[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF ILLINOIS INSTITUTE OF TECHNOLOGY]

The Melting Point–Composition Diagram of the Zirconium–Oxygen System[1]

BY DANIEL CUBICCIOTTI

The solidus curve of the zirconium–zirconium dioxide system has been investigated by observing the melting points of wires of the oxidized metal. The results show that near the melting points oxygen dissolves to the extent of 55 atom per cent. in solid zirconium metal, while zirconium dissolves in the solid dioxide to form a 15 mole per cent. solution. No evidence was found for compounds other than the dioxide.

Many investigators have remarked on the high solubility of oxygen in zirconium metal. Fast[2] found that samples containing as much as 40 atom per cent. oxygen still had the structure of zirconium metal. Guldner and Wooten[3] found no evidence for a zirconium dioxide structure in the X-ray patterns of samples containing as much as 38 atom per cent. oxygen. DeBoer and Fast[4] found that oxygen dissolved in the metal spread the α–β transition temperature into a range of temperatures in which the α and β forms were in equilibrium. These same authors[5] observed that the oxygen migrated as negatively charged particles when a current was passed through the metal.

The present study of the melting points of zirconium–oxygen solutions was made in order to add to the understanding of this interesting system.

Experimental

Preparation of Samples.—Samples of zirconium with known oxygen content were prepared by oxidizing samples of zirconium under controlled conditions. To prepare the samples, about 0.2 g. of 0.015-inch Foote Mineral zirconium wire was weighed, cut into three pieces, and bent into horseshoes. These pieces were suspended by a silica rod and heated in a porcelain tube in vacuum; they were then oxidized by admitting a known amount of 99.8% pure oxygen gas. When cool the wires were reweighed and the percentage of oxygen in the sample calculated from the weights.

The amount of oxidation, and hence the composition of the samples, was controlled by fixing the temperature of the oxidation and its duration. The oxidations were performed from about 650 to 850°. At temperatures much above 900° the wires burned to a slag when oxygen was admitted.

The samples resulting from this procedure were non-equilibrium mixtures of a zirconium metal core and a coating of zirconium dioxide containing zirconium in solution. The mixtures were equilibrated as described below.

Determination of Melting Points.—A horseshoe sample prepared as above was connected to two iron leads in a porcelain tube. The porcelain tube was fitted with an optically flat glass window and suitable glass tubing so that the system could be evacuated. Vacua of the order of 10^{-4} mm. or better were maintained in the system. The sample was heated to the melting point by an a.c. current, supplied through a constant voltage transformer and a variable transformer. The brightness temperature of the sample was measured with a Leeds and Northrup Optical Pyrometer. The brightness temperature at the melting points could be observed with a fair degree of precision. The observed melting points of several samples of pure zirconium, for example, ranged from 1675 to 1695° brightness.

In order to equilibrate the mixtures of metal and oxide formed by the oxidation, the samples were heated for about 20 minutes at a temperature approximately 200° below the expected melting point. This treatment was not essential, however, since some samples containing 40% oxygen that were melted without the equilibration were found to melt at the same temperature. The heating of the samples to the melting point from room temperatures was gradual (so that the sample did not melt unobserved) and took about 15 minutes. Apparently the gradual heating was sufficient to equilibrate the mixtures.

The method just described was adequate for samples containing as much as 30 atom per cent. oxygen. With increasing oxygen content the samples became more fragile. It was necessary to scrape the ends to make electrical contact and this treatment was too severe for samples with more than 30% oxygen.

For oxygen percentages greater than 30, another heating method was devised. The sample was placed in a close-fitting coil of 0.01″ tungsten wire, and the tungsten wire was heated electrically. In this method the brightness of the sample was difficult to distinguish from that of the wire. When the sample melted, the brightness of the wire and of the sample were very close. This method gave less precise results. At 57 atom per cent. oxygen the melting points observed for three pieces of the same sample ranged from 2190 to 2230° brightness.

