MIXED OXIDES OF THE TYPE MO2 (FLUORITE)-M2O3-I

OXYGEN DISSOCIATION PRESSURES AND PHASE RELATIONSHIPS IN THE SYSTEM CeO₂-Ce₂O₃ AT HIGH TEMPERATURES

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(Received 24 September 1963)

Abstract—Oxygen pressures in equilibrium with the cerium oxides have been determined by equilibration with CO/CO_2 or H_2/H_2O mixtures at temperatures from 636 to 1169°C. Partial and integral free energies, enthalpies and entropies have been calculated. The results are used to construct the cerium–oxygen phase diagram at these temperatures, between the compositions $CeO_{1.5}$ and $CeO_{2.0}$.

A CHARACTERISTIC property of MX_2 compounds crystallising with the fluorite structure is the readiness with which the cation lattice can incorporate quite a large proportion of altervalent ions to form "anomalous mixed crystals," for which the fluorite structure is apparently retained. Evidence that the cation lattice is virtually complete and the anion lattice highly defective has been obtained from a comparison of X-ray and pycnometric densities, so that depending on the nature of the altervalent ion, the mixed crystal is thought to contain either vacancies or interstitial anions. Moreover, the distribution of altervalent cations on cation sites, and of the anion defects, is generally assumed to be completely random.

The common fluorite-type oxides are ThO₂, UO₂, ZrO₂ (distorted fluorite), CeO₂, PrO₂, and TbO₂. Various studies of ternary anomalous mixed-crystal systems containing one of these in combination with one or other of the trivalent oxides of yttrium and the rare earth metals have been reported.⁽¹⁻¹¹⁾ In all of these systems, a wide range of fluorite-type solid solution was indicated by room-temperature X-ray investigation of samples quenched from high temperatures.

By contrast, the binary systems $Ce(IV)-Ce(III)-O_2$, $Pr(IV)-Pr(III)-O_2$, and $Tb(IV)-Tb(III)-O_2$ behave quite differently. The ceria system has been investigated at room temperature by X-ray diffraction techniques,^(12,13) which showed the existence

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of stoichiometric, intermediate phases $CeO_{1\cdot812}(Ce_{32}O_{58})$, $CeO_{1\cdot782}(Ce_{32}O_{56})$, and $CeO_{1\cdot719}(Ce_{32}O_{55})$, although these stoichiometries are now thought to be $CeO_{1\cdot818}$ - $(Ce_{11}O_{20})$, $CeO_{1\cdot778}(Ce_{9}O_{16})$ and $CeO_{1\cdot714}(Ce_{7}O_{12})$. A comprehensive series of investigations by EYRING and his collaborators⁽¹⁴⁻¹⁷⁾ has demonstrated very similar behaviour in the praseodymia and terbia systems. These "compounds" are thought to occur as a result of ordering in the cation and anion sub-lattices.

In an attempt to reconcile these differences, it has been suggested⁽¹²⁾ that many of the earlier results on ternary systems might refer to metastable states. The method of sample preparation commonly involved the mixing of two aqueous salt solutions in appropriate amounts, followed either by co-precipitation or evaporation to dryness. In both cases, a random dispersion of the two cations is likely to occur, and if this persists through the stage of conversion to the oxide, a mixed crystal results. This aspect of the problem of ternary systems is at present being studied in our laboratory. In binary systems, however, where a single chemical species occurs in two different oxidation states, this problem does not arise since electron exchange can take place readily.

It is not certain just how mobile these mixed-valence oxide systems are. EYRING's work suggests that, of the three, the terbia system is the least mobile, and our experience suggests that ceria is very mobile indeed, so much so that it is impossible to retain a high-temperature state even by rapid quenching techniques. The ternary systems, on the other hand, are unlikely to adjust significantly when quenched from high temperatures, and it is clear that direct comparison of room-temperature data for the two types is not justified. It is important, then, to obtain high-temperature data for the binary systems. Such data can be obtained either by high-temperature X-ray diffraction or by the measurement of equilibrium oxygen dissociation pressures. The latter approach is much wider in scope since it permits not only the determination of phase relationships but also the calculation of certain important thermodynamic functions. EYRING's group has determined oxygen dissociation pressures in the praseodymia and terbia systems, but these have been used only to indicate the stable intermediate phases; no thermodynamic data have been derived.

We chose to study the oxygen dissociation equilibria in the ceria system. As our experiments were nearing completion, BRAUER and GINGERICH⁽¹⁸⁾ published their results of a similar investigation, and shortly afterwards KUZNETSOV and his collaborators⁽¹⁹⁾ reported their data, based mainly on e.m.f. measurements, for the same system. There is, therefore, a considerable amount of information available.

