PROBLEMS OF THE CHEMICAL IDENTIFICATION OF NEW ELEMENTS

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Abstract - The relative role of the chemical and nuclear-physical evidence
for element discovery in the history of synthetic transuranium elements is
analyzed. The advantages of the thermochromatography of volatile inorganic
compounds for the chemical identification of transactinide elements are
outlined. The physico-chemical aspects of this approach are discussed, such
as the equilibrium and rates of reactions of recoil atoms, the principles
of selecting the chemically active constituents of the carrier gas, the
factors that determine the possibility of rapid thermochromatographic sepa-
ration, and problems involved in the interpretation of the results of expe-
riments with individual atoms. Description is given of a Monte-Carlo compu-
ter calculation technique for simulating thermochromatographic zones, which
is based on a simplified realistic model of the migration of molecules along
the column and permits various experimental details to be taken into account.
It proves possible to separate thermochromatographically heavy actinides
(up to mendelevium) in atomic state and to obtain information on the metallic
states of these elements. The experiments are described aimed at the search
for the spontaneously fissioning isotopes of element 107 -- ekarhenium --
in the products of the bombardment of berkelium-249 with neon-22. The tech-
nique used allows one to isolate rhenium isotopes in not more than one second.
Prospects for investigating future elements including superheavy ones are
discussed.

INTRODUCTION

The possibilities of obtaining new chemical elements depend on progress in nuclear physics
and technology. All the known elements with atomic numbers above 100 have been synthesized
in nuclear reactions induced by alpha particles and heavy ions ($Z > 2$) on targets made of ura-
nium, the reactor transuranium isotopes, as well as lead and bismuth. The production of in-
creasingly intense heavy ion beams is the only way to open up further prospects for discovery
of new elements, including superheavy ones (SHE), if long-lived isotopes of the latter are
not found in nature (see Refs. 1-5 for a review). New synthetic elements can be produced only
in atom quantities and have short lifetimes. These facts severely complicate their chemical
identification as a part of the discovery, and the further study of the chemical properties
of these elements -- the two problems that are closely related with each other. The concept
of an element bears a rich chemical content; therefore there still exist some enthusiasts who
are ready to overcome the major scientific and technical difficulties occurring in the course
of these investigations.

Strictly speaking, the chemical identification consists in separation of the new element from
all known elements according to the characteristic features of its chemical behaviour.
In fact, the discoverers of synthetic transuranium elements always with much success used
nuclear-physical data and arguments, and this permitted the reduction of the amount of the
necessary chemical evidence of the discovery (Refs. 6-8). First of all, these were radioactive
properties such as the α-decay energies and half-lives and their correlation, and the
spontaneous-fission half-lives. These quantities constitute rather specific characteristics,
and only a few heavy elements can, in principle, have isotopes similar in their radioactive
properties to the transfermium element sought for. Further, despite the fact that in the
course of the synthesis, the interaction between the bombarding heavy ions and the target nu-
clei proceeds through numerous channels, the possibility of producing many nuclides is so far
excluded by the laws of conservation or because the regularities of these processes lead to
negligible effective cross sections. As a strong evidence for the assignment of the atomic
and mass numbers was often advanced the genetic relationship of the new nucleus with some
known nuclides, but sometimes this could hardly be established. The classical method of cross
bombardments is of smaller importance for the new transfermium elements, since the set of
available targets and projectiles is very limited in the required combinations. The above
listed nuclear-physical aspects of the studies aimed at synthesis of transfermium elements

are discussed in more detail in other papers submitted to the present conference.

The history of transuranium elements saw the changing proportions of the nuclear-physical and chemical data required to prove the discovery. There follow a few examples.

The crucial proof of the discovery of neptunium-239 (Ref.9) was the establishment of its genetic relationship with the then known uranium-239; indicative was the constant ratio of the yields of the two activities under different conditions of neutron irradiation of uranium. Then, one succeeded in finding a procedure for the chemical isolation of neptunium from uranium, which was used to prove that neptunium was accumulated at a rate corresponding to the decay rate of uranium-239. The chemical evidence consisted of establishing that the chemical properties of uranium and neptunium were similar while isolation of neptunium from uranium and thorium was still feasible.

A similar situation occurred for plutonium (Refs. 10 & 11). It was found that the beta-decay of a neptunium isotope with at that time unknown mass number resulted in the formation of an alpha-activity (that was plutonium-238), which was expected to belong to element 94. The chemical evidence was limited to the proof that this alpha-activity could be separated from uranium.

Americium (Refs. 12 & 13) was first produced from plutonium-239 irradiated in a reactor, as a result of the capture of two neutrons and the beta-decay of plutonium-241. The synthesis method used provided very conclusive evidence for atomic number, and the researchers were entirely convinced that they had produced the new element after they had isolated it from plutonium.

Curium (Ref.14), berkelium (Ref.15), californium (Ref.16), and mendelevium (Ref.17) were synthesized for the first time by the alpha-particle bombardments of the appropriate target materials with atomic numbers by two units smaller. Reactions of the type $^{253}Es(\alpha,n)^{256}Md$ were used. The new elements were eluted from the cationic chromatographic column in accordance with the behaviour of their rare earth counterparts. This evidence only would be insufficient if the probability for reactions other than (α,xn) to occur were not practically ruled out. As an additional argument served the reliable prediction of nuclear properties, and establishment of the genetic relationship $^{256}Md \xrightarrow{EC} {}^{256}Fm$ in the case of mendelevium.

The first study of einsteinium and fermium is considered to be that published in 1955(Ref.18), in which isolation of these elements from the debris of a thermonuclear explosion was described. In the course of chromatographic separation of trivalent transuranium elements, the authors discovered new alpha-activities with the behaviour expected for two transcalifornium elements. However, the authors of this discovery appear to have felt confident of their discovery only after the independent synthesis of these elements had been performed using heavy ions (Ref. 19) and subsequently in a nuclear reactor (Ref.20), i.e. by the better studied nuclear transmutations.

Thus, from the beginning of the studies aimed at synthesizing transuranium elements a certain tradition was established. As the nuclear data pointed to a comparatively narrow range of the possible atomic numbers, the chemical experiments consisted of isolation of the new activity from the target element and from a small number of "suspicious" elements. The more detailed studies to show chemically that the element was not identical with some of the known ones, were always carried out later.

It is not difficult to follow another interesting regularity. Despite the fact that chemical identification was performed not in the strict sense of this term, the task appeared to be so hard that its solution often required the use of new, unconventional techniques which had not yet become classical ones. This essentially was the case for the discovery experiments on neptunium and plutonium and, in the first place, americium and curium (Refs. 12-14), where use was made of ion-exchange chromatographic separation on cationic resin with a complexing eluent, i.e. the method which had been used for lanthanide elements only shortly before that (Ref. 21).

The solution chemistry methods gave no results in searches for elements 102 and 103 as they did not permit work with isotopes having half-lives shorter than several minutes. Therefore, the most important factor involved in progress in the production and reliable identification of elements 102 and 103 at Dubna was the further development and improvement of nuclear-physical techniques for the assignment of the atomic and mass numbers (Refs.22-24). Except for $^{255}102$ with $T_{\frac{1}{2}}=$ 1 h (Ref. 25), all the known isotopes of element 102 and 103 were first identified by using no chemistry.

