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Conductivity Measurements on Cobalt and Nickel Oxides in Highly-Enriched Oxygen Atmospheres

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The pressure dependencies of the conductivities of nickel and cobalt monoxides have been investigated in the range 10^{-2} to 7.5×10^2 atmospheres at temperatures in the region of 1000° C. Conductivity saturation occurs in CoO due to the formation of Co_3O_4, and the experimental data correlates well with a model for the separation of the higher phase. NiO exhibits no saturation effect in the pressure range investigated and the $p^{1/5}$ dependence of the conductivity at 950° C with this oxide above 0.1 atm is interpreted in terms of the formation of singly ionised vacancies.

1. Introduction

Knowledge of the properties of oxide phases under conditions of high temperature and oxygen pressure are relevant to many metallurgical and ceramic applications. While high temperature thermodynamic data is becoming more complete, the influence of high oxygen pressures is still largely an unknown quantity. This gap in our knowledge is due to the experimental problem of containing high pressures of the gas at temperatures of interest in solid-state studies. Consequently, interphase relationships in oxide systems have not been well defined under conditions where the dissociation pressure of the highest phase is much greater than atmospheric pressure. Indeed, much of the confusion in the chemistry of the oxides of the later transition metals can be attributed to the lack of understanding of the role of oxygen pressure. The highest phase in these oxides often has to be prepared at lower temperatures than are desirable or has not been prepared in well characterised form due to the high dissociation pressure at the preparation temperature used. In favourable cases, therefore, it might be expected that new phases could be stabilised in high pressures of oxygen. Such a transformation should ideally be describable in terms of the non stoichiometry of the lower phase.

This paper reports the results of conductivity measurements on cobalt monoxide and nickel monoxide at about 1000° C and in up to 750 atm of oxygen. Conductivity measurements were made because they provided an *in situ* method of detecting phase changes. CoO was chosen as a standard since the pressure-temperature-composition data is well established up to 950° C where the equilibrium oxygen pressure at the monoxide-spinel phase boundary is 1 atm [1, 2]. Nickel oxide was chosen, because in this region of temperature spinel formation is unknown, although the formation of microdomains of spinel below 1000° C and in oxygen pressures less than atmospheric has been postulated on the basis of conductivity data [3].

2. Experimental

The high pressure conductivity cell is shown in fig. 1. It consisted of three parts; a drilled stainless steel rod (a) tapered at one end to fit an Autoclave Engineer's cone T-piece (b) into which was also screwed a standard A.E. thermocouple unit (c). This provided the entry into the cell for the thermocouple and conductivity measuring leads. Samples of oxide in pellet form (d) were mounted between fused alumina discs (e) above and below the conductivity measuring leads, and held in a stainless steel U-section tube (f) at the end of a four bore alumina tube (g) which supported the measuring leads over the distance between the sample assembly and the exit point from the cell (c). The conductivity measurements were made using a Wayne Kerr 0.1 % Autobalance Bridge and the circuit contact resistance was reduced by coating the pellets with Johnson Matthey N758 platinum paste. Conductivity data at oxygen pressures lower than atmospheric were obtained using a cell with an outer jacket of silica attached to a conventional vacuum line.

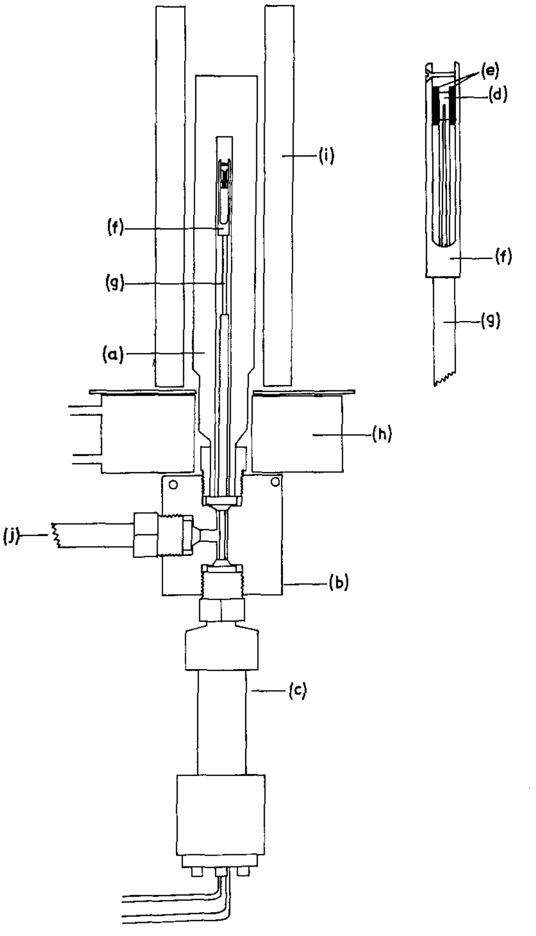

Figure 1 The high pressure conductivity cell. (a) Stainless steel cover; (b) cone T-piece; (c) thermocouple unit; (d) pelleted sample; (e) alumina discs with conductivity measuring leads on inner faces; (f) sample holder; (g) four-bore alumina rod supporting the conductivity and temperature measuring leads; (h) cooling tank; (i) furnace; (j) high pressure line.

