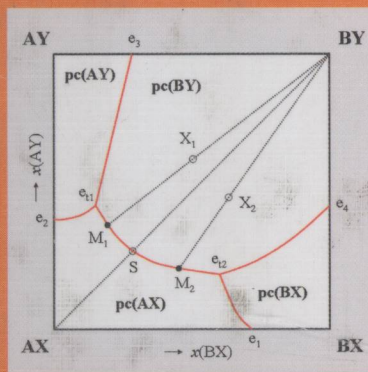
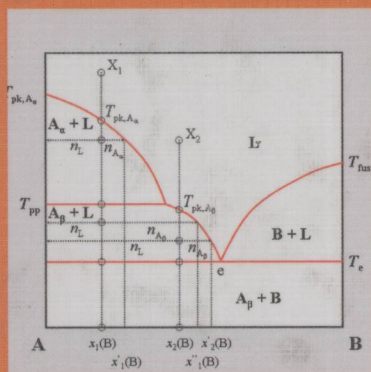


Physico-Chemical Analysis of Molten Electrolytes

Vladimír Danek



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PHYSICO-CHEMICAL ANALYSIS OF MOLTEN ELECTROLYTES

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PHYSICO-CHEMICAL ANALYSIS OF MOLTEN ELECTROLYTES

Dedicated to my wife Maria

Publisher's Note

Vladimír Daněk, 6 April 1940 – 28 November 2005

It is our sad duty to inform you that after submitting the manuscript for this book, Dr. Vladimír Daněk passed away after a short illness in November 2005.

In 1963 Dr. Daněk joined the Institute of Inorganic Chemistry of the Slovak Academy of Sciences in Bratislava, of which he was the director in the period 1991–1995. His main field of interest was the physical chemistry of molten salts systems; in particular the study of the relations between the composition, properties, and structure of inorganic melts. He developed a method to measure the electrical conductivity of molten fluorides. He proposed the thermodynamic model of silicate melts and applied it to a number of two- and three-component silicate systems. He also developed the dissociation model of molten salts mixtures and applied it to different types of inorganic systems. More recently his work was in the field of chemical synthesis of double oxides from fused salts and the investigation of the physicochemical properties of molten systems of interest as electrolytes for the electrochemical deposition of metals from natural minerals, molybdenum, the synthesis of transition metal borides, and for aluminium production.

During his career Dr. Daněk was also head of the Department of Molten Salts, chairman of the Scientific Board of the Institute, chairman of the Scientific Collegium for Chemical Sciences of the Slovak Academy of Sciences, and member of the Presidium, the Executive Board, and chairman of the Commission for Chemical Sciences of the Scientific Grant Agency of the Ministry of Education of the Slovak Republic and the Slovak Academy of Sciences.

In 1994 he was elected an active member of the New York Academy of Sciences. His numerous achievements were also recognized with the Award of the Czechoslovak Academy of Sciences, 1968; the Award of the Slovak Academy of Sciences, 1972, 1986 and 1989; the Dyonýz Štúr Silver Medal for Achievements in Natural Sciences, 1990; and the Dyonýz Štúr Golden Medal for Achievements in Natural Sciences, 2000. In the course of his distinguished career he published more than 240 papers in international journals and conference proceedings.

We extend our condolences to his wife Maria and further family on their sad loss.

Acknowledgement

Ing. Marián Kucharík, PhD, took on himself the task of correcting the proofs. Ing. Zdeněk Pánek, DrSc, was responsible for compiling the index.

Preface

The idea of this book came to me after seeing a multitude of young scientists carrying out their PhD studies on molten salts and attending various conferences, many of whom were eager for any new knowledge on molten salts. Many of them focused their study on problems that would contribute a little more to the understanding of the structure of the system of interest using sophisticated and very expensive equipment. On the other hand, while being mostly interested in the quantum chemistry and molecular dynamics simulation calculations, their knowledge of the physical chemistry of inorganic melts is often poor.

At the universities, we can also see another very encouraging development. After the resumption of relations between East and West at the end of the 1990s, a lot of young scientists from Eastern Europe and Asia came to the universities in Western Europe for a shorter or longer stay, or a PhD study. While in Eastern Europe and Asia, the measurement of physico-chemical properties is more frequent due to the lack of other expensive sophisticated physical equipment, in Western Europe and the United States, the emphasis is rather on the use of high-tech investigations.

