301. *The Oxides of Uranium. Part II.* The Binary System* UO_2–CaO.

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The phase diagram of the system CaO–UO_2 has been investigated in the temperature range 1650—2300° c. The eutectic temperature is 2080° $\pm$ 20°, and the eutectic composition about 45 moles % of UO_2 and 55 moles % of CaO. The CaO takes no detectable amount of UO_2 into solid solution, but the UO_2 forms solid solutions, with defective fluorite structure, the saturated solid solution containing 47 mols. % of CaO at the eutectic temperature. The concentration of CaO in the saturated solid solution decreases with falling temperatures, down to 20 moles % at 1650°. At 1750° and below, two compounds are formed: Ca_2UO_4 (= 2CaO,UO_2), a tetragonal double oxide of unknown structure; and $CaUO_3$ (= CaO,UO_2), having a cubic cell with $a = 10{\cdot}727 \pm 0{\cdot}002$ *kX*. The structure of the latter is equivalent to the Type-C rare-earth oxide structure, with $Ca^{2+} + U^{4+}$ replacing $2M^{3+}$.

Studies of binary oxide systems have brought to light a number of interesting regularities in the field of crystal chemistry, but few systems involving two species of large cations appear to have been studied hitherto. Uranium dioxide crystallises with the fluorite structure (a = 5·457 A.), the interatomic distance U–O being 2·363 A.; in calcium oxide the distance Ca–O is 2·398 A. The relatively large U^{4+} and Ca^{2+} cations are thus of closely similar effective radius, and it might be expected *a priori* that the system UO_2–CaO would display the formation of anomalous mixed crystals and of intermediate phases with structures not encountered in binary systems involving smaller cations. The work now described has shown that this is, indeed, the case, and it brings out clearly the trend from an ordered to a random arrangement of defect structures as the temperature is raised.

Uranium dioxide and lime are highly refractory, with melting points approximately 2700° and 2500°, respectively. The study of their phase equilibrium is therefore essentially a problem of high-temperature techniques. The literature contains relatively few equilibrium studies between such refractory substances. Above about 1850° the phase diagram for CaO–UO_2 found from the present work resembles that constructed by Zhirnova (*J. Appl. Chem. U.S.S.R.*, 1939, **12**, 1279) from fragmentary data for the ZrO_2–MgO system. The eutectic temperature is about 2080°, and a few temperatures on the solidus curve of the UO_2 phase were determined directly, at temperatures up to 2250°. The liquidus curves and the uppermost portions of the solidus curves can, however, be only sketched in the phase diagram in their probable positions. Direct measurements in those regions of the phase diagram lying at temperatures above 2300° would, indeed, involve considerable experimental difficulty.

Experimental.

All specimens were fired in a small tungsten-spiral vacuum furnace, described in detail elsewhere (Alberman, *J. Sci. Instr.*, 1950, 280). This furnished temperatures up to approximately 2500° within a useful volume of about 20 c.c., and with a maximum energy consumption of about 1200 watts. The energy consumption at high temperatures was shown by direct calibration (Alberman, *loc. cit.*) to be strictly proportional to T^4, and in the present work all temperatures were measured by the power input to the furnace. The ambient pressure was maintained at $<10^{-5}$ mm. by an efficient pumping system.

The oxides used as starting materials were "AnalaR" calcium oxide, and a very pure grade of uranium dioxide. Mixtures were made up synthetically to accurately known compositions. For this purpose, the lime was brought to constant weight at 800° in a platinum crucible, or in some cases was "dead burned" at considerably higher temperatures, and then finely ground with the appropriate quantity of uranium dioxide. The mixtures were pressed (under 15 tons/sq. cm.) into pellets of ⅜" diam. and of various lengths, suited to their purpose. This was done immediately before firing as absorption of moisture brought about disintegration. The pellets formed in this way had sufficient mechanical strength for careful handling with forceps.

Pellets for *X*-ray analysis were made about 1 in. long, so that when they were standing on the tantalum base of the furnace enclosure, the topmost ¼" was in the centre of the heated zone (Fig. 1). After being heated at temperatures between 1650° and 2100° for various times, the top portion of the pellet was broken away, ground in an agate mortar, and loaded into thin-walled Pyrex *X*-ray capillaries. Contamination by diffusion of tantalum from the base plate (see below) was thereby minimised. Two-phase materials, containing free lime as one solid phase, were leached with ammonium chloride solution, in order to dissolve the lime under nearly neutral conditions, thereby isolating the second phase for *X*-ray analysis.