Determination of Spectral Emissivities.—To convert the brightness temperature to true[6] temperature it is necessary to know the emissivity of a sample at the wave length of maximum transmission of the pyrometer. Spectral emissivities have been reported for zirconium metal. Thus it was only necessary to show how the emissivities of the samples changed as oxygen was dissolved in the metal.

For this purpose the room temperature reflectivities of the samples after melting were determined by a method used by Worthing and by Prescott.[7] A sheet metal cylinder 2.5″ in diameter and 12″ long was lined with white cotton velveteen. A 32-candlepower, 6-volt bulb was placed at either end of the cylinder, and, to diffuse the light from these bulbs, a single thickness of the velveteen was placed just in front of them. A 0.75″ square sighting hole was cut in the center of the cylinder wall. The brightness temperatures of the walls and of the samples were determined with the optical pyrometer. The reflectivity of the sample was calculated from the expression

$$r = \text{anti}\log_{10}\left[-\frac{2.303\,c\,(T - S)}{\lambda\,TS}\right]$$

in which r is the reflectivity of the sample, T the brightness temperature of the walls in degrees Kelvin and S that of the sample; c is a constant equal to 1.438×10^4 micron degrees and λ the wave length of maximum transmission of the pyrometer (0.65 micron). The emissivity, ϵ, of a body is related to its reflectivity as

$$\epsilon = 1 - r$$

Transmission of the Window.—The brightness of the wire samples was somewhat diminished by the glass window through which it was observed. A correction for this diminution was made by multiplying the spectral emissivity of the sample by the transmission coefficient of the window. The window was a Pyrex plate 2 mm. thick ground by the American Instrument Company. Its transmission was determined with a Beckmann Spectrophotometer. The transmission coefficient at 0.65 micron was found to be 0.908. Kanolt[8] has found a value of 0.904 for the transmission coefficients of several glasses.

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(1) This research was sponsored by the Office of Naval Research.

(2) J. D. Fast, *Metallwirtschaft*, **17**, 641 (1938).

(3) W. G. Guldner and L. A. Wooten, *Trans. Electrochem. Soc.*, **93**, 223 (1948).

(4) J. H. DeBoer and J. D. Fast, *Rec. trav. chim.*, **55**, 459 (1936).

(5) J. H. DeBoer and J. D. Fast, *ibid.*, **59**, 161 (1940).

(6) The true temperature of a body will be taken to mean its temperature defined by the International Scale.

(7) C. H. Prescott, Jr. in "Temperature, Its Measurement and Control," Am. Inst. Phys., Reinhold Pub. Co., New York, N. Y., 1941, p. 1200.

(8) Kanolt, quoted by P. D. Foote, *et al.*, "Pyrometric Practice," Bur. Stand. Tech. Papers, No. 170, p. 111, 1921.

Errors.—The method used in the present work is not capable of great precision and is open to several distinct uncertainties. First, the sample may have picked up oxygen and changed in composition during the heating period. To determine the magnitude of the effect a piece of pure zirconium wire was heated in the system for 20 minutes at about 1800–1900°. The melting point of this sample was found to be 75° higher than that of a sample brought rapidly to its melting point. Thus, estimating from Fig. 1, the sample had picked up enough oxygen to form a 5 atom per cent. solution. With larger concentrations of oxygen the additional oxygen uptake was apparently smaller. A 40% sample that was heated for 20 minutes melted at the same temperature as one that was not equilibrated. Therefore the compositions may have been richer in oxygen by as much as 5% for samples of low oxygen content, while for samples containing 40% oxygen or more the composition probably did not change by more than 1%.

Second, the uncertainty involved in matching the brightness of the sample at its melting point with that of the pyrometer filament was approximately 25°. Furthermore, the variation in surface condition from one sample to the next gave rise to variations in spectral emissivities. The variation in spectral emissivity was at most from 0.42 to 0.51, as indicated in Table I. At 2000° brightness, such a variation corresponds to a 50° variation in melting temperature. As a result of these errors inherent in the method, the true melting point of any one sample may have been in error by as much as 75°. The melting points relative to one another were probably in error by less than 50°.