The conductivity cells were heated externally by a furnace placed around the sample zone on the outer cover. Sample temperatures were measured with a Pt/Pt/13 % Rh thermocouple cemented to one side of the pellet. The oxide pellets used were 0.5 cm^2 by 0.1 cm thick, and they were compacted from spectroscopically pure powders supplied by Johnson Matthey Chemicals Ltd. Cobalt monoxide was made by decomposition of the carbonate, this operation being carried out before pelleting. Before mounting in the cells the compressed pellets were sintered at 1000° C in 1 atm of oxygen for 12 h.

The pumping system for raising the oxygen pressure consisted of an Autoclave Engineers HH15 pump and compression cylinder fitted with a motor drive. Mercury was used as pumping fluid and stringent precautions were taken to exclude any grease or oil from the high pressure line. For the relatively small volume of the cell and the gas line this simple pumping device provided a robust and rapid means of raising the gas pressure to 1000 atm in one cycle of the mercury. The oxygen required for the experiments was drawn from a reservoir of two BOC cylinders.

3. Results

Normalised data for the oxygen pressure dependence of the conductivity of the cobalt oxide samples is presented in fig. 2a for the interaction temperatures of 950, 1000, 1050 and 1100° C. For the two lower temperatures, it can be seen that the conductivity ceased to be a function of the oxygen pressure at 1 and 3 atm, respectively. The data at 1050 and 1100° C is not so definite, though a break does occur in the conductivity at 5 and 8 atm. However, X-ray analysis of samples of oxide quenched in atmospheres above and below these critical pressures confirm that the breaks in the conductivity-oxygen pressure relationship are due to the onset of spinel formation.

Similar data for the case of nickel monoxide are given in fig. 2b for the interaction temperature of 950° C. The conductivity of this oxide does not exhibit any saturation effect and varies as the $\frac{1}{5}$th power of the oxygen pressure up to a final pressure of 750 atm. Conductivity-pressure isotherms were not made above 950° C because of the danger of rupture of the steel vessel at the higher temperatures in oxygen pressures greater than 100 atm. This also placed a limit on the upper pressure in the higher-temperature CoO experiments. X-ray analyses of samples quenched from 950° C in 750 atm of oxygen did not indi-

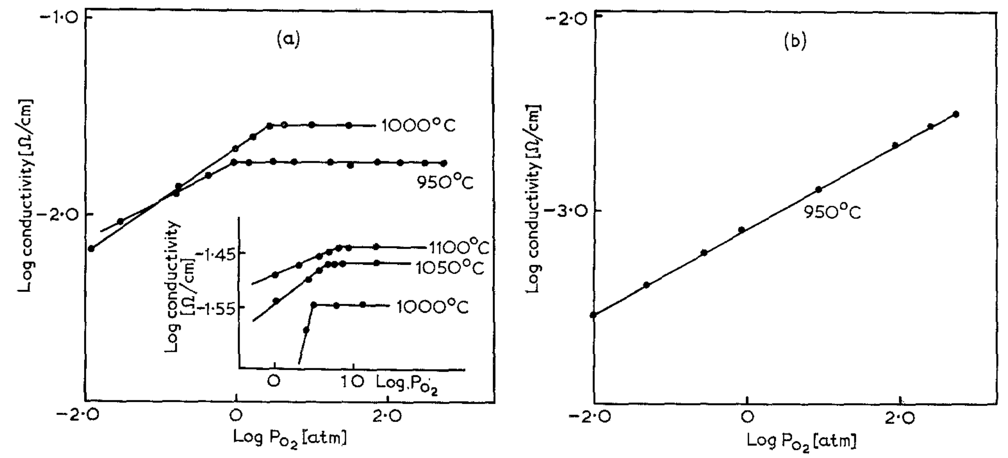

Figure 2 (a) The dependence of the electrical conductivity of cobalt monoxide on the oxygen pressure. (b) Similar data for nickel monoxide.

cate the presence of any new nickel oxide phases.