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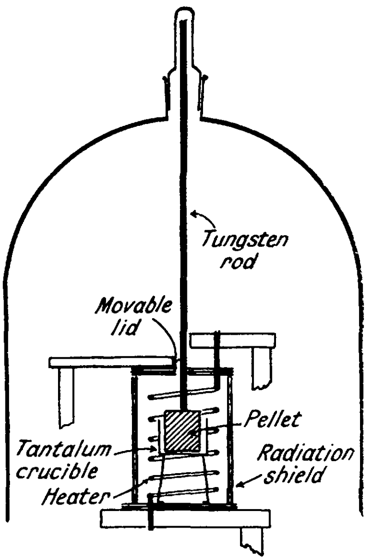
Pellets for thermal analysis were made about 1 cm. long, and were place in tantalum crucibles (7/16″ diam., $\frac{3}{8}$″ deep) made by deep-drawing 0·010″ tantalum sheet. The crucibles were suspended in the centre of the heated zone by a light spot-welded framework of tantalum and tungsten. Melting points were then determined directly by a simple technique. A long rod of tungsten rested on the top of the pellet, with its upper end projecting into a length of narrow tubing attached to the bell-jar which covered the furnace assembly (Fig. 1). The top end of the tungsten rod was observed through a cathetometer as the temperature of the furnace was gradually raised. When liquefaction commened, the rod sank through the contents of the tantalum crucible, at a rate depending on the proportions of liquid phase and unmelted solid. The m. p. was then determined from the power input at the commencement of fusion; the temperature scale was calibrated both by optical pyrometry and by determining a series of melting points between those of nickel (1455°) and iridium (2440°). The measurements were quite reproducible, seven measurements of the eutectic temperature, on compositions covering the full width of the equilibrium diagram, giving a value of 2080° with a standard deviation less than 20°.

FIG. 1.



X-*Ray Measurements.*—Diffraction patterns were taken on a 9-cm. Unicam camera, with filtered copper-$K\alpha$ radiation. Measurements of cell dimensions were extrapolated by Nelson and Riley's method (*Proc. Physical Soc.*, 1945, **57**, 160), the value of a_{100} at $\theta = 90°$ being obtained by combining the ten lines of highest diffraction angle recorded on the film, by the method of least squares. The values recorded are probably reliable to $\pm 0{\cdot}001$ *kX*.

Metallographic Examination.—This was used primarily to locate the eutectic composition, since the method of thermal analysis employed was not capable of fixing temperatures on the liquidus curve, but only gave the m. p. of the eutectic over the whole range of its existence. Portions of pellets from the m. p. experiments were mounted in Bakelite, and polished on a carborundum wheel. On examination under a metallurgical microscope, particles of primary phase could be seen embedded in a continuous matrix of eutectic, the appearance being similar to that of duplex metallic systems. On the lime-rich side of the eutectic, the primary phase (CaO) could be removed by etching with concentrated hydrochloric acid, leaving a network of eutectic. A specimen with 55 moles % of CaO and 45 moles % of UO_2 melted very sharply and showed no crystals of a primary phase under the microscope. It was concluded that this mixture was close to the eutectic composition.

Chemical Analysis.—The gross composition of all mixtures was adjusted synthetically to cover the requisite range, and the compositions of the saturated uranium dioxide solid solution phases were determined with considerable accuracy by the *X*-ray data. The validity of this method was checked, and the composition of the compounds in the system determined by direct chemical analysis. Two-phase products, consisting of lime + solid solution or lime + compound, were exhaustively leached of lime by means of ammonium chloride solution, which did not attack the solid phases containing uranium dioxide. The residue, for analysis, was dissolved in 50% nitric acid + hydrogen peroxide or by fusion with potassium hydrogen sulphate. Calcium was first precipitated as oxalate, and uranium then determined by precipitation with tannin (cf. Powell and Schoeller, " Analysis of Minerals and Ores of the Rarer Elements "). The tannin precipitates were tested for tantalum (and tungsten, which was not, however, detected in more than trace amounts) as described by Powell and Schoeller.