This book includes selected topics on the measurement and evaluation of physico-chemical properties of molten electrolytes. It describes the features, properties, and experimental measurement of different physico-chemical properties of molten salt systems used as electrolytes for the production of different metals, metallic layer deposition, as a medium for reactions in molten salts, e.g. precipitation of double oxide powders used for functional and construction ceramics, special parts for steel and copper production, etc.

The physico-chemical properties such as phase equilibria, density (molar volume), enthalpy (calorimetry), surface tension, vapor pressure, electrical conductivity, viscosity, etc. are the most important parameters of electrolytes needed for technological use. For each property, the theoretical background, experimental techniques, as well as examples of the latest knowledge and the processing of most important salt systems will be given. Most of the examples are among the published works of the author.

The aim of the book is not only to present the state of the art studies on different properties of molten salt systems and their measurement, but also to present the possibilities of modeling molten salt systems, to be able to forecast the properties of an electrolyte mixture from the properties of the pure components in order to avoid experimentally demanding, and in most cases, also expensive measurements. Some direct methods of study on the structure (ionic composition) of molten electrolytes are also presented.

During the last decades of the twentieth century, a substantial development of experimental and especially, computational techniques took place. Thus, new measurement methods and mathematical processing of data appeared. This new information is not given anywhere in a comprehensive form and therefore, a lot of people working in this field are not acquainted with it. This book thus fills a substantial gap in this field of science. The book also documents the latest research in molten salt chemistry and brings new results and new insights into the study of molten salt systems using the results of X-ray diffraction and XSAF methods, Raman spectroscopy, and NMR measurements.

On the other hand, it is not the goal of this book to present an exhaustive review of the measurement of physico-chemical properties carried out in the last two or three decades. This would certainly exceed the framework of this book. The electrochemistry of molten salts is not included in this book either, since in my opinion, this topic would need a separate book due to its complexity and wealth of applications. The quantum chemistry and molecular dynamics simulation methods are omitted as well.

However, recent books of this kind have been written by the Russian authors Antipin and Vazhenin (1964), and the American authors Blander (1964), Sundheim (1964), Mamantov et al. (1969), Lumsden (1966), and by Lowering and Gale (1983). Since then, new information on physical properties of molten salt systems has been disseminated only in papers in different journals.

This book should serve as a textbook for all people working in the field of molten salt chemistry. It is aimed at undergraduate students working on their diploma work, for students working on their PhD theses, and also for other graduates, e.g. teachers at universities, scientists in academic institutes, research institutes, and in industry, i.e. to all who need up-to-date information on this subject.

It is a pleasure for me to express my thanks to my teachers Professor Milan Malinovský, who taught me the theory of molten salts, Professor Kamil Matiašovský, who taught me his experimental skills, and Dr. Ivo Proks, who helped me to understand a little of thermodynamics. Professor Pavel Fellner of the Slovak Technical University is greatly acknowledged for his advice and comments which helped improve this book.

I am very thankful to my colleagues at the Institute of Inorganic Chemistry of the Slovak Academy of Sciences for their help and good friendship during my whole professional career.

Finally, my warm thanks and great admiration are devoted to my wife. Without her timeless patience, systematic support, and help, this book could not have been written.

Vladimír Daněk
2005

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Chapter 1

Introduction

Inorganic ionic melts represent a group of waterless solvents and solutions, which is interesting both from the point of view of fundamental research as well as with regard to their present and prospective use in technical practice. At present we find them used, e.g. in the metallurgical production of aluminum, magnesium, alkali, and refractory metals, where they are used as electrolytes; in black metallurgy, where they form slags gathering unwanted admixtures and reaction products in iron and steel production. Molten electrolytes are used in galvanic metal plating in melts, e.g. in aluminum plating, boriding, or in the deposition of refractory metal layers (Ti, Mo, Nb, etc.). Molten mixtures of alkali metal halides and zirconium, thorium, beryllium, and uranium are used as heat-bearing medium in primary circuits of nuclear plants.

Mixtures of molten alkali metal halides and hydroxides have a potential use in energy storage, where the relatively high value of the enthalpy of fusion is used. Molten carbonates of alkali metal halides are used as electrolytes in molten carbonate fuel cells. A big industrial field, where oxide melts are predominantly used, is the glass industry. Here, the high affinity of these melts to under-cooling and glass formation is exploited.

