THE ELECTRON AFFINITY OF UO$_3$

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The ion-molecule equilibria method was applied to study negative ions while U$_3$O$_8$ being vaporized. No UO$_3^-$ ions were found. It have led to the conclusion that the electron affinity of UO$_3$ is less than 205 kJ·mol^{-1}. That is in complete contradiction with the Gurvich's prediction EA(UO$_3$) = 500±50 kJ·mol^{-1}.

Molecules with high electron affinity change a lot the properties of slightly ionized gases. They form stable negative ions and make lower the electron concentration and the plasma frequency. At the same time this effect depends on the bond dissociation energy of the molecule either. The

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figure 1 demonstrates that fact using the results of the simple model calculation [1].

The table 1 shows some data for the molecules with high electron affinities. The transition metal fluorides have got the highest electron affinity while their bond dissociation energies are quite small. It makes that in real systems oxides change the electron concentration stronger than fluorides.

The uranium oxide lies aside from other molecules in table 1. High electron affinity 500 ± 50 kJ·mol^{-1} with its high dissociation energy places it out of competition. Based on that value of the electron affinity of UO_3 Magill et al [2] came to conclusion that concentration of charged particles in the vapors over UO_2 at temperatures higher than 2000 K would be about 30 %.

The electron affinity of UO_3 given was estimated in the reference book [3] (also see [4]). They got it while comparing the electron affinities of fluorides and oxides of molybdenum, tungsten and uranium and the procedure looks quite reasonable.

There are no any experimental data on thermodynamics of the negative ion UO_3^-. Plog et al [5] and Middleton [6] mentioned that UO_3^- has been seen by SIMS of uranium oxides.

EXPERIMENTAL

The work is carried out on the magnet mass spectrometer MKh-1303 (60°, 200 mm), adapted to study ion-molecule

equilibria. A platinum effusion chamber (12 mm x 12 mm) was used with (0.5 to 1.2 mm) effusion orifice. The temperature was measured with a Pt-Pt/Rh (10 %) thermocouple, the accuracy being ±4 K. Ionic currents were measured with a channel electron multiplier VEU-6. The substances U_3O_8, Cr_2O_3, V_2O_5 of chemical grade purity were used. The oxide V_2O_3 was synthesized with reduction of V_2O_5 by hydrogen.

The ratio of the partial pressures of ions is calculated from measured ion currents as follows

$$\frac{p(A^-)}{p(B^-)} = \frac{I(A^-)}{I(B^-)} \left\{\frac{M(A^-)}{M(B^-)}\right\}^{1/2} \frac{\gamma(B^-)}{\gamma(A^-)} \frac{i(B^-)}{i(A^-)}$$

where I is a measured ion current with multiplier, M is mass of the ion, γ is the multiplier gain, and i is the isotope abundance. The multiplier gain is assumed to be inversely proportional to a square root of ion mass.

NEGATIVE IONS IN THE VAPORS OF U_3O_8

Recently we have found that addition of small amounts of potassium chromate increases the electron concentration in the vapors of transition metal oxides and allows to register at 1400 K such negative ions as PtO_2^- [7], NiO_2^-, CoO_2^- [8], FeO_2^- [9], MnO_2^-, MnO_3^-, MnO_4^-, VO_3^-, $V_3O_8^-$, $V_4O_{10}^-$ [1].

In this work the results of application of ion-molecule equilibria method to study vapors of U_3O_8 are described. Preliminary calculations showed that if the electron affinity of UO_3 would be 500 kJ·mol^{-1}, then the

concentration of ions UO_3^- in the vapors of uranium oxide should be much higher than the experimental sensitivity level.

Uranium oxide with small additives was investigated, experiment I - {85.9 U_3O_8 + 4.7 K_2CrO_4 + 9.4 Cr_2O_3}, experiment II - {98.9 U_3O_8 + 0.5 K_2CrO_4 + 0.6 V_2O_3}. The composition is given in mole percent.

Negative ions found were as follows: CrO_3^- (10 000), CrO_4^- (14.6) in experiment I; VO_3^- (1.3), $V_3O_8^-$ (500), $V_4O_{10}^-$ (1000) in experiment II. Relative intensities at 1400 K are given in brackets.

Ion UO_3^- (mass number 286) has not been found. Yet from experimental data it is possible to estimate the upper limit of UO_3^- concentration. We assumed that ion current of UO_3^- is less than measured signal at mass number 286.