EXPERIMENTAL

General procedure

Oxygen dissociation pressures in the ceria system are not accessible by direct measurement. Incomplete reduction isotherms obtained by SCHENK and ROTERS⁽²⁰⁾ at 700°C and 900°C in static CO₂/CO mixtures indicated values of 10^{-8} atm. downwards. Accordingly, a first series of experiments

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- ⁽²⁰⁾ R. SCHENK and H. ROTERS, Z. anorg. allg. Chem. 211, 65 (1933).

was designed to use CO_2/CO mixtures. In later experiments H_2O/H_2 mixtures were used to establish very low oxygen pressures. The gas mixture was circulated over the heated ceria sample which was held in a Pt/Rh alloy container suspended from one end of a fused-quartz spring. The sample composition was thus determined *in situ* by direct weighing. Equilibrium was assumed when the sample reached constant weight.

With CO_2/CO mixtures, the rapidly circulating gas and the sample were brought to equilibrium at some known, constant temperature. The sample weight was a measure of its composition, while the composition of the gas phase was determined analytically by gas-volumetric methods. With H_2O/H_2 mixtures, the gas composition was preset and maintained while the sample attained its equilibrium composition. By these means, pressure-composition isotherms were obtained over a temperature range from 636°C to 1170°C.

Materials and apparatus

The ceria used in the experiments was prepared from A.R. ammonium ceric nitrate. Cerium (IV) was extracted with diethyl ether from a solution of this salt in 8 M HNO₃ and then back-extracted into water.⁽²¹⁾ Cerous oxalate was precipitated with oxalic acid from this weakly acid solution, washed, dried, and finally converted to CeO₂ by ignition in air at 800°C. The product obtained was almost white with a faint tinge of yellow. Its cell edge was found to be 5.4110 \pm 0.0005 Å, in good agreement with the latest published value for column-purified CeO₂, $a_0 = 5.4112 \pm 0.0003$ Å.⁽²²⁾ The lattice constant remained unchanged after ceria samples had been subjected to repeated reduction and reoxidation during the high-temperature studies. In the course of this treatment, however, a slight greyish surface discolouration was observed, which, with prolonged experimentation, permeated the whole sample. Spectroscopic analysis revealed slight contamination of the ceria by platinum from the sample container.

A diagram of the apparatus used in the CO₂/CO experiments is shown in Fig. 1. The furnace F_3 was wound with Kanthal wire and its temperature controlled to $\pm 1^{\circ}$ C by the combined use of a mains-voltage stabilizer and a Kelvin Hughes Proportional Controller (Mk 4). The reaction tube, which was part of the circulation system, and inside which the sample was suspended, passed through this furnace. Recrystallized alumina (Morgan Crucible Co. Purox) proved to be the most suitable material. The ends of this tube were bonded to glass with "Araldite" and the joints coated with "Glyptal". Frequent checks were made to ensure that the whole apparatus was vacuum-tight. Sample temperatures were measured with a calibrated Pt-Pt (13% Rh) thermocouple situated between the furnace tube and the inside of the reaction tube was found to be 1°C, so that this procedure seems justified.

The fused-quartz spring was obtained from The Thermal Syndicate Ltd. Its maximum load was 5 g and its sensitivity about 7.7 cm/g. The precautions to be observed in the use of such springs have been discussed by DELL and WHEELER.⁽²³⁾ The spring temperature was maintained constant to $\pm 0.05^{\circ}$ C at about 30°C by rapid circulation of thermostatted water around the spring compartment. Spring extensions were measured by a cathetometer relative to a fixed point inside the jacket. The final equation used to compute the oxide composition (expressed as the value of *n* in the formula CeO_n) was $n = 2 - [10.758(\Delta 1 - \Delta 1^{\circ})]/(S \cdot w^{\circ})$ where S is the spring sensitivity (determined by direct calibration), w° is the weight of the CeO₂ sample taken (2.5–3.5 g), and $\Delta 1$, $\Delta 1^{\circ}$ are the measured distances (cm) between the measuring and reference points when the oxide compositions are CeO_n and CeO₂ respectively. Buoyancy corrections were negligible. An assessment of all the errors involved in this computation suggests that the reduced oxide compositions are accurate to ± 0.002 in the value of *n*. Finally, after each isotherm had been determined, the sample was reoxidised in air to an assumed composition of CeO_{2.000} and the final $\Delta 1^{\circ}$ value compared with that obtained at the beginning of the experiment. This check ensured that no mechanical loss of sample occurred.

The gas-circulation pump was constructed entirely of glass from a design of WATSON.⁽²⁴⁾ Its

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maximum capacity proved to be about 5 l/min at atm pressure, and it performed satisfactorily at all pressures down to a few millimetres of Hg. In practice, linear flow-rates of 1-3 cm/sec in the reaction tube at pressures ranging from 10–70 cm of Hg were used. According to the data of DARKEN and GURRY,⁽²⁵⁾ such flow-rates are sufficient to make thermal segregation errors negligible.

The gas-analysis apparatus is shown on the left of Fig. 1, and forms part of the circulation system. A series of calibrated compression bulbs was used to obtain P.V.T. data. The calibrated flask B was used primarily to store gas mixtures for duplicate analyses, but could be used directly to facilitate analyses of low CO_2/CO mixtures. The liquid-air traps C_1 and C_2 were used to freeze CO_2 .

