for chloride solutions. K_m was found to be independent of Pu(IV) concentration in the range 3.6×10^{-4} to 2.9×10^{-3} *M* Pu(IV). Since K_m is smaller for chloride solutions than for perchlorate solutions, weak chloride complexing of Pu^{+4} is indicated. However, the precision of the experiments is not sufficient to warrant calculation of a stability constant.

A persistence of properties with changing atomic number would be expected for a "rare-earth-like" series (actinide, thoride or uranide) of the same oxidation number. The qualitative and quantitative similarity in the hydrolytic properties thus supports the assumption that uranium and plutonium are members of such a series. The similarity of the absorption spectra with each other and with the rare earths (see footnote 13) is further confirmation as is the weakness of the chloride complexes of these elements (strong chloride complexes would be expected if they were transition elements).

Uranium(IV) ($K_m = 0.032$, $\mu = 0.5$) is slightly more acidic than plutonium(IV) ($K_m = 0.025$, $\mu = 0.5$). This difference is barely outside the experimental error but appears to be significant. On the basis of simple "coulombic arguments" the reverse would be expected, since uranium(IV) is larger than plutonium(IV) as indicated by the metal–oxygen distances of the dioxides (U–O, 2.363 Å.; Pu–O, 2.332 Å.[22]). A similar but considerably more pronounced anomalous trend was found for the MO_2^+ and MO_2^{++} ions.[23] In the case of the M^{+4} ions, however, this trend is too small to provide an adequate basis for extensive interpretation.

Acknowledgment.—We are indebted to the Chemical Development Division of the Research Laboratory of Y-12 (Electromagnetic Plant), and particularly Mr. Albert Clark and Mr. G. H. Clewett for their helpful coöperation in connection with this problem.

Summary

1. Through *p*H measurements of UCl_4 solutions, U^{+4} was established to be the species of uranium(IV) in acidic solutions.

2. The acid constant of U^{+4} was determined as a function of ionic strength for chloride and perchlorate solutions through a spectrophotometric method. The molarity constants could be fitted approximately to a Debye–Hückel limiting law and the activity constant $K_a = 0.21 \pm 0.02$ was estimated for the equilibrium $U^{+4} + 2H_2O \rightleftarrows UOH^{+3} + H_3O^+$.

3. The stability constant for the reaction $U^{+4} + Cl^- \rightleftarrows UCl^{+3}$ was estimated to be K_c = *ca.* 0.63 ($\mu = 0.5$) and $K_c^0 = 7.0$ ($\mu = 0$).

4. The acid constant of Pu^{+4} ($K_m = 0.025$, $\mu = 0.5$) was found to be almost identical with though slightly smaller than that of U^{+4} ($K_m = 0.032$, $\mu = 0.5$).

5. The spectral data, the quantitative hydrolytic data and the observation that the chloride complexes of uranium(IV) and plutonium(IV) are weak, are confirmatory evidence of the hypothesis that these elements are members of a "rare-earth-like" series.

OAK RIDGE, TENNESSEE RECEIVED NOVEMBER 25, 1949

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[22] W. H. Zachariasen, Report MDDC-67 (June 1946).

[23] K. A. Kraus and F. Nelson, Report AECD-1864 (March 1948).

[CONTRIBUTION FROM RESEARCH LABORATORY, UNITED STATES STEEL CORPORATION OF DELAWARE]

The Composition of $CaO–FeO–Fe_2O_3$ and $MnO–FeO–Fe_2O_3$ Melts at Several Oxygen Pressures in the Vicinity of 1600°

BY R. W. GURRY AND L. S. DARKEN

As a step in the extension of the work on the iron–oxygen system[1,2] to steel-making slags it was thought desirable to investigate near 1600° the several ternary systems formed by the addition to iron oxides of each of the other important elements to be found in such slags. The investigations of Chipman and co-workers[3,4] on the activity of FeO in slags of the system $CaO(MgO)–SiO_2–FeO$ furnish a basis for our knowledge of slags in equilibrium with liquid iron, that is, at partial pressures of oxygen in the vicinity of 10^{-8} atmospheres at 1600°. This paper reports the results of some determinations of the composition of the liquid oxides in the systems Ca–Fe–O and Mn–Fe–O in the vicinity of 1600° at oxygen pressures up to one atmosphere. Similar data from the literature on the system Si–Fe–O have been included and tentative phase diagrams at 1600° for all three systems have been constructed. Some of the data here reported were accumulated several years ago when it was intended to make a more complete investigation; some are the recent by-product of another investigation. This partial report based on such fragmentary data is made now, since the more complete investigation is no longer planned for the immediate future.