The study of elements 102 and 103 by chemical methods followed long after the discovery of their first isotopes. In Berkeley, rather a sophisticated computer-controlled system (Ref. 26) was built which made it possible to repeat the simple ion exchange and extraction experiments many times in rapid sequence. These comprise the following steps: the accumulation of nuclear reaction products on the surface of some rabbit-collector during a certain period of time (typically one or two half-lives of the isotope being investigated);

the pneumatic transport of the rabbit from the target to the chemical apparatus; the washing of the activity from the collector and its deposition onto a chromatographic column; the passage of the solution through the column under pressure; the collection and drying of separate solution drops and, finally, the mechanical transfer of the latters to α-radiation detectors. The total duration of the experiment, i.e. the time passing from the delivery of the collector to the transfer of samples for measurement, should not much exceed the half-life of the isotope. By using this apparatus, there were performed experiments on the extraction behavior of element 103 using 20 atoms of the isotope ^{256}103 ($T_{\frac{1}{2}}$= 35 s) (Ref. 27), the ion exchange experiments on element 104 - kurchatovium (Ref. 28), in which some 17 atoms of this element were detected, and the extraction experiments on this element (Ref. 26) with not more than 5 atoms detected. The uncertainty in the number of the atoms registered was associated with the fact that the energy of the α-particle emitted from the daughter isotope ^{257}102 was the same as that of the parent isotope ^{261}Ku ($T_{\frac{1}{2}}$= 70 s). One could usually detect only a few per cent of the total number of the atoms produced by the target irradiation.

This situation in the field of the studies of the chemical properties of the elements of the second hundred can hardly be tolerated . In the early sixties, long before the works carried out using the Berkeley computer-controlled system, we at Dubna aimed at developing a new experimental technique, which could allow us to reach a high rate of separating elements and preparing samples for radioactivity measurements (Refs. 29 & 30). The solution was to use the gaseous compounds of nuclear reaction products, which were transported by flowing gas and separated by using the principles of gas adsorption chromatography or thermochromatography. The method developed by us has several evident advantages. These are the so far unsurpassed speed of operation down to tenth fractions of a second, high "utilization" of atoms produced in the nuclear reaction (up to 30-40% of the atoms are detected in the case of spontaneously fissioning isotopes with half-lives of the order of one second or more), which is conditioned by the continuous chemical processing and, finally, a rather simple, from a technical point of view, and flexible experimental setup,   as opposed to the mentioned automated aqueous chemistry apparatus.

As an example, Fig. 1 shows the experimental setup used in current experiments to search for the spontaneously fissioning isotopes of element 107 with half-lives exceeding one second among the products of the irradiation of ^{249}Bk with the ^{22}Ne ions (see below).
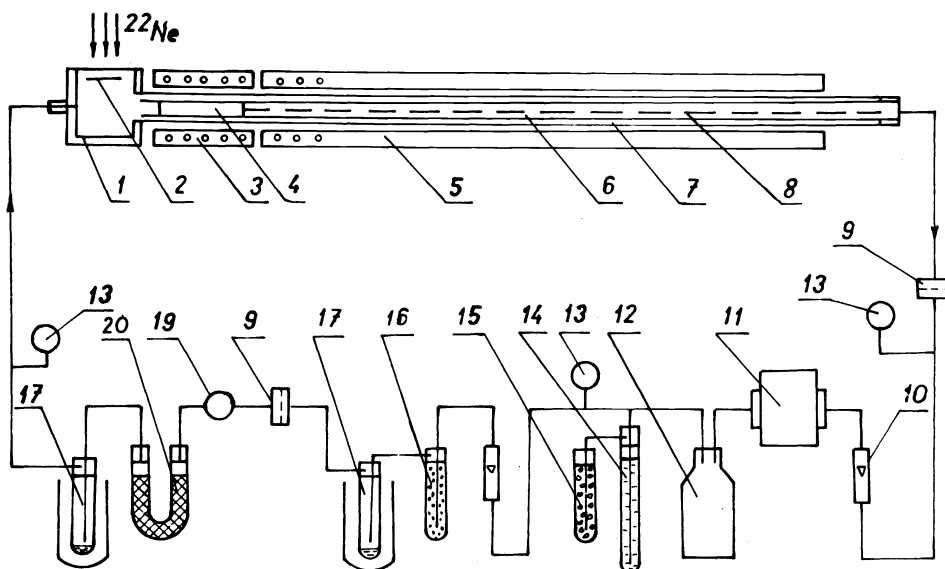

Fig. 1. Experimental setup for the chemical identification of element 107, ekarhenium. 1 - target chamber, 2 - berkelium-249 target, 3 - furnace, 4 - quartz wadding filter, 5 - temperature gradient furnace, 6 - quartz tube, 7 - stainless steel tube, 8 - fission track detectors (quartz), 9 - fiber filter, 10 - flow meter, 11 - peristaltic pump, 12 - 5-liter flask, 13 - manometer, 14,15 - safety system, 16-20 - carrier gas conditioning system.

Similar devices were employed in our earlier chemical studies of elements 102 (Ref. 31) and 103 (Ref. 32) with several hundreds of atoms of the isotopes ^{256}102 and ^{256}103.

Those experiments indicated the low volatility of the chlorides of elements 102 and 103, this being an evidence for their "actinide nature". Then followed the chemical identification of kurchatovium (the isotope ^{259}104, $T_{1/2}$ = 3 s) (Refs. 33-35) and nielsbohrium (^{261}105, $T_{1/2}$ = 2 s) (Refs. 35-37) with several tens of atoms. It consisted of the separation of the volatile halides of ekahafnium and ekatantalum from the halides of the actinide elements.

Some physicochemical and technical problems of the method are considered below.

CHEMISTRY OF VOLATILE COMPOUNDS

The most important processes involved when we use gaseous compounds in an "on-line" experiment with the cyclotron beam are the following ones (cf. Fig. 1):
(a) the recoil atoms (i.e. nuclear reaction products including the sputtered atoms of the target matrix) formed as a result of the interaction between the heavy ion beam and the target are ejected from the target material layer, if it is thin enough (typically $\approx$ 1 mg/cm^2 for projectiles heavier than boron), and are thermalized in a gas flow passing through a chamber behind the target. It is preferrable that the gas should contain chemically active components for production of the needed compounds of the elements being separated. If these species can cause the corrosion of the target, one uses formally "inert" gas (the radiolysis products and impurities may nevertheless be reactive). In this case the chemical state of the thermalized atoms is poorly determined and one adds chemically active substances downstream at the exit of the target chamber;
(b) the separation is carried out using the principle of gas-adsorption chromatography or thermochromatography. The latter is essentially chromatography in a column (mostly capillary and unpacked), along which there is negative temperature gradient in the direction of the flow. Various compounds are deposited on the column walls at characteristic temperature intervals depending on their volatility, or, to be more exact, on their energy of physical or chemical adsorption on the surface of the column material.

Under otherwise equal conditions, the position of the zone centre is determined by adsorption enthalpy and the actual duration of thermochromatographic procedure. The latter value in the case of short-lived isotopes is equal to their lifetime and is not directly related to the rated duration of the continuous experiment. The measurement of the position of the short-lived isotope zone is carried out in the simplest way in the case of spontaneously fissioning activities as it is possible to place solid-state detectors for fission fragments (mica, quartz, plastics) directly into the column.

Let us consider some processes affecting the chemical identification procedure (separation of elements) and, at the same time, discuss the question whether there is any specifity about this process and the interpretation of the data if we deal only with a few atoms of the element.

The recoil atoms are slowed down in a gaseous medium which undergoes intense irradiation with the heavy ion beam penetrating throughout the chamber behind the target. Under typical conditions, we deal with currents of about 10^{12} neon-22 ions per cm^2 of the chamber cross section. The gas in the chamber is replaced, on the average, in every 0.1 s or so. During this period of time, the beam energy absorbed should heat the gas by nearly 50-100°, yielding about 10^{17} electron-ion pairs per cm^3 of the gas (STP). However, the maximum ion concentration appears to be of the order of 10^{13} per cm^3 owing to fast recombination. In any case, since the molecule undergoes approximately 10^9 collisions with other molecules per second, the interaction with ions and electrons having a relative molecular concentration of 10^{-6} can, in principle, influence the chemical stabilization of the recoil atoms. Similarly, relative concentration of 10^{-7} is a limit for the content of any gas components including "impurities", the possible interaction with which should be taken into consideration because the atom, during thermochromatographic processing remains, as a rule, in the gaseous phase for about one second.