Recently, there has also been an increase in the importance of melts in their use as a reaction medium for chemical and electrochemical synthesis of compounds for functional and construction ceramics, e.g. double oxides with spinellitic and perovskite structure and binary compounds with prevailing covalent bond character, mainly borides and carbides of transition metals.

In order to decide the suitability of a certain melt in technical practice, an in-depth knowledge of its physico-chemical properties is unavoidable. The present database of the properties of inorganic melts is relatively broad. Many properties are known, such as phase equilibria, enthalpies of fusion, heat capacities, density, electrical conductivity, viscosity, surface tension, emf of galvanic cells of many molten systems, the measurement of which was stimulated first by their technological application.

Nevertheless, the published data on the physico-chemical properties of the molten systems are often incomplete and in many cases the results given by different authors may more or less differ. The reason is that the experimental measurement of the physico-chemical properties of inorganic melts is sometimes inadequate. First, because of the shortage of expensive construction material. Second, due to the relatively high costs connected with the construction of unique measurement devices.

It is obvious that the choice of a suitable melt for a concrete application, which is often a multi-component mixture, is given by the requisite optimum physico-chemical

properties at a given temperature. With regard to the experimental difficulty of direct measurement, in choosing a concrete melt it is much cheaper to use convenient structural models that enable us to forecast the values of the physico-chemical properties of multi-component molten systems on the basis of knowledge of the properties of the pure components. It is then necessary to know the mathematical description of the functional property – composition and property – temperature dependences. The definite form of such dependences is given first by the structure (ionic composition) of the molten systems, which in many cases is still not satisfactorily known. Recently, research on the structure of inorganic ionic melts has rapidly advanced. A substantial improvement in the experimental techniques, especially in high-technology electronics and computer techniques, has contributed to this. However, the present knowledge of the physico-chemical properties of molten systems is in many cases on a higher level than the possibility of their interpretation. First, it follows from the lack of an adequate knowledge of their structure. High-temperature X-ray diffraction analysis applied to the liquid phase has not principally contributed to the classification of the structure of melts, mainly due to the lack of suitable approaches in structural analysis. More success was attained recently by the exploitation of sophisticated methods of high-temperature infrared and Raman spectroscopy, NMR, MAS NMR, and some numerical methods, especially methods of quantum chemistry and of molecular dynamics.

While for the last mentioned methods of investigation the measuring devices could be acquired, with only small adaptations, devices for measurement of physico-chemical properties are not available on the market. The measurement, especially its precision depend on the skills of the scientists and the workers in the laboratory. For instance, the construction of a high-temperature torsional pendulum viscosimeter requires in-depth knowledge of many features of the technique. It should also be mentioned that for scientific purposes, the accuracy and precision of results must be at least one order higher than for industrial purposes. On the other hand, using generalized knowledge many industrial measurements could be avoided as necessary data could be estimated with good accuracy.

Generally, any electrolyte is composed of a mixture of alkali metal halides, which serve as solvent, and the compound of the deposited metal. In addition, there may be other additives, which may improve the properties of electrolyte or enhance the metal deposition.

For a certain purpose a concrete molten system must be used. For example, in the electro-deposition of metals from molten salts several types of molten systems were tested as electrolytes. From the analysis of literature and on the basis of the electro-active species used, they can be divided into two principal groups:

- systems containing halo-complexes of deposited metals,
- systems containing oxides or oxy-complexes of deposited metals.

In all of the investigated systems, one of the most important tasks to be solved is to find the proper composition of the electrolyte with regard to both the suitable physico-chemical properties and the desired character of the electrodeposited product. Both problems are closely related to the actual structure, i.e. the ionic composition of the melt.

Quite recently attention was paid to the role of oxides, either as electro-active species, as impurities or as additives in the electro-deposition of transition metals. This may be demonstrated, e.g. in the case of electro-deposition of molybdenum, where the electrolysis of neither pure K_2MoO_4 , nor the $KF-K_2MoO_4$ mixture yields a molybdenum deposit. However, introducing small amounts of boron oxide, or silicon dioxide to the basic melts, smooth and adherent molybdenum deposits may be obtained. Also, in the case of niobium and tantalum deposition, the presence of oxygen either from the moisture or added on purpose leads to the formation of oxohalo-complexes, which due to their lowered symmetry and thus lower energetic state, decompose easier at the cathode yielding pure metal.

