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STUDIES OF NON-STOICHIOMETRIC OXIDES BY THERMOANALYTICAL METHODS*

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ABSTRACT

Non-stoichiometric oxides can be divided into metal-deficient and oxygen-deficient oxides, and a few examples of each type are given in order to show the materials of interest in this field. After a short review of the methods used in the study of these oxides, an account is given of the methods used in and the results obtained from a recent thermogravimetric investigation in atmospheres of controlled oxygen pressure on cerium oxides, plutonium oxides and mixed uranium/plutonium oxides, which are all of special interest in research on fuels for nuclear power reactors.

INTRODUCTION

In classical chemistry and crystallography it was assumed that inorganic compounds had definite compositions determined by the valence of the atoms and that the atoms were arranged in an ideal structure with all sites occupied. From the early 1900's many inorganic compounds have been, however, found to be of variable composition and today it is recognized that an exact stoichiometric composition is an exception rather than a rule, and that it can only be obtained at definite partial pressures of the components at a given temperature. Deviations from stoichiometric composition are also very common in the inorganic oxides which are considered in this paper. Especially for the oxide systems where the cations can exist in several valence states, very large deviations have been observed at higher temperatures.

Today, it is also well established that the properties of inorganic oxides and other compounds are determined by the number and type of defects present at the non-stoichiometric composition. For the oxides of interest to the nuclear field—UO_2, PuO_2 and mixed U, Pu oxides—for instance, which can show considerable deviations from stoichiometry, important properties such as thermal conductivity, fission gas release, and compatibility with cladding materials all strongly depend on the degree of non-stoichiometry, and usually it is necessary to fabricate these fuels to fixed compositions in order to obtain a fuel with specified properties.

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The main purpose of this paper is to give a brief account of the different thermoanalytical methods normally used in the study of non-stoichiometric oxides, and secondly to demonstrate the applicability of the thermogravimetric technique widely used in these studies and to review some recent measurements on oxide systems of special interest to the nuclear field. First, however, a few examples of typical non-stoichiometric oxide systems will be given in order to define the type of compounds of interest to these studies.

NON-STOICHIOMETRIC OXIDE SYSTEMS

By statistical thermodynamic calculations it can be shown[1] that all compounds above the absolute zero temperature will contain an equilibrium concentration of point defects—vacancies (e.g., Schottky disorder consisting of V_M'' and $V_O^{\cdot\cdot}$) or interstitial atoms (e.g., Frenkel disorder consisting of $M_i^{\cdot\cdot}$ and V_M''). These point defects, which are termed primary or native defects and which are created without a reaction with a surrounding atmosphere, only give very small deviations from stoichiometry. Although they are important for the electrical and magnetic properties of many compounds, they are of minor importance for the description of grossly non-stoichiometric compounds.

Much greater deviations from stoichiometry than expected from primary defects can, however, be obtained when an oxide can react with gaseous oxygen in the surrounding atmosphere, especially if the cations exist in several oxidation states as pointed out in the introduction. Different types of defect can be envisaged to explain the deviations from stoichiometry and generally the oxide systems are classified according to the predominating defects into two main groups[1]:

(1) Oxygen-deficient oxides in which oxygen vacancies ($V_O^{\cdot\cdot}$) are formed. Alternatively the oxygen deficiency in these oxides can also be described as the presence of excess metal, in which case the predominating defects are considered as interstitial metal atoms or ions ($M_i^{\cdot}$).

(2) Metal-deficient oxides in which metal vacancies are formed (V_M'). Alternatively the metal deficiency may reflect the presence of excess oxygen in the form of interstitial oxygen ions (O_i'').

Oxides in which the cations can exist in several oxidation states, and where large deviations from stoichiometry can thus be expected, are primarily the transition metal oxides, the lanthanide oxides and the actinide oxides, and a few examples of the types of defect considered important for these oxides are shown in Table 1.