Experiments with CO_2/CO mixtures were carried out as follows. The ceria sample was loaded on the spring, heated in air to constant weight, and the initial $\Delta 1^{\circ}$ value determined. The system



Fig. 1

was evacuated and the sample temperature adjusted to the required value. Pure CO_2 , produced by thermal decomposition of A.R. CaCO₃ in the furnace F_1 (Fig. 1), was then introduced and circulated through the complete circulation system which included the gas-analysis section, the reaction tube, and a furnace containing graphite (F_2 Fig. 1), the temperature of which was adjusted to give some appropriate CO_2/CO ratio. Reduction of the sample occurred, and at some predetermined composition the graphite furnace was isolated from the system (Tap T₄ turned through 180°). The subsequent procedure does not warrant a detailed description. In outline, the total $CO + CO_2$ was first measured; this mixture was then circulated through the liquid–air traps to condense CO_2 , after which all the CO was pumped off; finally, the condensed CO_2 was expanded and measured. Duplicate analyses were in close agreement.

The oxide sample was subjected to both oxidation (addition of more CO_2) and reduction steps, and the isothermal reduction and oxidation curves were identical within experimental error. Moreover, identical data were obtained from different ceria samples.

One restriction on the use of CO_2/CO mixtures derives from the possible side reaction $2CO = CO_2 + C$. Thermodynamic calculations permit the prediction of conditions where this is likely to occur. Low temperature and low CO_2/CO ratio, together with high total pressure, favour the reaction.

⁽²⁵⁾ L. S. DARKEN and R. W. GURRY, J. Amer. Chem. Soc. 67, 1398 (1954).

However, in our experiments CO_2/CO mixtures have been used successfully in circumstances where carbon deposition is predicted. The occurrence of such deposition has been inferred from the fact that in some experiments a reduced oxide oxidised only very slowly in a CO_2 -rich atmosphere, whereas normally oxidation occurred rapidly at all temperatures. Carbon deposition was found to interfere seriously in attempts to reduce the sample beyond a certain point at temperatures below 700°C, and also at higher temperatures when the CO_2/CO ratio was less than 10⁻³. It was for this reason, and not because of the limitations of the gas analysis, that the isotherms at some more elevated temperatures could not be completed by CO_2/CO equilibration.

As a consequence of this restriction on the use of CO_2/CO mixtures to establish low oxygen pressures, the apparatus was modified to use H_2O/H_2 mixtures. Two methods were used to establish and maintain a known H_2O/H_2 ratio. The first made use of a cryostat constructed essentially to the design of Scott and BRICKWEDDE.⁽²⁶⁾ The constant temperature bath consisted of a eutectic mixture of chloroform and carbon tetrachloride (F.P. $-75^{\circ}C$) in which was immersed a coil of thin-walled glass tubing containing ice. The temperature of the bath was maintained to $\pm 0.01^{\circ}C$ and was measured with a copper-constantan thermocouple calibrated at the sublimation point of CO_2 .⁽²⁷⁾ The cryostat assembly replaced the furnace F_2 (Fig. 1) in the circulating system, from which the gas-analysis section was isolated. Carefully purified cylinder hydrogen at known pressure was circulated through the cryostat and over the sample in the reaction tube at a linear flow-rate of about 3 cm/sec. Water vapour-pressure values were obtained from International Critical Tables.⁽²⁸⁾ Identical isothermal data were obtained both in oxidation and reduction, and in the region of overlap with CO_2/CO data the agreement was excellent. However, for H_2O/H_2 ratios below 10^{-3} , when the cryostat temperature was raised, resaturation of the hydrogen with water vapour appeared to be very slow, and equilibrium in this region was established in reduction.

For diphasic* regions of the system, the equilibrium H_2O/H_2 ratio was determined by successive approximation. The oxide was reduced to some composition well within the diphasic region; the cryostat temperature was then adjusted to produce an oxide composition which remained constant with time over a period of several hours. However, the results obtained at lower temperatures where the equilibrium H_2O/H_2 ratios are low, are probably uncertain.

The second method used to produce known H_2O/H_2 ratios was exploratory. The cryostat was replaced by a furnace surrounding a recrystallized-alumina tube containing a mixed bed of pure chromium metal and Cr_2O_3 . Hydrogen was circulated over this heated bed, the temperature of which ranged from 900°C to 1200°C and was held constant to $\pm 1^{\circ}C$. At equilibrium the H_2O/H_2 ratio is determined by the standard free-energy change at temperature for the reaction $\frac{1}{3}Cr_2O_3 + H_2 = \frac{2}{3}Cr + H_2O$, provided that no side reaction interferes. Equilibration took longer with this arrangement, but provision of a more efficient contact between the gas and the bed might improve this situation. Further investigation is to be carried out in our laboratory.

RESULTS AND DISCUSSION

Oxygen dissociation pressures

 CO_2/CO experiments. Oxygen pressures were calculated from the equation

$$\frac{1}{2}\log P_{\rm O_{\bullet}} = -\log K + \log \left(P_{\rm CO_{\bullet}} / P_{\rm CO} \right),$$

where K is the equilibrium constant for the reaction $CO + \frac{1}{2}O_2 = CO_2$ at the sample temperature. Values of K were obtained by interpolation from tables compiled by the U.S. National Bureau of Standards.⁽²⁹⁾ The major error in the oxygen pressures

* The terms *mono*- and *diphasic* are used throughout to describe the state of the condensed system.