Side Reactions and Chemical Contamination.—The heated tantalum and tungsten parts of the furnace act as efficient " getters," and we have some evidence that the oxygen pressure within the heated enclosure is maintained at less than 10^{-8} mm. The dissociation pressure of most, even the more refractory, oxides becomes of this order of magnitude at temperatures between 2000° and 2500°, and we have, in fact, observed the decomposition of all except the most stable oxides (*e.g.*, ThO_2) under the conditions attainable in our vacuum furnace. In particular, at the point of contact with a tantalum crucible or tantalum floor, direct displacement of more volatile metals (*e.g.*, Ca, and even Th) can occur, leading to the entry of tantalum into the system (*e.g.*, with the formation of ternary solid solutions). In the absence of a liquid phase, diffusion of tantalum into the pellets was not excessively rapid, and the upper parts of pellets, used for *X*-ray analysis, were free from tantalum. With the occurrence of eutectic melting, reaction was rapid, and the interior of the bell-jar was rapidly covered with condensed calcium; in these circumstances as much as 14% of tantalum dioxide was found in the melt after complete fusion. Eutectic temperatures were, however, taken from the first signs of melting, and it is believed that no considerable errors were introduced from this source.

RESULTS AND DISCUSSION.

The UO_2–CaO *Mixed-crystal Phase and the Melting Equilibria.*—The addition of lime to uranium dioxide gives rise to a solid solution phase, with fluorite structure, having a considerable breadth of composition at 1900—2100°. The cubic unit cell shrinks quite regularly as $U^{4+} + 2O^{2-}$ is progressively replaced (see below) by $Ca^{2+} + O^{2-} + \square O$, where $\square O$ denotes a vacant oxygen site. The lattice parameter *a* varies linearly with the molar fraction of lime, and can therefore be used to determine the limiting composition of the solid solution phase, in material of duplex structure, richer in lime (Fig. 2). The compositions of the saturated solid solution at 1950° and at the eutectic temperature (2080°) were determined in this way as 43 and 47 moles % of lime. The composition of the saturated solid solution at 1950° was determined analytically as 40 moles %. Specimens that had been melted were invariably contaminated rather heavily with tantalum; analytical figures obtained on such material are therefore not significant. The composition of the limiting solid solution determined from *X*-ray measurements is, however, entirely consistent with the experimental evidence for the position of the solidus curve. The initial rate of cooling of a sample from temperatures around 2000° was so high that it is permissible to regard the switching off of the furnace as equivalent to a quenching process.

Mixtures richer in lime than the saturated solid solution showed the presence of lime as the second solid phase, with a cell dimension identical, within our limits of error (a = 4·797 ± 0·001 A.), with that of pure lime. It may be concluded that the lime phase does not take detectable amounts of U^{4+} cations into solid solution.

The limits of the eutectic melting range were thus fixed, and the eutectic temperature was determined directly. This eutectic composition was shown, by the metallographic examination and by the sharpness of fusion, to be close to 45 moles % of uranium dioxide. The m. p.s of the unsaturated uranium dioxide solid solutions rose very steeply with increasing dioxide content; it was proved that the mixture with 70 moles % of this oxide must melt well above 2300°. Hence the solidus curve could not be followed directly beyond the composition 60 moles % UO_2, 40 moles % CaO, but the data obtained experimentally are sufficient to enable the remainder of the equilibrium diagram to be filled in with considerable confidence (Fig. 3).

FIG. 2.

