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THERMODYNAMIC PROPERTIES OF SOLID SOLUTIONS
AT HIGH TEMPERATURES

Final Report

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ABSTRACT

The research carried out under this contract was concerned with the determination of thermodynamic properties of inorganic materials at high temperatures. Experimental methods were developed which permit accurate and reliable determination of activity-composition relations in solid solutions, and stabilities of end-member compounds. The data provide insight into the general laws governing the behavior of materials in high-temperature environments.

The phases selected for the experimental studies include orthosilicates, metasilicates, oxides of periclase structure, spinels and titanates. It has been shown that directions of conjugation lines between coexisting solid-solution phases provide a powerful tool for determining relative stabilities of end-member compounds and activity-composition relations of solid solutions. In general, oxide phases (including silicates and titanates) forming complete solid-solution series at high temperatures show less deviations from ideality in their activity-composition relations than do alloy systems. Deviations from ideality are particularly small for many solid solutions of relatively simple structures (e.g. oxides of periclase structure), whereas those of greater structural complexities (e.g. spinels) show larger deviations from ideality.

INTRODUCTION

The research program whose main results are summarized in this final report was carried out during the period May 1, 1961 - October 31, 1973. Details of the work performed and the results obtained have been set forth in Annual Progress Reports and in reprints of the numerous papers which have resulted from this work. These publications are listed at the end of this report. In the following we summarize the main developments, and present our appraisal of its significance and the present status of knowledge in the field concerned.

SUMMARY OF MAIN ACCOMPLISHMENTS,

AND AN APPRAISAL OF PRESENT KNOWLEDGE

At the inception of this research program some 12 years ago, knowledge of the thermodynamic behavior of oxide solid solutions, including silicates, was very deficient. Previous authors would often use misleading concepts based on molecular species that do not exist in these essentially ionic substances. Among the objectives of the present work was to define activity-composition relations in ionic solutions in terms of meaningful composition parameters, to design experimental methods by which activity-composition relations in terms of these parameters could be measured at elevated temperatures, and to interpret these observations in terms of general trends.

The first steps in our work was to develop methods by which standard free energies of formation of the various compounds from their oxide components could be obtained with a higher degree of reliability and accuracy than were previously available. Of paramount importance in this connection were the theoretical derivations of the importance of directions of conjugation lines in ternary systems, as adapted to ionic solutions on the basis of Wagner's treatment of alloys. This was followed by experimental measurements in a number of carefully selected ternary systems. Among the compounds for which standard free energies of formation were thus obtained are MgAl_2O_4 , MnAl_2O_4 , MnCr_2O_4 , Mn_2SiO_4 , MnSiO_3 , Mg_2SiO_4 , MgSiO_3 , $\text{Al}_6\text{Si}_2\text{O}_{13}$, Mg_2TiO_4 , MgTiO_3 , MgTi_2O_5 , Mn_2TiO_4 , MnTiO_3 , MnTi_2O_5 , Ni_2TiO_4 .

Because of the contamination problems encountered in investigations of activity-composition relations in oxide solid solutions (including silicates), it was found necessary to investigate thermodynamic properties of alloys formed between noble metals (Pt or Pd) and some of the transition elements of the oxide solid solutions (e.g. Fe, Ni, Co, Cr). Hence the scope of the work was

broadened to include experimental studies of equilibria between one or more oxide phases, a metal phase and a gas phase of known oxygen pressures and in which not only the oxide phases but also the alloy phase is of variable composition. Alloy systems whose activity-composition relations were studied in the course of this investigation include Pt-Co, Pt-Ni, Pt-Cr, Pd-Fe, Pd-Ni, Pd-Co, Pt-Cr.

Activity-composition relations in a number of oxide solid solutions (including silicates) were next determined. The general approach was to start with solutions of simple periclase structure and gradually turn to those of more complex structures, for instance silicates and spinels. Solid solutions whose thermodynamic properties have been studied experimentally under this research contract include MgO-NiO, MnO-NiO, MnO-CoO, MgO-CoO, MnO-"FeO", NiO-"FeO", MgAl_2O_4 - CoAl_2O_4 , MnAl_2O_4 - CoAl_2O_4 , MnCr_2O_4 - CoCr_2O_4 , Mn_2SiO_4 - Co_2SiO_4 , Mn_2SiO_4 - Fe_2SiO_4 , MnSiO_3 - FeSiO_3 , Mg_2SiO_4 - Fe_2SiO_4 , MgSiO_3 - FeSiO_3 , Ca_2SiO_4 - Fe_2SiO_4 , CaSiO_3 - FeSiO_3 , Mg_2TiO_4 - Fe_2TiO_4 , MgTiO_3 - FeTiO_3 , MgTi_2O_5 - FeTi_2O_5 , MgTiO_3 - NiTiO_3 , Mg_2TiO_4 - Co_2TiO_4 , MgTiO_3 - CoTiO_3 , MgTi_2O_5 - CoTi_2O_5 , Mn_2TiO_4 - Co_2TiO_4 , MnTiO_3 - CoTiO_3 , MnTiO_3 - NiTiO_3 . In the solid solutions of relatively simple structures (e.g. oxides of periclase structure), the activity-composition relations are determined largely by the relative sizes of the cations involved, whereas in the more complex structures (e.g. spinels) other factors significantly enter into the picture, for instance the distribution of cations on the different lattice sites.

We feel that great progress has been made during the course of this work toward an understanding of the energetics involved in compound- and solid-solution formation in oxide and silicate systems. It is our opinion that we now have a good knowledge of the general behavior of such systems. However, much remains to be done both experimentally and theoretically on details of individual systems, especially where complex structures and large deviations

from stoichiometry are involved. During the last year of this project, we were able to show the profound influence of oxygen non-stoichiometry on activity-composition relations in $\text{NiO}-\text{FeO}$ solid solutions in equilibrium with Ni-Fe alloys. We feel that further work on similar systems (e.g. $\text{CoO}-\text{FeO}$) and on spinels with large deviations from stoichiometry would provide much insight into the energetics of ionic substances and hence shed light on their interactions with alloys in a variety of materials' problems. We also feel that a better understanding of the effect of ionic size on the thermodynamics of solid solutions could be attained by further studies of some key systems, and that the time is ripe for further evaluations of interrelations between thermodynamic properties and structural characteristics of ionic solid solutions. Finally, we feel that the improved knowledge of the thermodynamics of solid solutions acquired to a large extent as a result of work on this project would form an excellent starting point for determination of similar parameters in liquid oxide and liquid silicate phases.

LIST OF PUBLICATIONS

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