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# Nonstoichiometric Compounds

As Chapter 1 emphasizes, the law of definite proportions was one of the principal pieces of evidence that led to the acceptance of Dalton's atomic theory. It is now recognized that a great many solid-state binary compounds do not have fixed and unvarying compositions but exist over a range of compositions in a single phase. Thus, FeO (wüstite) has the composition range Fe<sub>0.85</sub>O<sub>1.00</sub> to Fe<sub>0.95</sub>O<sub>1.00</sub> and is never found with its nominal 1:1 composition. The compounds NiO and Cu<sub>2</sub>S also deviate considerably from their nominal stoichiometries.

The explanation depends on the existence of more than one oxidation state for the metal. In wüstite, iron can exist in either the +2 or the +3 oxidation state. Suppose a solid were to begin at the hypothetical composition of  $Fe_{1.00}O_{1.00}$ , with iron entirely in the +2 oxidation state. For every two  $Fe^{3+}$  ions introduced, three  $Fe^{2+}$  ions must be removed to maintain overall charge neutrality. The total number of moles of iron is then less than that in the ideal FeO stoichiometry. The departure from the nominal stoichiometry can be far more extreme than that found

in wüstite. The composition of "TiO" ranges from Ti<sub>0.75</sub>O to Ti<sub>1.45</sub>O. Nickel oxide varies only from Ni<sub>0.97</sub>O to NiO in composition, but the variation is accompanied by a dramatic change in properties. When the compound is prepared in the 1:1 composition, it is pale green and is an electrical insulator. When it is prepared in an excess of oxygen, it is black and conducts electricity fairly well. In the black material, a small fraction of Ni<sup>2+</sup> ions are replaced by Ni<sup>3+</sup> ions, and compensating vacancies occur at some nickel atom sites in the crystal.

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# **Nonstoichiometric Compounds**

A.I. Gusev, A.A. Rempel, A.J. Magerl

#### **Nonstoichiometric Compounds:**

Transport in Nonstoichiometric Compounds George Simkovich, 2012-12-06 Prior to the 9th International Conference on Reactivity Solids in Krakow Poland a group of about 25 international scientists held a special conference entitled Transport in Nonstoichiometric Compounds in late Aug 1980 in Mogilany Poland near Krakow This conference was well received in view of the interaction between the participants as well as the resulting publication of the proceedings Elsevier Scientific Publishing Company 1982 edited by I Nowotny At this first conference the participants decided that it would be desirable to organize similar conferences at about two year intervals Thus a second meeting was held in late June early July at Alenya Pyrenees Orientales France This conference had a larger number of participants about 50 but still managed to promote excellent interaction between all the participants These proceedings with editors G Petot Ervas Hj Matzke and C Monty have also been published by Elsevier as a special edition of the journal Solid State lonics Vol 12 1984 In view of the success of the initial two conferences a third meeting was organized and held at The Pennsylvania State University University Park PA 16802 U S A from 11 June 84 to 15 June 84 The proceedings of this conference are presented in the Disorder and Order in Strongly Nonstoichiometric Compounds A.I. Gusev, A.A. Rempel, A.J. following text Magerl, 2013-03-09 long to understand that the phenomena associated with the redistribution of interstitial atoms and structural vacancies in non stoichiometric compounds represent an excellent model of analogous phenomena arising in solid state systems with mutual substitution of components Therefore methods of analysis and description proposed and developed for nonstoichiometric compounds are applicable to a number of systems with substitutional disorder In 1980 when we embarked on this work ordering in nonstoichiometric compounds was assumed to be a rare and accidental effect which hardly deserved close attention Now many people understand that ordering represents a general regular phenomenon in all non stoichiometric compounds Ordering effects which were not even mentioned or were referred to as something insignificant and negligible just 20 years ago proved to be numerous and comparable in magnitude with the change of properties in the whole homogeneity interval of non stoichiometric compounds Phase diagrams of binary systems of transition metals with carbon and nitrogen which remained unchanged from the time they were plotted in 1950 60s and containing one or two nonstoichiometric compounds were enriched with many ordered phases Unfortunately the accumulated experimental and theoretical knowledge has not so far been disseminated widely Nonstoichiometric Compounds Ronald Ward, American Chemical Society. Division of Inorganic Chemistry, 1963 Non-Stoichiometric Compounds J. Nowotny, W. Weppner, 2012-12-06 The material in this book is based on invited and contributed papers presented at the NATO Advanced Research Workshop on INon stoichio l metric Compounds held in Ringberg Castle Rottach Egern Bavarian Alps Germany July 3 9 1988 The workshop followed previous meetings held in Mogilany Poland 1980 Alenya France 1982 Penn State USA 1984 and Keele University UK 1986 The aim of these workshops is to present and discuss up to