For many of the oxygen-deficient oxides mentioned in the table the deviation from stoichiometry was previously considered to be due to interstitial cations instead of oxygen vacancies. Recent studies, for instance, of the oxygen self-diffusion in CeO_{2-x}[3], however, strongly support the oxygen vacancy model, which today is generally accepted for these oxides. This is also in accordance with the conclusions arrived at in a recent study of atomic radii in PuO_2[4], which show that the radii of oxygen atoms are smaller than the corresponding radii of the metal atoms forming a

TABLE 1

EXAMPLES OF PREDOMINATING DEFECTS IN NON-STOICHIOMETRIC OXIDES[1]

	Composition	*Oxygen-deficient oxides*		*Metal-deficient oxides*	
		$V_O^{\cdot\cdot}$ [a]	$M_i^{\cdot}$ [a]	V_M' [a]	O_i'' [a]
Transition metal oxides	TiO_{2-x}	+	+ (?)		
	$Mn_{1-y}O$			+	
	$Fe_{1-y}O$			+	
	$Fe_{3-y}O_4$			+	
Lanthanide oxides	CeO_{2-x}	+			
	PrO_{2-x}	+			
Actinide oxides	UO_{2+x}				+
	UO_{2-x}[b]	+			
	PuO_{2-x}	+			
	$(U, Pu)O_{2\pm x}$	+			

[a] Kröger's notation is used throughout this paper[2]. [b] Exists only at high temperatures in strongly reducing atmospheres.

very stable lattice. Many of the oxides shown in the table exist as non-stoichiometric compounds over an extended compositional range. It is, however, inconceivable that large concentrations of defects can remain randomly distributed as supposed in classical defect theories and some interactions between the defects must be expected. Clustering, long-range ordering into superstructures or perhaps even elimination of the defects by a crystallographic shearing mechanism, as proposed for the TiO_{2-x} system[5], must be considered when the nature of a non-stoichiometric oxide is studied.

THERMOANALYTICAL METHODS USED IN THE STUDY OF NON-STOICHIOMETRIC OXIDES

Of the many different methods used in studies of non-stoichiometric oxides, thermogravimetry in controlled atmospheres plays a dominant role. An important advantage of this method is that it is possible to determine the composition of the samples directly at the test temperature. Compared to the methods where the samples must be quenched after equilibration at high temperatures in order to determine the composition, this method gives much more reliable data. This is especially important for systems which rapidly respond to changes in the oxygen pressure as, for instance, the CeO_{2-x} oxides, where it is impossible to quench without changes in composition. Another advantage, which also improves the accuracy of the result, is that from the weight curve plotted during the experiment, it is possible, to judge directly when equilibrium has been obtained between the sample and the surrounding atmosphere. In the quenching experiments this is only possible after many and time-consuming experiments. In the next section the equipment and technique used in some recent thermogravimetric measurements on non-stoichiometric PuO_2 and CeO_2 will be reviewed in order to demonstrate the applicability of this method.

Compositional changes in non-stoichiometric oxides usually take place relatively slowly and these processes are not easy to investigate with DTA. This technique has thus only been used in studies of some of the ordered intermediate phases[6] existing in many of these oxides at low temperatures. Quantitative DTA measurements to determine the enthalpy changes involved during compositional changes in non-stoichiometric oxides would be very helpful, however. Today these data must be derived from the $\Delta\bar{G}_{O_2}$-values (relative partial free energy of oxygen) obtained in thermogravimetric experiments, which, of course, cannot give very accurate results. However, in order to verify the conclusion arrrived at in thermogravimetric experiments, enthalpies determined by a direct and independent method should be available. Some enthalpy measurements of non-stoichiometric oxides have previously been performed by bomb calorimetry[7], but the data obtained in these studies are not accurate either. Recently, however, very sensitive microcalorimeters, which can work up to 1500°C, have been developed in France[8,9]. Measurements with this technique have already been performed on systems such as UO_{2+x}, PuO_{2-x} and $(U, Pu)O_{2\pm x}$ and some interesting and accurate data have been reported for these oxides.

THERMOGRAVIMETRIC STUDIES OF NON-STOICHIOMETRIC Pu- AND Ce-OXIDES

The purpose of the experiments reviewed in this section was to determine thermodynamic data and phase relationships for the non-stoichiometric oxides PuO_{2-x} and CeO_{2-x} at higher temperatures. These measurements are thus primarily concerned with the α and α' phases, respectively, shown in the phase diagram in Fig. 1.

The thermogravimetric measurements were performed in atmospheres of closely controlled oxygen pressures, which were prepared by mixing CO and CO_2. Different types of experiments were carried out in the temperature range 900–1450°C:

(1) Isothermal experiments.

(2) Continuous heating and cooling in atmospheres of fixed composition. In order to maintain equilibrium between the sample and the atmosphere, a heating and cooling rate of 1 °C min^{-1} was used in these experiments.