Results and Discussion

The Brightness Temperatures on Melting.—The brightness temperatures of the melting points for the compositions observed are given in Fig. 1. The two kinds of points in the figure correspond to the two methods used to heat the samples.

As described above, the samples containing less than 30 atom per cent. oxygen were heated by their own resistance. After melting, all these samples were silvery and metallic in appearance. X-Ray diffraction patterns of these samples showed only lines due to the zirconium structure; however, the positions of some of these lines were shifted by the presence of oxygen as reported by DeBoer and Fast.[5]

At 28 atom per cent. oxygen, the melting point of the sample was determined by both heating methods. The two points are shown in Fig. 1, where it may be seen that the two methods agree within 15° for this composition.

For compositions greater than 30 atom per cent. oxygen, the samples were heated with a tungsten coil. The appearance of the melted samples was somewhat difficult to observe since only small samples were used. From about 30 to 50% oxygen, the samples were dark grey and shiny. The X-ray patterns of these samples after melting were those of zirconium metal plus those of tungsten.[9] At 57 and 60% the melted samples were dull black. For the compositions greater than 60%—that is, near the composition of zirconium dioxide—the melted samples were dull black in color.

The Emissivities.—In order to convert the melting points observed in brightness temperature to true temperature, values of the emissivites of the samples were required. These were determined by measuring the reflectivities as described above. Table I lists the values observed for several samples after they had been melted.

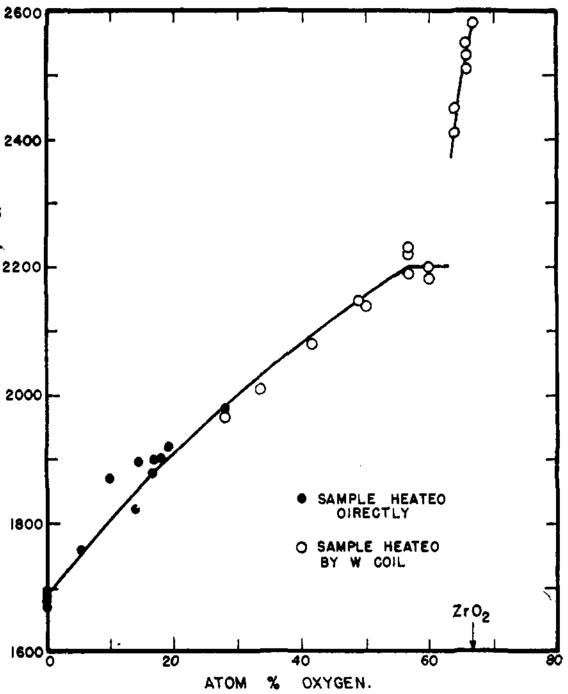

Fig. 1.—The melting point diagram for the zirconium–oxygen system in brightness temperature.

The precision of these measurements was not high, as witnessed by the discrepancies observed in duplicate measurements. However, the values agree within about 10% and there is no observable trend of the emissivities with oxygen content. The emissivities were therefore assumed to be independent of concentration with a value between 0.44 and 0.50 at room temperature.

TABLE I

THE SPECTRAL EMISSIVITIES OF SAMPLES WITH DIFFERENT OXYGEN CONTENT

Oxygen in sample, atom %	Brightness temp., °C. Of background		Reflectivity at 0.65μ	Spectral emissivity at 06.5μ
		Of sample		
Pure Zr	1035	982	0.49	0.51
	1078	1025	.51	.49
10	1025	983	.56	.44
	1065	1012	.50	.50
14	1025	983	.56	.44
22	1018	978	.58	.42
	1054	1002	.50	.50
28	1027	980	.53	.47

Zwikker[10] has determined the emissivity of both α- and β-zirconium. He found the spectral emissivities at 0.652 micron to be 0.48 for α- and 0.43 for β-zirconium. Since the alpha is the low temperature stable form, the present measurements should be compared with the 0.48 value. Burgess and Waltenburg[11] report values of 0.32 and 0.30 for the spectral emissivities of the solid and liquid metal respectively at the melting point. Since the present measurements agree with Zwikker's his value was used. Because the zirconium is the

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[9] Am. Soc. Testing Mat., "Orginal Set of X-Ray Diffraction Patterns," 1942, Card 3153.