- ⁽²⁷⁾ Temperature—Its Measurement and Control in Science and Industry p. 212. American Institute of Physics, Reinhold, New York (1941).
- ⁽²⁸⁾ International Critical Tables, 3, McGraw-Hill, New York (1928).
- ⁽²⁹⁾ D. D. WAGNER, J. E. KILPATRICK, W. G. TAYLOR, K. S. PITZER and F. D. ROSSINI, U.S. Bur. Stands. J. Res. 34, 143 (1945).

⁽²⁶⁾ R. B. SCOTT and F. G. BRICKWEDDE, U.S. Bur. Stands. J. Res. 6, 401 (1931).



FIG. 2.— \bigcirc CO₂/CO; \bullet H₂O/H₂—cryostat; \blacksquare H₂O/H₂—metal/metal oxide buffer.

derives from the uncertainty in K due to temperature variations of $\pm 2^{\circ}$ C. The errors in $\frac{1}{2} \log P_{O_2}$ were estimated to be ± 0.04 . Figure 2 shows plots of $\frac{1}{2} \log P_{O_2}$ (atm) against oxide composition for temperatures ranging from 636°C to 1169°C. We believe that oxygen pressures obtained from CO₂/CO experiments are true equilibrium dissociation pressures.

 H_2O/H_2 *Experiments*. Where the cryostat was used to establish known H_2O/H_2 ratios, oxygen pressures were calculated from the equation

$$\frac{1}{2}\log P_{\rm O_2} = -\log K + \log \left(P_{\rm H_2O} / P_{\rm H_2} \right).$$

Here K is the equilibrium constant for the reaction $H_2 + \frac{1}{2}O_2 = H_2O$ at the sample temperature. The values of this equilibrium constant were also obtained from the U.S. National Bureau of Standards compilation.⁽²⁹⁾ The errors in $\frac{1}{2} \log P_{O_2}$ were estimated to be ± 0.04 . These data are plotted in Fig. 2, and it is obvious that they agree well with the CO₂/CO results where comparison is possible.

In the Cr/Cr_2O_3 experiments oxygen pressures were derived from free-energy data quoted by KUBASCHEWSKI and EVANS⁽³⁰⁾ for the reactions

$$Cr_2O_3 = 2Cr + \frac{3}{2}O_2$$
: $\Delta G = 267,750 - 62.1T (\pm 4000 \text{ cal}).$

$$H_2 + \frac{1}{2}O_2 = H_2O(g)$$
: $\Delta G = 57,250 + 4.48T \log T - 2.21T (\pm 300 \text{ cal})$

The final computation was made from the equation

$$\frac{1}{2}\log p_{O_2} = \frac{-6,993}{T_1} - \frac{12,511}{T_2} - 0.979\log(T_1/T_2) + 4.524,$$

where T_1 is the temperature of the Cr/Cr₂O₃ bed and T_2 that of the ceria sample. Oxygen pressures so obtained were uniformly lower than the other concordant values. We have assumed that the discrepancy arises wholly from uncertainties in the equation for the free-energy of formation of Cr₂O₃, and have derived an equation

$$\frac{1}{2}\log P_{0_2} = \frac{-6,501}{T_1} - \frac{12,511}{T_2} - 0.979\log(T_1/T_2) + 4.371$$

which fits the CO_2/CO and H_2O/H_2 (cryostat) data. From this we have derived the equation

$$\Delta G = -261,000 + 60.0T (\pm 2000 \text{ cal})$$

for the free-energy of formation per mole of Cr_2O_3 . This procedure, whereby the free-energy of formation of an oxide as a function of temperature is determined from known oxygen dissociation pressures of a non-stoichiometric oxide, has certain merits and warrants further investigation.

The uncertain nature of the low-temperature diphasic equilibria has already been mentioned. There remains the question of whether or not the oxygen pressures obtained from the cryostat experiments at low H_2O/H_2 ($<10^{-3.5}$) ratios in apparently monophasic regions of the system are true equilibrium values. These results were obtained in reduction only, and the usual criterion for equilibrium (approach from both sides) was not applied. The reason for this has already been stated, namely, the supposedly slow establishment of the solid/vapour equilibrium over ice at low temperatures (below about -38° C). The evidence on which this was based was obtained from measurements at 636°C. An oxide of composition CeO_{1.994} was

⁽³⁰⁾ O. KUBASCHEWSKI and E. EVANS, Metallurgical Thermochemistry. 3rd Ed. Pergamon Press, London (1958).