(3) Continuous heating and cooling in atmospheres of fixed oxygen pressure. This was obtained by changing the CO_2/CO ratio at short intervals in a precalculated manner to keep the oxygen pressure constant as the temperature changes. This type of experiment is particularly useful to establish the existence of two-phase regions and of discrete phases.

EQUIPMENT

The experimental set-up used in these experiments is shown schematically in Fig. 2. It consists of:

(1) A Netzsch thermobalance with an accuracy of ±0.2 mg and with a temper-

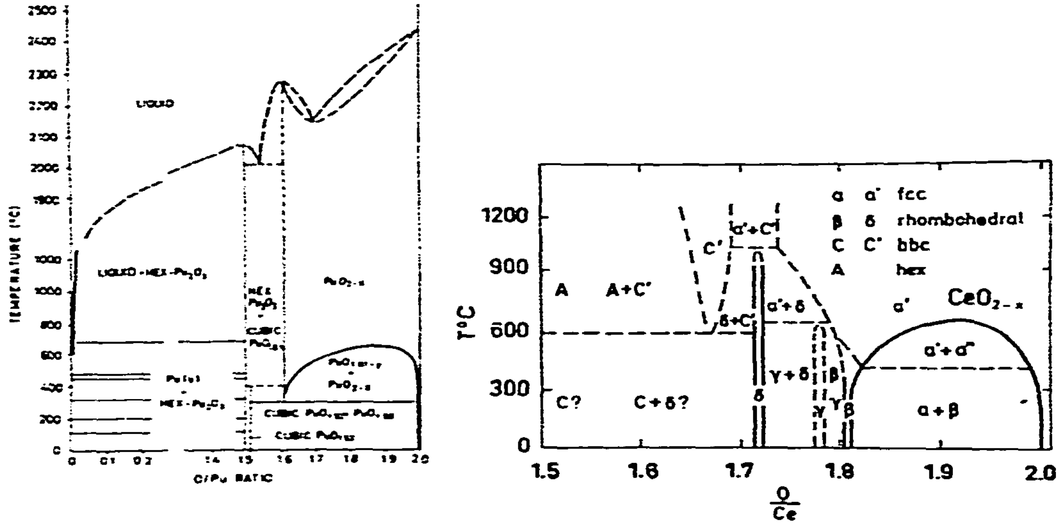

Fig. 1. Phase diagrams for the Pu-O and Ce-O systems.

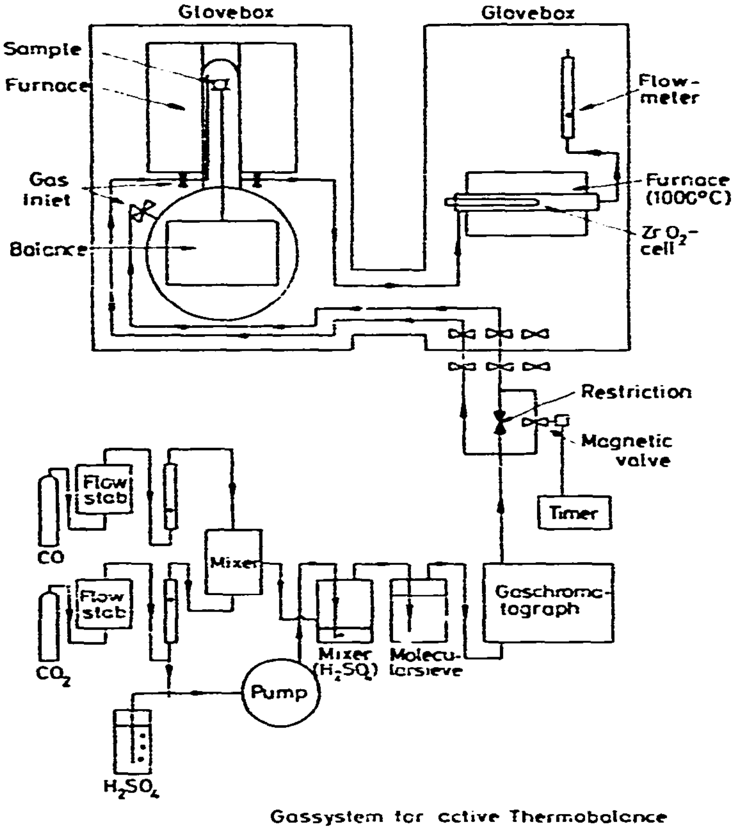

Fig. 2. Experimental set-up for thermogravimetric measurements on PuO_{2-x}.

ature range of 20–1550 °C. The balance was placed in a glove box for the measurements on PuO_2.

