to prevent actual diffusion during the run. Having made the run with iodine at room temperature, the measurements were carried up to the higher temperatures, preferably exactly that of the air run. Preliminary results are: T (absolute) = 300°; $P_{\text{air}} = 0.242$ mm.; $P_{\text{air}} + I_2 = 0.448$ mm.; $T = 908°$; $P_{\text{air}} + I_2 + I = 0.825$ mm.; $T = 925°$; $P_{\text{air}} + I_2 + I = 0.847$ mm.; $T = 1213°$; $P_{\text{air}} + I = 1.580$ mm.

In these runs the temperature of the furnace was determined by a calibration using the instrument as a gas thermometer. This calibration checked that using a thermocouple to within a few degrees except at the higher temperatures where there was reason to suspect that the thermocouple (which was a very imperfect one) was at fault. We should have liked to check this calibration optically, but the necessary pyrometer was not available at the moment. The most serious source of error came from the fact that the water used to cool the furnace was at a temperature lower than room temperature and therefore it was suspected that iodine was being deposited at the point (A). There was, therefore, considerable chance of the partial pressure of the iodine in the cold gas changing with the temperature of the furnace. Indeed, at the higher temperatures the pressure change is higher than that calculated on the assumption of complete dissociation of the iodine. However, the results at about 915° lead to a value for log k of 3.7 (Lewis and Randall calculate 3.4 ± 0.2).

Summary

A new method of measuring the temperature and molecular weight of gases has been described. A preliminary determination of the dissociation constant of iodine at 740° has been made.

BALTIMORE, MARYLAND

[CONTRIBUTION FROM THE GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 106]

THE EQUILIBRIUM BETWEEN ZIRCONIUM OXIDE AND CARBON AND THEIR REACTION PRODUCTS AT INCANDESCENT TEMPERATURES

BY C. H. PRESCOTT, JR.

RECEIVED JUNE 28, 1926 PUBLISHED OCTOBER 6, 1926

Plan of the Investigation

This research was begun in the fall of 1923 at the suggestion of Professor A. A. Noyes as an attempt to devise an apparatus and precision technique for the study of chemical equilibria at incandescent temperatures. The particular subject of interest was the investigation of the stability of refractory oxides. The reduction of zirconium oxide by carbon was chosen as the immediate subject for research.

This reduction has been studied by Troost,[1] Moissan,[2] and more recently by Wedekind.[3] All three report a carbide as the product, Moissan and Wedekind agreeing on the formula ZrC. Van Arkel and deBoer[4] prepared the carbide by passing zirconium tetrachloride, hydrogen and carbon monoxide over a hot tungsten filament which precludes the presence of free carbon, and checked their results with x-ray powder photographs. They report that the formula is ZrC and that the substance has a sodium chloride type of structure. The formula ZrC_2 reported in the International Critical Tables seems to be without justification.

The predominant feature of the present technique is the small size of the furnace. This allows the attainment and very accurate control of high temperatures with a minimum of power. It also makes it possible to enclose the apparatus completely in glass, and the energy evolved is not so great as to prevent thermostatting the furnace and so obtaining uniform conditions in the environment. The furnace is comparatively easy to manufacture and replace, which is essential as it is bound to deteriorate at the temperatures employed.

The limiting factor in the present technique is the temperature control, by pyrometer measurements, in the face of a fluctuating line voltage. The use of commercial power is not to be recommended. The chief fundamental limitation of the method is that it applies directly only to equilibria with one gaseous component, where the reaction is not limited by gaseous diffusion but progresses by direct displacement.

Acknowledgment is due to the Norman Bridge Laboratory of Physics for the loan of the optical pyrometer, to Dr. W. E. Forsythe and Dr. A. G. Worthing of the Nela Research Laboratory for assistance with the pyrometry, and to Dr. S. B. Hendricks for the x-ray work on the solid phases. This investigation was aided financially from a grant made to Professor A. A. Noyes by the Carnegie Institution of Washington.

The Temperature Measurements

The temperature was measured with a Leeds and Northrup optical pyrometer fitted with an auxiliary lens of 4 diopters which enabled it to be brought to a distance of 20 cm. from the furnace. At the close of the experiments this instrument was recalibrated against a standard lamp obtained from the Nela Research Laboratory. At the same time the transmission was measured of a water cell made of a section of a 1.5-liter Pyrex flask and a piece of window glass, which closely approximated the conditions of the furnace and thermostat windows with water between.

---

[1] Troost, *Compt. rend.*, **116**, 1227 (1893).

[2] Moissan, *ibid.*, **116**, 1222 (1893). Moissan and Lengfeld, *ibid.*, **122**, 651 (1896).

[3] Wedekind, *Chem.-Ztg.*, **31**, 654 (1907).

[4] Van Arkel, *Physica*, **4**, 286 (1924). Van Arkel and deBoer, *Z. anorg. Chem.*, **148**, 345 (1925).

The corresponding correction to the observed temperature was calculated from the Wien radiation law by the formula[5] $(1/S)-(1/\theta) = (\lambda \log t)/0.4343c_2$, where θ is the observed temperature, S is the brightness temperature of carbon, t is the transmission of the water cell (83.9%), λ is the effective wave length of the pyrometer color screen (0.66μ), and c_2 is 14330μ degree.

Since the new calibration agreed within 3° with the old Bureau of Standards calibration in the temperature range of the equilibrium measurements, corrections for the emissivity of carbon were used as determined on the old scale. A furnace with an 0.8mm. hole in the center of the wall had been mounted in furnace bulb No. 1 and the apparent brightness temperature of the adjacent wall compared with the temperature of the hole at a series of temperatures from 1250°K. to 2050°K. This correction is $T-S = 0.017\ S-8$ degrees.