Unfortunately the literature does not contain any pertinent data which could permit a detailed discussion of the chemical transformations of recoil atoms. Therefore, chemically active gas components were chosen such as to provide the transformation of the atoms into the required compounds even under extremely unfavorable conditions. These active substances fulfil the following functions: (a) to react either with the recoil atoms (to chlorinate, oxidize, etc.), or with intermediate molecules leading to the formation of the desired compounds; (b) to inactivate the possible "harmful" admixtures which could affect in an undesired way the chemical stabilization of the recoils; (c) to serve as "carriers", first of all, in the sense of modifying the properties of the column surface.

Fast synthesis of compounds.

The first function can be considered with the example of experiments on Ku (Refs. 33-35) and Ns (Refs. 35 & 36) chlorides. We had no possibility of introducing chlorides into the target chamber because of their high corrosivity. The recoil atoms were slowed down in helium or nitrogen and, despite the careful purification of the gases, the possibility for oxides

to form due to oxygen traces was not excluded. The formation of nitrides is less probable, as the reaction $Zr(g) + N_2(g) = ZrN(g) + N(g)$ has the enthalpy change $\Delta H^o_{298} = +91$ kcal.

It should be noted that, in contrast to solid-state compounds, the oxides of the IIIrd-Vth group transition elements are expected to be rather reactive in gaseous form and their inertness in the crystalline state results from a high lattice energy.

When analyzing the data presented in Fig. 2 for zirconium - a kurchatovium homolog -- we can see that there is a variety of conceivable paths for a zirconium atom to form tetrachloride with negative enthalpies at all bimolecular steps, both with and without taking into account possible interactions with the oxygen admixtures and atoms (radicals) produced by the gas radiolysis. Moreover, when a microcomponent (trace amounts) interacts with a macrocomponent, under equilibrium conditions the microcomponent will react almost quantitatively even at very low equilibrium constant values, i.e. at positive values of ΔH of the reaction. However, in view of the requirement that the chlorination should take a short time, some reactions being too slow, they might in principle hinder the conversion $Zr \longrightarrow ZrCl_4$.
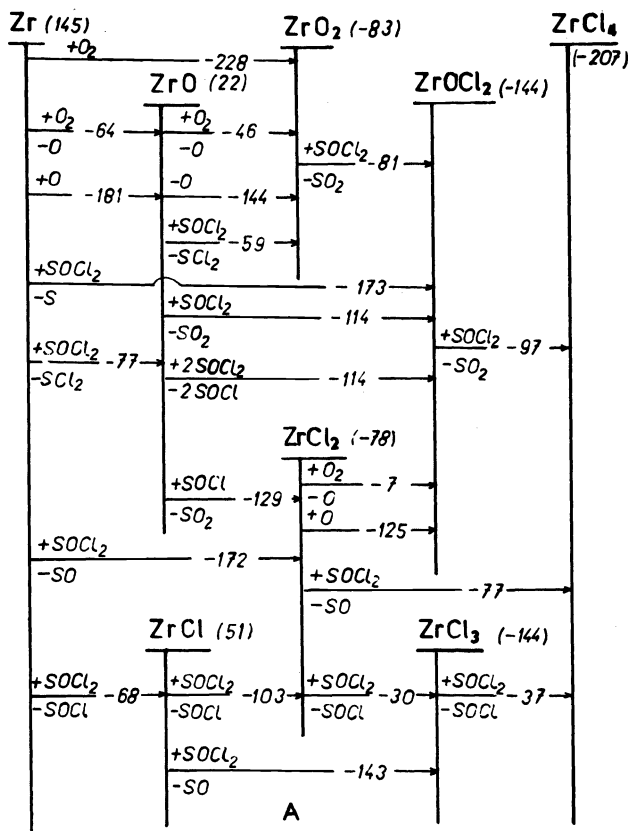

Fig. 2. The ways of transformation of zirconium atoms into a zirconium tetrachloride molecule in the interactions with (a) thionylchloride and (b) titanium tetrachloride in gaseous phase. The reacting constituent of the carrier gas is indicated above the arrow, the reaction product - below the arrow, and the enthalpy of reaction is given in the gap of the arrow. The values of enthalpy of formation of gaseous compounds of zirconium, ΔH^o_{298} (Refs. 40 & 41) are given in brackets.

Indeed, in a bimolecular reaction, the concentration of the nonreacting molecules of the microcomponent falls off exponentially with time as the reaction is the quasimonomolecular one and the average time for the microcomponent to react is equal to

$$\tau = (1/nZP)\exp(E_{act}/RT).$$

Here, n is the concentration of the chemically active macrocomponent (mole l^{-1}), Z is the number of the binary collisions of the microcomponent molecule with the molecules of the chemically active species (mole^{-1} l^{-1} s^{-1}), and P is the steric factor. As is known,

Zr (143)   ZrO₂(-83)   ZrCl₄ (-207)

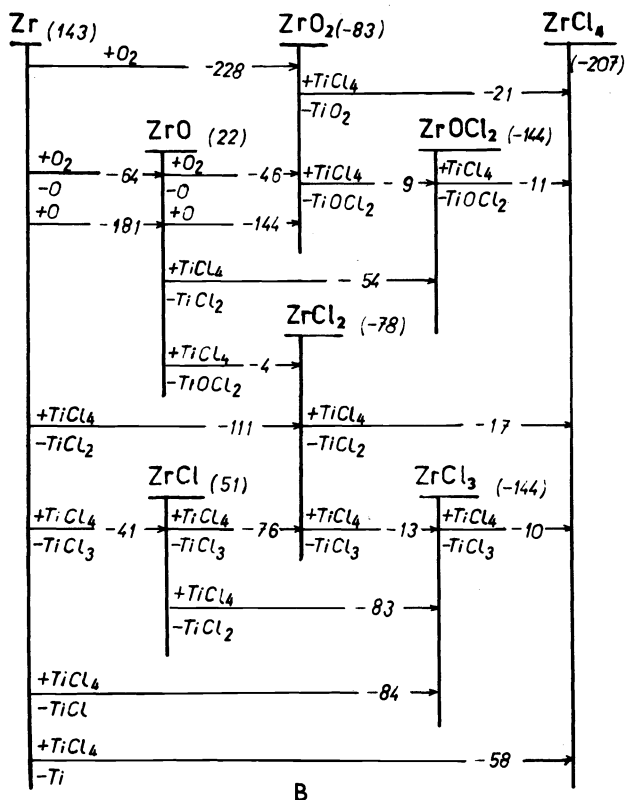ZrO (22)   ZrOCl₂ (-144)

ZrCl₂ (-78)

ZrCl (51)   ZrCl₃ (-144)

B

Fig. 2(b). See caption of Fig. 2.

$ZP \leq 10^{10}$, hence

$$\tau = (10^{-6}/p) \exp(E_{act}/RT),$$

where p is the partial pressure of the chemically active constituent in mm Hg. Thus the reaction is not fast enough if τ exceeds the characteristic experimental time t. This is the case if

$$E_{act}/RT \geq 14 + \ln(tp)$$

and, because of $E_{act} \geq \Delta H$, we obtain a similar limitation for the "admissible" values of ΔH. Of course, E_{act} is positive for negative values of ΔH as well. We know (Ref. 42) the relation which is satisfied for exothermic reactions involving radicals, which many of the reactions listed in Fig. 2 belong to, namely, $E_{act} = 11500 + 0.25 \Delta H$ (cal/mole).

This implies that at T = 500 K always $E_{act}/RT \leq 11.5$, so the exothermic reaction cannot play a negative role in the here considered processes except for, perhaps, the recombination reactions proceeding through ternary collisions.

Scavenging of impurities in the gas. In experiments with Ku and Ns, halogenating compounds fulfilled all the three functions indicated above, in particular, they scavenged the possible minor admixtures of water vapors and oxygen in inert gases. This was considered previously by using, as an example, experiments aimed at studying nielsbohrium pentabromide (Ref.39) when bromine and boron bromide served as active components of the carrier gas. The low corrosive activity of these species permitted their vapors to be introduced direct into the target chamber manufactured of nickel. Oxygen and water seem to be the most dangerous trivial impurities in helium: reactions with oxygen can lead to formation of slightly volatile oxybromides, or even oxides, while water vapors can hydrolize the bromides already formed.