(2) An external gas system for mixing CO and CO_2 in the desired ratios, which can be checked with a gas chromatograph. The gas flow to the balance is divided into two streams: one is passed directly over the sample (full flow), while the other is passed through a restriction before it enters the lower cylinder holding the weighing system of the thermobalance, and from which the gas passes into the sample compartment through a tube placed around the rod carrying the crucible. With the restriction used a flow ratio of 1/10 could be obtained between the two gas streams, which proved to give the smallest buoyancy corrections to the weight measurements.

(3) A solid electrolyte $ZrO_2(CaO)$ oxygen cell placed in a separate box in a furnace operated at 1000 °C. With this cell, which is shown schematically in Fig. 3 together with a typical calibration curve and which has been described previously[10], the oxygen pressure and thus the CO/CO_2 ratio in the exit gas could be monitored continuously.

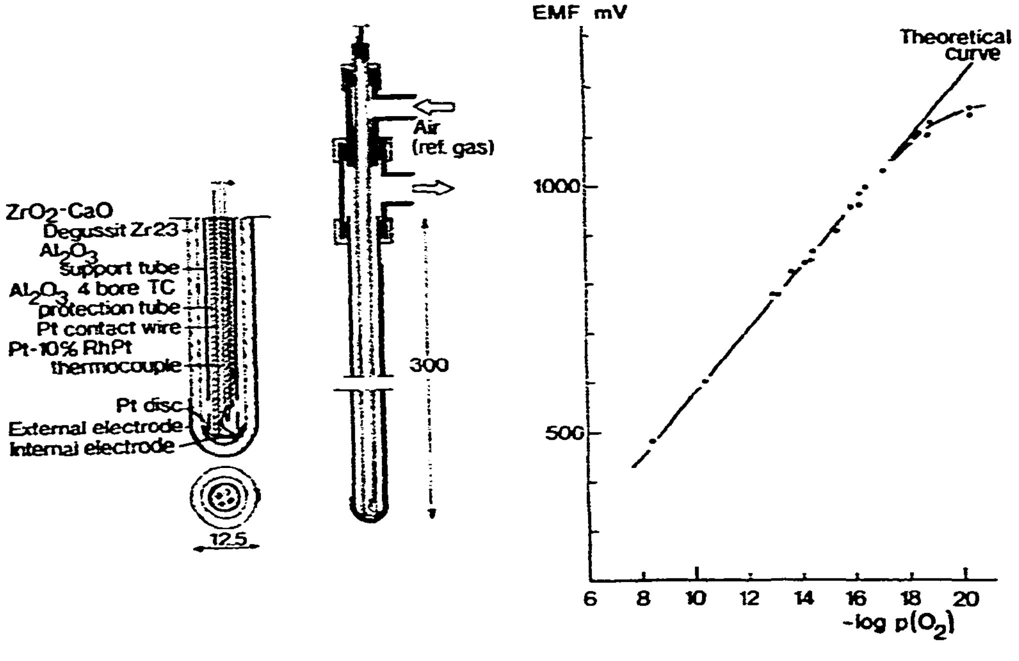

Fig. 3. (a). Principle of solid electrolyte ZrO_2 (CaO) cell for measurement of oxygen pressures. (b). Calibration curve for ZrO_2 (CaO) oxygen cell at 1000 °C.

RESULTS AND DISCUSSION

From the weight curve plotted during the measurements the composition of the samples can be determined as a function of temperature and oxygen pressure in the atmosphere used. In order to get accurate results, however, the weight readings must be corrected for the changes in the buoyancy which take place with changing temperature. In the present experiments these corrections were determined with an empty crucible using the same heating and cooling rates and the same atmospheres as used for the oxide samples. From the oxygen pressures in the atmospheres in equilibrium with the samples, the important thermodynamic quantity, $\Delta\bar{G}_{O_2}$ (relative partial free energy of oxygen), can also easily be calculated from the relation:

