PHYSICAL CHEMISTRY

V. V. RACHEV, L. M. KOVBA, E. A. IPPOLITOVA

1964

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

V. V. RACHEV, L. M. KOVBA, E. A. IPPOLITOVA

A CONTRIBUTION TO THE STUDY OF THE UO_2—UO_3 SYSTEM

(Presented by Academician V. I. Spitsyn, June 30, 1964)

The UO_2—UO_3 system has been intensively studied in recent years ($^{1-13}$). However, only in one work (^{1}) was X-ray photography at high temperatures used (up to 960°). Other authors studied quenched samples* ($^{9-12}$), or, in constructing the condensed-state diagram, used data on the dependence of oxygen pressure on composition, etc. ($^{4-7}$). In the present work the results are presented of a study of the UO_2—U_3O_8 system by the method of high-temperature X-ray photography, and the possibility is considered of constructing a phase diagram on the basis of the data obtained and a critical review of those published earlier.

Samples of uranium oxides of various composition were prepared by annealing mixtures of $UO_{2.02}$ and U_3O_8 for 20 h in sealed quartz ampoules at 1000°. Photography was carried out in a high-temperature chamber (^{14}) in the range 850—1150° (for samples $UO_{2.02}$—$UO_{2.40}$) and 20—1000° (for samples $UO_{2.50}$—$UO_{2.667}$). Temperature fluctuations did not exceed ±5°C; the radiation was CuK ($UO_{2.02}$—$UO_{2.40}$) and CuK_α ($U_{2.50}$—$UO_{2.667}$). The accuracy in determining the lattice parameters of cubic oxides was ±0.001 Å; for the parameters b and c of the rhombic subcells U_3O_8 and $U_5O_{13\pm x=1}$ it was ±0.002 Å, and for the period a, ±0.005 Å; deviations of composition did not exceed 0.003 in the oxygen index.

For determining the phase boundaries, data from qualitative phase analysis were used; for cubic phases in the $UO_{2.20}$—$UO_{2.25}$ region, semiquantitative phase analysis and calculation of compositions from lattice parameters were used (using the linear dependence of the parameter a of the UO_{2+x} phase on composition). The dependence of the lattice parameter on the composition of the UO_{2+x} phase at high temperatures is linear (Fig. 1); the coefficient of linear expansion is practically constant for this temperature interval, although it changes somewhat with composition.

Fig. 1. Dependence of the lattice parameters of cubic phases UO_{2+x} and U_4O_9 on temperature: 1 –$UO_{2.02}$; 2 –$UO_{2.17}$; 3 –$UO_{2.20}$; 4 –$UO_{2.22}$; 5 –U_4O_9.

The upper boundary of the homogeneity region of the UO_{2+x} phase shifts with temperature:

Fig. 1. Dependence of the lattice parameters of cubic phases UO_{2+x} and U_4O_9 on temperature: 1 –$UO_{2.02}$; 2 –$UO_{2.17}$; 3 –$UO_{2.20}$; 4 –$UO_{2.22}$; 5 –U_4O_9.

Figure 1: Fig. 1. Dependence of the lattice parameters of cubic phases UO_{2+x} and U_4O_9 on temperature: 1 –$UO_{2.02}$; 2 –$UO_{2.17}$; 3 –$UO_{2.20}$; 4 –$UO_{2.22}$; 5 –U_4O_9.

850° $x = 0.19$; 950° $x = 0.20$; 1100° $x \geq 0.22$.
900° $x = 0.195$; 1000° $x = 0.21$; 1150° $x \geq 0.25$.

In the oxide U_4O_9 the lattice parameter also depends linearly on temperature up to 1100°, while in the interval 1100—1150° an abrupt increase of the parameter occurs, and the oxide U_4O_9 merges with the homogeneity region of the UO_{2+x} phase (an order-disorder type transition); the transition temperature is thus 1125 ± 25°. The results obtained are in general agreement with the data of Roberts and Walter ([5]) and differ greatly from the results of Shener ([9]). The U_4O_9 phase coexists with the rhombic phase U_5O_{13-x}. The phase composition of samples $UO_{2.55}$—$UO_{2.667}$ is given in Table 1.

* In view of the high rate of phase transformations in the UO_2—U_3O_8 system, such data cannot be used to judge the phase composition of samples at high temperatures.

