



Interatomic Interactions in Binary Plutonium Compounds

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ABSTRACT

Based on the reference data on the density of substances in a condensed state, calculations of the concentration of electrons, the concentration of nucleons and the compaction coefficient for binary plutonium compounds are presented. It is proposed to use the concentration of electrons and the concentration as the structural characteristics of materials. It is shown that the concentration of electrons and the concentration of nucleons are applicable to characterize the structures of substances: in solid, liquid and gaseous states. The use of correlation analysis showed the uniqueness of the compaction of plutonium trichlorides and tribromides.

Key words: electron concentration, plutonium, density, structure.

INTRODUCTION

Previously, the results of calculations of interatomic [1-9] and intermolecular [10-13] interactions described through changes in volumes were presented.

Chemical interactions and phase transformations are traditionally characterized by thermodynamic parameters and phase diagrams. The transformations of substances are accompanied by thermal effects and changes in volume. Density, an important characteristic of substances, is the result of two indicators: 1) the mass, which is concentrated in the nucleons of the atoms, and 2) the volume, which is formed by the electron shells.

Interatomic and intermolecular interactions lead to the formation of chemical bonds in compounds, and these new bonds determine the properties and structure of new substances. Interaction is a process that is characterized by a simultaneous mutual change in the characteristics of interacting material objects (in our case, atoms). These material objects (atoms) act on each other with different intensities, obeying certain laws, and reproduce new structures with high accuracy. Chemical bonding is a consequence of both interatomic and intermolecular interactions. The concept of composition is quite definite and does not cause confusion. The concept of structure is still controversial due to the choice of structural units. With an equal chemical composition, differences in the properties of substances are determined by the difference in structures. The structure is a consequence of two factors: chemical composition and energy content. An amorphous structure contains more stored energy than a crystalline one. A substance in a gaseous state contains more energy than a liquid.

Thermal processes are discussed in sufficient detail in numerous works on chemical thermodynamics, and information on volume changes is not enough.

Chemical bonding is a consequence of both interatomic and intermolecular interactions. The concept of composition is quite definite and does not cause confusion. The concept of structure is still controversial due to the choice of structural units. With an equal chemical composition, differences in the properties of substances are determined by the difference in structures. The structure is a consequence of two factors: chemical composition and energy content. Any solid substance can be converted into gaseous by heating. Any gaseous substance can be converted into a solid state by cooling. For all transitions, solid $\leftrightarrow$ liquid $\leftrightarrow$ gaseous composition of a substance can be unchanged, but the structure changes. The structure changes as a result of changing electron clouds. The electron clouds are directly responsible for the formation of the structure. The quantity "electron concentration" is introduced, which can be used as a structural characteristic of a substance. The "concentration of nucleons" along with the concentration of electrons determines the similarity and difference of substances.

The space occupied by matter is filled with nucleons and electrons. To estimate the space occupied by matter, it is convenient to use the indicators of electron concentration and nucleon concentration.

The concentration of electrons for homonucleon substances is determined by formula 1:

$$C_{electron} = \frac{d}{M} Z \quad (1),$$

Where $C_{electron}$ is for the concentration of electrons in a unit of volume, mole/cm³;

d is for substance density in the condensed state, g/cm³;

M is for molecular weight, g/mole;

Z is for the ordinal number of the element in the Periodic table.

For chemical compounds the electron density is determined through the following expression:

$$C_{electron} = \frac{\text{number of electrons in compound (in one mole)}}{\text{volume of mole of compound (condensed state)}} \quad (1a)$$

A_aB_b type compound has a concentration of electrons

$$C_{electron} \approx \frac{aZ_A + bZ_B}{M/d} \quad (2),$$

A compound of the A_aB_b type has a concentration of nuclei (regardless of their class)

$$C_{nuclei} = \frac{a+b}{M/d} \quad (3)$$

Metal alloys are not simple mixture of various components, but represent different chemical compounds of the elements forming the alloy. To estimate the depth of interaction between

atoms it is convenient to compare the volumes of substances before the reaction ($V_{component}$) and the volumes of substances after the reaction ($V_{product}$). The value obtained is then standardized to the finished product volume. The result (in %) characterizes the change in the volume of the substances in the course of reaction. This value can be designated as a coefficient of consolidation :

$$K_{consolidation} = \left(\frac{\sum V_{component} - V_{product}}{V_{product}} \right) \times 100\% \quad (4)$$

The coefficient of compaction can be either positive or negative. This means that the reaction product may have a volume smaller than the sum of the volumes of the original elements, and may be larger than the sum of the original volumes (loosening of the electron shells).