During the calibration it was found that readings could be duplicated to about 1.5°. The emissivity correction probably introduces errors not greater than 4°, so the temperatures as reported are probably relatively good to 2° or 3°, and absolutely to 6° or 7°.

Apparatus and Procedure

The furnace, shown in Fig. 2 (where the dimensions are stated in inches), is a tube of Acheson graphite 5.7 cm. long, 0.635 cm. in diameter at the ends, and 0.318 cm. in the central section for a length of 2.54 cm., with a 0.04cm. wall. This is supported on tungsten rods pressed into the ends of the tube. The charge is retained at the center by graphite plugs resting loosely against the tungsten rods.

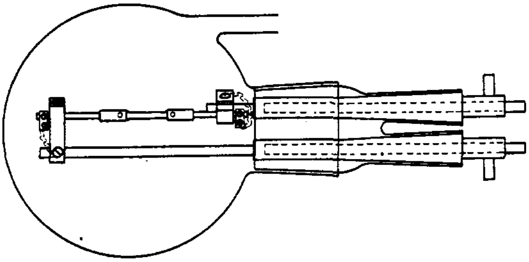

Fig. 1.—Furnace bulb No. 1.

The charge was in every case a pellet of compressed zirconium oxide and carbon, approximately 0.64 cm. long and 90 mg. in weight, fitting loosely into the furnace. The zirconium oxide was made by igniting Kahlbaum's zirconium nitrate. The carbon was Acheson graphite, the same as that of the furnace.

Furnace bulb No. 1 (Fig. 1) was found inadequate for equilibrium measurements, but was used to determine the emissivity of carbon and to run samples to completion in a vacuum. The furnace was horizontal, the tungsten rods resting in steel guides clamped to water-cooled copper leads. Electrical connection was made by flexible copper wire fastened to steel

---

[5] W. E. Forsythe, *J. Optical Soc. Am.*, **4**, 305 (1920); **5**, 494 (1921). Report of Standards Committee on Pyrometry.

clamps on the ends of the tungsten rods. The outer ends of the water-cooled leads were tapered to fit ground-glass seals in a Pyrex plug which in turn was ground to fit a 1-liter Pyrex flask. Seals were made with Dennison's banker's specie sealing wax, and the flask was permanently connected to the vacuum system.

In furnace bulb No. 2 (Fig. 2) the tungsten rods were welded to flexible copper wire through a nickel intermediary. The copper was melted completely over the nickel to prevent the formation of nickel carbonyl. The flexible cord was then welded to a 0.635cm. copper rod which was silver soldered through a copper disk seal in the end of a 1.9cm. Pyrex tube. The central section was a 2.54cm. tube with a window mounted 3 cm. from the axis, and a 2mm. connecting tube.

The extreme fragility of the furnace necessitated the flexible leads as well as the following assembling procedure. The lower lead was clamped vertically in a special support, and the furnace pushed onto the tungsten rod. Then the central tube was placed over the furnace and down against the seal. The top lead was then clamped somewhat above its final position and lowered gradually as the furnace was worked onto the tungsten rod. Finally, the central tube was raised into position and connected with a hand torch. Support, furnace and all were then placed in position and the connecting tube was sealed to the rest of the apparatus.

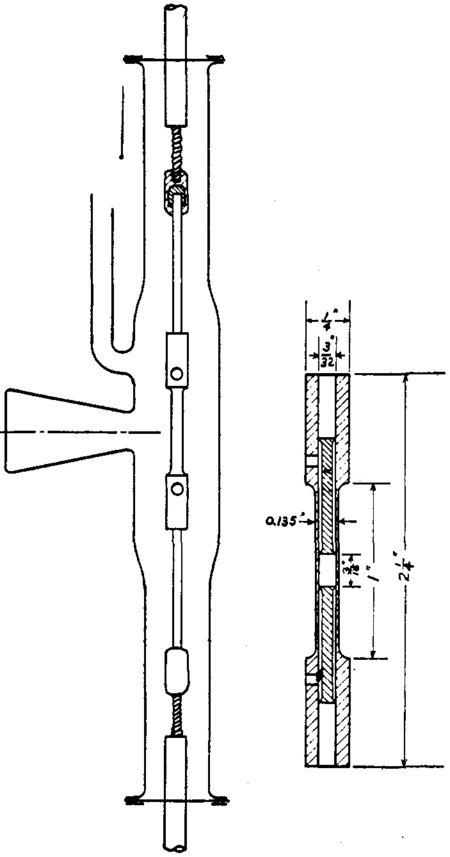

Fig. 2.—Furnace bulb No. 2 and furnace.

The furnace was connected (see Fig. 3) through a small trap T to the manometer M which had a range of 2 meters, and a piece of capillary tubing at the bottom of the column to damp out oscillations at high pressures. The outlet from the Toepler pump P and the connecting tube to the stopcock A comprised the rest of the enclosed gas space during measurements, which was all placed below the water level in a thermostat. This was of 300-liters capacity and equipped with a 500-watt heater and an electric fan at opposite ends of the same relay, and two stirrers, one located near the furnace so as to pass by it a constant stream of water from below. It was set at 35° and could dissipate an extra kilowatt of power without rise of temperature. The thermostat was set on a laboratory desk, and had a glass window through which the temperature measurements were made.