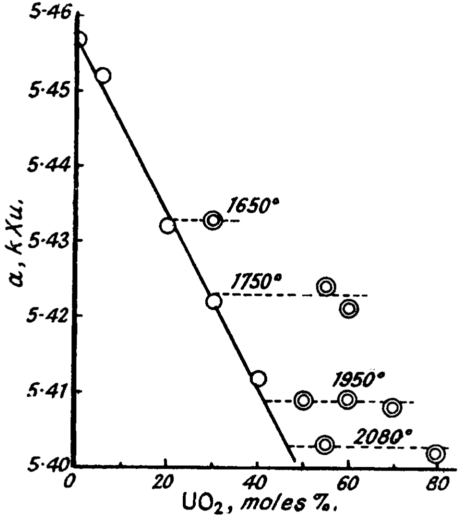
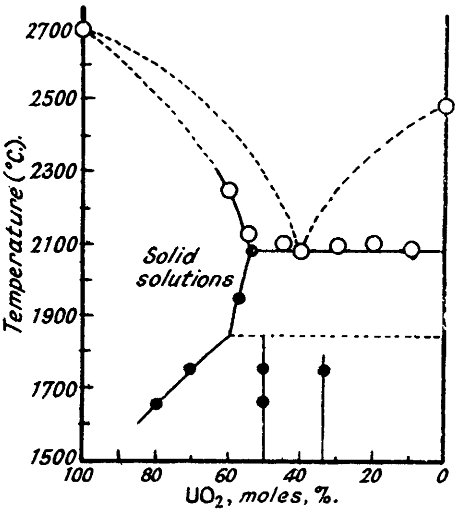


FIG. 3.



Intermediate Phases.—The tolerance of the uranium dioxide fluorite structure for lattice defects diminishes markedly as the temperature is reduced; the saturation concentration of calcium oxide decreased and the cell dimension of the uranium dioxide phase increased accordingly when materials with 50—70 moles % of the dioxide were annealed at temperatures below 2090°. The change in a was particularly marked at 1750° and 1650° (Table I). At the same time, in mixtures richer in lime (*e.g.*, 30 moles % UO_2 + 70 moles % CaO) a new phase appeared, having a diffraction pattern which could be largely indexed in terms of a fluorite cell much *smaller* than that found even for the solid solutions richest in lime. The formation of the new phase was not observed in mixtures with 50 moles % of uranium dioxide, and it was therefore first interpreted as a double oxide nCaO,UO_2, where $n > 1$. However, when specimens of the 70/30 and 80/20 CaO–UO_2 mixtures, well annealed at 1750°, were exhaustively leached with ammonium chloride solution, the resulting product was found by analysis to be CaO,UO_2 (Found : CaO, 17·30; UO_2, 83·16. Calc. : CaO, 17·19; UO_2, 82·81%), and gave a diffraction pattern which could be completely indexed in terms of the rare-earth " Type-C " structure, with a = 10·727 ± 0·002 A., 16 molecules of $CaUO_3$ per unit cell (Table III); hence in this double oxide, Ca^{2+} + U^{4+} are substituted for the $2M^{3+}$ cations of the rare-earth oxides. That the

TABLE I.

UO_2, moles, %.	M. p. (° c.).	Cell dimensions.				
		a (2080° c.).	*a* (1950° c.).		*a* (1750° c.).	*a* (1650° c.).
		UO_2.	UO_2.	CaO.	UO_2.	UO_2.
100	2700	—	5·4573	—	—	—
94·6	—	—	5·4516	—	—	—
80	—	—	5·4317	—	—	—
70	2300	—	5·4215	—	—	5·4329
60	2250	—	5·4120	—	—	—
55	2120	—	—	—	—	—
50	2060	5·4028	5·4093	—	—	—
45	2100	—	—	—	5·4243	—
40	2080	—	5·4087	—	5·4214	—
30	2090	—	5·4083	—	—	—
20	2100	5·4023	—	—	Polyphase region	—
10	2090	—	—	4·7962	Polyphase region	—
5	—	—	—	4·7971	—	—
0	2500	—	—	4·7977	—	—

TABLE II.

		2080°	1950°	1750°	1650°
Temp.					
Composition of saturated solution	CaO, moles %	47	43	29	20
	UO_2, moles %	53	57	71	80

TABLE III.

Diffraction pattern of $CaUO_3$.