Table 1 shows examples of liquids under normal conditions and their structure calculated according to formulas 2 and 3.

Table 1. Structural characteristics of fluids under normal conditions.

liquid	Chemical formula	Electron concentration mole/cm ³	Nucleon concentration mole/cm ³
acetone	CH ₃ -C(O)-CH ₃	0.436	0.136
toluene	C ₆ H ₅ -CH ₃	0.470	0.141
benzene	C ₆ H ₆	0.473	0.135
methanol	CH ₃ OH	0.445	0.148

Table 2 shows examples of gases under normal conditions and their structure calculated according to formulas 2 and 3.

Table 2. Structural characteristics of gases under normal conditions.

gas	electron concentration mole/m ³	nucleon concentration mole/m ³
O ₂	713,9	89,24
H ₂	89,24	89,24
Ar	804,6	44.7
F ₂	803,2	89.24
Cl ₂	1517,1	89.24
Kr	1609,2	44.7
F ₂ O	1162,2	133.8
CF ₄	1877,4	223.5

*** Concentrations of electrons and nucleons in the table are normalized to cubic meter.**

The works [14, 15] show the relationship between the characteristic "electron concentration" and the mechanical properties of substances and compounds.

The aim of the present work was to identify the possibility of using the normalized magnitude of the volume change as a characteristic that makes it possible to estimate the intensity of interaction between heterogeneous atoms, and the concentration of electrons and the

concentration of atomic nuclei, determined in units of mole/cm³, as a value that makes it possible to evaluate the structure of the material.

METHODS

The coefficient of compaction can be either positive or negative. This means that the reaction product may have a volume smaller than the sum of the volumes of the original elements, and may be larger than the sum of the original volumes (loosening of the electron shells).

RESULTS

Table 3 shows the characteristics of binary plutonium compounds.

Columns 2, 3 and 4 are filled on the basis of calculations using formulas 4, 2a and 3 using the data from [16,17].

Column 5 is filled with data from [18].

Plutonium in the solid state has a volume of one mole of atoms of 13.7 cm³, an electron concentration of 7.642 mole/cm³, and a concentration of nuclei of 0.081 mole/cm³.

Table 3. Structural characteristics of binary plutonium compounds.

1	2	3	4	5
compounds	$K_{consolidation}$, coefficient of consolidation	% of Concentration of electrons in the compound $C_{electrons}$ mole/cm ³	Concentration of nuclei in the compound C_{nuclei} mole/cm ³	$-\Delta H_{298}^0$ kJ /mole
PuH ₂	73.8	4.14	0.173	140
PuH ₃	112.7	3.85	0.159	
PuH _{2.7}	116.4	4.22	0.162	
Be ₁₃ Pu	-5.9	1.78	0.171	
PuB ₂	10.3	5.00	0.144	
PuB	2.9	5.56	0.112	
PuB ₄	5.9	3.75	0.164	
PuB ₆	-1.2	2.96	0.167	
PuB ₁₂	9.5	2.44	0.206	
PuB ₆₆	-10.1	1.20	0.189	
PuC ₂	1.6	4.42	0.125	
PuC	6.2	5.57	0.112	
Pu ₂ C ₃	7.4	5.09	0.124	
PuN	32.5	5.68	0.113	
Pu ₂ O ₃	1.9	4.66	0.110	
PuO ₂	11.1	4.65	0.127	1058
PuO	9.0	5.56	0.109	
PuF ₆	14.9	2.53	0.112	1753
PuF ₄	-3.9	2.39	0.092	1734
PuF ₃	35.5	4.15	0.127	1552
Mg ₂ Pu	-30.1	1.98	0.050	
PuMg ₆	-24.5	1.29	0.054	