The experimental technique including the method of analysis was substantially that reported in our earlier investigations. The vertically mounted tubular globar furnace was used

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[1] Darken and Gurry, THIS JOURNAL, **67**, 1398 (1945).

[2] Darken and Gurry, *ibid.*, **68**, 798 (1946).

[3] Fetters and Chipman, *Trans. Am. Inst. Min. Met. Eng.*, **145**, 95 (1941).

[4] Taylor and Chipman, *ibid.*, **154**, 228 (1943).

exclusively. Premelts (12 to 30 g.) were first made in a platinum crucible from analytical grade chemicals (Fe_2O_3, $CaCO_3$, $MnCO_3$). The sample for equilibration was suspended in a platinum crucible in the controlled atmosphere of the inner porcelain tube of the furnace. The approximate weight of the sample was in some measurements eight-tenths of a gram, in which case four crucibles with different contents were usually equilibrated simultaneously; in other instances it was four grams. Prior experience[1,2] and the preliminary melts indicated that two hours were sufficient for equilibration at 1600°. The smaller samples were quenched in mercury, the larger ones in water; in the water quench only the outside of the crucible, not the sample itself, was exposed to water. The principal experimental difficulty lay in adequately quenching the specimens equilibrated with one atmosphere of oxygen. The results from the smaller samples in this atmosphere (especially in the Ca-Fe-O system) were particularly erratic. Those from the larger samples were more consistent. Greater faith in the results of the larger sample is further justified by the fair agreement of top and bottom analyses indicated in the last entry of the four gram samples in Table I; the slightly higher Fe_2O_3 content of the top portion is undoubtedly due to air oxidation. The four gram melts of the $CaO-FeO-Fe_2O_3$ system (Table I) were prepared as part of an investigation of the quaternary system including sulfur (sulfate). For these the atmosphere contained small amounts of SO_2 (not over 8% except in one case so designated); the partial pressure of oxygen is so near one atmosphere that no correction is deemed necessary. The sulfur content of these melts as given in Table I is very low and any appreciable influence on the $FeO-Fe_2O_3$ ratio thereby seems highly unlikely. Justification of this view is to be found in a comparison of the data for the two four-gram melts at 1618°.

The results for the $CaO-FeO-Fe_2O_3$ system are given in Table I and are shown graphically in Fig. 1. The termini of the curves on the $FeO-Fe_2O_3$ side of the diagram are taken from previous work of the authors (Table III). The dashed curves for 1400°, 1500° and 1600° at one atmosphere pressure of oxygen represent the work of White.[5] These are shown for comparison and to indicate the temperature coefficient. The agreement is seen to be fairly good. From the data of White and of Krings and Schackmann[6] curves for 0.2 atmosphere of oxygen are also shown. The work of the latter authors is obviously in discord with both the present investigation and that of White.

TABLE I

COMPOSITION OF $CaO-FeO-Fe_2O_3$ MELTS[a]

Temp., °C.	Time, hours	Initial composition[b]	Final composition,[d] wt. % FeO	Fe_2O_3	S
		0.8-g. Samples in O_2[c]			
1574	1	3	3.20	67.85	....
1600	1	1	0.55	57.67	....
		2	1.64	62.30	....
1603	2	1	0.38	56.94	....
		2	2.95	67.88	....
		3	12.24	77.14	....
		4	1.54	61.05	....
		4-g. Samples in O_2 (+SO_2)[c]			
1621	4	7	0.32	52.91	0.37
1624	17	5	4.61	67.8	.008
1618[e]	5.5	6	1.95	62.08	.14
1618	5.5	6	1.75	62.78	.018
1600	18.5	9	21.94	78.05	<.01
1610	4	8 top	8.11	75.32	....
		bottom	9.07	74.42	....
		0.8-g. Samples in CO_2[c]			
1603	2	1	7.38	53.06	....
		2	8.24	54.35	....
		4	30.07	59.51	....
1608	4	1	8.74	54.17	....
		2	7.71	53.74	....
		3	13.67	57.01	....
		4	32.09	58.89	....