The partial pressure of oxygen and the upper limit of $\dfrac{I(UO_3^-)}{I(CrO_3^-)}$ were computed in the experiment I (see table 2). The partial pressure of oxygen is determined from the ratio of ion currents CrO_3^- and CrO_4^-
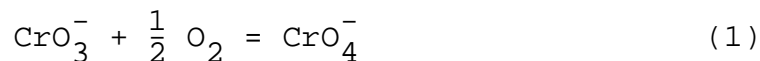
$$\{p(O_2)/p^O\}^{1/2} = \frac{p(CrO_4^-)}{p(CrO_3^-)} \frac{1}{K^O(1)}$$

Thermodynamic data of CrO_3^- and CrO_4^- were taken from ref. [10] to get numerical values of equilibrium constants $K^O(1)$ *

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* The standard state p^O = 101325 Pa is used

of the reaction

$$CrO_3^- + \frac{1}{2} O_2 = CrO_4^- \tag{1}$$
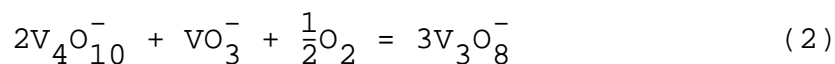
The partial pressure of oxygen, the activity of V_2O_3 and the upper limit of $\dfrac{I(UO_3^-)}{I(VO_3^-)}$ were estimated in the experiment II (see table 3). The partial pressure of oxygen results from the ratio of ion currents $V_3O_8^-$, VO_3^-, $V_4O_{10}^-$ as follows

$$\{p(O_2)/p^o\}^{1/2} = \frac{p^3(V_3O_8^-)}{p(VO_3^-)\ p^2(V_4O_{10}^-)}\ \frac{1}{K^o(2)}$$

were $K^o(2)$ is the equilibrium constant of the reaction

$$2V_4O_{10}^- + VO_3^- + \frac{1}{2}O_2 = 3V_3O_8^- \tag{2}$$

The activity of V_2O_3 is obtained on the same way

$$a(V_2O_3) = \frac{p(VO_3^-)\ p^4(V_4O_{10}^-)}{p^5(V_3O_8^-)}\ \frac{1}{K^o(3)}$$

were $K^o(3)$ is the equilibrium constant of the reaction

$$V_2O_3(s) + 5V_3O_8^- = 4V_4O_{10}^- + VO_3^- \tag{3}$$
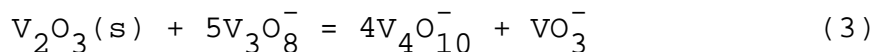
To get numerical values of $K^o(2)$ and $K^o(3)$ the experimental data from Kaibicheva's thesis [11] were used. We are going to publish them elsewhere.

It might be mentioned that other examples of determining the oxygen partial pressure by ion-molecule equilibria can be found in ref. [12].

ESTIMATION OF THE ELECTRON AFFINITY OF UO_3

To estimate an electron affinity by the equilibrium method the relation is used as follows

$$EA(UO_3) = -\Delta_r H_0^O(1) = T\{R \ln K^O(5) - \Delta_r \Phi^O(5)\} \qquad (4)$$

where $K^O(5)$ is the equilibrium constant of the reaction

$$UO_3 + e = UO_3^- \qquad (5)$$

The equilibrium constant $K^O(5)$ is a product of the partial pressure of UO_3 and the ratio $p(UO_3^-)/p(e)$. To estimate the latter ions emerging from additive are used – CrO_3^- in the first experiment and VO_3^- in the second one. Thermodynamic properties of these ions are known (see table 5) and in this work they will be employed as ion-standards. It means that it is possible to compute equilibrium constants of the reactions

$$\tfrac{1}{2} Cr_2O_3(s) + \tfrac{3}{4} O_2 + e = CrO_3^- \qquad (6)$$

$$\tfrac{1}{2} V_2O_3(s) + \tfrac{3}{4} O_2 + e = VO_3^- \qquad (7)$$
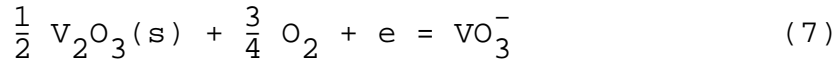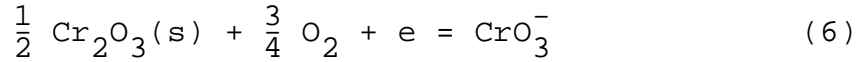
from the literature data. Using $K^O(6)$ and $K^O(7)$ one can eliminate the partial pressure of electrons and as the result we have

$$\frac{p(UO_3^-)}{p(e)} = \frac{p(UO_3^-)}{p(CrO_3^-)} \; K^O(6) \; \{p(O_2)/p^O\}^{3/4} \; \mathbf{a}(Cr_2O_3)^{1/2}$$

in the experiment I and

$$\frac{p(UO_3^-)}{p(e)} = \frac{p(UO_3^-)}{p(VO_3^-)} \; K^O(7) \; \{p(O_2)/p^O\}^{3/4} \; \mathbf{a}(V_2O_3)^{1/2}$$
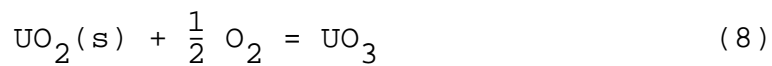
in the experiment II.