$$\Delta\bar{G}_{O_2} = RT \ln p_{O_2} \tag{1}$$

Nevertheless in order to determine what relation is to be expected between this quantity and the composition of the samples, x in MO_{2-x}, defect theories should be considered. The formation of oxygen vacancies during reduction of the oxides can be written as[1]:

$$O_O + 2M_M = V_O^{\cdot\cdot} + 2M_M' + \tfrac{1}{2}O_2 \tag{2}$$

where O_O and M_M represent oxygen and metal atoms on their respective sites in the crystal lattice, $V_O^{\cdot\cdot}$ represents a double positively charged oxygen vacancy and M_M' a negatively charged metal ion (e.g., Ce^{3+}) in the normal cation lattice, which has taken up one of the electrons liberated during ionization of the oxygen vacancies. Assuming that the law of mass action is valid for this equilibrium, by introducing the neutrality condition

$$[M_M'] = 2[V_O^{\cdot\cdot}] \tag{3}$$

and by expressing $[V_O^{\cdot\cdot}]$ as the fraction of unoccupied sites in the oxygen lattice, i.e., $[V_O^{\cdot\cdot}] = x/2$, it can be shown that $x \propto p_{O_2}^{-1/6}$. Other exponents will be obtained if the oxygen vacancies are singly charged $(-1/4)$ or neutral $(-1/2)$, or if other types of defects or defect clusters are formed, but generally $x \propto p_{O_2}^{-1/n}$ can be expected. Substituting this proportionality into eqn (1) the following relationship between $\Delta\bar{G}_{O_2}$ and the composition is obtained:

$$\Delta\bar{G}_{O_2} \propto -nRT \ln x \tag{4}$$

If this treatment is valid a linear relationship should be found when $\Delta\bar{G}_{O_2}$ is plotted against $\ln x$ at constant temperature if n is constant, i.e., if one type of defect prevails in a subregion within the non-stoichiometric phase range.

The $\Delta\bar{G}_{O_2}$ values obtained for PuO_{2-x} and CeO_{2-x} are shown in Figs. 4 and 5, respectively, as a function of $\log x$ together with data obtained in other investigations. Considering all the available data for the two systems, it is interesting to note that the expected linear relationship is really obtained. The non-stoichiometric phases can apparently be considered as consisting of several subregions, which can each be characterized by a certain value of n in eqn (4), corresponding to that one type of defect is predominantly formed within each subregion. From the values obtained for n it should in principle be possible to determine the type of defect formed within the different subregions, but this can only be rather speculative since the defect theories outlined above are based on assumptions which are probably not fulfilled in practice—randomly distributed non-interacting defects. In the more sophisticated statistical thermodynamic approach (Atlas[11] for CeO_{2-x}) an attempt is made to take interactions between the defects into account. Although this treatment can predict the major trends in the experimental data, it has not been possible in this way to account for the finer details probably because ordering reactions of the defects into superstructures have been neglected. For the CeO_{2-x} system, high temperature X-ray diffraction measurements have recently shown that ordering of the defects takes place at higher temperatures.

Information on the phase relationships of the systems can also be obtained from the $\Delta\bar{G}_{O_2}$ versus log x plots. If a two-phase range, for instance, exists, the system will