[a] Specimens in a group indicated by a common temperature and time were equilibrated simultaneously. [b] Initial compositions:

	Weight, % FeO	Fe_2O_3		Weight, % FeO	Fe_2O_3
1	0.49	57.37	5	5.73	66.66
2	1.46	62.45	6	2.55	62.08
3	1.22	71.46	7	0.00	49.20
4	12.00	79.70	8	.00	91.26
			9	.00	100

[c] Total pressure one atmosphere. [d] Balance CaO. [e] 17.35% SO_2 in O_2.

The approximate boundaries of the phase regions at 1600° are included in Fig. 1. The composition of the liquid in equilibrium with solid CaO in the binary $CaO-Fe_2O_3$ system was taken from Sosman and Merwin.[7] The composition of the liquid containing about 20 weight per cent. CaO in equilibrium with iron and that of the liquid in equilibrium with both solid CaO and metallic iron are from Fetters and Chipman.[3] The curve representing the composition of the liquid in equilibrium with solid CaO was drawn to conform with thermodynamic principles governing the relative positions of the field boundaries intersecting at the point representing the composition of the liquid in equilibrium with solid CaO and iron.

The composition at 1600° of the liquid oxide in the binary system $FeO-Fe_2O_3$ in equilibrium with liquid iron and also with each of the various atmospheres, taken from previous work by the present authors,[2] is given in Table III. The

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(5) J. White, *Iron and Steel Inst., Carnegie Schol. Mem.*, **27**, 1 (1938).

(6) Krings and Schackmann, *Z. Elektrochem. angew. physikal. Chem.*, **41**, 479 (1935).

(7) Sosman and Merwin, *J. Wash. Acad. Sci.*, **6**, 532 (1916)