To estimate partial pressures of UO_3 the literature data on thermodynamics of uranium oxides were used. It has been supposed that the admixture of chromium oxide and vanadium oxide should not change the activity of the chief ingredient in large extent. While being heated U_3O_8 becomes

nonstoichiometric U_3O_{8-z} and later on is converted to lower oxides. At temperatures lower than 1400 K firstly U_3O_{8-z} is changed to U_4O_{9-y}, and then to UO_{2+x}. At temperatures upper than 1400 K U_3O_{8-z} instantly goes to UO_{2+x}. Thermodynamics of all these phases is well known [3, 13-21], while satisfactory agreement seeing among different authors.

The figure 2 presents the stability diagram of uranium oxides as a function of the partial pressure of oxygen in the system. Last experimental data of Nakamura & Fujino [20] are used for UO_{2+x}. Comparison with previous works is given in ref. [20]. The lines of heterogeneous equilibria between UO_{2+x}, U_4O_9 and U_3O_8 are taken from Kotlar et al [13]. The experimental oxygen partial pressures are also given on this picture.

Thus measurement of oxygen partial pressures in the course of the experiment allows to monitor the composition of uranium oxides. Having compared the experimental oxygen partial pressures and the stability diagram one may conclude that in the experiments U_3O_8 decomposed with formation of UO_{2+x}, where $x \approx 0.2$. Notice that the same way was used in investigation of negative ions in the vapors of nonstoichiometric Fe_3O_{4+x} [9].

Let us express the partial pressure of UO_3 with the help of the equilibrium constant of the reaction

$$UO_2(s) + \frac{1}{2} O_2 = UO_3 \qquad (8)$$

Along with relation for $p(UO_3^-)/p(e)$ it gives the final result

$$K^O(5) = \frac{p(UO_3^-)}{p(CrO_3^-)} K^O(6) \ K^O(8)^{-1} \ *$$

$$\{p(O_2)/p^O\}^{1/4} \ \mathbf{a}(Cr_2O_3)^{1/2} \ \mathbf{a}(UO_2)^{-1} \qquad\qquad (9a)$$

for the experiment I and

$$K^O(5) = \frac{p(UO_3^-)}{p(VO_3^-)} K^O(7) \ K^O(8)^{-1} \ *$$

$$\{p(O_2)/p^O\}^{1/4} \ \mathbf{a}(V_2O_3)^{1/2} \ \mathbf{a}(UO_2)^{-1} \qquad\qquad (9b)$$

for the experiment II.

The equations (9) express the equilibrium constant of the reaction (5) through the experimentally measured quantities. Substituting $K^O(5)$ to the equation (4) one can get the electron affinity of UO_3.

It should be mentioned that it might be possible to use the other way besides the equations (9) and (4). As the example the first experiment will be used. The equilibrium constants and the enthalpy of reaction

$$UO_2(s) + CrO_3^- = UO_3^- + \tfrac{1}{4} O_2 + \tfrac{1}{2} Cr_2O_3(s) \qquad\qquad (10)$$
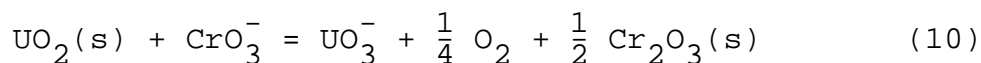
might be obtained from the same experimental data as used in the equation (9). Then the electron affinity of UO_3 may be evaluated as follows

$$EA(UO_3) = \Delta_f H_0^O(UO_3) - \Delta_r H_0^O(10) - \Delta_f H_0^O\{UO_2(s)\}$$

$$- \Delta_f H_0^O(CrO_3^-) + \tfrac{1}{2} \Delta_f H_0^O\{Cr_2O_3(s)\}$$

Such two ways are equivalent and give completely the same results.

Table 4 presents the calculations according formulas

(9). The upper limits, the oxygen partial pressure and activity of V_2O_3 are computed from the experimental data (see tables 2 and 3). To determine the activity of chromium oxide by ion-molecule equilibria it is necessary to get ion current of $Cr_2O_6^-$ [22]. In present work ion $Cr_2O_6^-$ was absent and it was assumed that $\mathbf{a}(Cr_2O_3) < 1$. It gives even stronger inequality for the upper limit $K^O(5)$. The equilibrium constants of the reactions (6)-(8) are evaluated from literature thermodynamic data showed in table 5.