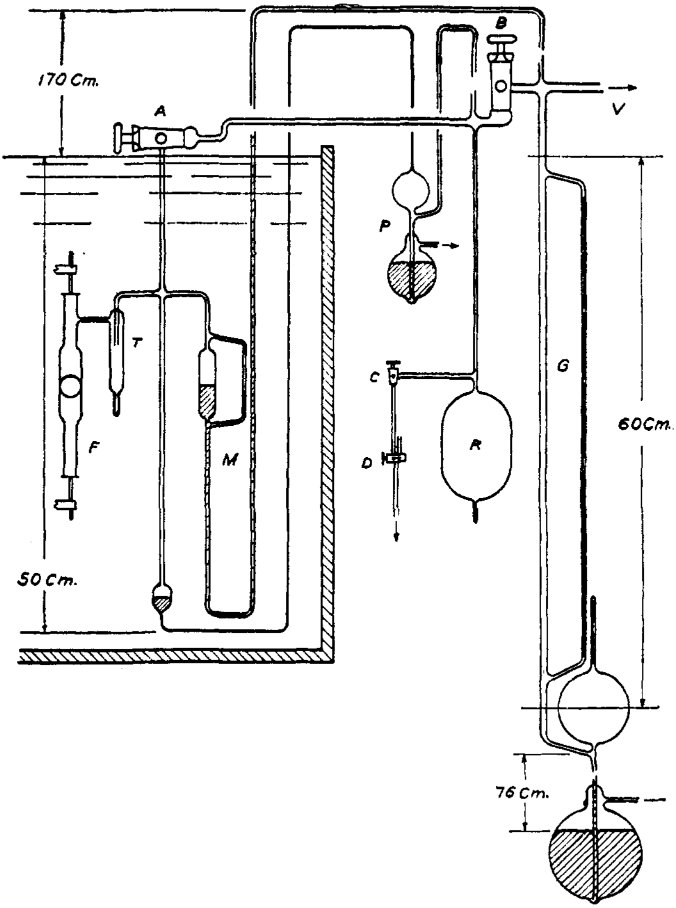

Fig. 3.—Apparatus for high-temperature equilibria.

Current was supplied by a 1-kilowatt transformer with an 8.5ohm control resistance in the primary. The furnace current was of the order of 150 amperes at 6 volts.

In Fig. 3 the essential features also of the apparatus outside the thermostat are shown: a Toepler pump P to force gas into the furnace bulb, a gas reservoir R, and a stopcock B which isolates them from the McLeod gage G and the vacuum pumps which are connected at V, a single-stage mercury-diffusion pump backed by a Hyvac oil pump. The top of the manometer is also brought back to the high-vacuum line so as to give absolute pressure measurements. Due to the high pressures sometimes used, the delivery tube and compensating arm of the Toepler pump extend upwards to the same height as the manometer. The stopcocks A, B and C were set in sealing wax and warmed with a hand torch when turned. A and B were of 1cm. bore to facilitate evacuation and prevent clogging. They withstood differences of pressure up to 2.5 atmospheres and remained tight for many turnings.

After the furnace was assembled and installed and the thermostat filled, the whole system was evacuated with Cocks A and B open, C closed and Pump P connected to the fore vacuum. When a pressure of 10^{-4} mm. was obtained, it was assumed that the furnace was tight, and the furnace was run for a few minutes to drive off any adsorbed inert gases. Then C was opened, and when vacuum was reëstablished, B was closed. Carbon monoxide was generated from sodium formate and sulfuric acid, washed in sodium hydroxide and sulfuric acid, passed through phosphorus pentoxide, and admitted to the apparatus through D, a greased three-way stopcock. Simultaneously, the vacuum was released on the pump P. The apparatus was filled, usually to one atmosphere, but several times to one-half atmosphere as the pressure in the reservoir had to be below that in the furnace. Then Cocks C and A were closed. Additional gas was pumped into the furnace bulb by applying pressure to P from the compressed-air line or an oxygen tank. To set the pressure precisely, the Toepler pump was operated with the furnace running. The pressure could be reduced to that of the reservoir by opening the cock A. As the thermostat had to be drained a couple of inches whenever this cock was turned, runs were made as much as possible in the order of increasing pressure.

The rate of reaction was so slow, and the quantity of material so small, corresponding to a total change of 30 cm. pressure in the enclosed volume of 100 cc., that it was impracticable to wait for the system to attain equilibrium. Instead, it was merely used as an indicator of the distance from equilibrium. Each run constituted a measurement of the rate of reaction at a predetermined temperature and pressure.

The current was first thrown on and the furnace brought to the approximate temperature. Then gas was pumped in to the proper pressure. Readings were next made on the optical pyrometer and the furnace current adjusted till the temperature was that set for the run. Then the pressure was read on the manometer. The temperature was adjusted before each of the pressure readings, which were taken at intervals of three to ten minutes for periods of one to three hours. The temperature fluctuated considerably, commonly 5°, often 10°, occasionally as much as 30°, as a result of the rapid changes in line voltage.

With the apparatus and procedure described above it was found impossible to obtain interpretable results until allowance was made for the emission of carbon monoxide produced by the oxygen adsorbed on the carbon furnace. With a blank pellet of powdered graphite, rates of emission were found entirely comparable with previously supposed rates of reaction, increasing with the temperature, but entirely independent of the pressure. After baking for five hours at 2000° and 1.5 atmospheres, the rates were zero at lower temperatures. After 12 hours more, the rate was also zero at 2000°. There was, however, a slight emission for a few minutes, presumably of adsorbed carbon monoxide, after the furnace had been standing for some time at room temperature. It was concluded, as was also found in subsequent experiments, that satisfactory runs could be obtained, provided the furnace was baked overnight at the highest