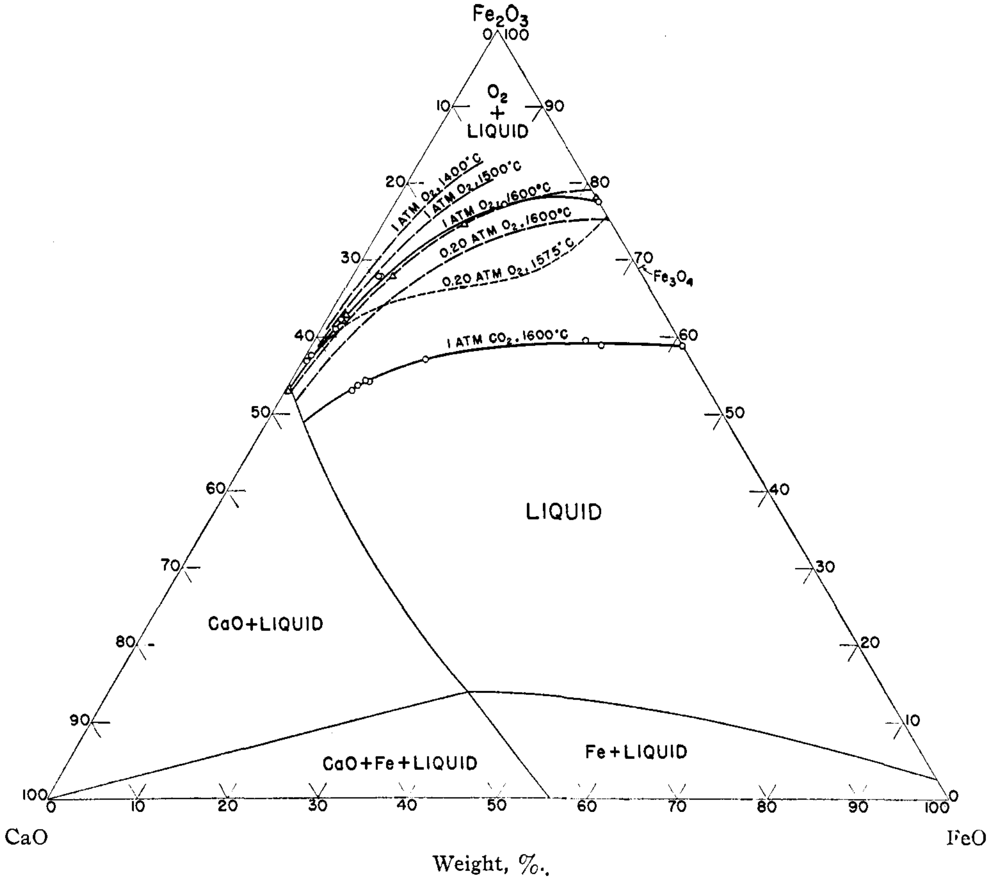

Fig. 1.—The system CaO–FeO–Fe_2O_3 at 1600°: ——, this investigation, O, 0.8-g. sample; △, 4.0-g. sample; - - - - - - Krings and Schackman; — — —, White.

largest discrepancy between White's data and ours seems to occur here—namely, at the iron-oxide boundary of the three component diagrams. Also included in Table III is the oxygen pressure

TABLE II

COMPOSITION OF MnO–FeO–Fe_2O_3 MELTS[a]

Temp., °C.	Time, hours	Initial composition[b]	Final composition,[d] wt. % FeO	Fe_2O_3
		Samples in O_2[c]		
1600	1	10	14.98	73.80
		11	6.72	71.57
		12	0.37	66.55
		13	0.36	54.85
1597	2	10	13.90	74.48
		11	6.78	71.15
		12	0.12	67.17
		13	0.12	54.49
		Samples in CO_2[c]		
1600	2	10	30.44	58.48
		11	21.98	55.50
		12	13.80	53.16
		13	5.49	49.58
1600	4	10	30.40	57.89
		11	19.79	58.14
		12	13.69	52.61
		Samples in CO–CO_2[c]; $p_{CO}/p_{CO_2} = 0.920$		
1618	2.2	11	50.18	17.40
		12	44.15	16.92
		13	32.95	15.61

[a] Specimens in a group indicated by a common temperature and time were equilibrated simultaneously. [b] Initial compositions:[d]

	Wt. %FeO	Wt. %Fe_2O_3
10	20.54	68.22
11	10.10	68.11
12	4.27	62.90
13	0.24	55.19

[c] Total pressure one atmosphere. [d] Balance MnO.

TABLE III

OXYGEN PRESSURE OF VARIOUS ATMOSPHERES AND COMPOSITION OF THE IRON OXIDE IN EQUILIBRIUM WITH THEM AT 1600°

Atmosphere	Oxygen pressure, atm.	Composition of oxide, wt. % FeO	Fe_2O_3
1 atm. O_2	1	22.4	77.6
0.2 atm. O_2	0.20	27.1	72.9
1 atm. CO_2	3.6×10^{-3}	41.1	58.9
$p_{CO}/p_{CO_2} = 0.920$	2.3×10^{-7}	83.4	16.6
(Liq. Fe and pure iron oxide)	6.9×10^{-9}	97.3	2.7

