[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY, UNIVERSITY OF CHICAGO]

The Chemical Properties of Elements 93 and 94

BY A. V. GROSSE

In December of 1932 we[1] expressed the possibility of producing new isotopes and even elements, with artificial radioactive properties, by nuclear bombardment. With surprising rapidity this anticipation came true through the discoveries of F. Joliot and I. Curie.[2] Using neutrons E. Fermi[3] was able to attack successfully also the nuclei of heavy elements. In the products of uranium bombardment he thought to have found element 93, disintegrating into element 94. For the correct interpretation of Fermi's results[4] as well as for future experiments, a discussion of the properties of element 93 and 94 is advisable.

Two possibilities have to be considered, of which the first one seems to be more probable. Either elements 93 and 94 are the *highest homologs* of *manganese* and *iron*, respectively, and then they can be correctly termed according to Mendelejew, ekarhenium (En) and ekaosmium (Eo), *or* they belong to the *second group* of *rare earth* elements in N. Bohr's sense.

The Properties of Ekarhenium and Ekaosmium.—If the electron distributions of elements 93 and 94 are according to the table below, they will be normal higher homologs of rhenium and osmium, respectively, and their properties can be readily deduced from the properties of the surrounding elements (see Table II).

This task is now considerably simpler than a few years ago, because thanks to the pioneer work of the Noddacks, the properties of rhenium and its compounds are now well known.[5]

Ekarhenium (En) will have a valency from a maximum of 7 down to 2 and even 1. The highest oxide, En_2O_7, will be stable, like Re_2O_7, and unlike Mn_2O_7; it will be volatile and probably sublime and melt below 375°. Hydrogen will reduce it at elevated temperatures first to lower, non-volatile oxides and later probably to the metal itself. It will form in water solution the acid, $HEnO_4$, with water soluble salts like $KEnO_4$, $Ba(EnO_4)_2$, etc. Since the basicity increases with the period number, $HEnO_4$ might also be basic enough to form water soluble salts with strong acids (HNO_3, HCl), analogous to uranyl salts. In any case it will remain in solution in highly acid media.

Ekarhenium hexa- or hepta-fluoride (EnF_7) will be very volatile and will be immediately hydrolyzed by water into HF and hydrated oxides.

Ekaosmium will also have different valencies, 8 being the highest. The highest oxide—the tetroxide, EoO_4—will sublime and boil below 200°, dissolve in water and alkalies similarly to OsO_4, but will be a weaker oxidizing agent than OsO_4.

The highest halides, especially the fluorides, will be volatile and readily hydrolyzable.

The Second Possibility.—According to N. Bohr[6] we have to expect somewhere beyond uranium a "second group of rare elements," *i. e.*, elements with very similar properties, where the additional electron as we go from element to ele-

TABLE I

The electron distribution of the elements given is based on the analogy with their lower homologs

Element	Quantum numbers n..l...s	2 s	2 p	3 s	3 p	3 d	4 s	4 p	4 d	4 f	5 s	5 p	5 d	5 f	6 s	6 p	6 d f	7 s	Highest valency
91 Et		2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	3	2	5
92 U		2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	4 (5)	2 (1)	6
93 En		2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	5 (6)	2 (1)	7
94 Eo		2	2	6	2	6	10	2	6	10	14	2	6	10		2	6	6 (7)	2 (1)	8

TABLE II

Group / Period	4	5	6	7	8			
4	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	
5	40 Zr	41 Nb	42 Mo	43 ..	44 Ru	45 Rh	46 Pd	
6	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	
7	90 Th	91 Et	92 U	93 En?	94 Eo?			

(1) A. V. Grosse, *Chem. Bulletin* of the Chicago Section of Amer. Chem. Soc., **20**, 15 (1933).

(2) I. Curie and F. Joliot, *Compt. rend.*, **198**, 254 (1934).

(3) E. Fermi, *Nature*, **133**, 757 (1934).

(4) A. V. Grosse and M. S. Agruss, *Phys. Rev.*, **46**, 241 (1934).

(5) I. and W. Noddack, "Das Rhenium," Leopold Voss, Leipzig, Germany, 1933.