To estimate the activity of UO_2 the Gibbs-Duhem equation for UO_{2+x} phase

$$d \ln \mathbf{a}(UO_2) + \frac{x}{2} d \ln p(O_2) = 0$$

was applied. Thus

$$\ln \mathbf{a}(UO_2) = - \int_0^x \frac{x}{2} d \ln p(O_2)$$

Measuring the oxygen partial pressure allowed to estimate nonstoichiometry index of uranium dioxide UO_{2+x} formed out of U_3O_8 ($x \approx 0.2$, see figure 2). Yet for bigger reliability the lower limit of UO_2 activity was estimated. It corresponds the heterogeneous equilibrium between UO_{2+x} and U_3O_8 ($x = 0.245$ at 1430 R and $x = 0.25$ at 1515 R [18]). Dependence of $\ln p(O_2)$ from x in the range $x > 0.003$ is taken from ref. [20], and in the range $0 < x < 0.003$ is approximated by the straight line.

The upper limit of the equilibrium constants of the reaction (5) brings to the upper limit of the electron

affinity of UO_3. The free energy functions of UO_3, UO_3^- and electron are taken from the reference book [3]. The first experiment shows that the electron affinity of UO_3 is less than 205 kJ·mol^{-1} and the second experiment does EA(UO_3) < 325 kJ·mol^{-1}. As a recommended value we chose the lower one EA(UO_3) < 205 kJ·mol^{-1}.

DISCUSSION

Thus our experimental results - absence of negative ion UO_3^- in the vapors of uranium oxides - show that the electron affinity of UO_3 is at least on 295 kJ·mol^{-1} less than as estimated in the reference book [3].

The difference in an enthalpy on 295 kJ·mol^{-1} leads to the difference in an equilibrium constant at 1400 K on 10^{11} times. Nothing in the formula (9) couldn't bear such error. The error propagation law shows that inaccuracies of the literature thermodynamic data in table 5 gives inaccuracies as follows $\Delta\{\ln K^O(6)\}$ = 1.0, $\Delta\{\ln K^O(7)\}$ = 1.2, $\Delta\{\ln K^O(8)\}$ = 1.4 at 1400 K. It means the inaccuracy of the equilibrium constants $K^O(6)$, $K^O(7)$, $K^O(8)$ is about three - four times. The errors of the partial pressure of oxygen and of the estimated UO_2 activity obtained are also not bigger than several times.

The only possibility to get an error as high as eleven orders of magnitude is to suggest full absence of equilibrium in the systems under study. Such hypothesis couldn't be ruled out but it seems to be quite improbable.

We observed non equilibrium while studying systems of cobalt and nickel oxides with potassium sulfate [8]. Yet it was easily detected due to time and composition dependence of the apparent equilibrium constants. In the present case potassium chromate with chromium oxide or vanadium oxide were used as additives. The same admixture was applied to study negative ions in the vapors of some transition oxides - nickel and cobalt oxides [8], iron oxide [9], manganese and vanadium oxides [1]. Worthy of notice is that the conditions of the experiments were about the same. In all cases negative ions produced from molecules with the electron affinity of about 250 kJ·mol^{-1} were found but not UO_3^-. It is hard to imagine that vaporization of uranium oxides so different that the negative ion of the molecule with the electron affinity 500 kJ·mol^{-1} couldn't be registered.

To show it more clearly let us roughly estimate $K^O(5)$ by the straight way. Pure stoichiometric UO_2 have got quite low work function 298 kJ·mol^{-1} [22-24] and it should be quite high concentration of electrons $1.6 \cdot 10^{-5}$ Pa at 1400 K over it. When UO_2 have been oxidized its work function goes up to 434 kJ·mol^{-1} and the electron concentration goes down to $3.2 \cdot 10^{-10}$ Pa at 1400 K. The addition of chromium oxide according our calculations [8] raise the electron concentration back up to the same level as over stoichiometric UO_2.

The sensitivity level of registering negative ions even in the worst case should be less than $1 \cdot 10^{-9}$ Pa. The

partial pressure of UO_3 at 1400 K in our experiments was roughly $2.8 \cdot 10^{-3}$ Pa. So in the worst conditions the absence of UO_3^- in the vapors over uranium oxides means that $K^O(5)$ is less than $1.1 \cdot 10^8$ and the electron affinity of UO_3 is less than 247 kJ·mol^{-1}.

Besides we will mention two studies with uranium-containing negative ions where UO_3^- has not also been found. Sidorova et al [25] investigated ion-molecule equilibria with uranium oxyfluorides and saw UF_6^-, UOF_5^-, and $UO_2F_3^-$. Yokozeki et al [26] studied electron attachment to volatile uranil compounds with atom uranium coordinating six atoms of oxygen and again did not see UO_3^-.