PuAl	-8.6	4.13	0.077	
AlPu ₃	-7.6	5.33	0.072	
Al ₂ Pu	-7.2	3.30	0.083	
Al ₃ Pu	-5.9	2.87	0.086	
Al ₄ Pu	-5.5	2.57	0.088	
PuSi ₂	14.0	3.77	0.093	
Pu ₅ Si ₃	-4.1	4.75	0.074	
Pu ₃ Si ₂	-5.8	4.54	0.073	
PuSi	-10.6	3.81	0.071	
Pu ₃ Si ₅	1.8	3.62	0.082	
PuP	0.4	4.03	0.074	
Pu ₂ S ₃	8.8	3.48	0.074	
PuS	14.3	4.31	0.078	
PuS ₂	18.2	3.33	0.079	
PuCl ₃	9.7	2.40	0.066	961
Pu _{0.6} Sc _{0.4}	-7.4	4.23	0.065	
PuMn ₂	-1.9	4.97	0.103	
Pu ₆ Fe	2.3	6.76	0.080	
PuFe ₂	0.4	5.25	0.108	
Pu ₆ Co	1.2	6.73	0.080	
Pu ₃ Co	-9.8	5.83	0.076	
Pu ₂ Co	-10.7	6.63	0.079	
Co ₁₇ Pu ₂	-4.0	4.41	0.130	
Co ₃ Pu	-4.8	4.94	0.113	
Co ₂ Pu	1.2	5.54	0.112	
PuNi	-12.8	5.24	0.086	
PuNi ₃	-5.0	5.04	0.113	
PuNi ₄	-4.1	4.93	0.120	
PuNi ₅	-5.2	4.75	0.122	
Pu ₂ Ni ₁₇	-2.8	4.63	0.132	
PuCu ₂	-13.1	4.73	0.093	
PuCu ₃	-11.7	4.56	0.101	
PuCu ₄	-14.8	4.26	0.101	
PuCu ₆	-12.8	4.14	0.108	
PuZn ₂	-8.7	4.39	0.085	
Pu ₂ Zn ₁₇	0.4	3.83	0.104	
Pu ₁₃ Zn ₅₈	-7.6	3.86	0.092	
Pu ₃ Zn ₂₂	-2.9	3.77	0.100	
Pu _{0.79} Zn _{0.21}	-4.2	6.05	0.075	
Pu _{0.25} Zn _{0.75}	-25.7	3.31	0.072	
PuGa ₃	5.5	4.01	0.086	
PuGa ₆	4.5	3.46	0.086	
PuGa ₄	7.5	3.84	0.088	
PuGa	-3.7	4.72	0.075	
Pu ₅ Ga ₃	-0.1	5.41	0.077	
PuGa ₂	-4.1	4.01	0.077	
Pu ₃ Ga	-4.0	5.68	0.073	
PuGe ₂	17.1	4.51	0.086	
Pu ₅ Ge ₃	-0.3	5.16	0.073	

Pu ₂ Ge ₃	-1.3	4.10	0.072	
PuAs	-11.4	4.20	0.066	
PuSe	3.0	4.37	0.068	
Pu ₃ Se ₄	4.7	4.09	0.069	
PuSe ₂	6.2	3.69	0.068	
Pu ₂ Se ₃	-1.0	3.74	0.064	
PuBr ₃	33.1	2.91	0.058	740
Pu ₂₈ Zr	1.6	6.83	0.74	
PuZr ₃	0.7	3.86	0.072	
PuRu	-5.2	6.02	0.087	
PuRu ₂	-5.4	5.79	0.095	
Pu ₃ Ru	-7.4	6.14	0.075	
Pu ₅ Ru ₃	-6.9	6.06	0.080	
Pu ₅ Rh ₃	-16.3	5.42	0.072	
Pu ₅ Rh ₄	-14.0	5.50	0.076	
PuRh ₂	-4.1	5.82	0.095	
PuRh ₃	-1.7	5.83	0.102	
Pu ₃₁ Rh ₂₀	-9.1	5.87	0.078	
Pd ₄ Pu ₃	-13.9	5.25	0.079	
Pd ₅ Pu ₃	-11.9	5.28	0.083	
Pd ₃ Pu	-2.9	5.60	0.097	
PuPd	-21.0	5.13	0.073	
PuAg _{3.64}	-7.8	4.78	0.084	
Ag ₅₁ Pu ₁₄	-9.9	4.57	0.082	
Cd ₆ Pu	-4.3	3.99	0.073	
Cd ₁₁ Pu	-2.4	3.87	0.075	
InPu ₃	-10.0	5.25	0.063	
InPu	-7.1	4.52	0.063	
In ₃ Pu	3.1	4.08	0.068	
PuSn ₃	0.6	4.09	0.067	
Pu _{0.225} Sn _{0.775}	-20.6	3.13	0.052	
Pu ₃ Sn	-8.1	5.38	0.065	
PuSn ₂	-1.7	4.24	0.066	
PuSb	-12,7	3,96	0,055	
PuSb ₂	1,2	3,95	0,061	
Pu ₂ Te ₃	-4,9	3,69	0,054	
PuTe ₃	3,2	3,45	0,055	
PuTe ₂	5.0	3.92	0.058	
PuTe	-4.2	4.10	0.056	
PuI ₃	2.2	2.85	0.045	560
Pr _{0.95} Pu _{0.05}	1.2	3.01	0.049	
Pu _{0.05} Sm _{0.95}	-1.2	3.21	0.050	
Gd _{0.80} Pu _{0.20}	-2.5	3.64	0.052	
Pu _{0.25} Tb _{0.75}	-3.3	3.90	0.054	
Ho _{0.06} Pu _{0.98}	8.1	7.14	0.077	
Hf _{0.06} Pu _{0.94}	2.3	6.93	0.075	
HfPu ₄	2.8	6.75	0.075	
HfPu ₂₈	0.2	6.83	0.073	
PuRe ₂	-5.4	7.36	0.091	