θ.	*d* (uncorr.), A.	*hkl*.	*d*, calc.
9·17°	4·831	Compound C	—
10·66	4·158	(211 or Compound C)	4·379
14·31	3·112	222	3·097
15·14	2·948	Compound C	—
16·63	2·689	400	2·682
17·93	2·499	411, 330	2·528
18·47	2·430	Compound C	—
18·95	2·370	420	2·398
21·74	2·078	431, 510	2·103
23·86	1·902	440	1·897
24·40	1·863	433, 530	1·840
26·72	1·712	532, 611	1·740
27·32	1·677	602	1·696
28·44	1·617	622	1·617
29·32	1·572	631	1·582
29·83	1·547	444	1·548
31·10	1·490	640	1·488
32·24	1·443	721, 633 642	1·460 1·434
33·29	1·403	730	1·409
35·80	1·316	811, 741	1·320
37·60	1·261	822, 660	1·264
38·75	1·230	662	1·230
39·45	1·211	752	1·214
39·92°	1·199	840	1·199
41·13	1·170	842	1·173
41·92	1·152	921, 761, 655	1·157
43·54	1·117	930 932	1·131 1·107
44·72	1·094	844	1·095
48·17	1·033	1022, 666	1·033
49·25	1·0160	1031, 952	1·023
50·62	0·9958	1040, 864	0·9959
51·63	0·9816	1033, 961	0·9875
52·58	0·9690	1110, 954	0·9711
53·44	0·9583	1121, 1051	0·9556
54·17	0·9493	880	0·9481
55·06	0·9388	970, 1130	0·9407
57·15	0·9162	1060, 866	0·9198
58·07	0·9069	1062	0·9066
59·41	0·8940	1200, 884	0·8939
63·91	0·8569	1073	0·8533
65·40	0·8465	1240	0·8480
68·42	0·8277	10·82	0·8276
70·01	0·8190	1066	0·8178
72·04	0·8091	12·44	0·8085
73·31	0·8035	1330,994	0·8039
79·72	0·7822	1341, 1174	0·7865
81·37	0·7785	1093	0·7781

$a = 10{\cdot}727 \pm 0{\cdot}002$.

formation of $CaUO_3$ is observed only in mixtures containing an excess of free lime is explicable if the double oxide is formed by the phase reaction

$$\underset{\text{(solid solution phase)}}{Ca_{(1-x)}U_x\,O_{(1+x)}} + (2x-1)CaO \longrightarrow \underset{\text{(Type-C phase)}}{xCaUO_3} \qquad . \quad . \quad . \quad . \quad . \quad (1)$$

occurring at the interface between crystals of lime and of the solid solution. The *X*-ray measurements are summarised in Table II. The type-C oxide structure contains two sets of cation positions: 8 cations on Wyckoff's 8 (*e*) ($\pm\ \tfrac{1}{4}\ \tfrac{1}{4}\ \tfrac{1}{4}$ and its permutations), and 24 cations on 24 (*e*) ($\pm\ u0\tfrac{1}{4}$ with $u = ca.\ -0{\cdot}030$). Hence $16Ca^{2+}$ and $16U^{4+}$ could be accommodated (*a*) with Ca^{2+} and U^{4+} distributed statistically over all positions, (*b*) with $8U^{4+}$ on 8(*e*) and $8U^{4+} + 16Ca^{2+}$ on 24(*e*), or (*c*) with $8Ca^{2+}$ on 8(*e*) and $16U^{4+} + 8Ca^{2+}$ on 24(*e*). These alternatives lead to different relative intensities for certain " non-fluorite " reflections, though only a few lines are available for comparison and not obscured by coincidences. The observed intensity data are in best accord with alternative (*a*) *i.e.*, random distribution of Ca^{2+} and U^{4+} over all cation sites.

In attempting to identify the double oxide (later proved to be $CaUO_3$) by bracketing the compositions $3CaO,UO_2$, etc., it was found that a second intermediate phase, phase C, appeared on prolonged annealing of 80/20 and 90/10 $CaO–UO_2$ mixtures, being formed apparently by a second phase reaction between $CaUO_3$ and CaO. This was finally isolated by the same method as used for isolation of $CaUO_3$, and although it remained a little uncertain whether the product was, in fact, still contaminated with $CaUO_3$, the analytical results indicated that the second compound was $2CaO,UO_2$ ($= Ca_2UO_4$). The diffraction pattern indicated a tetragonal cell with at least one rather large dimension; the measurements, listed in Table IV, could be quite well indexed in terms of a cell with $a = 16{\cdot}760$, $c = 9{\cdot}208$ *kX*, $c/a = 0{\cdot}549$, which could contain 32 molecules of Ca_2UO_4 in conformity with Zachariasen's data for the spatial requirements of Ca^{2+}, O^{2-}, and U^{4+}

TABLE IV.