date knowledge in the study of non stoichiometry and its effect on materials properties as well as to indicate the most urgent research pathways required in this field Since the subject of non stoichiometry is interdisciplinary the workshops bring together solid state physicists and chemists surface scientists materials scientists ceramists and metallurgists. The present workshop which gathered 42 scientists of an international reputation mainly considered the effect of surfaces grain boundaries and structural defects on materials properties From discus sions during this meeting it emerged that correct understanding of properties of ceramic materials requires urgent studies on the defect structure of the interface region Progress in this direction requires the development of the interface defect chemistry. This is the task for materials scientists in the near future The present proceedings includes both theoretical and experimen tal work on general aspects of non stoichiometry defect structure and diffusion in relation to the bulk and to the interface region of such materials as high tech ceramics solid electrolytes electronic cera mics nuclear materials and high Tc oxide superconductors Transport in Nonstoichiometric Compounds G. Petot-Ervas, Claude Monty, 1984 **Disorder and Order in Strongly** Nonstoichiometric Compounds A.I. Gusev, A.A. Rempel, A.J. Magerl, 2001-08-13 Deals with the influence of stoiciometry and order disorder on materials properties It summarizes the knowledge available in a comprehensive way **Inorganic Synthetic Chemistry** Ruren Xu, Yan Xu, 2017-02-11 Modern Inorganic Synthetic Chemistry Second Edition captures in five distinct sections the latest advancements in inorganic synthetic chemistry providing materials chemists chemical engineers and materials scientists with a valuable reference source to help them advance their research efforts and achieve breakthroughs Section one includes six chapters centering on synthetic chemistry under specific conditions such as high temperature low temperature and cryogenic hydrothermal and solvothermal high pressure photochemical and fusion conditions Section two focuses on the synthesis and related chemistry problems of highly distinct categories of inorganic compounds including superheavy elements coordination compounds and coordination polymers cluster compounds organometallic compounds inorganic polymers and nonstoichiometric compounds Section three elaborates on the synthetic chemistry of five important classes of inorganic functional materials namely ordered porous materials carbon materials advanced ceramic materials host quest materials and hierarchically structured materials Section four consists of four chapters where the synthesis of functional inorganic aggregates is discussed giving special attention to the growth of single crystals assembly of nanomaterials and preparation of amorphous materials and membranes The new edition s biggest highlight is Section five where the frontier in inorganic synthetic chemistry is reviewed by focusing on biomimetic synthesis and rationally designed synthesis Focuses on the chemistry of inorganic synthesis assembly and organization of wide ranging inorganic systems Covers all major methodologies of inorganic synthesis Provides state of the art synthetic methods Includes real examples in the organization of complex inorganic functional materials Contains more than 4000 references that are all highly reflective of the latest advancement in inorganic synthetic chemistry Presents a comprehensive coverage of the key

issues involved in modern inorganic synthetic chemistry as written by experts in the field Understanding Solids Richard J. D. Tilley, 2005-09-27 A modern introduction to the subject taking a unique integrated approach designed to appeal to both science and engineering students Covering a broad spectrum of topics this book includes numerous up to date examples of real materials with relevant applications and a modern treatment of key concepts The science bias allows this book to be equally accessible to engineers chemists and physicists Carefully structured into self contained bite sized chapters to enhance student understanding Questions have been designed to reinforce the concepts presented Includes coverage of radioactivity Relects a rapidly growing field from the science perspective Intermetallics Research Progress Yakov N. Berdovsky, 2008 Intermetallics is concerned with all aspects of ordered chemical compounds between two or more metals and notably with their applications This book covers new and important research on the crystal chemistry and bonding theory of intermetallics determination and analysis of phase diagrams the nature of superlattices antiphase domains and order disorder transitions the geometry and dynamics of dislocations and related defects in intermetallics theory and experiments relating to flow stress work hardening fatigue and creep response of deformed intermetallics to annealing magnetic and electrical properties of intermetallics structure and properties of grain and interphase boundaries the effect of deviations from stoichiometry on physical and mechanical properties crystallisation of intermetallics from the melt or amorphous precursors Chemistry of Non-stoichiometric Compounds Koji Kosuge, 1994-01-13 This unified presentation of the chemistry of non stoichiometric compounds is the first monograph on the subject for two decades Based on statistical thermodynamics and structural inorganic chemistry with descriptions of modern examples and applications this will be useful to both researchers in industry and undergraduates in solid state chemistry and physics

Non-Stoichiometric Oxides of 3d-Metals Andrzej Stokłosa, 2015-03-18 In the present work in Part I new elements widening the bases of the defects theory are shown particularly this work discusses the mechanism of the formation of defects as a result of elementary processes the work also presents a description of the equilibrium state by one equation taking into account the concentrations of defects and their changes during the process of reaching the equilibrium The equation relates the concentrations of defects dependent on the standard Gibbs energies of their formation with the equilibrium pressure of oxygen The obtained relations and the discussion have lead to the development of a method for determination of complete diagrams of concentrations of the point defects which allows taking into account the minority defects Part II presents the results of the calculations of the diagrams of point defects concentrations for a series of pure and doped oxides of transition metals 3d with different composition M O ratio crystallographic structure and point defects structure A critical analysis of the results of the studies of the deviation from the stoichiometry and the electrical conductivity obtained so far by most research groups has been also performed A new interpretation of these results concerning concentrations and types of ionic defects present has been performed and the mobility of electronic defects and its