4. Discussion

In fig. 3 the dissociation pressures for Co_3O_4 as determined from the conductivity data are compared with the sub-atmosphere values compiled by Maun [1] as a log P against $1/T$ plot. The incorporation of the present data leads to a discontinuity in the relationship and the slope has values -9200 and -14880 above and below a critical $1/T$. In cobalt monoxide Fischer and Tannhauser [2] following Kevane [10] have identified three regions of conductivity, functions of both temperature and pressure of oxygen, in which association between positive holes and cation vacancies leads to a different oxygen pressure dependence. The ionisation energy required to separate a hole-vacancy pair is estimated to be about 0.5 eV and it is suggested that at high oxygen pressures (about 1 atm in this region of temperature) significant concentrations of unionised vacancies are present, thus leading to a reduced pressure effect. We suggest that this may be the reason for the change in the slope of the log P graph. Below 1000° C unionised vacancies are present at the phase boundary limit of the monoxide due to the high equilibrium pressures in the gas phase.

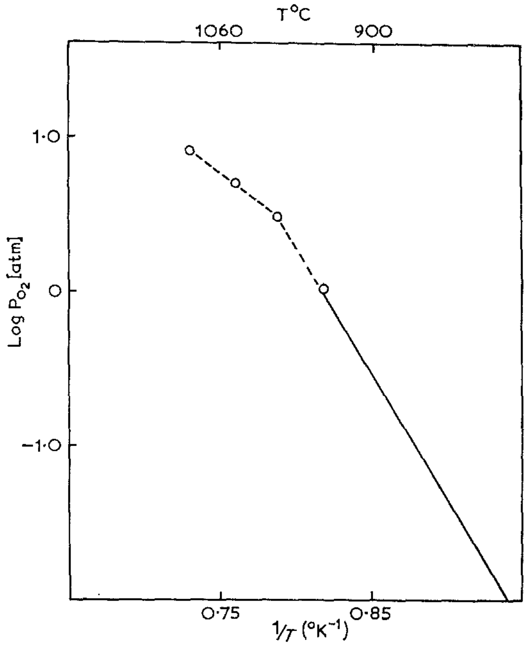

Figure 3 Literature and present values of the equilibrium oxygen pressure for the system $CoO/Co_3O_4/O_2$ as a log p versus inverse temperature plot (-O-). This work. Solid line is best fit to data in [1].

In order to examine this model further, it is necessary to assign the components of the heat term equivalent to the slopes of the lines in fig. 3, and this requires a model for the separation of the higher order Co_3O_4 phase. Various attempts have been made to account for this type of transition in solids in terms of the non-stoichiometry of the lattice in contact with the vapour of one or other component [4-6]. Essential to all the statistical thermodynamic theories is the concept that aggregation of the lattice defects occur due to the existence of a defect interaction energy, thus providing nuclei of the higher phase in the lower. The accurate computation of the contribution to the partition function of the lattice defects rests with the successful calculation of the configurational term. This is relatively straightforward where only random distributions of the individual defects are considered as was demonstrated by Anderson [4]. Where more complicated interactions are important the rigorous combinatorial problem rapidly becomes insoluble, though a fruitful less-exact approach appears to be the one in which random solution of particular clusters of different energies is considered [6]. For the cobalt oxygen system we assume a random distribution of equal numbers of positive holes and cation vacancies (m of each) on the cation sites (N_B in number). The conductivity of the single-phase monoxide region can be associated as a function of the oxygen pressure with the reaction,

$$\tfrac{1}{2}O_2 + 2m^{2+} \rightarrow 2p + \square^{+} + [O^{2-}|\square^{-}] \quad (1)$$

where p represents a positive hole, i.e. a trivalent cation that can occupy either a normal cation site or an interstitial position, $\square^{+}$ a cation vacancy and $[O^{2-}|\square^{-})$ an oxygen on an anion site. Because of the observed pressure-dependence of the conductivity, only one hole is designated to be free from each vacancy.