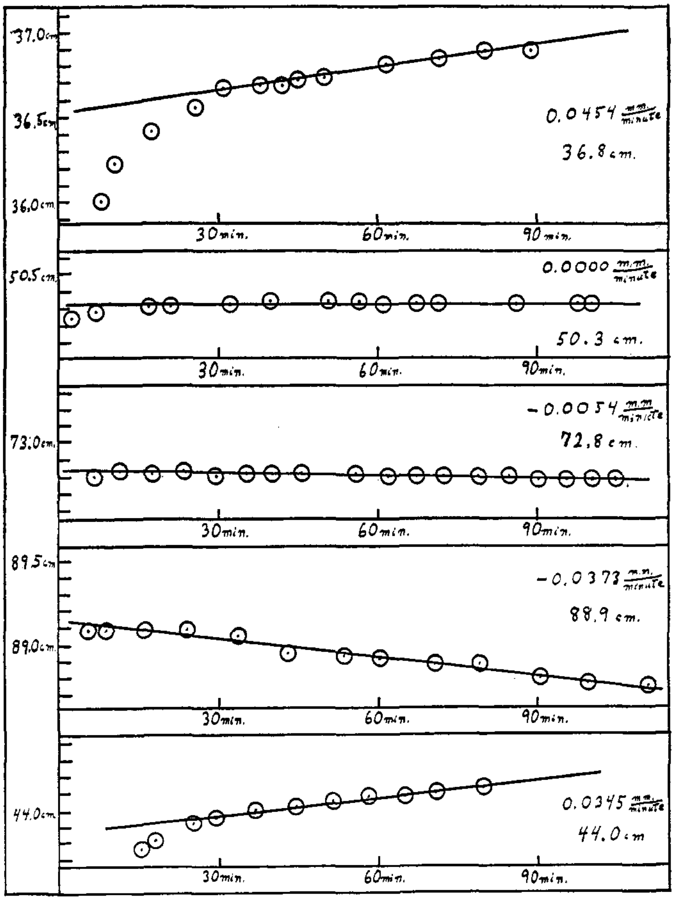

Fig. 4.—Original data at 1914°K.

temperature to be used in the early life of the furnace. Pressures were employed above the equilibrium pressure of the zirconia-carbon system so that the initial state should be known after baking.

Results of the Equilibrium Measurements

In working up the data the pressures during a run were plotted against the time. The slope of the best straight line gave the rate for the run. Rates at the same temperature were then plotted against the mean pressure for the run. If possible, a straight line was then drawn through these rates and its intercept was taken as the equilibrium pressure for that temperature. If the data were not good enough for this, an estimate was made from the graph as to the most probable pressure at which the rate should become zero. Finally, equilibrium pressures were converted to atmospheres, and a plot made of log p against $10^4/T$. The results are shown in Figs. 4–10. Fig. 4 gives all the original data at 1914°K., which series of runs was selected as a typical example. The rest of the data are presented only in summarized form.

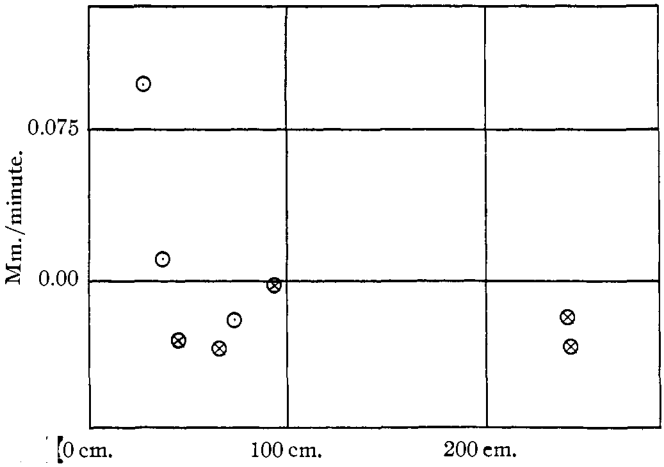

Fig. 5.—T = 1880°K.; p = 39.7 cm. = 0.522 atm.

Pellet A was used only at 1880°K. The furnace was evacuated and closed off. It was run for ten minutes, developing a pressure of 10 cm. This was pumped off and the furnace filled to one atmosphere and closed. A short run indicated a rapid rise, as was to be expected from adsorbed oxygen. The pressure was then raised to three atmospheres, but fluctuated too much to observe a rate over a short period of time. Next morning the pressure had dropped 2 cm. (Fig. 2), and continued during the day. The pressure was lowered to one atmosphere, and a very slight drop continued overnight. The system was then evacuated and a controlled run of three hours was made in which the pressure rose to 10 cm.

This ran the reaction ahead so that the pellet was more active thereafter. Two more uncontrolled runs were made, and then three in which the reaction was followed according to the outlined procedure (points in circles), before an accident terminated the series. The equilibrium pressure was estimated as 0.522 atmosphere, the least certain of the determinations due to the lack of more controlled runs.

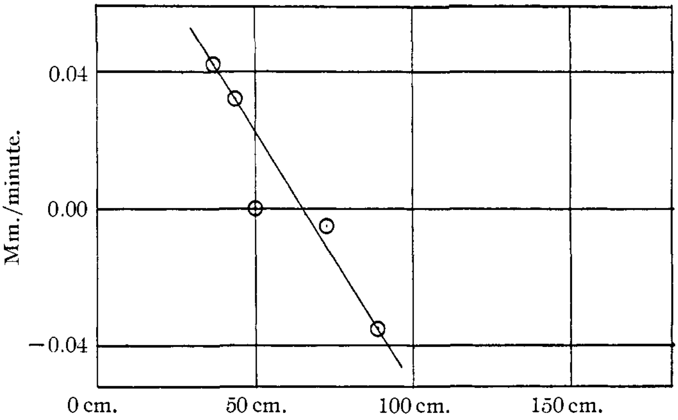

Fig. 6.—T = 1914°K.; p = 65.0 cm. = 0.856 atm.