Now let us briefly discuss the logic of estimating the electron affinity of UO_3 made in reference book [3]. The differences of the electron affinities of hexafluorides and trioxides of molybdenum and tungsten were calculated {EA(MoF$_6$) = 347±20 kJ·mol^{-1}, EA(WF$_6$) = 338±20 kJ·mol^{-1}, EA(MoO$_3$) = 285±25 kJ·mol^{-1}, EA(WO$_3$) = 325±30 kJ·mol^{-1}}. Later on it was assumed that about the same difference should be for uranium hexafluoride {EA(UF$_6$) = 538±35 kJ·mol^{-1}} and uranium trioxide. On such way the electron affinity EA(UO$_3$) = 500±50 was obtained.

After the reference book [3] was published the new thermodynamic data had arrived EA(MoF$_6$) = 369±18 kJ·mol^{-1} [27], EA(MoF$_6$) = 398 kJ·mol^{-1} [28], EA(MoO$_3$) = 277±19 kJ·mol^{-1}, EA(WO$_3$) = 380±19 kJ·mol^{-1} [10], EA(WO$_3$) = 321±$^8_{14}$ kJ·mol^{-1} [29], EA(UF$_6$) = 488±19 kJ·mol^{-1} [27]. They slightly differ

from those used in the reference book [3], but nothing is changed in estimating the electron affinity of UO_3.

Much higher electron affinities of molybdenum and tungsten hexafluorides $\{EA(MoF_6) > 496$ kJ·mol^{-1}, $EA(WF_6) > 496$ kJ·mol^{-1} [31,32]$\}$ were received with ionization by fast alkali atoms. They are discussed in ref. [32,33] and seems to be less reliable. For example, they have been disregarded in the reference book [3]. Yet even we will use them to estimate the electron affinity of UO_3 it brings to still larger values than the upper limit obtained in this work.

For our opinion the logic used in the reference book [3] is quite reasonable and there is nothing wrong with it. At the same time such great difference with the experimental results shows that the way of changing of the electron affinity at transition from molybdenum and tungsten oxides to uranium oxide have an anomaly.

REFERENCES

1. E.B. Rudnyi, E.A. Kaibicheva, L.N. Sidorov, **Struktura i Energetika Molecul. Trudy V Vsesoyusnogo soveshchaniya po isucheniyu molecul v gasovoi fase (Structure and energetics of molecules. Proceedings of the V all-union seminar on structure of molecules in the gas phase)**, p. 124, Ivanovo (1990).

2. J. Magill, G.J. Hyland, M.H. Rand, **J. Chem. Phys.** 88, 4101 (1988).

3. **Termodinamichekie Svoistva Individual'nykh Veshchestv (Thermodynamic Properties of Individual Substances),** V.P. Glushko: editor, Nauka: Moscow, 1978-1982, vols. 1 to 4.

4. D.L. Hildenbrand, L.V. Gurvich, V.S. Yungman, **The Chemical Thermodynamics of Actinide Elements and Compounds. Part 13 - The Gaseous Actinide Ions**, IAEA, Vienna, 1985

5. C. Plog, **Surf. Sci.** 67, 565 (1977).

6. R. Middleton,, **Nucl. Instr. Methods** 144, 373 (1977).

7. E.B. Rudnyi, O.V. Kuznetsova , E.A. Kaibicheva , L.N. Sidorov, **Teplofiz. Vys. Temp.** 28, 1135 (1990); **High Temp. USSR** (English transl) 28, 864 (1990).

8. E.A. Kaibicheva, E.B. Rudnyi, L.N. Sidorov, I.D. Sorokin, **Zhurnal Fiz. Khimii**, 65, 919 (1991).

9. E.A. Kaibicheva, E.B. Rudnyi, L.N. Sidorov, **Zhurnal Fiz. Khimii**, to be published.

10. E.B. Rudnyi, O.M. Vovk, E.A. Kaibicheva, L.N. Sidorov,

J. Chem. Thermodynamics, 21, 247 (1989).

11. E.A. Kaibicheva. **Ion-molecule Equilibria in Vapors of Oxides of 3d-Elements** (In Russian), Cand. thesis (1990) 189 pp. (Available at V.I. Lenin USSR State Library, Moscow).