We assume that at the moment of mixing helium with the bromine and boron bromide vapors the helium-based gaseous mixture contained BBr_3, Br_2, HBr, H_2O, and O_2 with a partial pressure of 10^{-4}, 10^{-2}, 10^{-4}, 10^{-4}, and 10^{-4} (in atm), respectively. For the reaction of
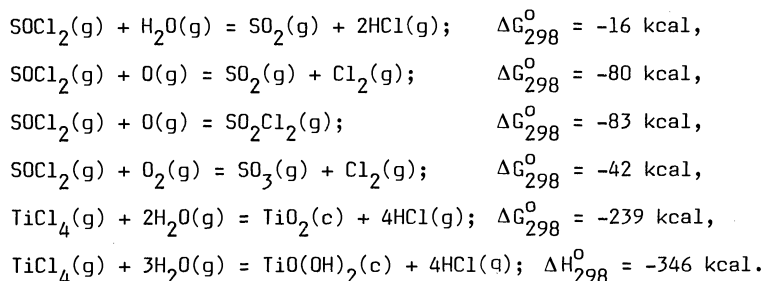
water vapors

$$3H_2O(g) + 2BBr_3(g) = B_2O_3(c) + 6\,HBr(g),$$
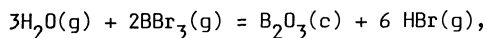
the change in free enthalpy and the equilibrium constant are equal to $\Delta G^o_{298} = 87$ kcal and $k_p \approx 10^{40}$, respectively.

The thermodynamics of this and other expected reactions implies that the equilibrium residual content of free water and oxygen molecules should be of the order of 10 molecules/cm^3.

The substantial role of boron tribromide was shown by direct experiments; namely, in its absence, with helium and bromine vapors only, the formation of volatile Ge, As, Se, Ga, and Zn bromides has been observed, but no higher bromides of Zr, Nb, and Ta were apparently produced because of formation of almost involatile and stable oxides and oxybromides. As boron tribromide was introduced into the carrier gas, volatile Hf, Nb, and Ta bromides were produced with high yields. Boron tribromide is known to be an active brominating agent, which is capable of converting the solid oxides of transition and other metals into higher bromides. Therefore it is possible that in our experiments there has occurred the bromination of oxides in the gaseous phase or of molecules adsorbed on the surface. However, it is not evident that such reactions should be fast enough, and we incline to believe that just the thorough purification of the gas from water and oxygen free molecules provides the possibility of fast synthesis of the higher bromides of niobium, nielsbohrium, and other elements.

Similarly, in experiments with chloride compounds in which thionylchloride and titanium tetrachloride vapors were introduced into the carrier gas, water and oxygen admixtures can, in principle, be removed rather efficiently (although some of them can be slow at the experimental temperature) by the following reactions:

$$SOCl_2(g) + H_2O(g) = SO_2(g) + 2HCl(g); \quad \Delta G^o_{298} = -16 \text{ kcal,}$$

$$SOCl_2(g) + O(g) = SO_2(g) + Cl_2(g); \quad \Delta G^o_{298} = -80 \text{ kcal,}$$

$$SOCl_2(g) + O(g) = SO_2Cl_2(g); \quad \Delta G^o_{298} = -83 \text{ kcal,}$$

$$SOCl_2(g) + O_2(g) = SO_3(g) + Cl_2(g); \quad \Delta G^o_{298} = -42 \text{ kcal,}$$

$$TiCl_4(g) + 2H_2O(g) = TiO_2(c) + 4HCl(g); \quad \Delta G^o_{298} = -239 \text{ kcal,}$$

$$TiCl_4(g) + 3H_2O(g) = TiO(OH)_2(c) + 4HCl(g); \quad \Delta H^o_{298} = -346 \text{ kcal.}$$

Thermochromatographic separation. Since a high speed of separation is required, it is particularly important to understand what the width and generally the profile of the thermochromatographic zone (peak) depend on. The problem of the zone profile, even in the simplest cases, does not seem to have an analytical solution. We investigated the effect of various experimental variables and other factors by using Monte-Carlo calculations. For this purpose we proposed a simplified model of migration of molecules along the column in the form of a series of displacements of random length ℓ with the probability density

$$\rho(\ell) = (1 - 1/\nu_1\eta)\,\delta(\ell) + (1/\nu_1\eta)(1/\eta)\exp(-\ell/\eta),$$

where $\delta(\ell)$ is Dirac's delta function, η is some characteristic displacement, and ν_1 is the average number of collisions of a molecule with the column wall in a column section of unit length, obtained from the equations of the kinetic theory of gases.

Such an expression for $\rho(\ell)$ corresponds to the following picture of molecular movement along the column. The molecule, in a random sequence, either (i) undergoes a series of collisions with the column wall, the statistical average number of collisions in this series being $\nu_1\eta$ and its random value N being distributed with the probability

$$P(N) = (\nu_1\eta-1)^{N-1}/(\nu_1\eta)^N;$$

in this case the molecule does not advance along the column ($\ell = 0$);
or (ii) the molecule moves a comparatively large distance (of the order of several centimeters) along the column, without striking the wall, the random length of the displacement being distributed exponentially with the average value of η.

Further we suggested that as a result of one series of collisions, the molecule spends in the adsorbed state the period of time $N\tau_0 \exp(-\Delta H_a/RT)$, where τ_0 is the period of oscillations of the molecule, perpendicular to the adsorbent surface (Ref. 44) and ΔH_a is adsorption enthalpy. We remember that N is a random quantity and T is a coordinate function in thermochromatography. In the Monte-Carlo computations, we calculated for a molecule sequential sums of displacements and the times of adsorption delays. After the total delay had

first exceeded the duration of experiment for the given molecule (see below for the defi-
nition of this quantity), its coordinate was recorded in the computer memory. After calcula-
ting the set number of the "histories" of individual molecules we constructed a histogram of
the zone.

In the case of isothermic chromatography,an analytical solution of the problem on the zone
dispersion is known (Ref. 43) for a laminar flow in the capillary column. It is natural to
require that our model give coincident results for the coordinate of the zone centre and for
the dispersion. It turns out that this is achieved provided that η is calculated by
the formula

$$\eta = (11 - 16\,\mathcal{R} + 6\mathcal{R}^2)\,Q/48\,\pi D^2 ,$$

where D is the diffusion coefficient
and $\mathcal{R}$ is the ratio of the velocity of the migration of the zone centre to the linear
velocity of the carrier gas, i.e.

$$\mathcal{R} = 1/[\,1 + (Q/\pi r^2)\,\nu_1 r_0 \exp(-\Delta H_a/R\,T)\,].$$

Here, Q is the flow rate of the gas and r is the column radius.

We used this function in calculating thermochromatograms. We note that η increases as
temperature decreases, due to the proportionality of Q/D to $1/\sqrt{T}$, and with an infinite
increase in $|\Delta H|$, i.e. at $\mathcal{R} \to 0$, it has a limiting value

$$\lim \eta = 11\,Q/\,48\,\pi D .$$

The calculational flow sheet described here has been obtained by considerably improving the
approach described earlier (Ref. 39). The calculation program at a BESM-6 computer allows one
to take into account the diverse factors and real experimental conditions. In particular,
it is possible to set not only the constant gradient, but also any temperature distribution
along the column length. Only ΔH_a and r_0 are adjustable parameters.