The other equilibrium measurements were made on Pellet B. After the preliminary treatment, the system was evacuated and run for an hour at 1948°K., until the pressure rose to 8 cm. Then a run was made at 46 cm. which gave a good forward rate (Fig. 7), at 92 cm. where the rate was zero, and at 143 cm. where the rate was reversed. Six more runs were made at intermediate pressures. Zero rate persisted over quite a range of pressure. This seems to be connected with the fact that the line voltage was

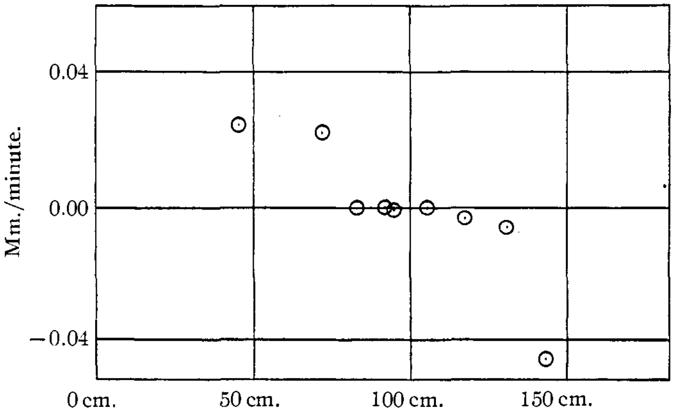

Fig. 7.—T = 1948°K.; p = 92.2 cm. = 1.21 atm.

fluctuating considerably. The visibility became bad because of the eye strain coming from the constant readjustment of the temperature, and this added to the difficulties of the temperature regulation. The effective rate should be an average over the temperature fluctuations. The persistence of a zero rate may be due to the necessity of building up an interface before the rate could become appreciable. This interface would be rapidly destroyed in a momentary reversal of the reaction, while there would be an appreciable lag before it could be reëstablished. Thus, if the set pressure corresponded to equilibrium at a temperature within the range of fluctuation, the resultant rate might be much reduced.

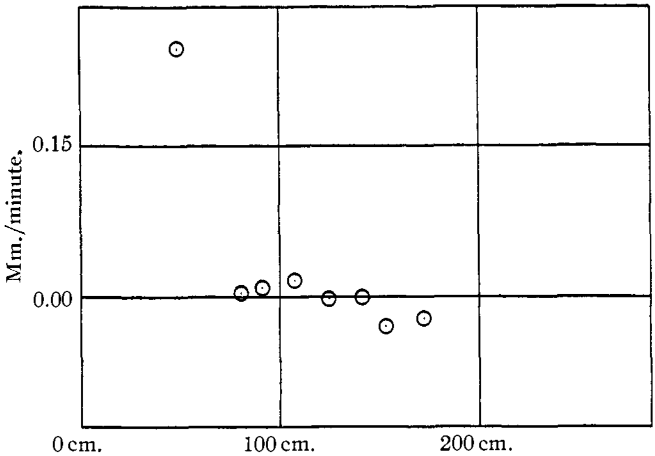

Fig. 8.—T = 1982°K.; p = 127.0 cm. = 1.67 atm.

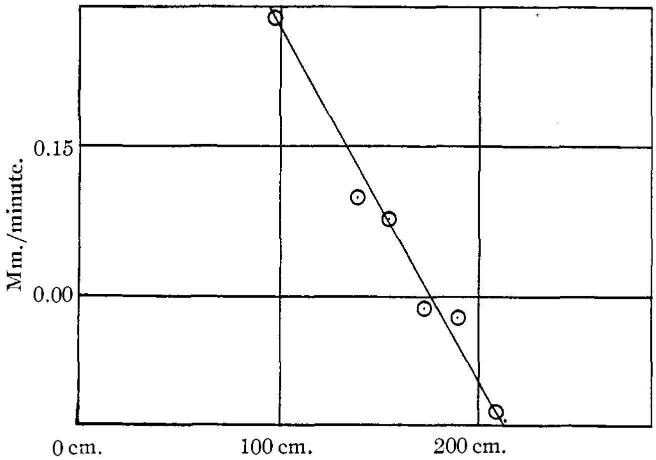

Fig. 9.—T = 2015°K.; p = 176.2 cm. = 2.32 atm.

In the series at 2015°K. conditions seemed much better (Fig. 9). There were no zero rates, though this may well be due to the higher temperature. However, at 1914°K. (Fig. 6) the visibility was again exceptionally good, the temperature requiring only occasional readjustment. In both these series the rates seem to bear a linear relation to the pressure, and the intercepts of the lines drawn on the graphs appear to afford the best determinations of the equilibrium.

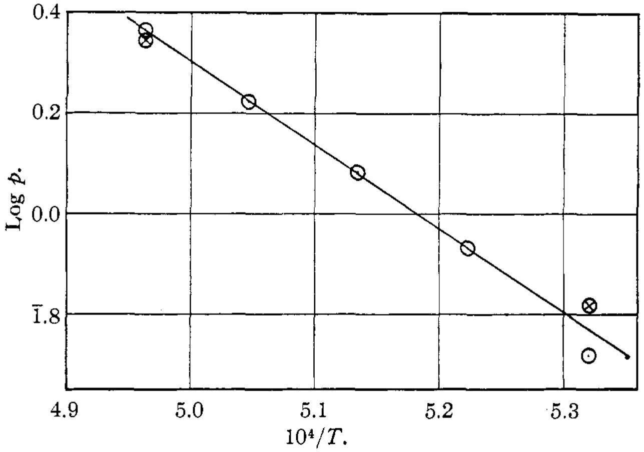

Fig. 10.—$ZrO_2 + 3C = ZrC + 2CO$. Log $p = 8.592 - (16{,}580/T)$; $\Delta F^\circ = 151{,}800 - 78.68T$; $\Delta H = 151{,}800$ cal.

