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Thermodynamics of actinide redox reactions in potassium phosphotungstate solutions

E.A. Erine*, A.A. Baranov, A.Yu. Volkov, V.M. Chistyakov, G.A. Timofeev

State Scientific Centre, Research Institute of Atomic Reactors, 433 510 Dimitrovgrad-10, Ulyanovsk, Russia

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Abstract

The paper represents the results of the investigation of kinetics and thermodynamics of the M(IV) reduction reactions (M=Am, Cm, Bk, Cf) and also those of the Am(V) disproportionation reaction and the reaction between Am(V) and Am(III) in aqueous solutions of potassium phosphotungstate, $K_{10}P_2W_{17}O_{61}$ (KPW). From experimental data the thermodynamic parameters of activated complex formation for the M(IV) ions reduction process through the chemical route have been calculated. Linear correlation has been ascertained between the $\Delta G^{\neq}_{298}$ values and the oxidation potentials of the M(IV)–M(III) pairs in KPW solutions and on this basis the estimation of the $\Delta G^{\neq}_{298}$ values has been made for U, Pu and Np. In the case of the Am(V) disproportionation and the reaction of the interaction between Am(V) and Am(III) ions the enthalpy component introduces the main contribution into the $\Delta G^{\neq}_{298}$ change. At the same time the contribution of the entropy component into the $\Delta G^{\neq}_{298}$ change in KPW solutions is considerably lower than for perchloric acid solutions. © 1998 Published by Elsevier Science S.A.

Keywords: Actinides; Phosphotungstate; Redox behaviour

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1. Introduction

Up to the present numerous papers on the study of actinide in KPW solutions have been published [1–6]. However, experimental data concerning the thermodynamic parameters of these elements transformation processes in KPW solutions are practically absent.

This work is concerned with the results of the investigation of kinetics of the M(IV) reduction reactions (M=Am,Cm,Bk,Cf) and also with the Am(V) disproportionation reaction and with the interaction between Am(V) and Am(III) in KPW aqueous solutions at different temperatures. On this ground the calculations of the thermodynamic parameters of formation of appropriate activated complexes have been carried out.

2. Experimental

The utilized preparations of Am, Cm, Bk and Cf, the methods of their production in tetravalent and in pentavalent state for Am, the procedure of spectrophotometric measurements were such as in [3–5]. The studies were carried out using the following initial concentrations: $[KPW]=6\times10^{-3}$ M; $[M]=(0.5–1.5)\times10^{-3}$ M; pH=3.0; Fig. 1 shows the effective rate constant of tetravalent Am, Cm, Bk and Cf ions reduction as a function of temperature with these conditions.

The investigation of the influence of temperature on the rate of reduction–oxidation reactions was performed in the temperature interval 25–50°C with an error of +0.2°C. From obtained values of activation energy (E_{act}) and reaction rate constants changes of the Gibbs free energy ($\Delta G^{\neq}_{298}$), enthalpy ($\Delta H^{\neq}$) and entropy ($\Delta S^{\neq}$) of activated complex formation were calculated using known Arrhenius and Eiring equations.

3. Results and discussion

3.1. The thermodynamics of the reduction reaction of tetravalent Am, Cm, Bk and Cf species

Previously in [3,4] we showed that tetravalent ions M(IV) (M=Am, Cm, Bk, Cf) are reduced to trivalent state in KPW solutions. This process is described by the rate equation

$$-\mathrm{d}[M(IV)]/\mathrm{d}t = k_0 + k_1[M(IV)] \tag{1}$$

where [M] is a current concentration of tetravalent species.

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*Corresponding author. Tel. (7-84235) 35801; fax: (7-84235) 35648.

