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PREDICTION OF THE PROPERTIES AND OCCURRENCE OF ELEMENT 114

(Voraussage von Eigenschaften Und Vorkommen Des Elements 114)

By

P. Hoffmann and K. Bachmann

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PREDICTION OF THE PROPERTIES AND OCCURRENCE OF ELEMENT 114

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Using an extrapolation method the boiling point /910-1200 °C/, the heat of vaporization /23 - 29 kcal/mole/ and the entropy of vaporization /18.7 - 21.2 cal/mole. deg/ of element 114 were determined. Due to these results the geochemical behaviour and the enrichment or depletion resp. in technical processes are discussed.

On the basis of the prediction of a higher stability of the nucleus with 114 protons, a number of studies have appeared which deal with the chemical and physical properties of element 114 and its chemical compounds [1-7]. In part, they are based on theoretical calculations and in part on extrapolation. These studies have suggested a similarity of the properties of element 114 with those of lead and other homologs of the fourth main group of the periodic system. For this reason, element 114 was sought in nature where a lead or tin concentration had been found [8-17]. The object of the present study was to obtain concrete data on the possible geological properties of element 114 during the formation and extraction of minerals so that a specifically oriented exploration would be possible. The properties of element 114 which have been described in the literature to date and are used in this study are listed in Table 1.

The geochemical behavior of an element is determined by the following properties:

1) Simultaneous occurrence as sparingly soluble salts in accordance with chemical properties [18].

Table 1. Properties of element 114.

Description	Value	Lit.
Most probable state of oxidation	+2	5
Metallic radius (Å)	1.85 1.80	1 5
Boiling point (°C)	147 2840	1 3
Heat of vaporization (kcal/mol)	9	1
Vaporization entropy (cal/mol.degr.)	20	1
Standard enthalpy H°_{298} (kcal/mol)	16	4
Atomic volume (cm^3)	20	6
Electronegativity	1.36	6

Examples: a) Ag_8GeS_6 = argyrodite
b) $Ag_8(Ge,Sn)S_6$ = canfieldite
c) $PbSnS_2$ = teallite
d) PbS = galenite with Sn in the lattice
e) $Pb_2(Cu,Fe)_{21}S_{15}$ = betechtinite

2) Common occurrence according to similar atomic and ionic radii [18].

Examples: a) Occurrence of Ge in gersdorffite (atomic radii: Ge 1.37 Å, As 1.39 Å, Ni 1.24 Å)
b) Formation of solid solutions of Ag_2S and GeS_2 (atomic radii: Ge 1.37 Å, Ag 1.44 Å)
c) Possibility of ion substitution in crystal lattices
Ti^{4+} (0.68 Å) for Sn^{4+} (0.71 Å)
Ca^{2+} (0.99 Å) for Sn^{2+} (1.12 Å)
$2Zn^{2+}$(0.74 Å) for Sn^{4+} (0.71 Å)

3) Similar properties on the basis of the similar volatility of the elements or their compounds [19-23]. In this connection, Anders and Larimer have shown that the volatility of elements and their sulfides determines their incidence in meteorites (except for Hg).

If the above three properties are considered in relation with the problem to be discussed, the following statements can be made concerning the properties of element 114:

Re 1: On the basis of analogy considerations (provided that element 114 belongs to group IVa), one might expect a stable sulfide 114S, so that an association with lead and tin is possible in nature.

Re 2: If we consider the metallic radius of element 114 of 1.80 or 1.85 Å (see Table 1), it can be recognized that a substitution of lead (atomic radius 1.75 Å) as well as of thallium (1.71 Å) and bismuth (1.70 Å) by 114 should be easily possible. The indicated atomic and ionic radii were derived from literature [24].

Re 3: An evaluation of the classification of element 114 according to its volatility is not possible on the basis of available literature data (see Table 1) since these diverge greatly. For this reason we attempted to obtain additional volatility data with the use of a method which has proved useful in the determination of boiling points and other thermodynamic properties of alkyl compounds and hydrides [6].

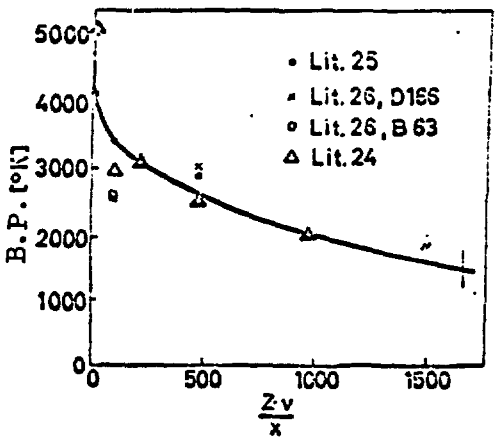

Fig. 1. Boiling points of the elements of main group 4 as a function of a quantity which is a composite of atomic number Z, atomic volume v and electronegativity x.