OsPu ₁₉	2.6	7.11	0.076	
Os _{2.6} Pu _{49.4}	2.4	7.09	0.076	
Os ₃ Pu ₅	-7.2	6.91	0.079	
PuOs ₂	-5.0	7.65	0.093	
PuIr ₂	-4.0	7.72	0.093	
Pu ₅ Ir ₃	-2.5	6.71	0.077	
Ir ₄ Pu ₅	-13.4	6.55	0.076	
Pu ₂ Pt	-17.5	6.01	0.068	
PuPt	-19.9	6.32	0.074	
PuPt ₂	-3.9	7.53	0.090	
PuPt ₃	-1.7	7.86	0.096	
PuPt ₄	-21.3	6.38	0.079	
PuPt ₅	-6.7	7.63	0.095	
Pu ₅ Pt ₃	-16.3	6.15	0.070	
Pu ₃₁ Pt ₂₀	-16.3	6.17	0.070	
Pu ₁₁ Hg ₄₅	5.0	5.96	0.072	
Pu ₃ Tl	-8.0	5.72	0.063	
PuTl ₃	-4.9	5.33	0.058	
Pu ₃ Pb	-7.3	5.61	0.062	
Pu ₅ Pb ₃	-11.2	5.16	0.058	
Pu ₅ Pb ₄	-7.7	5.21	0.059	
Pb ₅ Pu ₄	-4.4	5.14	0.059	
PuPb ₂	-0.2	5.08	0.060	
PuPb ₃	2.4	5.08	0.060	
PuBi	-9.2	4.59	0.052	
Pu ₇ Th ₃	3.8	5.98	0.064	
Pu ₃ U	-4.3	6.68	0.071	
PuU _{1.22}	8.0	7.69	0.083	
NpPu ₄	-1.5	6.96	0.074	
NpPu	-9.6	6.68	0.071	
Pu _{6.9} Np _{9.1}	5.5	7.88	0.084	
Pu _{0.5} Am _{0.5}	-4.7	5.72	0.061	

DISCUSSION

It follows from Table 1 that seals in binary plutonium compounds have a minus sign. This can be interpreted as the low reactivity of plutonium.

Considering interatomic interactions, it should be noted that in different combinations the volumes of interacting atoms vary differently. In [1-6], a correlation was established between the coefficient of compaction and the thermodynamic characteristics. The established correlations indicated the patterns of chemical transformations.

The presented results for plutonium halides show no correlation between heat effects and compaction. It turns out that the interaction of plutonium with bromine is more intense than with chlorine (by compaction). At first glance, this may be an incorrect calculation of volumes. Thermal effects decrease monotonically from fluorine to iodine. Verification of the calculations for uranium and thorium chlorides and bromides showed the same effect. Compaction is more intense in bromides than in chlorides. A check of the calculations for lanthanide chlorides and

bromides showed that the same effect appears for these compounds. It is clear that the calculations are correct with a high degree of probability. It is not yet possible to give a logical explanation for the established fact on the basis of existing information.

Comparison of the volumes of substances before and after reaction makes it possible to reveal the interaction of atoms and molecules more fully than thermal effects permit.

It is more convenient to consider the structure of the crystalline state through indices that can characterize the space filled with atomic nuclei and electrons. The nuclei of atoms form the skeleton of the structure, and the electrons form the interaction between the atoms.

Presented in tables 1, 2, 3, the concentration of electrons and the concentration of nucleons of atoms are able to reflect the differences and similarities in the structures of substances.

CONCLUSIONS

1. The results of the normalized characteristics of the change in volumes in binary plutonium compounds are presented.
2. It is proposed to use density as one of the quantities capable of characterizing the interaction of atoms in a condensed system to evaluate the properties of substances.
3. Coefficients of compaction can be used as relative chemical potentials for elements entering into chemical compounds.
4. It is proposed to use the values of the electron concentration and the concentration of the nuclei of the atoms of the compounds, defined in units of mole/cm³, as the structural characteristics of the material.
5. To evaluate the degree of interaction of the initial components during the formation of the compound, it is suggested to use the compaction factor.

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