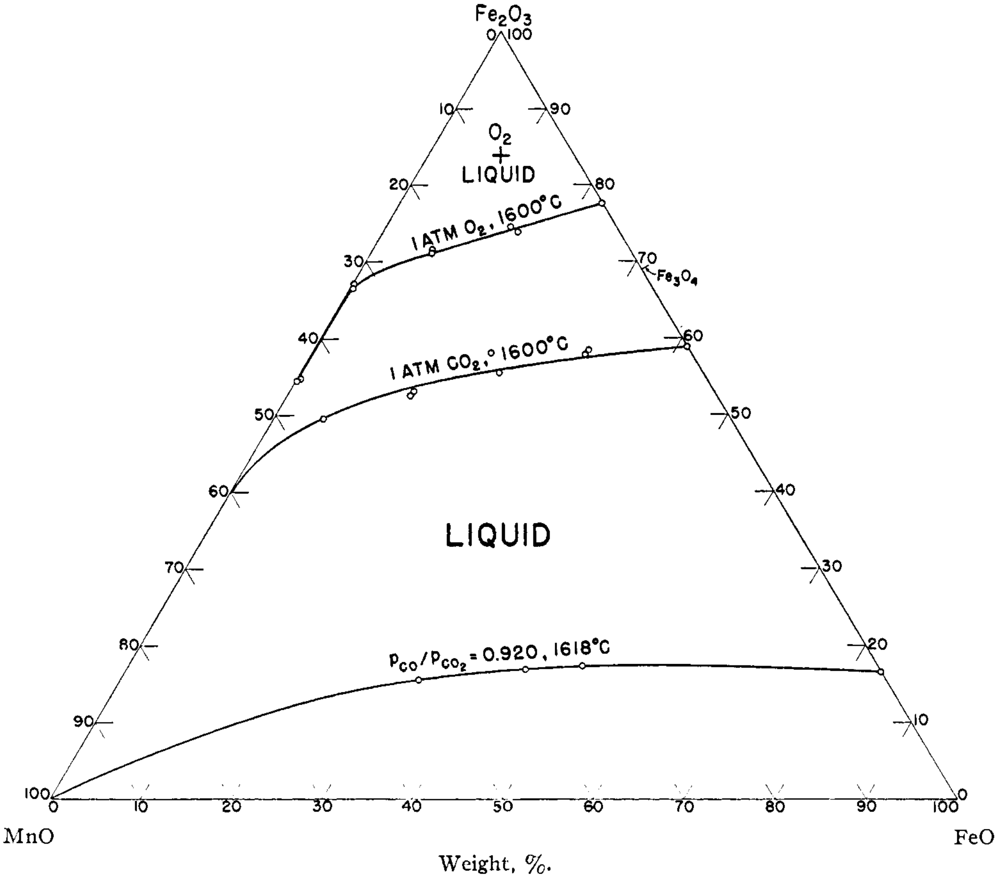

Fig. 2.—The system $MnO-FeO-Fe_2O_3$, at 1600°: O, this investigation.

associated with each atmosphere and with the equilibrium between iron and its pure oxide at 1600°. The curve on the diagram for each atmosphere at 1600° is seen to be an oxygen isobar and, in order to cover the liquid field completely, isobars covering a range of a factor of about 10^{10} in oxygen pressure are required.

Along any oxygen isobar, starting with pure iron oxide and increasing the CaO content, the ratio of Fe_2O_3 to FeO in the melt is seen to increase. Thus CaO may be said to be a flux for Fe_2O_3 and vice versa. This behavior is undoubtedly associated with the fact that calcium being more electropositive than ferrous iron, favors the formation in the melt of an atomic grouping involving oxygen, possibly the $Fe_2O_5^{4-}$ ion suggested by Chipman and Chang.[8]

The results for the $MnO-FeO-Fe_2O_3$ system are given in Table II and are shown graphically in Fig. 2. At 1600° and one atmosphere total pressure the liquid field covers substantially this whole diagram except for the upper corner which represents the two phase field of oxygen gas and liquid. As the amount of MnO increases along an oxygen isobar the ratio of Fe_2O_3 to FeO increases, as in the previous case. The similarity of the isoactivity curves for oxygen in this and the preceding diagram is rather striking and would seem to indicate that manganese is only slightly less electropositive than calcium in iron oxide melts; alternatively it may be said that MnO appears only slightly less basic than CaO.[9]

The diagram for the system $SiO_2-FeO-Fe_2O_3$, upon which no data are here reported is shown in Fig. 3. This figure is included on account of the importance of this system in steelmaking slags and to show the contrast between the effects of relatively basic CaO or MnO and relatively acidic SiO_2 when added to the $FeO-Fe_2O_3$ system. The 1600° isobars at one atmosphere and at 0.2 atmosphere of oxygen are taken from the data of White.[5] One point from Krings and Schackmann[6] at 0.2 atmosphere of oxygen and 1575° is shown. The composition of the liquid in equilibrium with silica and iron is from

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(8) Chipman and Chang, *Trans. Am. Inst. Min. Met. Eng.*, **185**, 191 (1949).