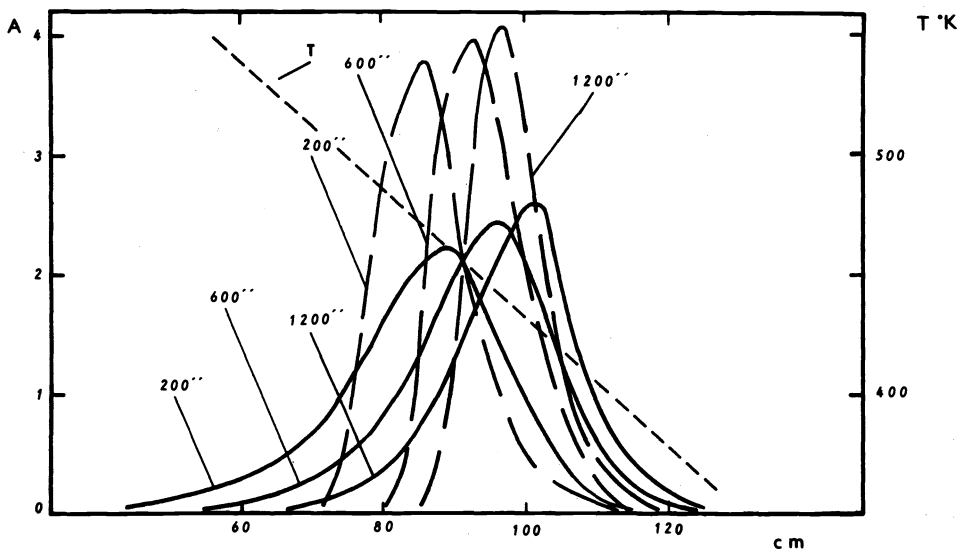Some results of calculations are given in Fig. 3.

Fig. 3. The calculated shape of thermochromatographic zone for a long-lived
isotope of element with $\Delta H_a = -23$ kcal/mole and $r_0 = 1 \times 10^{-12}$ s at
different durations of experiment (dashed curves, t_e is indicated), and for
short-lived isotopes of the same element with different half-lives at
$t_e = 10000$ s (solid curves, $T_{1/2}$ is indicated). The experimental conditions are
$Q = 0.5$ l/min; $r = 0.15$ cm, $D_{298} = 0.1$ cm^2/s; the temperature plot is shown
in the Figure.

The dashed curves show how the thermochromatograms change with the duration of the experiment
t_e in the case of elution thermochromatography with long-lived radioisotopes ($T_{1/2} \geq t_e$).
In this case all molecules move along the column during equal periods of time t_e.

The solid curves present the thermochromatograms of short-lived products of nuclear reactions -- the isotopes of one and the same element with different half-lives. It is implied that the coordinate of the point where the atom decays (see below for information on spontaneous fission detectors placed in this column) is recorded. The actual duration of the experiment, for each given atom, is equal to its random lifetime value. If $T_{\frac{1}{2}} \leq t_e$, then the change in the rated duration of experiment, t_e, practically does not influence the shape of the thermochromatogram. The profile and position of the zone are practically identical in the elution and frontal modes of separation. In practice, for the short-lived isotopes produced with small yields at an accelerator, of course, only the frontal mode is possible. A considerable broadening of the zones of short-lived isotopes as compared to the dashed curves is explained by the exponential character of the probability density distribution for the lifetimes.

By analogy with discussing the influence of minor admixtures on the fate of individual atoms in the gaseous phase, one can consider also the problem of relatively rare active sites of adsorption, which, in principle, can exist on the column surface. By definition, the adsorption heat on active sites $|\Delta H_{aa}|$ considerably exceeds $|\Delta H_a|$, the average value for all the rest of the surface. These sites can apparently affect the results of the experiments only under special conditions. First of all, we note that in a thermochromatographic experiment the number of collisions of the molecule with the wall, leading to adsorption, lies in the range $10^3 - 10^4$. It is proportional to the coordinate of the zone centre and, therefore, slightly depends in the order of magnitude on the lifetime of the atom and on other experimental variables. In the case of localized adsorption, the active sites can play a role only if their relative surface concentration f_s exceeds the inverse value of the collision number, i.e. $f_s > 10^{-4}$. If σ_0, the total number of adsorption sites, is taken to be equal to $10^{15}/cm^2$, the limit of f_s corresponds to nearly 10^{11} sites per cm^2 and their number in the element adsorption zone should be not less than 10^{12}. Therefore, if only $f_s > 10^{-4}$ and the number of atoms N_e introduced into the column is less than 10^{12} in the order of magnitude (subnanogram quantites), the shape of the thermochromatograms should not depend on N_e and will remain the same in an experiment with individual atoms (molecules).

One may argue that the adsorbed molecules generally possess some surface mobility which makes it possible for them, in the adsorbed state, to "visit" many sites and this should lead to the lowering of the indicated limits of f_s and N_e. In fact, ν_{as}, the frequency of the jumps of molecules between the adsorption sites, is determined by the expression (Ref. 44)

$$\nu_{as} = (1/\tau_0') \exp(E_{as}/RT)$$

where τ_0' is the period of oscillations close to τ_0 in the order of magnitude (see above), and E_{as} is the activation energy of surface diffusion ($|\Delta H_a| > E_{as} > 0$). The limiting value of f_s, above which the active centres can already influence the formation of the thermochromatogram, will decrease by a factor of about $\nu_{as} T_{\frac{1}{2}}$ (or by a factor of $\nu_{as} t_e$, if $t_e < T_{\frac{1}{2}}$); correspondingly, the upper limit of N_e will also decrease. Unfortunately, it is difficult to estimate E_{as} a priori. If this value is small, the limits of f_s and N_e decrease sharply.

However, we so far did not take into account the effect of a nonisotopic carrier. It is capable of depressing the active sites to a considerable extent, i.e. it can decrease their effective surface concentration. In accordance with the Langmuir adsorption isotherm, $1 - \theta_s$, the fraction of the adsorption sites not occupied by the carrier molecules, will be defined by the following expression (Ref. 44):

$$1 - \theta_s = \sigma_0/[\sigma_0 + n\tau_0 \exp(-\Delta H_a/RT)]$$

where n is the number of molecular collisions per unit area per unit time (from the equations of molecular kinetics). At a partial pressure of 1 mm Hg in the gas, the carrier with ΔH_a = -20000 cal/mole and ΔH_{aa} = -30000 cal/mole at T = 600 K will leave unoccupied the 0.4th and 10^{-4}th fractions of the sites, respectively, while at T = 500 K, these values will be 0.02 and 10^{-6}, respectively. This indicates that the active sites will be deactivated to a considerable extent, whereas a large part of the rest of the surface will remain free for adsorption. This is the "modifying action of the carrier".

The further progress of such estimations goes beyond the scope of the present paper. Experimental evidence too contradicts the anticipated influence of active sites. Since it is impossible either to expect the reproducibility of the concentration of active sites in different columns, or to repeat exactly the conditions of their preliminary treatment and experimental parameters, we were to observe irreproducible thermochromatograms, which did not occur in practice.

Thermochromatography of metallic actinides. The recent experiments performed at our Laboratory (Refs. 45 & 46) on the thermochromatography of heavy actinides in atomic state with a titanium column confirm experimentally the correctness of the conclusions and estimates presented above. We worked with long-lived isotopes in the elution mode of separation with an off-line experimental setup. It was expected to be difficult to retain the extremely reactive actinides in atomic state in the atmosphere of an "inert" gas. Therefore, the elements were

evaporated at 1150°C from liquid lanthanum, i.e. in the form of atoms, and sodium and calcium vapors were introduced into the He carrier gas. The dissociation energy of binary atomic oxides of lanthanides is larger than that of sodium and calcium oxides. Therefore, the action of Na and Ca vapors consists rather in the final purification of the gaseous helium and in the modification of the surface, than in the reduction of the oxides of actinide elements, if such had formed.