reduced in a H₂O/H₂ mixture for which log (P_{H_2O}/P_{H_2}) was -4.759 ($\frac{1}{2} \log P_{O_2} = -16.12$ at 636°C). Over a period of 12 hr the composition changed to CeO_{1.818}; after a further 3 hr the composition was CeO_{1.810}, and 12 hr later a composition CeO_{1.802} was reached. The approach to equilibrium was clearly very slow. At this point the temperature of the cryostat was raised slightly to give a nominal value of $\frac{1}{2} \log P_{O_2} = -15.98$. Some hours later the composition was CeO_{1.801}, and this composition remained constant for successive 2-hr periods as nominal values of $\frac{1}{2} \log P_{O_2}$ were increased to -15.82, -15.48 respectively. A further increase in the nominal value of $\frac{1}{2} \log P_{O_2}$ to -15.32 produced oxidation of the sample to a composition CeO_{1.818} when the cryostat temperature was lowered slightly ($\frac{1}{2} \log P_{O_2} = -15.50$). These non-equilibrium data for the 636°C isotherm fall in the hatched area (Fig. 2). At this temperature, values of $\frac{1}{2} \log P_{O_2}$ greater than -15.0 were obtained both in oxidation and reduction and were assumed to be true equilibrium values.

In retrospect, it seems likely that our explanation of this non-equilibrium behaviour may be only partially correct, and it is unfortunate that this assumption influenced our procedure in the subsequent experiments at temperatures up to 872° C where data for compositions below CeO_{1.80} were obtained only in reduction. Above this temperature data were obtained both in oxidation and reduction and are believed to represent true equilibrium.

EYRING'S results on the terbia system⁽¹⁵⁾ show that for certain regions of composition, below a certain temperature the approach to equilibrium is very slow, and more recently CZANDERNA and HONIG⁽³¹⁾ have observed hysteresis loops in the praseodymia system. FAETH and CLIFFORD⁽³²⁾ have studied this phenomenon in more detail and obtained different "equilibrium" oxygen pressures in oxidation and reduction for the same composition. It might be inferred, therefore, that similar behaviour occurs in the ceria system, and that some of the results which we have obtained in reduction at temperatures below 872°C are not, in fact, equilibrium values. This possibility will be checked. These considerations, however, are important in the discussion that follows.

Phase relationships and thermodynamic data

Examination of the isotherms plotted in Fig. 2 suggests that there exists a single non-stoichiometric solid phase between $\text{CeO}_{2\cdot00}$ and $\text{CeO}_{1\cdot72}$ at all temperatures above 685°C. However, some reservation must be attached to this conclusion because of the uncertain character of "equilibrium" data at lower temperatures in the neighbourhood of the $\text{CeO}_{1\cdot72}$ composition. Below 685°C there is clear evidence for a diphasic region. This is in agreement with the results of high-temperature X-ray investigations⁽³³⁾ and with BRAUER's tensimetric study.⁽¹⁸⁾ Two other diphasic regions are also indicated. In the composition range $\text{CeO}_{1\cdot72-1\cdot70}$ the high-temperature isotherms are clearly horizontal, although this property is not so well-defined at lower temperatures, probably for the reason that equilibrium had not been established. The second region occurs over the ranges $\text{CeO}_{1\cdot65-1\cdot50}$ at 1169°C and $\text{CeO}_{1\cdot67-1\cdot50}$

⁽³¹⁾ A. W. CZANDERNA, Ph.D. Thesis, Purdue (1957).

⁽³²⁾ P. A. FAETH, Ph.D. Thesis, Purdue (1961).

⁽³³⁾ G. BRAUER and K. A. GINGERICH, Angew. Chem. 69, 480 (1957).



FIG. 3.—Partial molal free energy plotted against temperature.

at about 1000°C. Between these two, a monophasic region, diverging with increasing temperature, is revealed. Neither BRAUER nor KUZNETSOV observed the diphasic region, $\text{CeO}_{1.72-1.70}$, but apart from this, the three sets of data are in fair agreement. The discrete low-temperature phases which occur at compositons $\text{CeO}_{1.818}$ and $\text{CeO}_{1.778}$ are not indicated.

A more detailed analysis of the phase relationships can be made when certain derived thermodynamic data are considered. For this purpose oxygen potentials $(\frac{1}{2} RT \ln P_{O_2})$ at various monophasic compositions have been computed for various temperatures. Plots of $\frac{1}{2}RT \ln P_{O_2}$ against temperature are shown in Fig. 3. (For clarity in presentation, these plots have been exploded in the $\Delta \bar{G}$ direction—the 10 K cal





interval shown serves to indicate the range of $\Delta \bar{G}$ values covered for each composition.) They are clearly linear over the whole temperature range for all oxide compositions between CeO_{2.00} and CeO_{1.84}, and the slopes give values of the partial entropies of solution of $\frac{1}{2}O_2$. At compositions below CeO_{1.84} they show some positive deviation from linearity at lower temperatures, and it can be seen that the temperature at which this deviation is first apparent becomes higher as the degree of reduction of the oxide increases. This curvature is not removed when a reasonable value for $\Delta \bar{C}_P$ is assumed and $\Delta \bar{G} + \Delta \bar{C}_P T (2.3 \log T - 1)$ plotted against T. It is significant, however, that these are just the temperatures below which there is uncertainty with regard to equilibrium at that composition. On this point the non-equilibrium results obtained at 636°C in the range CeO_{1.84} to CeO_{1.80} are of importance. The uncertainty represented by the hatched section of that isotherm (Fig. 2) is also shown in Fig. 3 for the compositions CeO_{1.83}-CeO_{1.80}, and it is clear that the extrapolated straight line lies within the hatched region. For temperatures above 872° C, where the assumption of genuine equilibrium seems justified on experimental grounds, the results plotted in Fig. 3 fall on straight lines for all compositions down to CeO_{1.73}.