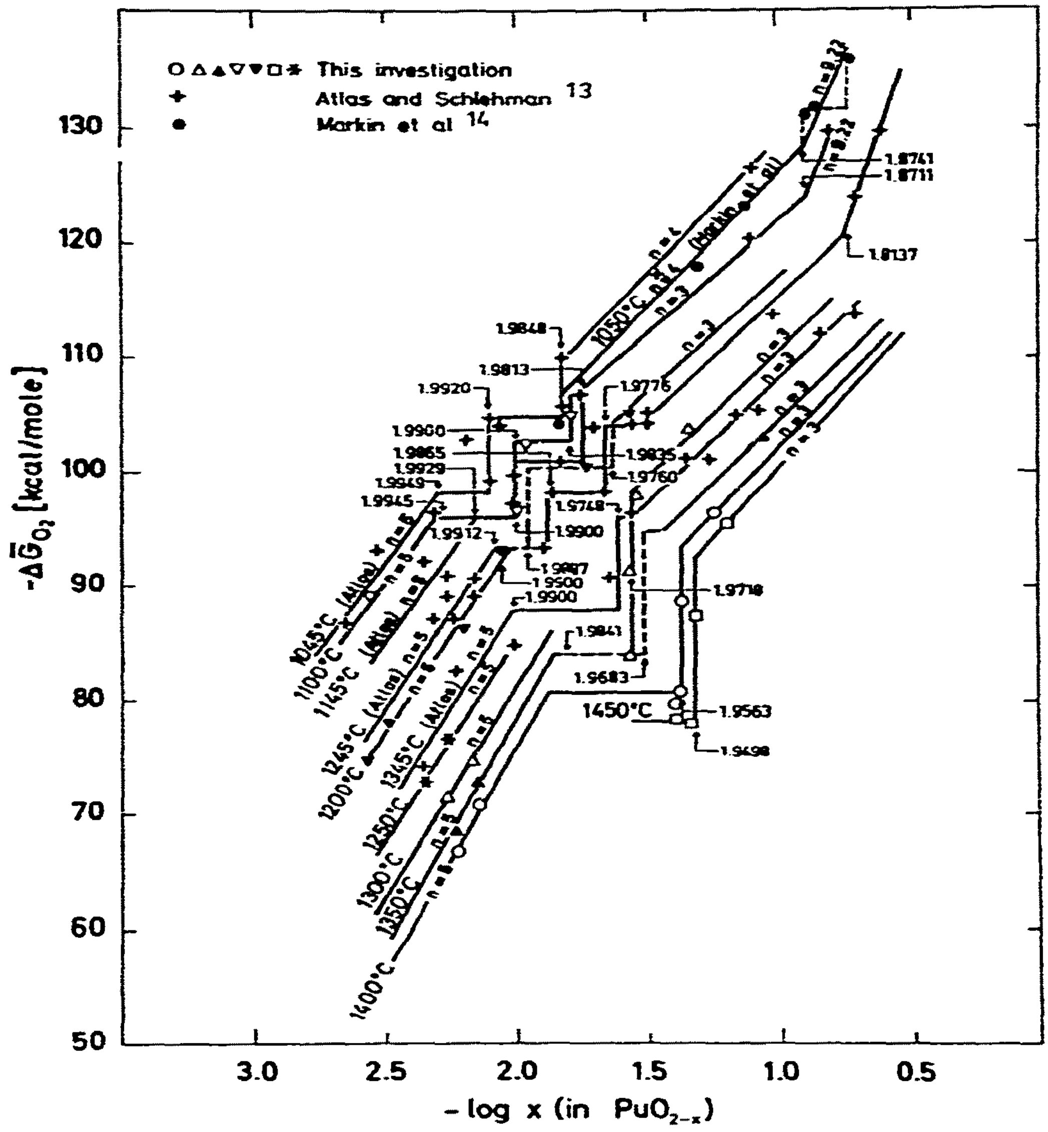

Fig. 4. $\Delta\bar{G}_{O_2}$ versus log x for PuO_{2-x}.

according to the phase rule only have one degree of freedom and a horizontal line should be observed. Near-vertical lines can in the same way be assumed to prove the existence of discrete phases of a narrow composition range, whereas lines with an intermediate slope indicate the existence of a single non-stoichiometric phase or a continuous sequence of discrete phases as found for the TiO_{2-x} system[12]. As shown