Now, the number of nearest neighbours around any defect is given by $\tfrac{1}{2}z(2m)^2/N_B$ and since this includes hole-hole, vacancy-vacancy and hole-vacancy pairs the concentration of each type of complex is $z(2m)^2/6N_B$, where z is the co-ordination number of a cation site in the CoO lattice (i.e. $z = 6$). At high oxygen pressures therefore, neutral vacancy formation in the lattice contributes $4m^2E_{12}/N_B$ to the energy of the system. Then following the same procedure as Anderson [4] the activity of oxygen, the non-metal component in this system, is given by the expression,

$$\lambda_B = \frac{1}{q(T)}\left[\frac{\theta/2}{1-\theta}\right]^2 \exp - [E^h_x - 8\theta E_{11} - 4\theta E_{12}]/kT \quad (2)$$

where θ is $2m/N_B$ and E_{11} and E_{12} are the interaction energies between like and unlike pairs of defects, no distinction being made between vacancy-vacancy or hole-hole interactions. E_{12} is, of course, the ionisation energy required to remove a hole from a neutral vacancy, and the remaining symbols are those used by Anderson. The modified isotherm therefore is

$$\tfrac{1}{2}\ln\,[p_\theta/p_{\frac{1}{2}}] = \left[\frac{\theta}{1-\theta}\right]^2 \exp\,[2\theta - 1]\,[E]/kT \quad (3)$$

obtained by dividing the particular solution for $\theta = \tfrac{1}{2}$ into the general activity equation, and for convenience at this stage making the substitution $4E_{11} + 2E_{12} = E$.

The critical pressures for conductivity saturation are readily identified as being $p_{\frac{1}{2}}$ values. Limiting and intermediate values of the vacancy density ($\tfrac{1}{2}\theta$) have been obtained from the gravimetric results of Fischer and Tannhauser [2] and in table I the extrapolated maximum vacancy densities, the total interaction energies and the critical temperatures calculated for the observed limiting pressures at the four temperatures used, are given. In fig. 4 the calculated values of the function $\tfrac{1}{2}\ln(p_\theta/p_{\frac{1}{2}})$ from the experimental data are compared with the theoretical values based on the isotherm for each of the four interaction temperatures in this investigation.

TABLE I

Temperature (°C)	$p_{\frac{1}{2}}$	Maximum vacancy density	Total interaction energy (kcal/mole)	Critical temperature (°K)
950	1	0.006	−21.6	2725
1000	3	0.009	−20.6	2600
1050	5	0.01	−20.6	2600
1100	8	0.013	−20.6	2570

By equating the expressions for the activity of the non-metal component in the solid and the gas phase Anderson derived the relation

$$\frac{d\,\ln\,p_{\frac{1}{2}}}{d\,(1/T)} = -[2E^h_x - 2E_{hh} - D] \quad (4)$$

where E^h_x is the energy of vacancy formation, D is the heat of dissociation of the gas and E_{hh} is the interaction energy between cation vacancies, the only defects assumed to be present on the cation sites in the simple model. A similar analysis for the present case reveals that this interaction energy should be $4E_{11} + 2E_{12}$. Thus if the change in overall heat term can be attributed to the formation of neutral vacancies below 1000° C, the value of E_{12} compares favourably with that reported by Fischer and Tannhauser. Certainly, Kevane's analysis [10] of the exact role of oxygen pressure in determining vacancy concentrations suggests the existence of quite critical pressures for the ionisation of