The phases U_3O_{8-x} and U_5O_{13+x} differ in the axial ratio a/b (1.685 and 1.695), in the character of their thermal expansion, and in the type of superstructure. With increasing temperature (Fig. 2B), the parameters a and b of the U_3O_{8-x} phase change differently–the parameter a increases, while b decreases (in agreement with the data of previous works ([1,8])), and a gradual transformation into the hexagonal modification takes place.

Table 1

Phase composition of $UO_{2.55}$–$UO_{2.667}$ samples at various temperatures*

Temperature, °C	$UO_{2.55}$	$UO_{2.57}$	$UO_{2.61}$	$UO_{2.63}$	$UO_{2.65}$	$UO_{2.667}$
20	A + B	B	B	B	B	C
100	A + B	–	B	B	B	C
200	A + B	B	B	B	B	C
300	A + B	–	B	B	B	C
400	–	–	B	–	B	D
500	–	–	B	–	B	D
600	A + B	–	B	B	D	D
700	A + B	–	B	–	–	D
800	A + B	–	B	B	–	D
900	A + B	–	B	D**	–	D

Temperature, °C	$UO_{2.55}$	$UO_{2.57}$	$UO_{2.61}$	$UO_{2.63}$	$UO_{2.65}$	$UO_{2.667}$
1000	–	–	B	–	–	D

* A –U_4O_9; B –U_5O_{13+x}; C –U_3O_{8-x} (orthorhombic phase); D –U_3O_{8-x} (hexagonal phase).
** 950°.

The thermal expansion of the $U_5O_{13\pm x}$ phase (Fig. 2A) is extremely small, and the transition U_5O_{13+x} to U_3O_{8-x} (hexagonal) in the case of the $UO_{2.65}$ and $UO_{2.63}$ samples occurs discontinuously.

For the $U_5O_{13\pm x}$ phase, which has a considerable homogeneity range, the lattice parameters practically do not change with composition ($a = 6.733$; $b = 3.665$; $c = 4.142$), but they differ noticeably from the parameters of U_3O_8 ($a = 6.713$; $b = 3.990$; $c = 4.147$). The parameter values agree with the literature data ([1,2,10,12]).

As can be seen from Fig. 2, in the case of U_3O_8 above 900° there is a sharp increase in the parameter a; this is evidently explained by a partial loss of oxygen. If the lattice parameters of the hexagonal phases $UO_{2.65}$ (500 and 600°) and $UO_{2.63}$ (950°) are plotted on the graph, they will lie on a straight line parallel to the analogous line for U_3O_8, on whose continuation fall the values of the parameters of the U_3O_8 phase at 1000 and 1100°.

If only stable phases are considered, then the U_3O_8–γ-UO_3 region is two-phase, and both oxides have narrow homogeneity ranges ([13]). On the basis of the foregoing, one may construct a condensed state diagram of the UO_2–UO_3 system that includes only stable oxides.

Fig. 2. Dependence of lattice parameters on temperature: A –for the U_5O_{13} phase, B –U_3O_8
(1 and 2 –data for the compositions $UO_{2.65}$ and $UO_{2.63}$, respectively)

All the other uranium oxides are metastable, and their formation in a number of processes (exclusively low-temperature ones) is connected with kinetic factors and is due to the closeness of the structures of the metastable phases to the structures of the initial oxides: UO_{2+x} and U_3O_7 to UO_2, α-UO_3, ε-UO_3, U_2O_5 to U_3O_8. Thus, as a result of oxidation of unstable uranium dioxide at room temperature, cubic oxides UO_{2+x}, with $x < 0.40$, are formed ([16]). Probably in a number of cases they were mistakenly taken for products formed upon reduction of uranium oxides: U_8O_{17} oxide in work ([17]). Stable dioxide, upon oxidation, gives tetragonal oxides, close in composition to U_3O_7 (α-U_3O_7 and β-U_3O_7). During thermal decomposition of amorph-

of uranium trioxide, a hexagonal[16] or pseudohexagonal[13] oxide UO_{3-x} is formed. As we have shown earlier,[15] the formation of various modifications of uranium trioxide (α and ε, in particular) during the oxidation of uranium dioxide is explained by the structural similarity of these oxides to the original uranium dioxide.