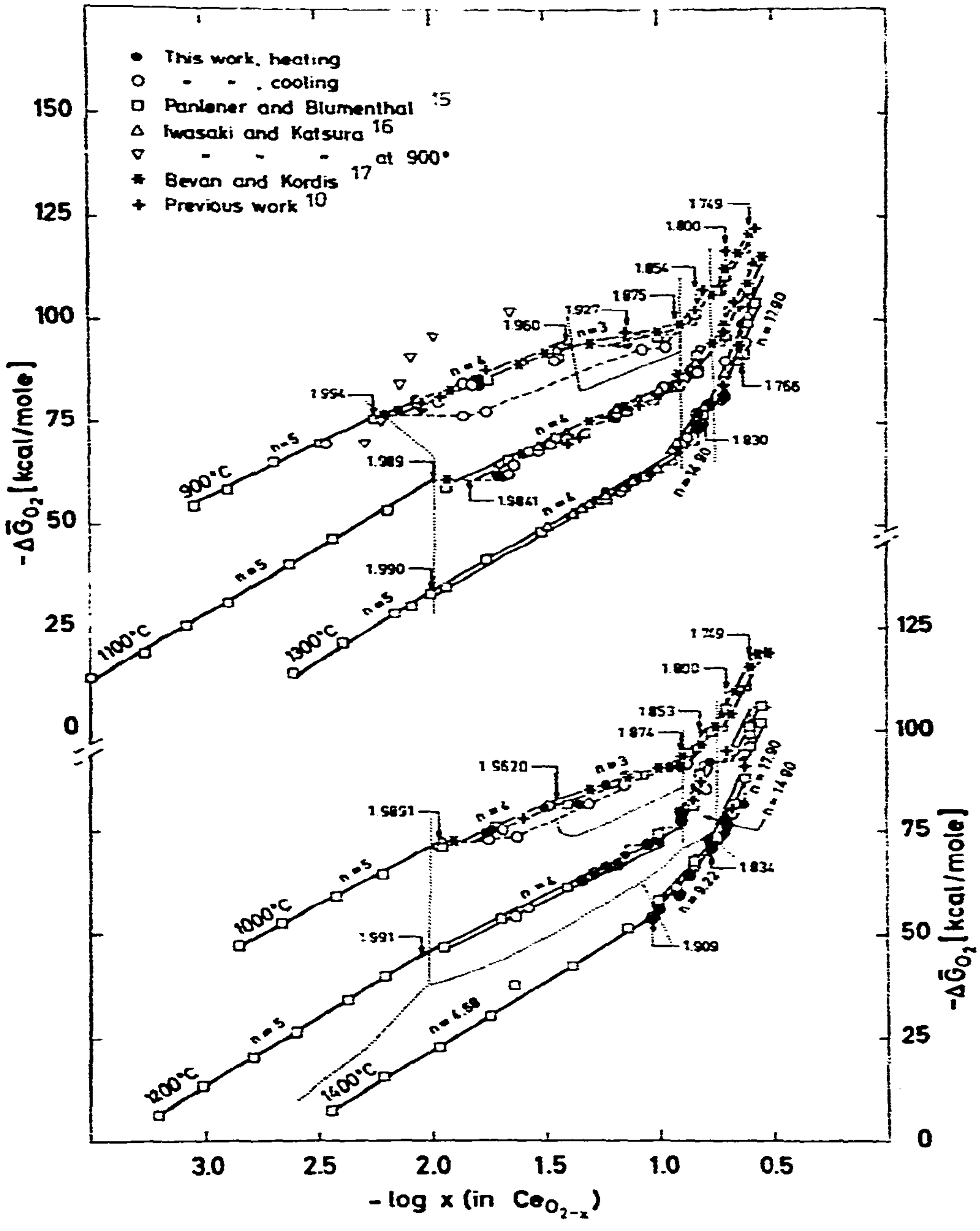

Fig. 5. $\Delta\bar{G}_{O_2}$ versus log x for CeO_{2-x}.

in Figs. 4 and 5, two-phase regions as well as discrete phases are found in the two oxide systems between the subregions, which according to the phase rule criteria can be considered as non-stoichiometric single phases. The finer details of the experimental points for the CeO_{2-x} system (Fig. 5) for the subregions with $n > 6$, however, also give a clear indication of the existence of a whole series of discrete phases, separated by two-phase regions in accordance with the above criteria. It is interesting to note that the composition of most of these discrete phases seems to follow the series M_nO_{2n-2}, which also describes the intermediate phases existing at lower temperatures in the Ce–O system (Fig. 1).

From the experimental $\Delta\bar{G}_{O_2}$ values other thermodynamic quantities such as $\Delta\bar{S}_{O_2}$, relative partial entropy of oxygen, and $\Delta\bar{H}_{O_2}$, relative partial enthalpy of oxygen, can be calculated from standard thermodynamic equations. This was also done for the different subregions observed for the two oxide systems examined, and good agreement, supporting the thermogravimetric results, was obtained between the calculated $\Delta\bar{H}_{O_2}$'s and those determined by microcalorimetry by Chereau et al.[9] for the PuO_{2-x} system, and by Camperveux and Gerdanian[8] for the CeO_{2-x} system.

From this brief review, it is clear, that thermogravimetric analysis is an important method in the study of non-stoichiometric oxides. Besides thermodynamic data, it can give interesting indications of the phase relationships and possible defect types. It must, however, be recognized that thermogravimetry is an indirect method and in order to study the real nature of these oxides, other more direct methods, such as high temperature X-ray diffractometry and electron microscopy (electron diffraction and lattice image techniques), should also be used.

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