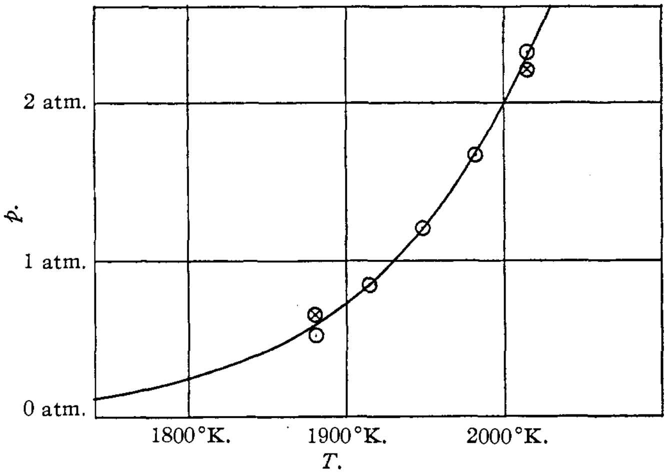

Fig. 11.—$ZrO_2 + 3C = ZrC + 2CO$. Log $p = 8.592 - (16{,}580/T)$; $\Delta F^\circ = 151{,}800 - 78.68T$.

In the series at 1982°K. (Fig. 8) the physical conditions were at their worst, but enough rates were taken to justify a fairly close estimation of the equilibrium pressure. In the middle of this series the apparatus was evacuated and run till 4 cm. pressure had developed, now carrying the reaction somewhat over half way to completion instead of a third as before. The agreement of this series and of the subsequent series at 1914°K. with the rest of the data affords evidence that the equilibrium has but one degree of freedom.

However scattering some of the data may be, the most probable value of the equilibrium pressure can be estimated in every case to better than 10% corresponding to 730 calories in the free-energy change. The points were estimated from the plots quite independently of other considerations, and before the recalibration of the temperature scale. These points are plotted in Fig. 10, the plot of log *p* against the reciprocal temperature, and in Fig. 11, in the original coördinates, as points in circles. These values are given in Table I.

TABLE I

EQUILIBRIUM PRESSURES OF THE REACTION

Temp., ° K.	1880	1914	1948	1982	2015
Pressure, atm.	0.522	0.856	1.21	1.67	2.32

The cross and circle at 2015°K. represents an estimate made neglecting the linear relation of rate to pressure at this temperature. The similar point at 1880°K. represents the intercept of a straight line connecting the two controlled rates nearest the equilibrium pressure. Neither of these can be regarded as inconsistent with the experimental data at those temperatures, but the most probable value of the equilibrium pressure over the range of the experiments was taken as represented by the straight line in Fig. 10, with which the agreement of the individual estimates is better than was anticipated. This gives for the equilibrium pressure p in atmospheres the relation $\log_{10} p = 8.592-(16580/T)$.

Nature of the Solid Phases

Determinations were made of the zirconium content of samples of the different pellets, weighing 9 to 20 mg., by igniting on a platinum foil and weighing as zirconium oxide. Pellets were made of two different compositions, one corresponding to the formation of ZrC_2 and the other to ZrC as the final product, also one of pure ZrO_2, and run under different conditions. The results are consistent with the equilibrium relations found, and with the formation of ZrC as the product. The history and analyses of these pellets are given in Table II together with the original composition of the pellet and the calculated composition it should finally assume on going to completion with formation of ZrC.

I am greatly indebted to Dr. S. B. Hendricks of this Laboratory for taking x-ray powder photographs and for giving me the following report, which completely determines the nature of the solid phases in the system.

The possible solid phases of the system are monoclinic ZrO_2 (baddeley-

Table II

Composition and History of Samples

Sample	Zr, %	Conditions of heating		
		Temp., °K.	Pressure, atm.	Time, hours
Initial	53.7			
Final	78.8[a]			
A	75.8	See account of equilibrium measurements		
B core	80.0			
core	78.6			
powder	64.7			
C	76.0	1880	0	22
D	78.7	2100	0	8
Initial	56.3			
Final	86.1[a]			
E	71.9	2000	2	
F	57.4	1880	2	20
G	69.0	1880	0	3
H	73.7	1880	0	19
I	85.7			
	85.0	2200	0	10
Initial	73.9[b]			
Final	88.3[c]			
J	75.4	2000	0	24

[a] Calculated.

[b] ZrO_2.

[c] ZrC.

ite), cubic ZrO_2, Zr_2O_3, ZrO, ZrC_2, ZrC, Zr, C, or solid solutions. Of these compounds the crystal structures have been determined as follows. Cubic zirconium oxide has a calcium fluoride type of structure with the length of the edge of the unit cube[4] $a_0 = 5.08$ Å. Zirconium carbide has a sodium chloride type of structure[6,4] with $a_0 = 4.76$ Å., 4.71 Å., and zirconium is reported to give reflections indicating a hexagonal, close-packed arrangement.[7]

In order to determine which of the above compounds were present in the solid phases, powder photographs were made of some of the more important samples. Monoclinic zirconium oxide, obtained by ignition of zirconium nitrate on a platinum foil, mixed with graphite from a powdered furnace tube, was used as a reference substance. The photographs from Samples B, D, H, I and J gave only lines corresponding to those on the reference photograph and lines that would result from reflection from planes of a face-centered cubic substance with $a_0 = 4.70$ Å. (One other line was noted as is shown in (B) of Fig. 12.) Sample I was nearly pure cubic substance. The intensities of the reflections could best be accounted for on the basis of a unit containing 4ZrC, having the sodium chloride structure. This is in close agreement with the previously reported data

[6] Becher and Ebert, *Z. Physik*, **31**, 863 (1925).