The variation of $\frac{1}{2}$ RT ln P_{0_2} with temperature for diphasic regions is also plotted in Fig. 3. As before, we have assumed equilibrium values for temperatures above 872°C. For the region CeO_{1.65-1.50}, only the value for the temperature 797°C lies off the straight line. For the region CeO_{1.72-1.70} the plot has been drawn to show two linear sections which intersect at a temperature of about 1300°K (1023°C). The significance of this will appear later. Again, only the 797°C point is not in line.

We now make the hypothesis that, for any monophasic oxide of constant composition, and for the diphasic regions of the system, the equilibrium values of $\frac{1}{2}$ RT ln P_{O_2} vary linearly with temperature in the range investigated. This hypothesis permits the calculation of "equilibrium" data at lower temperatures from true equilibrium data obtained at high temperatures. The blocked circles in Fig. 4 represent such calculated "equilibrium" values of $\frac{1}{2} \log P_{O_2}$ for those cases where the experimental data do not lie on the ΔG versus T line.

For convenience in what follows we shall designate the wide monophasic region indicated on the left of Fig. 2 as the "fluorite phase" and the other, narrower monophasic region as the "type-*C* phase", since at room temperature quenched oxides of composition within this field crystallise with the rare-earth type-*C* structure.⁽¹²⁾ The results actually obtained (Fig. 2) suggest that the right-hand boundary of the fluorite phase occurs at about CeO_{1.72} and that its composition is virtually independent of temperature. The calculated monophasic equilibrium data plotted in Fig. 4, however, show the occurrence of monophasic states, for temperatures below 1023°C and at certain compositions with n > 1.72, which are clearly unstable with respect to some diphasic equilibrium—an oxygen-rich fluorite phase on the left and an oxygendeficient phase on the right. The fluorite phase-boundary, although not obviously defined below 1023°C appears to move left as the temperature decreases (i.e. to higher values of *n*).

The nature of the oxygen-deficient phase on the right can only be inferred. If it is the type-*C* phase, the experimental isotherms in this region must be interpreted as reduction* branches of broad hysteresis loops, an interpretation which is not unreasonable in the light of FAETH's and CLIFFORD's results for the praseodymia system. However, this implies that at lower temperatures the composition $\text{CeO}_{1.714}$ has no significance, although the room-temperature X-ray data have shown the existence of a discrete, stoichiometric phase of this composition. In the praseodymia system this phase is stable to 1055°C ,⁽³⁴⁾ and a similar stability for $\text{CeO}_{1.714}$ would be expected.

There are two other features which, in our view, exclude the possibility of a diphasic region between the fluorite and type-C phases below 1023°C. The experimental data for the region $\text{CeO}_{1\cdot72-1\cdot70}$, plotted as $\Delta \bar{G}$ versus T (Fig. 3), fall on two straight lines which, we assume, describe two diphasic equilibria. At the three highest

^{*} For temperatures below 872° C all data for compositions with n < 1.80 were obtained in reduction: at 872°, 916°, and 971° C the isotherms were traced both in oxidation and reduction, but it transpires that all measurements taken in the relevant range (1.70 < n < 1.75) were in reduction.

⁽⁸⁴⁾ D. J. M. BEVAN, B. G. HYDE and L. EYRING, To be published in Proc. Roy. Soc. (Lond.)

temperatures the equilibrium is between the fluorite and type-*C* phases, so that at temperatures below 1023°C, another equilibrium obtains with a type-*C* phase on the right. It is most reasonable to assume the left-hand phase to be $\text{CeO}_{1.714}$ which is stable to 1023°C, above which it decomposes to form the fluorite and type-*C* phases. Occurrence of such a peritectoid decomposition should be reflected in discontinuities in the fluorite and type-*C* phase-boundaries at the peritectoid temperature. Such a discontinuity is clearly in evidence for the fluorite boundary, and occurs, although less obviously, in the type-*C* boundary. Between 636°C and 1023°C, then, we believe that $\text{CeO}_{1.714}$ exists in equilibrium with a fluorite phase, $\text{CeO}_{1.72+x}$, on the left and with a type-*C* phase, $\text{CeO}_{1.70-x}$, on the right. For this equilibrium situation, the experimental isotherms would be interpreted as showing non-equilibrium character in the region $\text{CeO}_{1.72+x}$ – $\text{CeO}_{1.714}$. The $\text{CeO}_{1.714}$ phase is highly ordered,⁽³⁵⁾ whereas the fluorite phase is disordered, so that such behaviour might not be unexpected.