We interpret the distribution of various alkali, alkali-earth and rare-earth elements in the column (Figs. 4 and 5) as a correlation between the metallic valence of elements and their volatility or the adsorptivity of trace amounts.
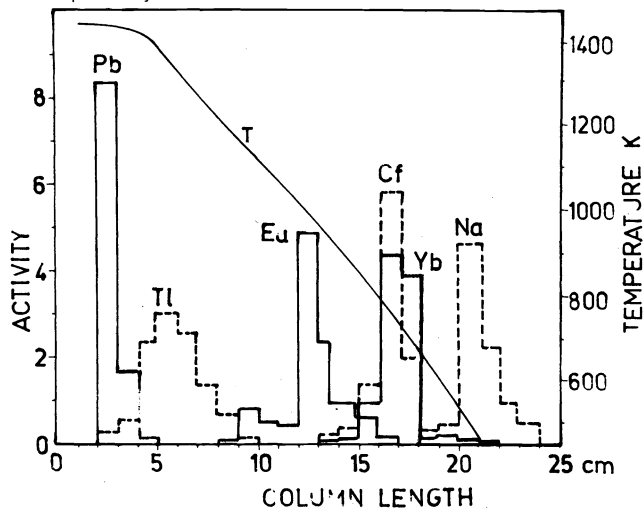

Fig. 4. Thermochromatography of actinide elements, the homologs of SHE and sodium, on a titanium column.
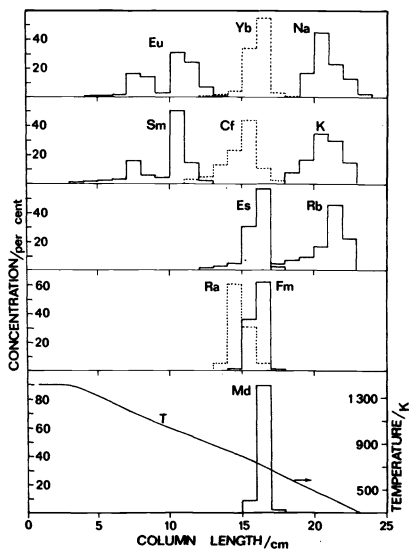

Fig. 5. Thermochromatogram of the mixture of heavy actinide elements on a titanium column (for convenience, the positions of different elements are shown on separate plots).

One can add to the data presented in Figs. 4 and 5 that americium and trivalent lanthanides little evaporated from the molten lanthanum during the experiment and deposited on the titanium within the section having a starting temperature of 1150°C, i.e. at considerably higher temperature than did divalent actinides. From the results obtained one can conclude that the metallic valency of elements from californium to mendelevium is equal to 2. This is the first experimental information of this kind on fermium and mendelevium. Some separation of the pairs of neighboring actinide elements has been achieved on a molybdenum column

apparently owing to the differentiated participation of the d-levels of actinides in the surface bonding. This allows one to hope that in the future it will be possible to use the thermochromatography of elements in metallic state even for the identification of actinides.

So far, however, thermochromatography continues to promise to give important results, first of all, in investigations of transactinide elements and in the identification of new elements in this region. This is exemplified by experiments aimed at the chemical identification of the possible spontaneously fissioning isotope of element 107.

EXPERIMENTS ON ELEMENT 107

In Ref. 47, an activity with a half-life of a second or so has been detected among the spontaneously fissioning products of the neon-22 bombardment of berkelium-249. This activity may belong to element 107. In this connection we have developed a thermochromatographic technique of identifying such an isotope of element 107 with intrinsic operation time of not more than one second. Based on the regularities of the Mendeleev Periodic Table and on the experimental localization of the actinide series, which was performed by investigating the chemical nature of elements 104 and 105, one should expect element 107 to be the homolog of rhenium. The most thoroughly studied stable and volatile compounds of the transition elements of the VIIth group (M denotes an element) are MO_3Cl, M_2O_7, HMO_4 and MO_3. Atom quantities cannot yield the molecules of M_2O_7; if these were required, one would have to use Re_2O_7 vapors as a carrier and count on the formation of $(107)ReO_4$ as a result of a fast exchange reaction. It is not necessary to use a chemically similar carrier in the case of compounds of the other types. The compound MO_3Cl does not suit as the chemical form of a particular oxychloride is difficult to fix because rhenium forms several volatile oxychlorides. In addition, oxychlorides are known also for tungsten, the homolog of element 106, from which it is desirable to separate element 107 during the identification. Therefore, the experiments were aimed at obtaining compounds of the type MO_3 or HMO_4 and the carrier gas of air was purified from the possible traces of chlorine-containing species. As early as 1972, we carried out some on-line experiments (Ref. 48) with rhenium radioisotopes by using humid air. In the experiments described below we kept the partial pressure of water vapors at a level of about 4 mmHg, the carrier gas flow rate was 0.5 l/min and the inner diameter of the quartz column was 4 mm. A specific feature of these experiments was the absence of a nonisotopic carrier close in volatility to the compounds being separated (if H_2O is not considered to be such). We used the experimental setup shown in Fig. 1. Under certain conditions, we observed the formation of a volatile compound of rhenium deposited at a temperature of 100-120°C in the zone centre for the isotope rhenium-177 with a half-life of 15 min (Fig. 6). A detailed study has shown that the reaction proceeds via the formation of an intermediate compound with a deposition temperature around 350°C, but sufficiently fast, for less than 2 seconds. Special attention was paid to the separation of involatile compounds since the summarized cross section for producing mendelevium-256 and fermium-256, the main spontaneously fissioning product of the neon-22 bombardment of berkelium-249, exceeds more than 10^4 times the cross section for production of the proposed isotope of element 107 (Ref. 48). By using in the column a filter of quartz wadding about 15 cm in length we succeeded in separating the rare earth elements (including the isotope scandium-44) hafnium and tantalum, which are the homologs of the actinides, elements 104 and 105, respectively, with a purification factor of above 10^5. Tungsten, the homolog of element 106, partially (5-8%) passes through the filter and deposits in the temperature interval between 800 and 400°C (cf. Ref. 48).
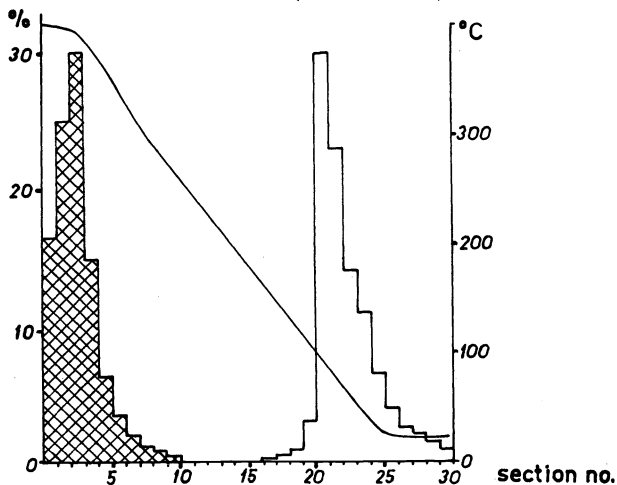

Fig. 6. Thermochromatograms of volatile compounds of rhenium in experiments with dry air (high-temperature peak) and with humid air (low-temperature zone).

To produce the isotope $^{267}107$, we bombarded berkelium-249 with neon-22 ions of an energy in the range 116-119 MeV. The target about 2.5 cm^2 in area and with a density of 130 $\mu g/cm^2$ of berkelium oxide contained from 2 to 15% of the daughter californium -249. In order to produce rhenium activity simultaneously, we introduced 40 μg of terbium into the target. The fluence of the neon-22 ions bombarding the target in one experiment (a total of 8 one to two day bombardments were performed) lay in the range from 4×10^{16} to 1.3×10^{17} particles. About 25% of the produced spontaneously fissioning nuclei of element 107 were expected to be detected. The results of the experiments do not so far make it possible to conclude that the products of bombardments contain a spontaneously fissioning isotope of the element close to rhenium in its chemical properties.

FUTURE SYNTHETIC ELEMENTS. SUPERHEAVY ELEMENTS.

Even if the proposed island of relative nuclear stability against spontaneous fission is really not pronounced in the chart of isotopes and the related "superheavy elements" (SHE) do not exist in nature because of their insufficient lifetimes, there is still the hope that a number of isotopes of elements with $Z \geq 107$, for which one can expect lifetimes of several tenths of a second and more can be synthesized in nuclear reactions.

So far, no attempts have been made to chemically identify element 106 -- ekatungsten. Under certain conditions, tungsten forms oxide compounds or oxychlorides (Refs. 49 & 50), which are volatile enough compared with the compounds of rare-earth elements, hafnium and tantalum. Thus, tungsten can be isolated rather selectively, if separation from the elements of the closest, lower subgroups of the Periodic Table is required.