[7] Hull, *Phys. Rev.*, **17**, 571 (1921).

on zirconium carbide. Table III shows the agreement between the calculated and observed intensities. In this table, Cols. 2 and 3 give the observed order of intensity and the order of intensity calculated for a sodium chloride type of structure; the calculated value was obtained by using the relationship: intensity $\propto J(A^2 + B^2)(d_{hkl}/n)^{2.35}$, where J is the number of reflecting planes in a particular form, $(A^2 + B^2)$ is the structure factor, and d_{hkl} the interplanar distance. Cols. 4, 5 and 6, give the calculated intensities for a sodium chloride, zinc sulfide and calcium fluoride type of structure, respectively (the 2.35 power being omitted). In these calculations it is assumed that the relative reflecting powers for Zr:C are as 9:1. Col. 7 gives the factor due to zirconium alone when the structure is any of the above three. The agreement with the sodium chloride type of structure is evident.

TABLE III

CRYSTAL STRUCTURE OF ZIRCONIUM CARBIDE

Plane	a_0[a]	Order of intensity Obs.	Order of intensity Calcd.	$(A^2 \div B^2)\,J$ NaCl	ZnS	CaF_2	Zr atoms
111	4.815	(1)	(1)	8.18	11.31	11.17	11.17
200	4.800	(2)	(2)	9.60	6.14	4.70	8.37
220	4.750	(3)	(3)	19.20	19.20	23.64	16.64
311	4.710	(4)	(4)	24.36	33.93	33.51	33.51
222	4.710	(7)	(9)	12.80	8.19	6.27	11.17
400	4.700	(10)	(17)	9.60	9.60	11.82	8.37
331	4.705	(6)	(8)	24.36	33.93	33.51	33.51
420	4.705	(5)	(5)	38.40	24.56	18.81	33.51
422	4.690	(7)	(6)	38.40	38.40	47.28	33.51
333–511	4.705	(9)	(11)	32.54	45.24	44.68	44.68
440	4.702	(18)	(18)	19.20	19.20	23.64	16.74
531	4.690	(11)	(10)	48.72	67.86	67.02	67.02
442–600	4.690	(12)	(7)	48.00	30.72	25.08	41.85
620	4.695	(17)	(12)	38.40	38.40	47.28	33.51
533	4.695	(19)	(20)	24.36	33.93	33.51	33.51
622	4.690	(19)	(15)	28.40	24.36	18.81	33.51
444	...	(21)	(21)	12.80	12.80	15.49	11.17
711–551	4.698	(15)	(16)	48.72	67.86	67.02	67.02
640	4.695	(16)	(19)	38.40	24.36	18.81	33.51
642	4.700	(13)	(13)	76.80	76.80	96.56	67.02
731–553	4.700	(14)	(14)	73.08	104.79	100.53	100.53

[a] $a_0 = 4.700$.

Fig. 12 gives a representation of the spacing and intensities of the lines in several of the photographs, intensity being plotted against $n\lambda/2 \sin \theta$. Sample J is chiefly monoclinic zirconium oxide with a small amount of zirconium carbide. Sample B shows a very equal mixture of zirconium carbide and of monoclinic zirconium oxide. All of the lines on photographs of Samples B, D, H, I and J corresponded to zirconium carbide or oxide lines (see previous exception). Thus the possibility of any of the other previously mentioned solid phases appearing is eliminated.

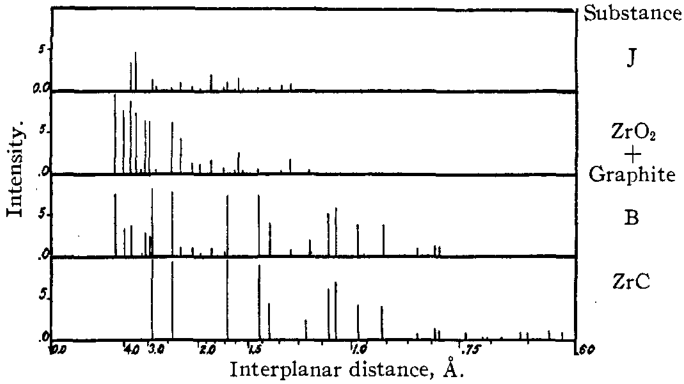

Fig. 12,

Thermodynamic Calculations

The x-ray study of the solid phases described in the preceding section shows that the reaction is as follows. ZrO_2 (monoclinic) + 3C (graphite) = ZrC (cubic) + 2CO (gas). We may now proceed to calculate the free-energy increase (ΔF) and the heat-content increase (ΔH) attending this reaction when the carbon monoxide pressure is one atmosphere.

The value of ΔF may be derived from the equilibrium pressure p by the familiar thermodynamic equation $\Delta F^\circ = -RT \ln K$, where $K = p^2$. From the determinations of the equilibrium pressure p tabulated in Table I we thus obtain the values given in Table IV.

Table IV

Free-Energy Increase Attending the Reaction

Temp., °K.	1880	1914	1948	1982	2015
ΔF°, cal.	4865	1184	−1478	−4045	−6746

From the expression for $\log_{10} p$ derived in the same section we similarly obtain the relations $\Delta F^\circ = 151{,}800 - 78.68T$, and $\Delta H = 151{,}800$ calories. At 1930°K. the free-energy change is zero and the actual equilibrium pressure is one atmosphere.