(9) The 1600° isotherms at one atmosphere of oxygen for these systems appear to cross at low FeO content. This may be due to experimental error or may reflect the presence of a higher oxide of manganese the composition of which lies outside the field of this diagram. In this connection, it is possible that the melts of highest manganese content in oxygen may contain more oxygen than corresponds to mixtures of MnO and Fe_2O_3; the method of analysis would not detect this.

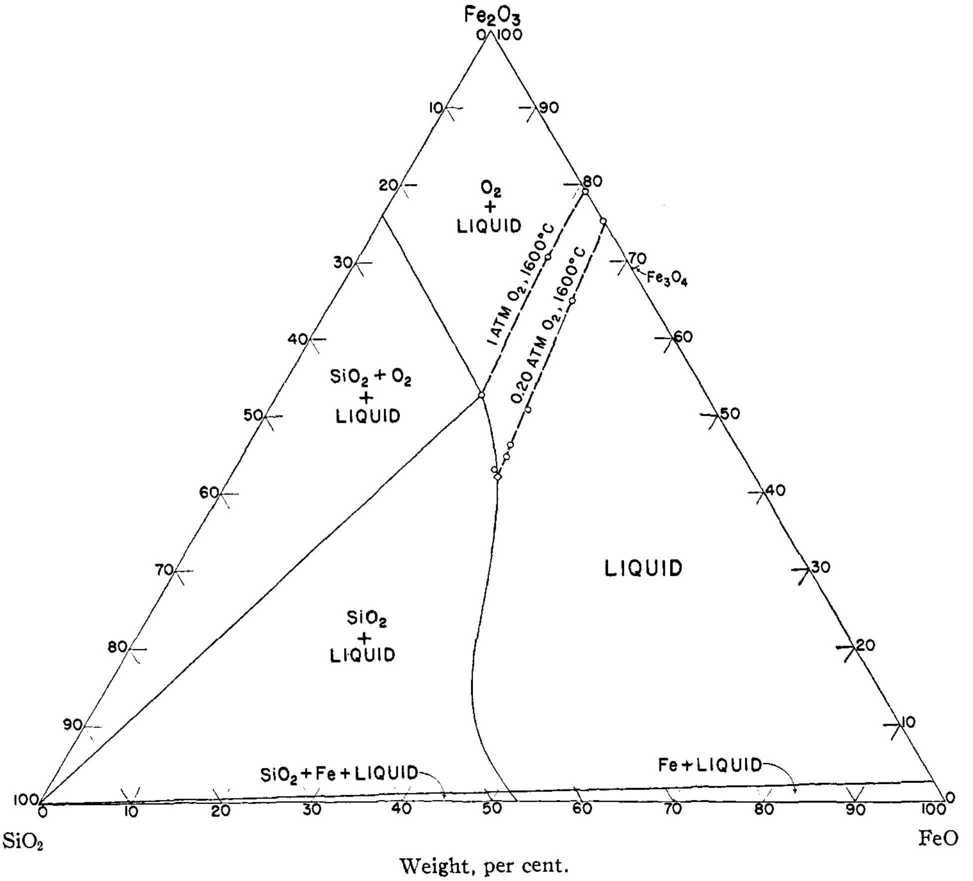

Fig. 3.—The system SiO_2–FeO–Fe_2O_3 at 1600°: O— — — —, White, 1600°; ◇, Krings and Schackman, 1575°.

Bowen and Schairer.[10] In the absence of any further data the line representing the composition of the liquid in equilibrium with iron was drawn straight. The curve representing the composition of the liquid in equilibrium with silica is shown inflected in order to conform to the thermodynamic requirement as to relative slopes in the vicinity of the point representing the composition of the liquid in equilibrium with silica and iron.

Summary

Analysis of CaO–FeO–Fe_2O_3 and MnO–FeO–Fe_2O_3 melts equilibrated in various atmospheres at 1600° has given the oxygen activity at several levels over the liquid fields in these systems. From these and other data tentative equilibrium diagrams at 1600° have been constructed for these systems and also for the SiO_2–FeO–Fe_2O_3 system.

Kearny, New Jersey Received February 24, 1950

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(10) Bowen and Schairer, *Am. J. Science*, **24**, 177 (1932).