Diffraction pattern of Ca_2UO_4.

$a = 16{\cdot}760$; $c = 9{\cdot}208$ A.; $c/a = 0{\cdot}549$.

θ.	d (uncorr.).	*hkl.*	d, calc.	Intensity.
9·21°	4·809	301	4·778	w
9·45	4·688	320	4·647	w
10·73	4·134	321	4·148	ms
		400	4·188	
14·92	2·989	332	2·997	w
15·16	2·943	440	2·963	s
15·55	2·871	530	2·875	w
		203	2·882	
17·72	2·529	621	2·547	vw
18·08	2·480	630	2·499	vw
		442	2·491	
18·47	2·429	522	2·439	vw
18·91	2·375	602	2·388	vw
21·71	2·081	800	2·095	m
23·94	1·897	802	1·907	vw
24·36	1·866	840	1·874	w
24·69	1·843	524	1·851	vw
26·53	1·723	803	1·730	m
		544	1·728	
27·22	1·683	770	1·693	m
28·47	1·615	724	1·628	vw
28·86	1·595	951	1·603	vvw
		843	1·599	
30·91	1·498	1101	1·503	vvw
		545	1·506	
31·45	1·475	880	1·481	w
32·01	1·452	705	1·460	vvw
		326	1·457	
33·26	1·403	882	1·410	vvw
33·74	1·386	516	1·390	vvw
35·41	1·328	1212	1·332	vvw
		883	1·334	
35·70	1·319	1240	1·325	vvw
36·15	1·305	1080	1·309	vw
		905	1·309	
36·69	1·288	925	1·294	vw
		706	1·292	
37·37	1·268	1242, 1171	1·273	vw
38·17	1·245	1260, 945	1·249	w
39·10	1·220	826, 507	1·224	vw
40·76	1·179	1224	1·182	w
41·57	1·160	1055	1·163	vw
42·10	1·148	008, 1440	1·151	vw
42·79	1·133	776	1·137	vw
43·27	1·123	1371	1·126	w
44·23	1·099	1372	1·102	vw

The two intermediate compound phases were not formed in any experiments carried out at 1900—1950°, and so must decompose between 1750° and 1950°. From the trend in the compositions of the limiting UO_2 solid solutions it would appear that the upper limit of occurrence of the phase reaction (1) is somewhere about 1850° ± 50° (giving the final phase diagram shown in Fig. 2).

The compound $CaUO_3$ appears to be the first example of a double oxide, ABO_3, crystallising with the Type-C rare-earth oxide structure. It thus extends our knowledge of the systematics of a class of compound which clearly reflects the influence of ionic radii upon the stability of alternative crystal structures. The simple oxides A_2O_3 formed by small cations ($r_A : r_O < 0{\cdot}60$) crystallise with the corundum structure, and double oxides ABO_3 for which $r_A : r_O$ and $r_B : r_O$ are both $<0{\cdot}6$ assume the related ilmenite structure. Examples are $FeTiO_3$, $LiNbO_3$. Larger tervalent cations give rise to A_2O_3 oxides with the cubic Type-C structure ($0{\cdot}6 < r_A : r_O < 0{\cdot}8$) or the hexagonal type-A structure ($r_A : r_O > 0{\cdot}8$). ABO_3 double oxides described hitherto, containing at least one fairly large cation, have all had the perovskite structure, which has a remarkable range of stability; it includes double oxides with radius ratios as diverse as those of $YAlO_3$ ($r_Y : r_O = 0{\cdot}67$, $r_{Al} : r_O = 0{\cdot}36$), $LaAlO_3$ ($r_{La} : r_O = 0{\cdot}82$, $r_{Al} : r_O = 0{\cdot}36$), and $BaCeO_3$ ($r_{Ba} : r_O = 0{\cdot}96$, $r_{Ce} : r_O = 0{\cdot}72$). It would appear, therefore, that the $CaUO_3$ type, related to the type-C structure in the same way that the ilmenite type is derived from the corundum structure, is probably formed only where the cations A and B are not merely appropriate, but also similar in size.

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