Fig. 1 shows the boiling points of the elements of the fourth main group [24-26] versus a quantity which is a composite of atomic number, atomic volume and electronegativity [6]. The curve resulting from this plot can be extrapolated and we thus obtain a boiling point of about 1200°C for element 114. A shortcoming of this plot resides in the marked scatter of data for carbon, silicon and tin, resulting in a high uncertainty in the extrapolation. We therefore used a second method in which the boiling point is calculated from the heat of vaporization and vaporization entropy (Trouton constant) of every element. For this purpose, the vaporization heats and entropies of the known elements were plotted against the same quantity which was used in Fig. 1 (Figs. 2 and 3). These plots show data scatter for all elements, so that no averaging was done; instead, the values from one literature source were connected by a curve, resulting in different values for element 114 in the extrapolation. Then new boiling points were calculated from the corresponding data for the heat and entropy of vaporization. The extrapolated and calculated values are compiled in Table 2. This table shows that although different extrapolated values are obtained as a function of the data set employed, the boiling points obtained, having values between 950 and 1200°C, are relatively similar.

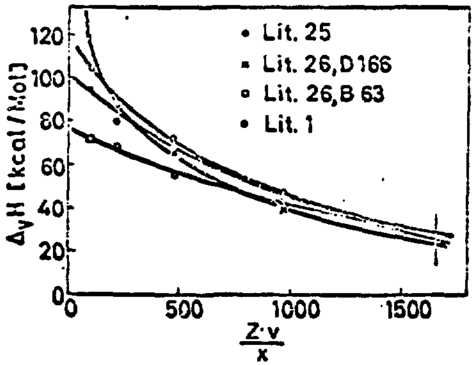

Fig. 2 Heats of vaporization of the elements of the fourth main group as a function of a quantity which is a composite of the atomic number Z, atomic volume v and electronegativity x.

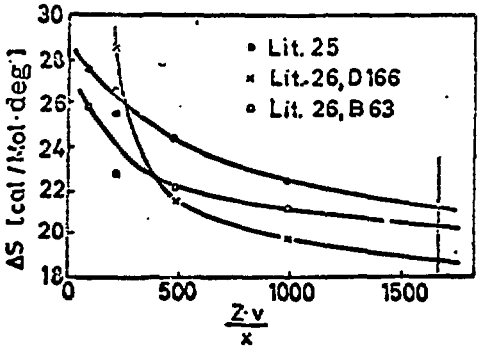

Fig. 3. Entropies of vaporization of the elements of the fourth main group as a function of a quantity which is a composite of the atomic number Z, atomic volume v and electronegativity x.

Table 2. Extrapolated values for the heat of vaporization, entropy of vaporization and boiling point of elements 114 and literature source for the data of the homologous elements used in the extrapolation.

Heat of vaporiz. /kcal/Mol/	Vaporiz. entropy /cal/Mol. deg/	B.P. /°C/	Literature
26	21,2	950	25
23	18,7	955	26
29	20,2	1150	26
28	-	-	1
-	-	1200	24,25,26

When this value is compared with the data of Anders and Goles [21], element 114 in terms of its volatility tends to the group Tl, Pb, Bi and In which is greatly depleted in chondrites.

According to the properties of element 114 discussed above, it seems indicated to consider it equivalent to Tl, Bi and Sb on the basis of its volatility, while Pb should be the preferential partner on the basis of chemical properties and the atomic radius of Pb. Since Pb has been assigned to the group containing Tl and Bi according to Anders [20, 21], it seems reasonable to search for element 114 in nature together with lead. More exact data could be offered if the theoretical frequency of occurrence of element 114 were known.

If we assume that in nature element 114 were preferentially enriched with lead, it would not necessarily have to be present in refined metallic lead, since ores are subjected to a number of reactions and extraction steps which take place at relatively high temperatures (600-1100°C). For example, cadmium and thallium can be found in an amount of about 75% in the flyash of the roasting and reduction process, while antimony, arsenic and tin are removed as oxides together with the slag.

On the basis of these considerations, it seems plausible that element 114 should be sought primarily in the flyash obtained in the lead production process; it is true that the other fractions, such as slag, speiss and rocks are also of some interest [16] since the chemical (reactivity) and physicochemical (volatility) properties of the oxides and sulfides of element 114 can be predicted only with great difficulty because inadequately exact data are available for the other elements of the fourth main group.

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