12. E.B. Rudnyi, M.V. Korobov, O.M. Vovk, E.A. Kaibicheva, L.N. Sidorov, **High. Temp. Sci.**, 26, 165 (1988/1989).

13. A. Kotlar, P. Gerdanian, M. Dode, **J. Chim. Phys. Phys.-Chim. Biol.** 65, 687 (1968).

14. A. Kotlar, P. Gerdanian, M. Dode, **J. Chim. Phys. Phys.-Chim. Biol.** 64, 1135 (1967).

15. C. Picard, P. Gerdanian, **J. Nucl. Mat.** 99, 184 (1981).

16. A. Caneiro, J.P. Abriata, **J. Nucl. Mat.** 126, 255 (1984).

17. T.B. Lindemer, T.M. Besmann, **J. Nucl. Mat.** 130, 473 (1985).

18. J.F. Babelot, R.W. Ohse, M. Hoch, **J. Nucl. Mat.** 137, 144 (1986).

19. J.F. Babelot, M. Hoch, **J. Nucl. Mat.** 167, 25 (1989).

20. A. Nakamura, T. Fujino, **J. Nucl. Mat.** 167, 36 (1989).

21. A. Nakamura, T. Fujino, **J. Nucl. Mat.** 149, 80 (1987).

22. E.B. Rudnyi, E.A. Kaibicheva, L.N. Sidorov, M.T. Varsavskii, A.M. Men', **J. Chem. Thermodynamics,** 22, 623 (1990).

22. G.A. Haas, J.T. Jensen, **J. Appl. Phys.** 34, 3451 (1963).

23. J.P. Hiernaut, J. Magill, R.W. Ohse, M. Tetenbaum,, **High Temp. - High Press.** 17, 633 (1985).

24. W. McLean, H.L. Chen, **J. Appl. Phys.** 58, 4679 (1985).

25. I.V. Sidorova, A.T. Pyatenko, L.N. Gorokhov, V.K. Smirnov, **Teplofiz. Vys. Temp.** 22, 1120 (1984); **High Temp. USSR** (English transl) 22, 857 (1984).

26. A. Yokozeki, E.L. Quitevis, D.R. Herschbach, **J. Phys. Chem.** 86, 617 (1982).

27. A.Ya. Borshchevskii, O.V. Boltalina, I.D. Sorokin., L.N. Sidorov, **J. Chem. Thermodynamics,** 20, 523 (1988).

28. M.I. Nikitin, **Teplofiz. Vys. Temp.** 27, 868, (1989).

29. C.W. Walter, C.F. Hertzler, P. Devynck, G.P. Smith, J.R. Peterson, **J. Chem. Phys.** 95, 824 (1991).

30. B.P. Mathur, E.W. Rothe, G.P. Reck, **J. Chem. Phys.** 67, 377 (1977).

31. R.N. Compton, P.W. Reinhardt, G.D. Cooper, **J. Chem. Phys.** 68, 2023 (1978).

32. L.N. Sidorov, A.Y. Borshchevskii, E.B. Rudny, V.D. Butsky, **Chem. Phys.** 71, 145 (1982).

33. P.M. George, J.L. Beauchamp, **Chem. Phys.** 36, 345 (1979).

Table 1. Thermodynamic properties of molecules forming the most stable negative ions [1]

M	EA(M)	D(M)	M	EA(M)	D(M)
PtF_6	675±34	149±12	PO_2	367±21	497±10
CoF_4	615±31	154±11	PO_3	433±51	479±10
CeF_4	367±39	399±25	BO_2	417±18	546
UF_6	488±19	312	CrO_3	351±17	459±21
UF_5	361±21	380	MoO_3	277±19	594±21
MoF_6	368±18	385	WO_3	380±19	594±21
MoF_5	334±17	375	UO_3	500±50	566±25
FeF_3	349±13	339			
RhF_4	523±29	202			
MnF_4	533±22	215			
IrF_6	627±37	270			

Table 2. The experimental data for the system U_3O_8-K_2CrO_4-Cr_2O_3(s)
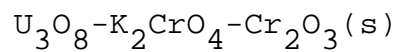
T(K)	$\ln \dfrac{I(UO_3^-)}{I(CrO_3^-)}$	$\ln \dfrac{I(CrO_4^-)}{I(CrO_3^-)}$	$\dfrac{p(O_2)}{Pa}$
1344	<-5.22	-6.77	0.42
1430	<-7.39	-6.53	2.2
1473	<-7.92	-6.57	3.6
1515	<-7.16	-7.16	1.9

Table 3. The experimental data for the system U_3O_8-K_2CrO_4-V_2O_3
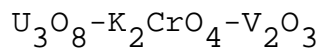
T(K)	$\ln \dfrac{I(UO_3^-)}{I(VO_3^-)}$	$\ln K_I(2)$ [a]	$\dfrac{p(O_2)}{Pa}$	$\ln K_I(3)$ [b]	$a(V_2O_3)$
1344	<3.87	5.50	0.16	−3.81	0.32
1430	<2.28	4.59	0.54	−3.23	0.18
1473	<1.09	3.65	0.33	−1.83	0.44

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[a] $-\ln \dfrac{I^3(V_3O_8^-)}{I(VO_3^-)\, I^2(V_4O_{10}^-)}$ is given