Metastable U_2O_5 oxide is likewise formed only as a result of a low-temperature process—acid treatment of uranium dioxide.[16]

The oxide U_3O_{8+x}, which is also formed as a result of the decomposition of amorphous UO_3 and UO_{3-x}, is extremely unstable—as a result of more prolonged calcination it is converted into U_3O_8.[16]

None of these oxides is obtained as a result of interaction between stable oxides,* and they should not be placed on the phase diagram. As is known,[2,18] uranium dioxide above 900° loses oxygen, giving an oxide of composition $UO_{2.64}$, which is very close to the lower boundary of the hexagonal phase U_3O_{8-x}. We observed that samples $UO_{2.667}$—$UO_{2.63}$, calcined above 900°, upon quenching give the metastable phase β-U_3O_8 (sometimes together with the stable phase U_5O_{13+x} or U_3O_{8-x}). On the heating curves of such samples an exothermic effect is observed at 130°. X-ray phase analysis showed that this effect corresponds to the transition of β-U_3O_8 into U_5O_{13+x} or U_3O_{8-x}. The formation of the β-U_3O_8 phase upon quenching samples of U_3O_8 calcined above 900° in sealed ampoules confirms the supposition of its partial decomposition under these conditions. It seems to us that, for U_3O_8 itself, such a transition is unlikely because of the gradual nature of the transformation of rhombic U_3O_8 into hexagonal, whereas in the oxide $UO_{2.65}$ it occurs abruptly; thus, β-U_3O_8 has a composition close to $UO_{2.65}$—$UO_{2.66}$.

Fig. 3. Phase diagram of the UO_2—UO_3 system:
I—UO_{2+x}, *II*—$U_4O_{9\pm x}$, *III*—$U_5O_{13\pm x}$, *IV*—U_3O_{8-x} (rhomb.), *V*—U_3O_{8-x} (hexagonal), *VI*—γ-UO_3. *A*—two variants of the possible structure of point *A*; the dashed line indicates the assumed boundaries of the two-phase region.

Moscow State University
named after M. V. Lomonosov

Received
15 V 1964

REFERENCES

1. F. Grønvold, *J. Inorg. and Nucl. Chem.*, **1**, 357 (1955).
2. H. R. Hoekstra, S. Siegel et al., *J. Phys. Chem.*, **59**, 136 (1955).
3. H. R. Hoekstra, S. Siegel, Report P/737 USA to the International Conference on the Peaceful Uses of Atomic Energy, Geneva, 1955.
4. P. E. Blackburn, *J. Phys. Chem.*, **62**, 897 (1958).

5. L. E. J. Roberts, A. J. Walter, *J. Inorg. and Nucl. Chem.*, **22**, 213 (1961).

6. S. Aronson, J. Belle, *J. Chem. Phys.*, **29**, 151 (1958).

7. K. Kiukkola, *Acta chem. scand.*, **16**, 327 (1962).

8. S. Siegel, *Acta crystallogr.*, **8**, 617 (1955).

9. B. E. Shaner, *J. Nucl. Materials*, **2**, 110 (1960).

10. H. Hering, P. Perio, *Bull. Soc. chim. France*, 1952, 351.

11. K. B. Alberman, J. S. Anderson, *J. Chem. Soc.*, 1949, Suppl. 303.

12. R. E. Rundle, N. C. Baenziger et al., *J. Am. Chem. Soc.*, **70**, 99 (1948).

13. H. R. Hoekstra, S. Siegel, *J. Inorg. and Nucl. Chem.*, **18**, 154 (1961).

14. V. G. Kuznetsov, *ZhNKh*, **1**, 1548 (1956).

15. L. M. Vidavskii, E. G. Lavut et al., *DAN*, **154**, 1371 (1964).

16. L. M. Kovba, E. U. Kuzmicheva, E. A. Ippolitova, *Vestn. Moscow Univ.*, No. 3, 34 (1964).

17. P. Margottin, W. Stuckens, R. Durand, *C. R.*, **252**, 4005 (1961).

18. P. P. Budnikov, S. G. Tresvyatskii, V. I. Kushakovskii, *DAN*, **128**, 85 (1959).

* As we have shown,[16] Perio' s data,[10] concerning the formation of tetragonal oxides as a result of the reaction of UO_2 with U_3O_8, are inaccurate—the only reaction product is U_4O_9.

Note: Figure translations are in progress. See original paper for figures.

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.