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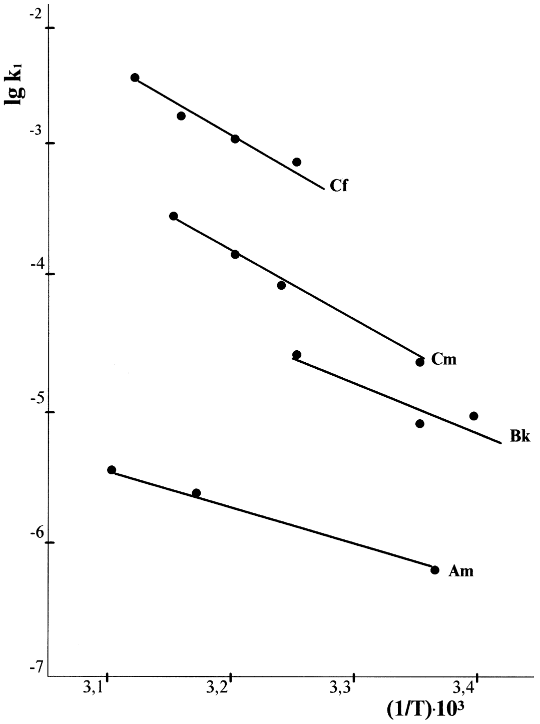

Fig. 1. Effective rate constant of tetravalent Am, Cm, Bk and Cf ions reduction as a function of temperature. [KPW]$=6\times10^{-3}$ M; [M]$=(0.5$–$1.5)\times10^{-3}$ M; pH$=3.0$.

Thus, the reduction of the M(IV) ions takes two parallel courses: a radiation–chemical (k_0) and a chemical one (k_1). Investigations have been performed of reaction rate of the M(IV) ions reduction through the chemical route at different temperatures. It is determined that the values of k_1 obtained by experiment fall well on straight lines in coordinates 'log $k_1 - 1/T$'. The thermodynamic parameters of activated complex formation for the chemical step of reduction of the tetravalent Am, Cm, Bk and Cf ions are calculated according to [7] and are presented in Table 1. It can be seen that the contributions of energetic and structural components to the $\Delta G298^{\neq}$ change for the examined elements are different. It should be noted that in the case of the reduction of the Am and Bk ions $\Delta S^{\neq}$ has a negative value and in the case of the Cm and Cf ions $\Delta S^{\neq}$ has a positive value. A considerable contribution of the $\Delta S^{\neq}$ value to the $\Delta G^{\neq}_{298}$ change for the Am, Cm, Bk and Cf ions testifies to the essential structural change in the process of their reduction.

Table 1

Thermodynamic parameters of activation complex formation in reaction of M(IV) reduction to M(III) by chemical route in KPW solutions ([KPW]$=6\times10^{-3}$ M, [M]$=(0.5$–$1.5)\times10^{-3}$ M, pH$=3.0$)

Element	Parameter			
	E_{act} kJ mol^{-1}	$\Delta G^{\neq}_{298}$ kJ mol^{-1}	$\Delta H^{\neq}$ kJ mol^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
Am	69.5	109.0	67.0	−140
Cm	101.5	95.5	99.0	+8
Bk	72.7	102.0	70.2	−106
Cf	111.0	88.7	108.5	+66

The analysis of the thermodynamic values shows that in the row of elements Am–Cm–Bk–Cf there is a linear correlation between activation entropy and activation enthalpy (Fig. 2).

$$\Delta H^{\neq} = \Delta H_0^{\neq} + T_0\Delta S^{\neq} \tag{2}$$

It may signify that the same reaction lies in the base of chemical step of the reduction of M(IV) to M(III) ones. Interaction between the M(IV) ions and water molecules appears to take place in the present case.

$$M^{4+} + \tfrac{1}{2}H_2O = M^{3+} + H^{+} + \tfrac{1}{4}O_2 \tag{3}$$

The course of this reaction was experimentally found out in the work [8] in the investigation of Am(IV) reduction in phosphoric acid solution.

Using experimental values of activation free energy $\Delta G^{\neq}_{298}$, obtained for Am, Cm, Bk and Cf, and values of real oxidation potentials (E^{r}_0) of the pair M(IV)–M(III) we plotted $\Delta G^{\neq}_{298}$ as a function of E^{r}_0 (Fig. 3). The values E^{r}_0 for Am ($E^{\text{r}}_0=1.38$ V) and Bk ($E^{\text{r}}_0=0.68$ V) were determined by experiment for concentrations KPW$=6\times10^{-3}$ M, [M]$=1.5\times10^{-3}$ M and pH$=3.0$ [9]. The values of E^{r}_0 for Cm and Cf were estimated using potential displacement by 0.95 V to the negative side relative to the values of the standard potentials of aqua-ions [1,10,11]. By extrapolation of this relationship to the side of the values for Pu (E^{r}_0 is taken from [2]) and also for Np and U (E^{r}_0 are obtained from the displacement analogous to Cm and Cf) the values of the $\Delta G^{\neq}_{298}$ were estimated for the above mentioned