[b] $-\ln \dfrac{p(VO_3^-)\, p^4(V_4O_{10}^-)}{p^5(V_3O_8^-)}$ is given

Table 4. Estimating the electron affinity of UO_3^-

exp. N	T(K)	ln K^*	ln $K^O(8)$	$a(UO_2)$	ln $K^O(5)$	$\dfrac{EA(UO_3^-)}{kJ \cdot mol^{-1}}$
I	1344	14.38	-11.55	>0.54	<19.09	<242
	1430	13.60	-10.13	>0.43	<15.37	<214
	1473	13.24	-9.48	>0.40	<14.02	<205
	1515	12.89	-8.90	>0.40	<13.69	<208
II	1344	16.44	-11.55	>0.54	<29.62	<359
	1430	15.38	-10.13	>0.43	<25.79	<338
	1473	14.88	-9.48	>0.40	<23.85	<325

* $K^O(6)$ is given for the experiment I and $K^O(7)$ is given
  for the experiment II (standard state is 101325 Pa)

Table 5. Auxiliary thermodynamic data

Compound	$\Delta_f H_0^O$	Φ_{1200}^O	Φ_{1400}^O	
	kJ·mol^{-1}	J·K^{-1}·mol^{-1}	J·K^{-1}·mol^{-1}	
Cr_2O_3(s)	−1134.8±1.7	143.8±7.5	160.2	[3]
V_2O_3(s)	−1211.7±5.0	157.7±2.0	174.9	[3]
UO_2(s)	−1081.2±1.0	116.0±1.1	126.8	[3]
O_2	0	217.9±0.0	222.8	[3]
e	0	29.0±0.0	32.2	[3]
CrO_3^-	−669±9	311.5±4.0	322.1	[10]
VO_3^-	−754±11	301.5±5.2	311.8	[1, 11]
UO_3	−795±15	343.6±3.3	354.5	[3]
UO_3^-		353.4±7.6	364.8	[3]

FIGURES CAPTIONS

Figure 1. The partial pressure of electrons in slightly ionized gas as function of an electron affinity (EA) and a dissociation energy (D in $kJ \cdot mol^{-1}$) of admixure molecules.

The results are given for model system consisted from inert gas, potassium (0.01%) and molecules M (1%), forming negative ions M^-. There are reactions of potassium ionization $K = K^+ + e$, attachment of electrons by molecules $M + e = M^-$ and dissociation of molecules to two fragments $M = A + B$.

Figure 2. Stability diagram of uranium oxides.

o – partial pressure of oxygen obtained in experiment I.