[10] C. Zwikker, quoted by: (a) J. H. DeBoer, *Ind. Eng. Chem.*, **19**, 1266 (1937); (b) J. H. DeBoer, P. Clausing and J. D. Fast, *Rec. trav. chim.*, **55**, 450 (1936).

[11] G. K. Burgess and P. G. Waltenburg, *Bull. Nat. Bur. Stand.*, **11**, 591 (1915).

beta form at the melting point, the emissivity was taken to be 0.43.

For those samples which were heated by a tungsten spiral, it was difficult to distinguish the brightness of the sample from that of the wire. However, the spectral emissivity of tungsten in this temperature range is also 0.43,[12] and the correction from brightness to true temperature could therefore be made unequivocally regardless of whether the brightness was that of the sample or the heater.

The conversion from brightness to true temperature was made by means of the formula

$$1/T - 1/S = \lambda/c \ln \epsilon \cdot t$$

where T is the true temperature and S the brightness temperature on the absolute scale, λ is 0.65 micron, c is 1.438×10^4 micron degrees, ϵ is the spectral emissivity at 0.65 micron, and t the transmission coefficient of the glass window, 0.908.

In order to check the accuracy of the method, the melting points of wires of several metals were determined when they were heated by their own resistance. A comparison of the observed melting points with literature values is given in Table II. For zirconium the observed values agree with the literature within about 10°, while for the other metals differences of as much as 60° are noted. Whether these large differences arise from inaccurate values of the emissivity used or from errors in measuring the brightness when the wire melted cannot be decided from these measurements.

In Table II is included the brightness melting point observed for zirconium dioxide. This sample was made by oxidizing a sample of 65.7 atom per cent. oxygen until it no longer had the grey color indicative of excess zirconium in the oxide. If one uses a value of 0.43 for the emissivity of the sample, the melting point calculated is 250° above the literature value. Such a large difference indicates an erroneous value of the spectral emissivity. Therefore, the value of the spectral emissivity necessary to reconcile the brightness melting point with the literature value was calculated to be 0.76.

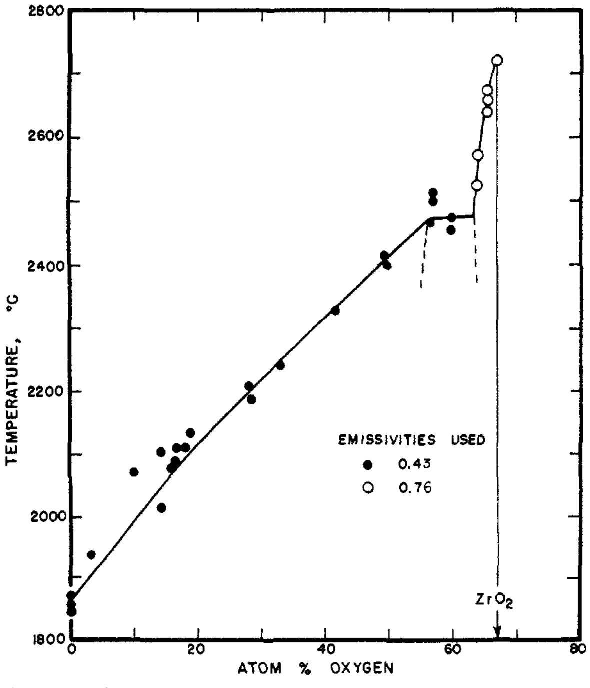

Fig. 2.—The solidus curve for the zirconium–oxygen system.

This value of the emissivity would indicate that the body observed was dark in color, and, in fact, the sample after melting was quite dark. The dark color may have been caused by partial dissociation of the zirconium in the oxide.