dependence on the temperature and oxygen pressure have been determined Structure Processing Properties Relationships in Stoichiometric and Nonstoichiometric Oxides Speranta Tanasescu, 2020-11-04 The interrelation among composition microstructure and properties of stoichiometric and nonstoichiometric compounds is a major field of research for both scientific and technological reasons As such this book focuses on metal oxides which present a large diversity of electrical magnetic optical optoelectronic thermal electrochemical and catalytic properties making them suitable for a wide range of applications By bringing together scientific contributions with special emphasis on the interrelations between materials chemistry processing microstructures and properties of stoichiometric and nonstoichiometric metal oxides this book highlights the importance of tightly integrating high throughput experiments including both synthesis and characterization and efficient and robust theory for the design of advanced materials **Introduction to Condensed** Matter Chemistry Jihong Yu, Ruren Xu, Wenfu Yan, 2024-06-06 Introduction to Condensed Matter Chemistry offers a general view of chemistry from the perspective of condensed matter chemistry analyzing and contrasting chemical reactions in a more realistic setting than traditional thinking Readers will also find discussions on the goals and major scientific questions in condensed matter chemistry and the molecular engineering of functional condensed matter Processes and products of chemical reactions should not be determined solely by the structure and composition of these basic species but also by the complex and possibly multilevel structured physical and chemical environment together referred to as their condensed state Relevant matters in condensed state should be the main bodies of chemical reactions which is applicable not only to solids and liquids but also to gas molecules as reactions among gas molecules can take place only in the presence of catalysts in specific condensed states or after their state transition under extreme reaction conditions. This book provides new insights on the liquid state chemistry definitions aspects and interactions summarizing fundamentals of main chemical reactions from a new perspective Helps to establish the new field of Condensed Matter Chemistry Highlights the molecular engineering of functional condensed matter Focuses on both liquid and solid state chemistry Nonstoichiometric Oxides O.T. Soerensen, 2012-12-02 Nonstoichiometric Oxides discusses the thermodynamic and structural studies of nonstoichiometric oxides This eight chapter text also covers the defect defect interactions in these compounds The introductory chapters describe the thermodynamic properties of nonstoichiometric oxides in terms of defect complexes using the classical thermodynamic principles and from a statistical thermodynamics point of view These chapters also include statistical thermodynamic models that indicate the ordered nonstoichiometric phase range in these oxides The subsequent chapters examine the transport properties such as diffusion and electrical conductivity Diffusion theories and experimental diffusion coefficients for several systems as well as the electrical properties of the highly defective ionic and mixed oxide conductor are specifically tackled in these chapters. The concluding chapters present the pertinent results obtained in nonstoichiometric oxide structural studies using high resolution electron microscopy and X ray and neutron diffraction Inorganic chemists and

inorganic chemistry teachers and students will greatly appreciate this book Nonstoichiometric Compounds, 1963 Fundamentals of Ceramics Mr. Rohit Manglik, 2024-01-08 EduGorilla Publication is a trusted name in the education sector committed to empowering learners with high quality study materials and resources Specializing in competitive exams and academic support EduGorilla provides comprehensive and well structured content tailored to meet the needs of students across various streams and levels Inorganic Chemistry Tina Overton, Jonathan Rourke, Fraser A. Armstrong, 2018 Leading the reader from the fundamental principles of inorganic chemistry right through to cutting edge research at the forefront of the subject Inorganic Chemistry Seventh Edition is the ideal course companion for the duration of a student s degree The authors have drawn upon their extensive teaching and research experience to update this text the seventh edition retains the much praised clarity of style and layout from previous editions while offering an enhanced section on expanding our horizons The latest innovative applications of green chemistry have been added to clearly illustrate the real world significance of the subject This edition also sees a greater used of learning features including substantial updates to the problem solving questions additional self tests and walk through explanations which enable students to check their understanding of key concepts and develop problem solving skills Providing comprehensive coverage of inorganic chemistry while placing it in context this text will enable the reader to fully master this important subject Online Resources Inorganic Chemistry Seventh Edition is accompanied by a range of online resources For registered adopters of the text DT Figures marginal structures and tables of data ready to download DT Test bank For students DT Answers to self tests and exercises from the book DT Tables for group theory DT Web links DT Links to interactive structures and other resources on www chemtube3D com Functional and Smart Materials Zhong-lin Wang, Z.C. Kang, 2012-12-06 In the search for new functional materials a clear understanding about the relationship between the physical properties and the atomic scale structure of materials is needed Here the authors provide graduate students and scientists with an in depth account of the evolutionary behavior of oxide functional materials within specific structural systems discussing the intrinsic connections among these different structural systems Over 300 illustrations and key appendices support the text Handbook of Solid State Electrochemistry P. J. Gellings, 2019-04-24 The Handbook of Solid State Electrochemistry is a one stop resource treating the two main areas of solid state electrochemistry electrochemical properties of solids such as oxides halides and cation conductors and electrochemical kinetics and mechanisms of reactions occurring on solid electrolytes including gas phase electrocatalysis The fund Nonstoichiometric Compounds Charles Richard Arthur Catlow, William Carlysle Mackrodt, 1987

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