It is thus the aim of the present book to serve as a guide in the measurement of the physico-chemical properties of molten salts and to characterize briefly the properties and the structure of different types of molten salt systems. In this book, only direct methods of measurements and different methods of processing the measured data are discussed. Computer simulation methods are not considered.

Chapter 2

Main Features of Molten Salt Systems

The transition from the solid to the liquid state is so commonplace that ancient scholars tried to explain this phenomenon. The development of the natural sciences in the sixteenth and seventeenth centuries enabled its deeper understanding, especially in connection with the development of suitable methods for the measurement of volume and heat. The first experiments to apply thermodynamic principles to the melting process of substances arose approximately at the time of the formulation of the second law of thermodynamics, i.e. in the middle of the nineteenth century.

As it is known, the main advantage of classical thermodynamics lies in the fact that it is not necessary to know the structure of the investigated system. This enabled some of the most important classical thermodynamic conclusions on the melting process to be made before the general idea of the atomic structure of a substance was accepted. However, as the latter observations showed, melting depends on the structure of the crystalline state of matter and due to the great variability of the crystal structure of matter, different features of this phase transformation have to be investigated. Today it is obvious that, without the thorough knowledge of the crystal structure of solid substances, it is not possible to study the structure of the melt. It should be, however, also emphasized that X-ray structural analysis, which was broadly exploited for the study of the crystal structure of solids, did not enable explanation of all structural aspects of the molten state. For deeper understanding of the structure of melts obviously, new experimental and theoretical approaches are needed.

From the general structural classification, the crystalline substances can be divided into four groups:

- (a) molecular,
- (b) ionic,
- (c) metallic,
- (d) network forming.

At melting, each group forms its own type of melt. Of course, melts having the features of two of these groups may also occur. For example, silicate melts belong to the network forming as well as to the ionic melts.

The structure of inorganic melts is, in spite of their relative simplicity, not completely understood. The earlier calculations and simple models of molten salts were built up rather on intuition. However, they were the necessary first step for more sophisticated approaches.

In general, inorganic melts increase their volume at melting. The number of substances that decrease their volume at melting is surprisingly low. From among the more common substances, we have e.g. Sb, Bi, Ga, H_2O , and RbNO_3 . These substances are characterized by a low coordination of atoms, which indicates an “open” structure of the solid. At melting, their structure partially collapses, which is followed by a volume contraction.

At a sufficiently high temperature, molten salts are miscible in any ratio. At lower temperatures, a limited miscibility can be observed. Partially miscible salts are in general mixtures of halides of multivalent metals with prevailing covalent bonds, like e.g. Al, Bi, and Sb, with halides having a high ratio of ionic bonds, e.g. CaCl_2 and KCl . The shape of the dependence of the given property on composition gives certain information about the structure of these mixtures. The comparison of the values of molar volumes of mixtures of alkali metal halides and the mixtures of alkali metal halides with PbCl_2 can be mentioned as an example. In the former case, the molar volume changes almost additively, which indicates that in the mixtures, the cations and anions are arranged more or less equally as in the pure salts. In the latter case, the change in molar volume on composition is almost additional only in the system NaCl-PbCl_2 , and from potassium to cesium, there is always a more expressive minimum. This trend indicates that in these melts, structural changes causing deviation from ideal behavior take place.

However, the molar volume of molten salt mixtures is in general not influenced much by structural changes, since the changes in the ionic ordering cannot be great. More sensitive in this direction is the electrical conductivity, which shows larger changes with the change in composition. An additive change of the electrical conductivity on composition is not known. For instance in the systems of alkali metal halides, in contrast to the molar volume, negative deviations in the concentration dependence of conductivity from the additivity can be observed. This effect supported the supposition of the formation of associates, leading to lowering the number of conducting ions in the melt. Even though until now, no further data supporting these ideas are available, it is clear that between cations of uneven size, an important interaction exists.

The concept of “complexing” in molten salt mixtures is somewhat different from that for solutes in aqueous or organic solvents. In water solutions, every ion is separated from the other ions by the solvation wrapping of water. Ions, simple or complex, are mutually influenced only by weak forces and each ion behaves independently.

In molten salts, the positively and negatively charged ions are in close contact and the interaction forces are great. The heats of formation of complex anions, except for the stable ions like $[\text{SO}_4]^{-2}$, $[\text{NO}_3]^{-}$, etc., are in the order of a few $\text{kJ} \cdot \text{mol}^{-1}$. These values are lower than that of the activation energy of diffusion, which in these melts is