TABLE II

COMPARISON OF OBSERVED MELTING POINTS WITH LITERATURE VALUES

Metal	Brightness at m.p., °C.	Spectral emissivity used	True temp. of melting, °C.	Lit. value, °C.
Zr	1685	0.43	1862	1857[10a]
	1688		1866	
	1690		1868	
Fe	1415	.35[12]	1577	1530[13]
	1425		1588	
	1430		1593	
Ni	1330	.36[12]	1471	1452[13]
Pt	1520	.30[12]	1730	1770[13]
	1527		1738	
	1540		1757	
ZrO_2	2580	.43	2974	2715[13]
	2580	.76	2715	

Since the observed melting points of the samples of composition near to that of zirconium dioxide were approximately the same as that of the oxide, the same value of the emissivity (0.76) was used to correct those melting points. In view of the arbitrary selection of the emissivity, the true temperatures calculated in that region of the system are possibly open to large errors. However, the shape of the curve is probably not greatly in error.

As a check that the emissivity of a solid solution of zirconium in its dioxide can have a value near 0.76, reflectivities were measured for several sheet samples of zirconium oxidized to varying degrees. The oxide coating on the metal can vary from pure white to jet black depending on the degree of oxidation.[14] The differences in color are probably due to differences in concentration of zirconium dissolved in the oxide observed. The emissivities varied from about 0.77 to 0.90 for the dark colored oxides.

The Phase Diagram.—The interpretation of the melting points into a phase diagram is not unique. In particular, in the region from 55 to 63% oxygen it is possible (1) that the melting points go through a maximum due to a compound of composition Zr_2O_3 or (2) that the melting points are constant due to a region of solid immiscibility of two phases.

To clarify this point, X-ray diffraction patterns were made of samples of 55.5, 61 and 63% oxygen that had been heated at 2000° for 30 minutes, and samples of 57 and 60% that had been melted. The patterns from all these samples, except the one at 60%, were those of zirconium metal and zirconium dioxide in addition to the tungsten lines

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[12] W. F. Roeser and H. T. Wenzel, ref. 7, p. 1318, 1313.

[13] K. K. Kelley, Bur. Mines Bull. No. 393, 1936.

[14] D. Cubicciotti, THIS JOURNAL, **72**, 4138 (1950).

from the heating coil. The pattern of the 60% sample was that of zirconium dioxide plus tungsten. Since no structures appeared other than those of the metal and the dioxide, it was assumed that no new compound formed in the 55 to 63% region. Thus that region was one of two immiscible solids, namely, zirconium and zirconium dioxide.

In Fig. 2 is given the phase diagram for the system as interpreted from the present results. Since the points represent the melting points of the samples, the curve is the solidus line for the system. The dotted lines drawn downward from the horizontal portion of the curve are included to indicate that a region of solid immiscibility exists and are not intended to mark the actual limits of solubility.

The diagram indicates that near the melting points only two solid phases are stable—those of zirconium metal and zirconium dioxide. The metal phase is capable of dissolving oxygen to form a solid solution of 55 atom per cent. oxygen, while the dioxide can form a solid solution with as much as 15 mole per cent. zirconium in zirconium dioxide.[15] In particular the diagram shows that no compound such as ZrO or Zr_2O_3 is stable at its melting point. The compound ZrO has been postulated to account for a number of phenomena,[16,17,18] however, in general it is possible to explain these on the basis of a solid solution of metal in the dioxide.

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(15) The value of 15 mole per cent. represents the mole fraction of Zr in ZrO_2. It is obtained by a simple calculation from the solubility limit of 63 atom per cent. oxygen in zirconium shown in Fig. 3.

(16) E. Friederich and L. Settig, *Z. anorg. Chem.*, **145**, 127 (1925).

(17) H. Jacobs, *J. Appl. Phys.*, **17**, 596 (1946).

(18) C. A. Zapffe, *J. Am. Ceramic Soc.*, **27**, 293 (1944).