An attempt has been made to estimate the phase-boundary compositions as a function of temperature for both the fluorite and type-*C* phases. The linear $\Delta \bar{G}$ vs *T* plot (Fig. 3) of experimental data below 1023°C in the region CeO_{1.72-1.70} was extrapolated to give low-temperature "equilibrium" values of $\Delta \bar{G}$ for the assumed equilibrium CeO_{1.714}/type-*C*. Similar plots were constructed for various compositions within the monophasic type-*C* region. The temperatures of intersection of these with the plot for the diphasic equilibrium represent the temperatures at which the left-hand type-*C* boundary has the particular compositions of the respective monophasic plots. A similar procedure was carried out to determine the right-hand boundary where the type-*C* phase is in equilibrium on the right with CeO_{1.51}. It is of interest to note that the linear $\Delta \bar{G}$ vs *T* plots for the two diphasic regions (CeO_{1.714}/type-*C* and type-*C*/CeO_{1.5}) intersect at about 600°C, at which temperature the type-*C* phase, as defined above, must cease to exist. Two possibilities for the equilibrium situation below 600°C are envisaged:

(i) The type-C decomposes below this temperature to form $\text{CeO}_{1.714}$ and $\text{CeO}_{1.5}$ —a eutectoid reaction.

(ii) At ~600° a disordered type-C phase orders on cooling to a stoichiometric phase of composition CeO_{1.67}(Ce₃O₅). Below this temperature, two diphasic regions exist—CeO_{1.714}/CeO_{1.67} for 1.67 < n < 1.714 and CeO_{1.67}/CeO_{1.5} for 1.5 < n < 1.67. These two possibilities are illustrated in Fig. 5.

These predictions are not necessarily invalidated by the room-temperature X-ray data which indicated a type-*C* phase between the compositions $CeO_{1.688}$ and $CeO_{1.651}$. Type-*C* phases in the X-ray investigations were prepared and annealed at 1050°C before they were quenched. These products were not pyrophoric, as were more highly-oxidized samples, and were more difficult to oxidize, all of which indicates reduced mobility. It is possible, therefore, that high-temperature equilibria in this region can be frozen by a rapid quench to room-temperature.

Determination of the fluorite phase-boundary, where this phase is in equilibrium on the right with CeO_{1.714} below 1023°C, is more difficult. Extrapolation of the linear $\Delta \bar{G}$ vs T (T > 1023°C) plot of experimental data in the region CeO_{1.72-1.70} can only yield $\Delta \bar{G}$ values at lower temperatures for a metastable fluorite/type-C equilibrium, for which the equilibrium pressures will be intermediate between those for the stable

⁽³⁵⁾ L. EYRING and N. C. BAENZIGER, J. App. Phys. Supp. 33, 428 (1962).



FIG. 5.—Derived phase diagram.

equilibria, fluorite/CeO_{1.714} and CeO_{1.714}/type-C respectively. These calculated metastable equilibrium pressures are shown in Fig. 4. One approximation to the fluorite phase-boundary would correspond to the intersections of the horizontal lines through these values with the corresponding monophasic isotherms (corrected as above to describe equilibrium situations). However, the true boundary is given by the intersections of these isotherms with the horizontal lines drawn through the appropriate unknown values of $\frac{1}{2} \log P_{O_2}$ for the stable fluorite/CeO_{1.714} equilibrium. Since these are higher than those for the metastable equilibrium, the true boundary will lie still further to the left.

One consequence of this interpretation is that certain data (see Fig. 4), which had been judged to describe equilibrium monophasic fluorite states, must relate to monophasic states which are metastable with respect to the fluorite/CeO_{1.714} equilibrium. We have already suggested that the conversion of a disordered fluorite phase to the ordered CeO_{1.714} is likely to be difficult, and that the measured dissociation pressures, as a function of composition in this region, reflect this. It is reasonable, then, to suppose that a monophasic equilibrium isotherm measured in reduction should extend into a metastable region.

At 715° and 636°C those calculated parts of the isotherms which have been assumed to describe stable or metastable monphasic equilibrium states lie above the measured isotherms. This behaviour most probably derives from a combination of slower reduction rates at lower temperatures and low rates of oxygen transfer in the gas stream at very low H_2O/H_2 ratios (~10⁻⁴). The fluorite phase-boundary sketched in Fig. 4, then, is based on the above rationalizations. It is very approximate and represents only a reasonable probability. On the same basis we have drawn proposed isothermal equilibrium paths for the region in question.

Not a great deal can be said about the low-temperature phases of ideal composition $CeO_{1.818}$ and $CeO_{1.778}$. The fluorite phase-boundary as drawn is continuous over the temperature range $1023^{\circ}C-636^{\circ}C$, and approaches a composition $CeO_{1.81-1.82}$ at temperatures below $636^{\circ}C$. This is in accord with the result obtained by BRAUER and GINGERICH⁽³⁶⁾ in a high-temperature X-ray investigation, where an oxide of composition



FIG. 6.—Partial molal enthalpy and entropy.