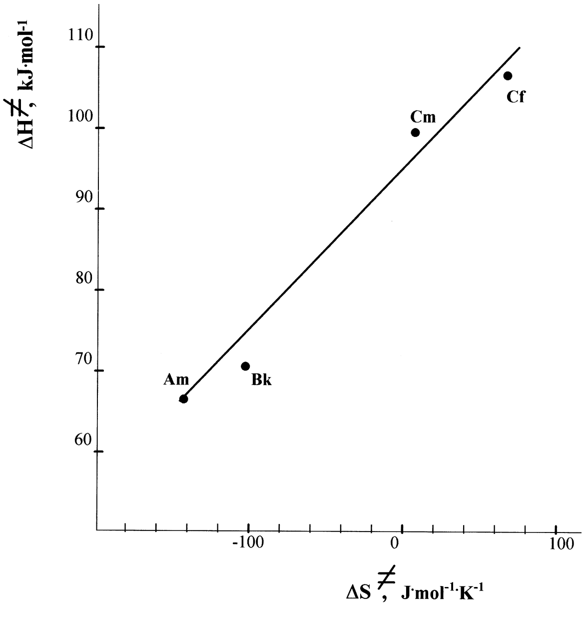

Fig. 2. Relationship between activation entropy $\Delta S^{\neq}$ and activation enthalpy $\Delta H^{\neq}$ of chemical step of tetravalent Am, Cm, Bk and Cf ions reduction.

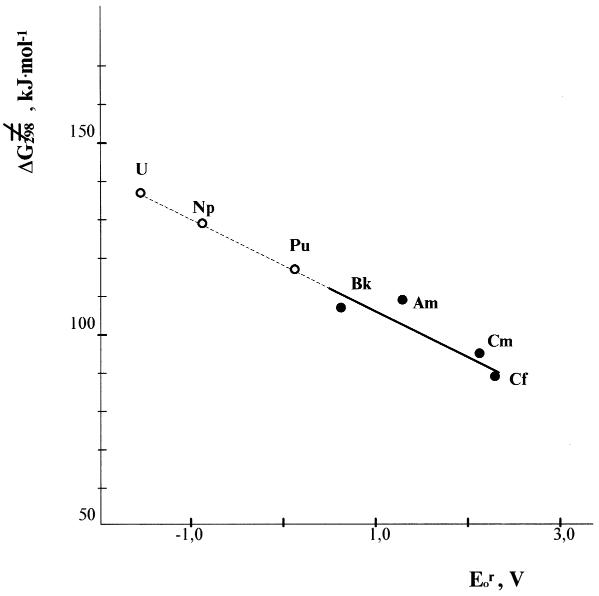

Fig. 3. Dependence of $\Delta G^{\neq}_{298}$ on the M(IV)–M(III) pair oxidation potential.

elements. From the obtained data it can be seen that the stability of the activated complex, formed by M(IV), increases in the row from Cf to U. The confirmation of the present assertion is the fact observed by experiment: in the air in KPW solutions trivalent Np spontaneously oxidizes to tetravalent state in several minutes.

3.2. Thermodynamics of reactions in KPW solutions with Am(V) species participation

In investigating the behaviour of the Am(V) ions in KPW solutions it is established that the reaction of its disproportionation proceeds in the pH range 1.0-4.0 [5]:

$$2\mathrm{Am(V)} = \mathrm{Am(IV)} + \mathrm{Am(VI)} \qquad (4)$$

However, as distinct from mineral acid solutions, where the reaction Eq. (4) proceeds in accordance with the second-order rate law relative to the Am(V) concentration, in KPW solutions kinetic curves of decrease of the Am(V) concentration are described by the equation

$$-\,\mathrm{d}[\mathrm{Am(V)}]/\mathrm{d}t = k_2[\mathrm{Am(V)}] \qquad (5)$$

An intramolecular transformation of the Am(V) in phosphotungstate complex was assumed to be the rate-determining step of the spontaneous transition of the Am(V) to different valent forms in KPW solutions [5]. Thus, the transformation of the Am(V) ions in KPW solutions and in mineral acid solutions takes different mechanisms. On this view it was of interest to study the thermodynamics of the conversion of the Am(V) in KPW solutions.