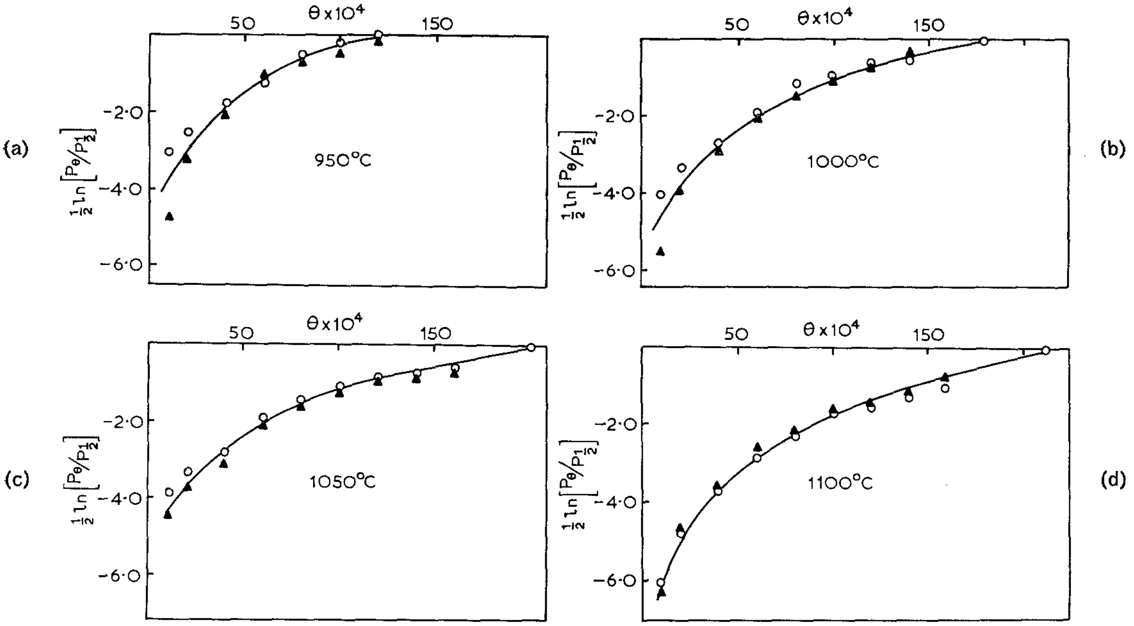

Figure 4 Correlation of the data with equation [3]. (○) Experimental points; (▲) calculated on the basis of the θ values.

vacancies, but even so, such a sharp break in the heat term is unexpected. In any case, the model must be deficient in many respects, and this is certainly reflected in the high value for the energy of vacancy formation that is obtained using equation 4 (cf [7]). We have taken no account of the size of the hole-vacancy complex compared with the volume available for each lattice site. The role of the interstitial positions has not been defined, though these may provide neighbouring sites to accommodate either the hole of the hole-vacancy pairs or the free holes. Thirdly second order interactions between the aggregated defects have not been considered though these must have an important bearing on the separation of the new phase. On the other hand the model does remove the problem of attributing the aggregation of the defects to an attraction between like defects. If E_{12} is about 0.5 eV for cobalt monoxide, then a small repulsive force exists between like defects. In the present case, this would imply that the critical temperature for mutual solubility of the two phases lies not much higher than the experimental region investigated here. The kinetic data of Baur and Fassell [11] tend to support this, in that these authors found no evidence for rate saturation in the oxidation of cobalt above 1150° C even though the extrapolated saturation pressure from fig. 3 should lie about 17 atm.

Kevane's analysis [10] suggests two reasons for an observed $p^{1/5}$ dependence of conductivity. Either the experiments are located in the first intermediate region for the formation of oxygen vacancies, when a limited agreement with this relationship is to be expected, or if the relationship extends over more than six orders of magnitude of oxygen pressure, the vacancy mechanism cannot be operative. In NiO, Pizzini and Morlotti [3] report a $p^{1/6}$ dependence up to 0.1 atm oxygen in agreement with other investigations, but suggest that the apparent change in the relationship is a saturation effect due to the formation of domains of Ni_3O_4. Our data in the pressure region 10^{-2} to near 10^3 atm conforms to a $p^{1/5}$ relationship and so we conclude that in NiO this is the pressure range in which singly ionised vacancies increase significantly in concentration at 950° C.

If it is assumed that the ordering energy terms are the same in NiO and CoO it is possible to estimate the gas-phase oxygen pressure required to stabilise an analogous spinel phase on NiO at 950° C. The necessary θ value for the calculation has been obtained by extrapolating Mitoff's data, [8] and the substitution of the assumed total interaction energy and a θ value of about 5×10^{-4} at 950° C and 500 atm into the isotherm equation leads to a compatible dissociation pressure for the hypothetical Ni_3O_4 phase of about 10^9 atm. The two major factors likely to substantially account for the difference in the dissociation pressure of the two spinels are the relative ease of vacancy formation in the monoxides and the crystal field contributions to the lattice energies of the spinels. The dominant feature of the first term is probably the third ionisation potential of the metal and this would certainly alone account for a much increased dissociation pressure in Ni_3O_4. The crystal field contributions must appear in the interaction energy and the extra stabilisation of the inverse spinel structure of Ni_3O_4 probably invalidates the assumption of identical ordering energies in both monoxides. However, it is pertinent to note that high dissociation pressures for new phases of the transition metal oxides have been predicted by Roy [9] on the basis of phase solubility limits in model systems.

5. Conclusions

This investigation represents the preliminary results of a general survey of the properties of materials in highly enriched oxygen atmospheres. Our suggestion that unionised vacancies predominate at the phase boundary below 1000° C in CoO at oxygen pressure of about 1 atm is in reasonable agreement with the estimated vacancy ionisation energy. The good fit of the data to a model which assumes the aggregation of vacancies and positive holes to be the controlling factor in positioning the oxygen-rich phase-boundary raises a number of interesting questions. In particular, one can inquire where the phase boundary would lie in a cobalt oxide in which the vacancies had been removed, e.g. by the incorporation of Li_2O. If the phase transition requires an oxygen to metal ratio of 1.006 in the oxide at 950° C for cobalt monoxides, then a very rapid increase in the dissociation pressure of the spinel phase should be observed with lithium doping. This system is the subject of a current investigation.

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