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[CONTRIBUTION FROM THE STERLING CHEMISTRY LABORATORY OF YALE UNIVERSITY]

Studies in the Theory of the Polarographic Diffusion Current. V. Effects of Certain Variables on *m* and the Residual Current

BY LOUIS MEITES

Data are presented on the effects of pressure, supporting electrolyte, applied potential, temperature and gelatin concentration on *m* and the residual current.

Experimental

The apparatus and technique have been described in preceding papers.[1-3]

Data and Discussion

Factors Affecting *m*. The Effective Pressure.—The theory underlying the variation of *m* with the applied pressure has been discussed by Kolthoff and Lingane,[4] and has been tested by Maas.[5] Assuming $\sigma = 400$ dynes/cm.[4]

$$m = k_1 (h_{\text{eff.}} - 3.1\, [mt]^{-1/3}) \qquad (1)$$

Table I summarizes the data for a typical capillary giving drop times between 1.8 and 7.6 sec. *Within these limits* equation (1) is satisfied with a mean error of ± 0.10%, and hence may be used with confidence so long as no better accuracy than this is required. However, the data clearly show small but significant deviations from the theory: k_1 is lower at both high and low pressures than at intermediate pressures. Over five hundred measurements of *m* with fourteen capillaries of widely varying characteristics, nearly all with more than one supporting electrolyte, indicate that k_1 increases about 2% as the drop time is increased from 0.5 to about 4 sec. and decreases about 1.5% from $t = 6$ to 19 sec. As most of these variations occur at drop times below 2 sec. and above 10 sec., it is plain that equation (1) cannot be relied on for capillaries with very short or very long drop times.

TABLE I

EFFECTS OF APPLIED PRESSURE AND SUPPORTING ELECTROLYTE ON *m*

Data for capillary C (marine barometer tubing) at $E_{\text{d.e.}} = -1.00$ v. *vs.* S.C.E. The value of the back pressure term in equation (2) was 1.57 ± 0.01 $\text{sec.}^{1/3}\text{mg.}^{-1/3}$; $T = \theta = 25.0°$

h, cm. of Hg	*m*, mg./sec. in 0.1 *F* KNO_3	$m/(h - 1.57) \times 10^2$	*m* in 0.1 *F* KCl	*m* in 0.1 *F* KCl–0.1 *F* HCl
107.78	4.2730	4.023	4.2432	4.2747
98.78	3.9133	4.025	3.8840	3.9129
89.78	3.5514	4.026	3.5291	3.5545
80.78	3.1837	4.019	3.1649	3.1830
71.78	2.8277	4.027	2.8052	2.8304
63.78	2.5062	4.028	2.4875	2.5032
57.78	2.2645	4.028	2.2468	2.2669
52.78	2.0640	4.030	2.0492	2.0653
47.78	1.8644	4.034	1.8524	1.8634
42.78	1.6625	4.033	1.6518	1.6602
38.78	1.5019	4.035	1.4896	1.5020
34.78	1.3357	4.021	1.3285	1.3347
31.78	1.2155	4.022	1.2098	1.2147
28.78	1.0952	4.024	1.0888	1.0958
26.78	1.0118	4.012	1.0064	1.0140

The Supporting Electrolyte.—Typical data for *m* of a single capillary in three supporting electrolytes are shown in Table I. The values of *m* in 0.1 *F* potassium nitrate and in 0.1 *F* potassium chloride–0.1 *F* hydrochloric acid are practically identical. In 0.1 *F* potassium chloride, however, *m* is appreciably lower: the difference varied somewhat among capillaries but was always between 0.4 and 0.9%. In ordinary polarographic work, therefore, it is justifiable to assume that *m* is independent of supporting electrolyte composi-

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(1) L. Meites and T. Meites, THIS JOURNAL, **72**, 3686 (1950).

(2) L. Meites and T. Meites, *ibid.*, **73**, 395 (1951).

(3) L. Meites, *ibid.*, **73**, 1581 (1951).

(4) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1941, pp. 62–69.

(5) J. Maas, *Collection Czechoslov. Chem. Commun.*, **10**, 42 (1938).