The thermodynamic parameters of the activated complex formation for the reaction Eq. (4) are given in Table 2. Data obtained for the Am(V) disproportionation in perchloric acid are also presented here for comparison [12]. It is seen that for the reaction Eq. (4) in KPW and $HClO_4$ solutions the $\Delta G^{\neq}_{298}$ values are different. In both systems the main contribution into the Gibbs energy change introduces the energy component. At the same time in perchloric acid solutions the contribution of the structural component $\Delta S^{\neq}$ into the $\Delta G^{\neq}_{298}$ is considerably higher than for KPW solutions. Consequently, in KPW aqueous solutions the Am(V) occurs in the form which is different on reactivity from the form of its existence in mineral acid solutions. This reason may account for the difference of the Am(V) transformation reaction in indicated media.

Special features of a reaction mechanism were also noted in studying the Am(V) reproportionation reaction [13] where the Am(V) was one of the reactants. If at first the Am(III) ions are introduced in a KPW solution and then the Am(V) ions are, direct interaction is going on according to the stoichiometric equation

$$\mathrm{Am(III)} + \mathrm{Am(V)} = 2\mathrm{Am(IV)} \qquad (6)$$

Different results are obtained if the sequence of the reactants introduction is changed. In this case, as kinetic investigations showed, the formation of the Am(IV) is the result of two consecutive reactions: the reaction of the Am(V) disproportionation and the reaction of the interaction of hexavalent americium, forming by the reaction Eq. (4), with trivalent americium, i.e.

$$2\mathrm{Am(V)} = \mathrm{Am(IV)} + \mathrm{Am(VI)} \qquad (7)$$

Table 2
Thermodynamic parameters of activation complex formation in reactions with Am(V) ions participation

Reaction	Parameter			
	E_{act} kJ mol^{-1}	$\Delta G^{\neq}_{298}$ kJ mol^{-1}	$\Delta H^{\neq}$ J mol^{-1} K^{-1}	$\Delta S^{\neq}$ J mol^{-1} K^{-1}
Am(V) disproportionation[a]	88	90.3	85.5	−16.5
Am(V)+Am(III)[a]	86	85.5	83.5	−6
Am(III)+Am(V)[a]	97	84.5	94.5	+34
Am(V) disproportionation[b]	81	100.8	78.5	−76

[a] [KPW]=6×10^{-3} M, [M]=(0.5–1.5)×10^{-3} M, pH=3.0.

[b] Perchloric acid, 4 M.

$$\mathrm{Am(VI)} + \mathrm{Am(III)} = \mathrm{Am(V)} + \mathrm{Am(IV)} \quad (8)$$

giving rise to

$$\mathrm{Am(V)} + \mathrm{Am(III)} = 2\mathrm{Am(IV)} \quad (9)$$

In both cases the first-order reaction relative to the Am(III) or Am(V) current concentration is the step which determines the observed rate of the Am(IV) accumulation. Observed from kinetic studies, characteristic properties of the Am(V) and Am(III) interaction mechanism depending on the reactants sequence must be reflected in the thermodynamic parameters of the reactions Eqs. (6) and (9).

The results of these investigations are summarized in Table 2. One can see that the Gibbs free energy change for the reactions Eqs. (6) and (9) are approximately equal and sufficiently close to the $\Delta G^{\neq}_{298}$ value of the reaction Eq. (4). The main contribution in the $\Delta G^{\neq}_{298}$ change introduces an energy component. The entropy variation in the case of the reaction Eq. (9) has a negative value which is comparable to that of $\Delta S^{\neq}$ for the Am(V) disproportionation reaction in KPW solutions. The $\Delta S^{\neq}$ proximity to zero indicates that appreciable structural changes in the process of the reactions Eqs. (4) and (9) are not realized. Another picture is observed in the case of the reaction Eq. (6): the entropy change is considerably higher than zero and has a positive value.

The obtained results signify that different complex forms of americium and activated complexes of different composition are apparently generated in KPW solutions depending on the Am(V) and Am(III) introduction sequence.

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