The available data (Refs. 51-53) allow one to hope that element 108, the homolog of osmium, can be selectively separated from the lighter elements, owing to the formation of an extremely characteristic tetraoxide. OsO_4 is even more volatile than the oxycompounds of rhenium. An interesting possibility of obtaining additional information is to study the conditions of reducing the gaseous oxide compounds of elements 107 and 108.

It is possible that elements with $Z \gtrsim 108$ belong to the region of SHE. Attempts are being made not only to synthesize them in nuclear reactions, but also to search for their long-lived isotopes in nature (Refs. 3-5).

For the convenience of discussion of chemical problems, we shall conventionally consider $108 \leq Z \leq 118$ to be the boundaries of the nearest island of stability. In principle, there exist many promising ways of synthesizing SHE, such as the bombardment of uranium and trans-uranium targets with xenon and uranium ions, which can produce many superheavy isotopes simultaneously. However, the nuclear-physical theory as yet cannot indicate what element belonging to the island of stability should be produced in the irradiated target with the largest yield and "convenient" properties of isotopes. The same uncertainty is involved in the prediction of superheavy nuclides, which are likely to exist in nature. Thus, apart from the extreme complexity of the chemical composition of the initial materials (the bombarded targets, natural samples, etc.), the problem of the chemical identification of SHE is complicated by the additional factor -- so far, new transuranium elements have been discovered and investigated in the order of increasing atomic numbers, whereas now one shall possibly have to extract a new element before the properties of its precursors are investigated. Attempts are being made to identify the new activities that are suspected to be SHE, by various methods including, in the first place, nuclear-physical techniques. It is possible that the measurements of total kinetic energy of spontaneous fission or induced fission fragments (Ref. 4) may allow one to reliably assign the nuclide to the SHE island, although they are incapable of giving the exact atomic number. If only one succeeds in using the mass-separator technique for exact determination of the mass number, then, by using the known function for the line of beta-stability, it will be possible to indicate Z with an accuracy not worse than one unit. It should be noted that finding optimal conditions for producing SHE ions from the ion source (the temperature of heating the sample and the composition of the auxiliary gas) will allow one to judge somehow the chemical properties of this element or, on the contrary, the considerations concerning its chemical nature will help in choosing the operating conditions of the ion source.

It is however not excluded that the atomic number of the SHE detected will be determined mostly by chemical studies. Such a problem seems to be solvable for a number of Z in the region of SHE, by thermochromatographic methods if different carrier gases are combined (to create oxidizing or reducing atmospheres), if chemically active filters are used for absorption of some gaseous compounds and, finally, if the columns made of different materials are used. At our laboratory a considerable amount of experimental data has been accumulated on the behaviour of the known elements. For instance, on the basis of the properties of homologs it is possible to propose some principles to be followed in separation of SHE and in their isolation from actinides. We note first of all that actinides do not evaporate either in oxygen or hydrogen atmosphere, at any rate, in the presence of SiO_2 (Refs. 54 & 55) up to a temperature of $1000^\circ C$. Elements 108-110 cannot be sublimed in an air stream, while elements 112-116 will undoubtedly be volatile. All the indicated SHE can be volatilized in

an oxygen flow at $T \leq 1000^{\circ}C$. In this case elements 115 and 116 can be absorbed by a calcium oxide filter, and elements 112-114 should not be absorbed by such a filter at a temperature of 1000 to 1100°C. The deposition temperatures of elements 112, 113, and 114, as well as of elements 115 and 116 (in atomic state) on a quartz thermochromatographic column should differ considerably. Experimental data on the separation of the known homologs (Refs. 56 & 57) are available and the temperature intervals of deposition for SHE are predicted (Refs. 57 & 58).

The data of Fig. 5 show that it is possible to create such conditions under which comparative-ly volatile elements are deposited at a sufficiently high temperature (in particular, above actinides). In the given case, on a titanium column, it is undoubtedly conditioned by the fact that Pb (the homolog of element 114) and Bi (the homolog of element 115) form with titanium the intermetallic compounds Ti_4Pb and Ti_4Bi, respectively. Titanium polonides (Po is the homolog of element 116) are also known. Thus, the use of columns manufactured of diffe-rent metals provide valuable information on the properties of elements and allows one to change, if desired, the (effective) volatility of elements. There are predictions concerning the nature of the interaction of SHE (Z=112-115) with many metals (Ref. 59). Some of these data are listed in Table 1.

TABLE 1. Enthalpy of sublimation of SHE and of the formation of SHE compounds with some metals.

	SHE (B)	112	113	114	115
metal (A)	$\Delta H^o_{298}(g)$	5.3 + 1.0	26.4 + 1.7	17.1 + 3.6	35.6 + 2.6
			$\Delta H^o_{298}(AB)$		
Ti		+6.3	-2.7	-3.1	-2.0
Zr		-0.9	-9.9	-10.6	-8.9
Mo		+32.4	+19.7	+20.1	+18.6
Fe		+26.4	+14.1	+14.5	+12.1
Cu		+11.3	+4.8	+5.3	+4.4
Ag		+10.3	+4.5	+5.3	+4.3
Au		+15.5	+5.2	+6.3	+2.9
Ni		+23.6	+8.1	+8.4	+5.3
Pd		+12.1	-2.8	-2.6	-7.4
Pt		+19.1	+3.1	+3.6	-1.9

$\Delta H^o_{298}(g)$ is the standard enthalpy of the formation of a gaseous element (Ref.58).

$\Delta H^o_{298}(AB)$ is the standard enthalpy of the formation of solid SHE-metal binary compounds (1:1) (Ref. 59).

The enthalpy of the formation of compounds with (1:1) composition is a measure for estima-ting the possible chemical interaction at adsorption. To distinguish between elements 108, 109, and 110 is still a complicated problem. For these elements, it is difficult to indicate sufficiently reliably the simple compounds that would be as characteristic of each given element as in the previous transactinides. The situation is complicated by the fact that Os, Ir, and Pt are polyvalent elements and not in all of them the highest oxidation state coinci-des with the group number in the Periodic System.

Element 111 seems to be even less volatile than gold and it is not expected to be volatilized in the oxidizing medium either. Although gold chlorides are volatile, the temperature of depo-sition of the chlorides of individual SHE will apparently differ not strongly and their sepa-ration from actinides will be complicated (Ref. 60). Therefore, chlorides can hardly be used for identification.

Many specific problems of the behavior of the homologs of elements are discussed in the papers in which isolation from a sample by high-temperature evaporation and subsequent separation were used to search for SHE in natural samples such as Allende meteorite (Refs. 54 & 55), among the products of concentration of heavy elements from hot brines, and in the targets irradiated at heavy ion accelerators (in off-line experimental setups, as a rule) (Refs.61-63).

As in the case of nuclear-physical methods, it is somewhat easier to prove that the new activity with specific radioactive properties belongs to the SHE group than to determine exactly its atomic number. In most cases it is possible to choose such conditions under which

only SHE, thus being separated from actinides, should produce sufficiently volatile compounds.

In attempts to extract and concentrate SHE, made so far by the methods of both gas chemistry and solution chemistry, the investigators, with few exceptions (see below), estimated the probable properties of SHE essentially on the basis of the simple downward extrapolation for the subgroups of the Periodic Table. The experimenter is interested, first of all, in such properties as the solubility of compounds (identification by coprecipitation), hydrolysis and complexing properties of ions in solutions (the use of ion exchange and extraction), oxidation states (the most important characteristic of the elements of the main subgroups), the standard oxidation potentials, and, finally, the volatility of elements and compounds. In accordance with the extrapolation, attempts were made to use the precipitation of sulfides (Refs. 64 & 67), the extraction of complexes with sulphur-containing reagents (Ref. 68), the extraction of halogenic complexes by anion exchangers (Refs. 69 & 70), the selective elution of bromide complexes from cationite (Refs. 66, 67 & 71), the spontaneous deposition on active metals (Ref. 69) and electrolysis (Ref. 72), and so on.