The molal heat capacities, C_p, of graphite and carbon monoxide were taken from Lewis and Randall,[8] and those of zirconium oxide and carbide estimated from Kopp's law according to the scheme given in Noyes and Sherrill.[9]

---

[8] Lewis and Randall, "Thermodynamics," McGraw-Hill Book Co., New York, **1923**, pp. 80, 569, 576.

[9] Noyes and Sherrill, "Chemical Principles," Macmillan Co., New York, **1922**, p. 93.

For C.................$C_p = 1.1 + 0.0048T - 0.0_512T^2$
For CO................$C_p = 6.50 + 0.0010T$
For ZrO_2...............$C_p = 14.2$
For ZrC...............$C_p = 8.0$

From the above-mentioned heat of reaction and the zero value of the free-energy change at 1930°K. the following equations are obtained and from them by extrapolation the following values at room temperature. $\Delta H = 159{,}500 + 3.5T - 0.0062T^2 + 0.0_512T^3$; $\Delta F^\circ = 159{,}500 - 3.5T \ln T + 0.0062T^2 - 0.0_66T^3 - 65.90T$; $\Delta H_{298} = 160{,}000$ calories; $\Delta F^\circ_{298} = 134{,}450$ calories.

Combining this heat of reaction with the heat of formation of carbon monoxide[8] at 25°C. and the heat of formation of zirconium oxide[10] at 18°C., gives a value for the heat of formation of zirconium carbide.

$ZrO_2 + 3C = ZrC + 2CO$	−160,000 cal.
$2CO = 2C + O_2$	− 52,280
$Zr + O_2 = ZrO_2$	+177,400
$Zr + C = ZrC$	− 34,880

The high-temperature heat of reaction is probably good to 5000 cal., and the extrapolation to room temperature probably not in error by more than 8000 cal. The determinations of Weiss and Neumann on the heat of formation of zirconium oxide are considerably better, provided their zirconium was pure. So the heat of formation of the carbide may well be good to 10,000 calories.

Summary

An apparatus and technique have been developed suitable for the study of equilibria between oxides and carbon at temperatures from 1000°K. to 2200°K., and at equilibrium pressures from a few centimeters to three atmospheres.

Temperatures were measured with an optical pyrometer. The furnace was a graphite tube 0.318 cm. in diameter with a 0.04cm. wall supported on tungsten rods and enclosed in Pyrex glass. The pressures were read on a mercury manometer. The enclosed gas space was about 100 cc. and was all below the water level of a thermostat at 35°.

Experiments were made on compressed pellets of zirconium oxide and graphite weighing approximately 90 mg. The procedure was to determine at a series of temperatures and pressures the rate of change of pressure with the time. From a series of such experiments at a single temperature and different pressures the equilibrium pressure was estimated.

The composition of the solid phases was determined from x-ray powder photographs. These showed the reaction to be $ZrO_2 + 3C = ZrC + 2CO$.

The increases in free energy and heat content that would attend this reaction between 1880°K. and 2015°K. at one atmosphere were found to

---

[10] Weiss and Neumann, *Z. anorg. Chem.*, **65**, 269 (1910).

be those given by the equations $\Delta F^\circ = 151{,}800 - 78.68T$, and $\Delta H = 151{,}800$ calories.

At 1930°K. the free-energy change becomes zero and the actual equilibrium pressure is one atmosphere.

PASADENA, CALIFORNIA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE MISSOURI SCHOOL OF MINES AND METALLURGY]

THE DETERMINATION OF SELENIUM AND TELLURIUM BY MEANS OF POTASSIUM PERMANGANATE

BY W. T. SCHRENK AND B. L. BROWNING

RECEIVED JUNE 28, 1926 PUBLISHED OCTOBER 6, 1926

Previous investigators have discovered that selenous and tellurous acids may be quantitatively oxidized by potassium permanganate in acid solution. Brauner[1] reported that in the reaction with tellurous acid, permanganate is not reduced to its lowest state of valence but to higher hydrated oxides. He also showed that the reaction is not quantitative in fairly concentrated sulfuric acid solution, due to loss of oxygen. Gooch and Danner[2] reduced the error to a negligible figure by carefully limiting the concentration of sulfuric acid. Gooch and Clemons[3] successfully determined selenous acid by oxidation with potassium permanganate.

The investigation showed that two difficulties must be overcome. The permanganate reacted with hydrochloric acid or chlorides present, and the manganese dioxide which precipitated was reduced very slowly by the ferrous sulfate. In many cases it was doubtful whether all the manganese dioxide was reduced at the apparent end-point, since a small amount remained as a stain on the glass.

It was found that the addition of phosphoric acid or disodium phosphate prevents the precipitation of manganese dioxide. Disodium phosphate was used since its addition does not increase the acid concentration. By dissolving the tellurium dioxide directly in sulfuric acid, the presence of chlorides was avoided and no difficulty was experienced from this source.

Procedure.—The following procedure for the determination of either selenium or tellurium was used and is recommended. A sample containing from 0.14 to 0.20 g. of the oxide is weighed and dissolved in 25 cc. of 40% sulfuric acid. In the case of tellurium dioxide, the sample must be heated until solution is complete. The solution is diluted to 150 cc., and 12 g. of disodium phosphate added. A standard solution of potassium permanganate is added to about 10 cc. in excess and the solution allowed to

[1] Brauner, *J. Chem. Soc.*, **59**, 238 (1891).

[2] Gooch and Danner, *Am. J. Sci.*, **44**, 301 (1892).

[3] Gooch and Clemons, *ibid.*, **50**, 51 (1895).