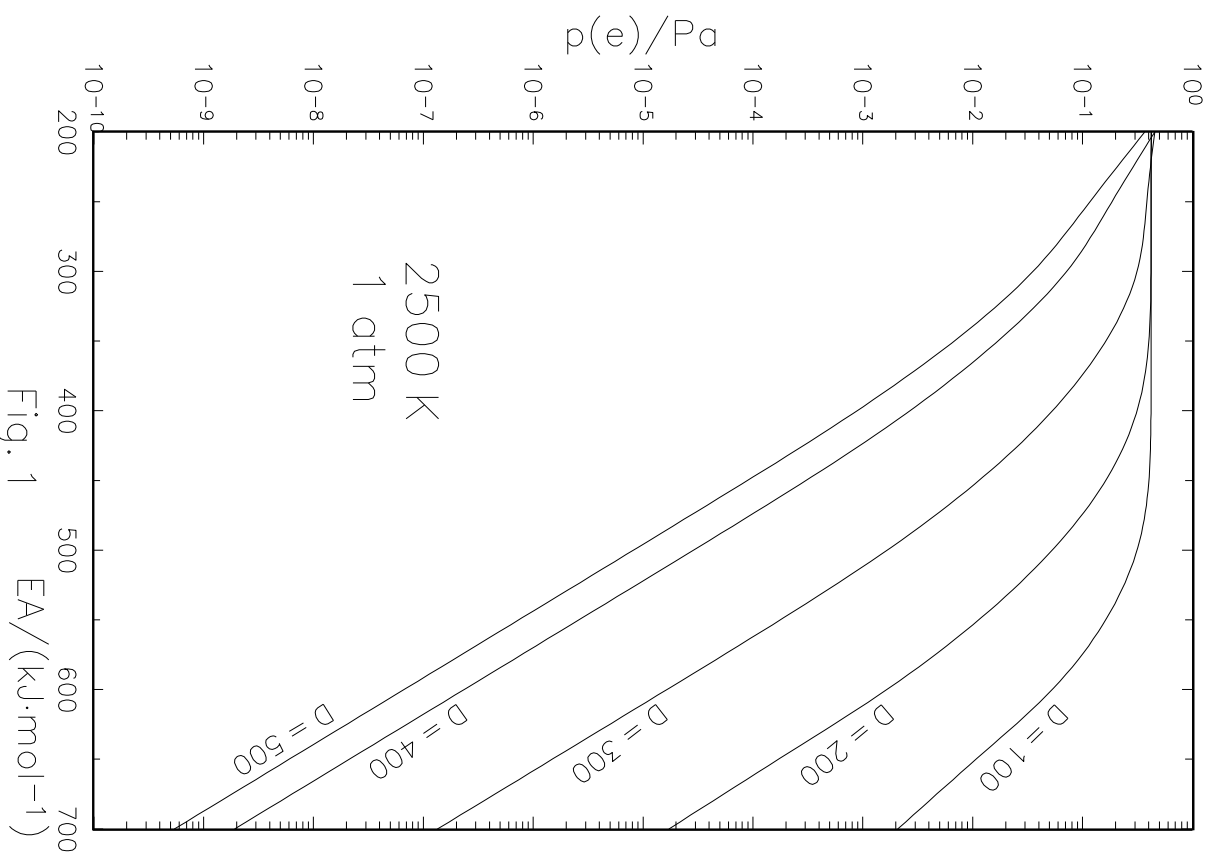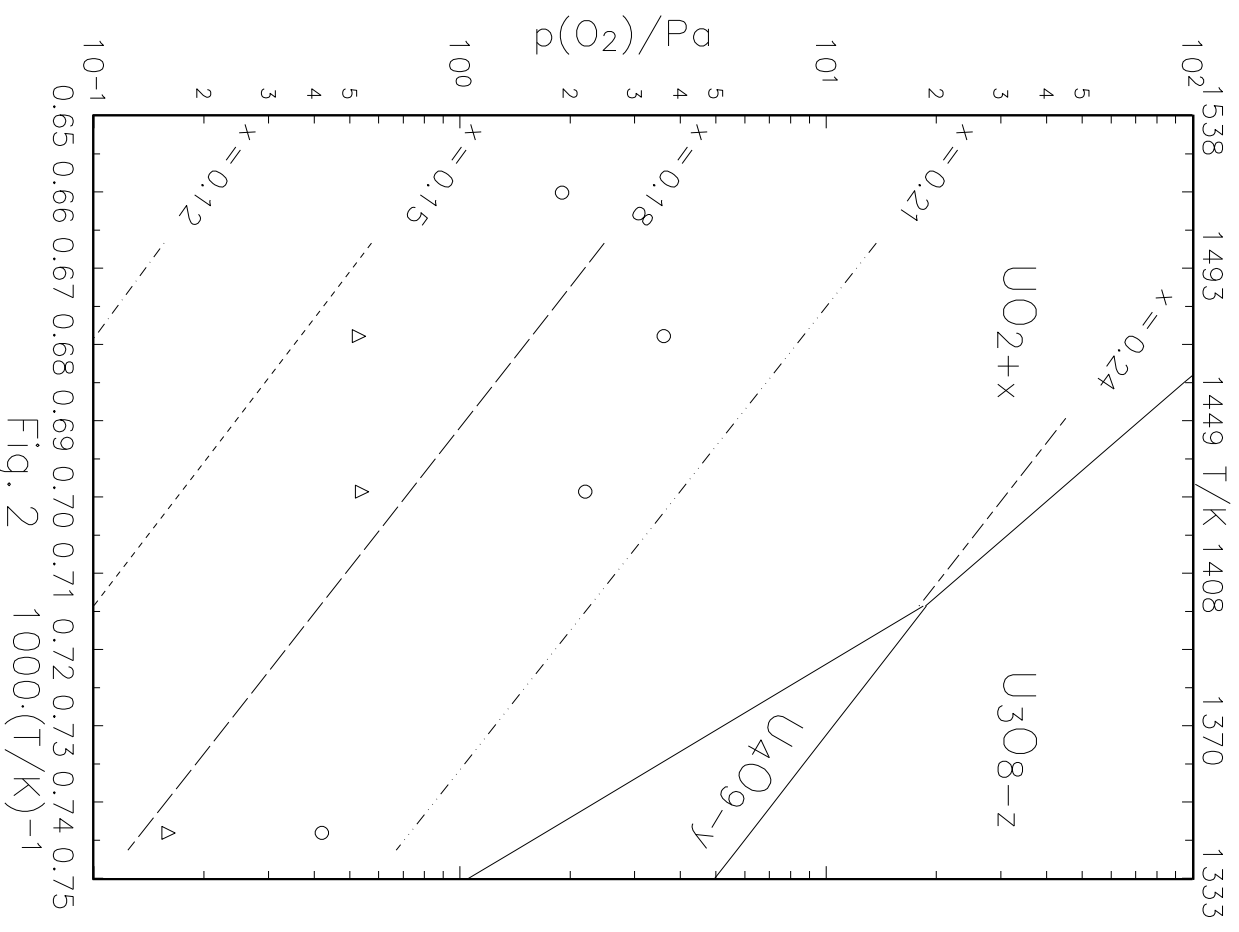Δ – partial pressure of oxygen obtained in experiment II.

Fig. 1

Fig. 2