(6) N. Bohr, *Z. Physik*, **9**, 1 (1922); *Ann. Physik*, **71**, 228 (1923); see also R. Swinne, *Z. tech. Physik*, **7**, 166, 205 (1926).

TABLE III

Element	Quantum numbers n / l	2 s	2 p	3 s	3 p	3 d	4 s	4 p	4 d	4 f	5 s	5 p	5 d	5 f	6 s	6 p	6 d	6 f	7 s	Highest valency
91 Et		2	2 6	2	6	10	2	6	10		2	6	10		2	6	3		2	5
92 U		2	2 6	2	6	10	2	6	10		2	6	10	1	2	6	4		1	6
93		2	2 6	2	6	10	2	6	10		2	6	10	2 (1)	2	6	4 (5)		1	5 (6)
94		2	2 6	2	6	10	2	6	10		2	6	10	3	2	6	4		1	5
95		2	2 6	2	6	10	2	6	10		2	6	10	4	2	6	4		1	5
etc.																				

ment will be bound in a lower quantum level and not be available as a valence electron.

We may assume that the filling of this lower quantum level has begun already in uranium; in this case the electron distribution would be given by Table III, according to the most reliable present knowledge.

Uranium would then correspond to cerium in the first group of rare earths and elements 93 and 94, also 95 and 96, etc., would all have properties very similar to element 91, just as the chemical properties of Pr, Nd, Sm, etc., are practically identical with La, and elements 93, and 94 in that case, would *not have* the properties of ekarhenium and ekaosmium.

It might also be that the filling up of the n_5 quantum level will begin at element 93, or 94, or even later; in the first case element 93 will be similar to uranium, just as Ce resembles La, and only in special cases resemble rhenium (like Ce ⟶ Zr).

A definite decision as to the real nature of these elements could be made after calculating the energy levels of the trans-uranium elements. For this purpose the energy levels of three last elements in the periodic table (Th, Et and U) should be known exactly. Unfortunately, the optical spectra of these elements have so far not yet been elucidated, due to their extreme complexity. We hope that the importance of these data for nuclear research may stimulate work in this direction.

Summary

The chemical properties of elements 93 and 94 are deduced (1) according to the periodic law and (2) according to the Bohr theory.

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[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

The Vapor Pressure of Binary Solutions of Ethyl Alcohol and Cyclohexane at 25°

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A previous investigation[1] indicated that solutions of ethyl alcohol in cyclohexane deviated widely from ideality. A further study of this system has been concerned with vapor pressure relationships. The total pressures and the partial vapor pressures of the components of solutions of ethyl alcohol and cyclohexane throughout the concentration range have been measured at 25°.

Materials

The ethyl alcohol and cyclohexane used in this investigation were obtained from the same sources and were purified by the same procedures as described in the previous investigation.[1] The resulting products were of the same quality as those there described. Merck C. P. silver nitrate was dissolved in redistilled water in preparing the solutions for the silver coulometer.

Method and Apparatus

Pearce and Snow's modification[2] of the air-bubbling method for measuring vapor pressure was adapted for this study. A mixture of hydrogen and oxygen, generated by the electrolysis of a 25% solution of sodium hydroxide contained in six large bottles, was saturated with the vapors of the mixtures under investigation. The amount of gas generated was calculated from the weight of silver deposited in a silver coulometer connected in series with the generators. The gas was dried with sulfuric acid before it entered the series of four bubblers, each of which contained from 8 to 10 cc. of the mixture being studied. The bubblers were connected in series by ground glass joints fitted with mercury seals. They were immersed in a constant temperature water-bath at the desired temperature. The vapors of the organic liquids were condensed out of the gas mixture in a tube immersed in a mixture of solid carbon dioxide and ether. Several determinations were made on alcohol rich mixtures and on pure alcohol using liquid air as the condensing medium.

The results thus obtained checked very closely those secured using solid carbon dioxide and ether and showed the latter condensing medium to be practically as efficient as the former.

The condensing tube was stoppered and weighed on an

(1) Vold and Washburn, THIS JOURNAL, **54**, 4217 (1932).
(2) Pearce and Snow, *J. Phys. Chem.*, **31**, 231 (1927).