However, there is no assurance that the actual properties of SHE do not substantially differ from the results of extrapolation. This would further complicate the problem of chemical identification. It is not excluded that the exact assignment of atomic number solely by chemical methods, without using the methods of atomic and nuclear physics, is not feasible. Of course, we do not take the liberty of predicting all the conceivable situations which may occur in the future.

Rather a large number of papers of speculative and theoretical nature, which predict SHE properties, have been published. Since they are reviewed in excellent and comprehensive review papers (Refs. 5, 74-77), here we shall restrict ourselves to making some comments.

It seems very important and interesting to employ the calculations of atomic electron structures using the Hartree-Fock and Dirac-Fock methods. Sometimes, the obtained results have no direct relation to what interests the experimental chemist who searches for SHE. Nevertheless, the calculations confirm the nature of soft acids in the cations of SHE of the main subgroups and the further lowering of the stability of the higher valent states in the corresponding subgroups. The latter deserves special attention. The calculations give a very large energy split of the electron p-subshells over the total angular momentum j as a consequence of the sharply increasing relativistic effects at $Z > 100$ for the electrons approaching the nucleus very closely. This fact intensifies the known tendency to decreasing stability of the higher valent states. The realization of the latter requires the promotion of the $p_{1/2}$ electron to the valent state including the orbitals $p_{3/2}$, and the energy spent is no more compensated for by the energy of bonding. This leads to the unexpected prediction that element 115 -- ekabismuth -- will be characterized mostly by the oxidation state +1 (Ref. 79), which is unknown for bismuth.

The extreme supporters of these effects even predict that elements 112 and 114 should not react chemically and may possess the properties of noble gases (Ref. 80). At Darmstadt (Refs. 81 & 82) and at Berkeley (Ref. 83) special experiments have been carried out, in which only activities with properties of noble gases ($T_{1/2} > 1$ s) were continually chemically extracted from the products of bombardment at the accelerator. Such separation can be performed rather selectively and is comparatively simple from a technical point of view. The activities are transferred by a helium stream and heavy noble gases are frozen out on a collector, which is faced by corpuscular radiation detectors. All the process is controlled by observing radon isotopes.

Unfortunately, neither the speculative, nor theoretical considerations of the chemical properties of SHE provide experimentalists with an unambiguous quantitative indication of the extent to what the SHE properties can deviate from those of their homologs. The majority of the authors believe that relativistic effects should somehow influence the SHE properties. As noted above, the physical and chemical proerties of a noble gas (without estimating the boiling point) or a rather volatile metal with the boiling point of 150°C (Ref. 78) are predicted for ekalead (114). However, there exists a prediction that neglects relativistic effects but, instead, is based on the seldom mentioned phenomenon of "double periodicity". The extrapolation from Si via Sn gives for ekalead the boiling point of 2840°C (Ref. 84). Such low volatility is characteristic of only covalent three-dimensional structures and transition metals, and, in our opinion, ekalead is very unlikely to have such properties. On the other hand, the 1st and 2nd ionization potentials of elements 114, 116 and 118 are calculated to be considerably smaller than the potentials of Xe, Rn, and Hg, which the potentials of element 112 are close to. Therefore, we believe that elements 114, 116, and 118 should be reactive taking into account also the expected high polarizability of their atoms.

CONCLUSION

Not detracting from the importance and possibilities of solution chemistry which has a long history and has been developed by many investigators and research groups for application to transuranium elements, we would like to stress the evident advantages of gas chemistry,

which so far has received less attention than it deserves. Undoubtedly, it must and will be developed to be employed not only in the studies of the newest elements. In fact, the experimental problems of research into transuranium elements are essentially a particular case of those daily encountered in the practice of radioanalytical and analytical chemistry. The advantages of the methods based on the volatility of compounds are the absence of the necessity to add ballast substances (reagents) to the sample investigated, thus increasing its mass, volume and the possibility of contamination and, secondly, the simplicity of prepa-rative separations which make it possible to obtain samples suitable for radioactivity measu-rements, X-ray fluorescence analysis, etc. Although the degree of separation is sometimes not high, the separation occurs, as a rule, fast owing to the acceleration of reactions at higher temperature. In view of the general tendency to improve the selectivity of the instru-mental methods of chemical analysis and of mass analysis, the economy of time is very import-ant in the preliminary separation or concentration of elements.

The individuality of an element is characterized, in the first place, by the properties of the elemental form and binary compounds, whose volatility is investigated by us.
 The important role of water and aqueous solutions in our life is, generally speaking, a result of the random coincidence of circumstances, and the invariant systems of chemistry and chemistry courses can in principle be built only on the basis of the systematization and consideration of anhydrous compounds. By the way, in predicting the properties of the missing elements of the Periodic Table, Mendeleev paid much attention to the properties of simple substances and binary compounds (Ref. 85).

Finally, we would like to make some comments on the "reliability"of identification of elements or 'the unambiguity of evidence", both chemical and nuclear-physical, for discovery. The history of the elements of the second hundred involves an abundance of inaccurate results and errors in the papers published, and this has led to priority disputes. The objective reasons why this situation has occurred are the extraordinary complexity of the investiga-tions, the necessity to constantly search for and develop new chemical and physical methods, which not at once become familiar for the majority of investigators, and, finally, the mani-festation of new regularities in the transuranium region. Unfortunately, the once published memorandum (Ref. 86) on the criteria for discovery of new elements, bears the seal of the aspiration to canonize the experimental approaches used in one of the leading laboratories of the world and to outlaw all the other ones. This is incompatible with the principles of scientific quest and, in a number of cases, contradicts both the investigations and data of the memorandum authors themselves.

We conceive that any work should be recognized to be the discovery of a new element, if it meets one of the following requirements:

(i) The new element has been chemically separated from the elements whose isotopes may have similar nuclear properties, or its atomic number has been assigned by the methods accepted in atomic physics (X-ray analysis, etc.); in this case there is no necessity to determine correctly the mass number of the isotope.

(ii) The atomic and mass numbers have been identified by nuclear-physical methods alone; such a work, however, should not be considered the discovery of an element if subsequently it turns out that the mass number of the isotope has been assigned erroneously. The attribut-ing of certain radioactive properties to a wrong mass number is useless and often harmful for nuclear physics since, once becoming the reference point of empirical systematics, this leads to erroneous predictions and to the slowing down of further progress. This has been the case more than once.

After the work of many years and discussions on new elements we have arrived at the conclu-sion that it is impossible to work out universal criteria to prove evidence for discovery of elements. An objective position is not enough to judge the reliability of indentification methods and supporting evidence; the experience of practical work with a concrete experimental approach is required. As the investigators advance into the region of heavy elements, they come across new nuclear and atomic properties, new regularities and phenomena. It has been shown above what complications the chemical properties can bring. Therefore, the evidence that may seem convincing at the moment of publication of the paper can become unconvincing and even wrong with the elapse of time. An illustrative example is the complicated history of discovery of elements 102 and 103 (Refs. 7, 23, & 24). These and other examples have led us to conclude that the discussion of the reliability of evidence for discovery cannot form the basis for the establishment of discovery priority. The first work containing the conclu-sions that have been confirmed in a subsequent independent study, in terms of the identifica-tion of an element and (or) an isotope and in terms of determination of their radioactive properties (with reasonable requirements to the accuracy of the half-life and radiation spect-rum measurements) should be recognized to be a discovery.

Doubting the possibility of establishing the criteria of reliability of evidence for discove-ry, we do not support the irresponsible attitude of authors to discovery claims. On the contrary, since we call for the reproduction of results at other laboratories, it is necessary that the experimental results and their interpretation be described in a great

detail, almost in the form of files. Only then it will be possible to prevent the arbitrary reinterpretation of results. In our view, elements should be named by their dicoverers. It seems appropriate to follow the existing tradition of memorizing the names of prominent naturalists who have made an important contribution to nuclear and atomic physics, and chemistry. The choice of the names is a great responsibility.

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