CeO_{1.787} retained its normal diphasic (CeO_{1.818} and CeO_{1.778}) character at 600°C, but converted to a single fluorite phase at 700°C. It is clear that even the lowest temperature used in our work is above the decomposition temperatures of these ordered phases. The data reported by BRAUER and GINGERICH suggest that ordered CeO_{1.818} (β -phase) converts to the disordered fluorite phase at about 420°C, and we suggest that ordered CeO_{1.778} (γ -phase) decomposes at a somewhat higher temperature to form a fluorite phase and CeO_{1.714}. Unequivocal evidence for the occurrence of such peritectoid decompositions in the PrO_n-O₂ system has been obtained recently.⁽³⁴⁾ Figure 5 shows a tentative (*T*, *x*) projection phase-diagram based on presently available information.

Derived thermodynamic data

The experimental plots of $\Delta \bar{G}(\frac{1}{2}O_2)$ as a function of temperature for various fixed compositions (Fig. 3) are linear for both monophasic and diphasic regions over the ⁽³⁶⁾ G. BRAUER and K. A. GINGERICH, J. Inorg. Nucl. Chem. 16, 87 (1960).

whole composition range from $\text{CeO}_{2\cdot 0}$ to $\text{CeO}_{1\cdot 5}$ at temperatures above 872°C. The best slopes of these lines were determined by a least squares analysis for 95 per cent confidence and give values of $\Delta \bar{S}(\frac{1}{2}O_2)$ for constant compositions which are independent of temperature. Values of $\Delta \bar{H}(\frac{1}{2}O_2)$ for constant compositions were also derived: these too are temperature-independent. The two sets of data, plotted as a function of composition, are shown in Fig. 6, for an arbitrary temperature of 1353°K. The errors in $\Delta \bar{S}$ are ± 0.8 e.u., and in $\Delta \bar{H} \pm 1.5$ kcal. The entropy and enthalpy changes for the reaction $2\text{CeO}_{1\cdot 5} + (\frac{1}{2}O_2) = 2\text{CeO}_2$ are given by

$$\Delta S = 2 \times \int_{1\cdot 5}^{2\cdot 0} \Delta \bar{S}\left(\frac{1}{2}O_2\right) \mathrm{d}n \quad \Delta H = 2 \times \int_{1\cdot 5}^{2\cdot 0} \Delta \bar{H}\left(\frac{1}{2}O_2\right) \mathrm{d}n$$

These have been calculated from a measurement of the areas under the curves shown in Fig. 6. Specific heat data for the two oxides were taken from the work of KUZNETSOV and his collaborators^(37,38) and for oxygen from a compilation by KUBASCHEWSKI and EVANS.⁽³⁰⁾ In fact, ΔC_p for the reaction between 298°K and 1353°K is very small

$$\left(\int_{298}^{1353}\Delta C \mathrm{p} \cdot \mathrm{d}t = -420 \mathrm{ cal}
ight)$$
,

which is significant in relation to the observed linearity of $\Delta \bar{G}(\frac{1}{2}O_2)$ with *T*, and values of the thermodynamic functions at 298°K are very little different from those determined at high temperatures. The figures obtained are:

$$\Delta H_{298} = -93.2$$
 kcal: $\Delta S_{298} = -32.0$ e.u.

The errors in such a computation are difficult to assess; we estimate them to be $\pm 1-2$ kcal and ± 1 e.u. respectively. By comparison, KUZNETSOV⁽¹⁹⁾ reports values of $\Delta H_{298} = -85.43$ kcal, obtained calorimetrically, and $\Delta S_{298} = -25.3$ e.u.

Finally, some comment on the shape of the plots in Fig. 6 is desirable. As the oxide is reduced below $\text{CeO}_{2\cdot0}$ within the broad, single fluorite phase region, the negative values of $\Delta S(\frac{1}{2}O_2)$ and $\Delta \overline{H}(\frac{1}{2}O_2)$ decrease sharply to a minimum at the composition $\text{CeO}_{1\cdot85}$ and then increase to a maximum in the composition range $\text{CeO}_{1\cdot80}$ -CeO_{1.75}. In fact, the results might be interpreted as exhibiting two maxima, since the points for the $\text{CeO}_{1\cdot80}$ composition lie outside the limits due to random errors. This would place the two peak compositions at $\text{CeO}_{1\cdot81}$ and about $\text{CeO}_{1\cdot78}$. At room temperature, two discrete "compounds" exist at these compositions, and it has been suggested that their particular stabilities and structures result from an ordering of lattice defects. The thermodynamic data are consistent with the view that ordering of some sort is significant at high temperatures within the monophasic region.

Acknowledgments—We gratefully acknowledge financial assistance for this work in the form of a Research Grant to one of us (J. K.) from the University of Western Australia, and of a general research grant for solid-state research from the Australian Atomic Energy Commission.

⁽³⁷⁾ F. A. KUZNETSOV and T. N. REZUKHINA, Zh. Fiz. Khim. 34, 2467 (1960).

⁽³⁸⁾ F. A. KUZNETSOV and T. N. REZUKHINA, Zh. Fiz. Khim. 35, No. 5 (1961).