

MATERIALS SCIENCE RESEARCH • Volume 4

KINETICS OF REACTIONS IN IONIC SYSTEMS

*Proceedings of an International Symposium on Special
Topics in Ceramics, held June 18-23, 1967,
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MATERIALS SCIENCE RESEARCH
Volume 4

KINETICS OF REACTIONS IN IONIC SYSTEMS

MATERIALS SCIENCE RESEARCH

- Volume 1:** Proceedings of the 1962 Research Conference on Structure and Properties of Engineering Materials
— *edited by H. H. Stadelmaier and W. W. Austin*
- Volume 2:** Proceedings of the 1964 Southern Metals/Materials Conference
— *edited by H. M. Otte and S. R. Locke*
- Volume 3:** Proceedings of the 1964 Conference on the Role of Grain Boundaries and Surfaces in Ceramics
— *edited by W. Wurth Kriegel and Hayne Palmour III*
- Volume 4:** Proceedings of the 1967 International Symposium on Kinetics and Reactions in Ionic Systems
— *edited by T. J. Gray and V. D. Fréchet*

Foreword

The kinetics of reactions in ionic solids is of profound importance not only in the understanding of the fundamental principles involved but also in many aspects of industrial research and development. These relationships, which are necessarily complex, cover a very broad spectrum, from the initial interaction through all stages of reaction to nucleation and growth of each individual phase. Their academic and applied implications touch on every varied aspect of solid-state reactions and merit even more attention than they have yet been accorded.

This Conference was held at Alfred University in June 1967 under the sponsorship of the U. S. Office of Naval Research and the U. S. Army Research Office, Durham, and was attended by more than 120 scientists. Ten foreign scientists attended and presented papers, including representatives of Sweden, Germany, France, the United Kingdom, Australia, and Canada. It was the fourth of a series of conferences on ceramic science. The previous conferences were titled "The Role of Grain Boundaries and Surfaces in Ceramics," at North Carolina State University at Raleigh, 1964, "Sintering," at the University of Notre Dame, 1965, and "Ceramic Microstructures," at the University of California at Berkeley, 1966.

The subdivisions of the text were determined on a very broad basis. The introductory lecture by J. G. Cohn reviews the many implications of reaction kinetics and is followed by a historical paper by the one scientist preeminently qualified to review what in many respects is autobiographical, Professor J. A. Hedvall of the Silikatforskningsinstitut, Göteborg, Sweden. A group of analytical papers follows, covering the kinetics of generalized solid-state reactions, including diffusion, reaction, nucleation, and crystal-growth kinetics. The kinetics of sintering is the subject of a second group of papers, while a third group deals with specific solid-state reactions, including the oxidation process.

We wish to express our sincere appreciation to the authors and other conference participants who made this volume possible. While preprinting for the conference was most arduous, our efforts were immeasurably assisted by C. H. Bloomquist of the State University of New York, College of Ceramics, who was responsible for the preparation of the photo-offset pre-prints, which materially aided the lively discussions and were subsequently of considerable assistance to the Editors in producing the final manuscript.

The cooperation of the many faculty and staff members from both Alfred University and the State University of New York, Agricultural and Technical College, who contributed unstintingly of their time and efforts to make the conference a success, is most gratefully acknowledged. The support of the Air Preheater Corporation of Wellsville, N. Y. and the Corning Glass Center of Corning, N. Y., and of Mr. W. Taylor, Jr., of the Pleasant Valley Wineries of Hammondsport, N. Y., with respect to our social activities, was appreciated by all. A special acknowledgment is due Dr. H. M. Davis of AROD, Dr. W. G. Rauch and Dr. A. M. Diness of ONR, and Dr. Cyrus Klingsberg of the National Academy of Sciences, both as representatives of sponsoring agencies and for their personal interest and assistance.

T. J. Grey
V. D. Fréchette

Alfred, N. Y.
October, 1968

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Chapter 1

General Introduction: Kinetics of Reactions in Ionic Systems

J. G. Cohn

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A review is given of studies of reactions in ionic solid systems and of the implications of these studies for industrial applications. Work on the kinetics of solid-state reaction systems is discussed, as are studies of reaction mechanisms and of the effects of process variables on product characteristics. As examples of the significance of these studies for industry the formation of ferrites and of other spinels by reaction in the solid state, the use of catalytic processes employing such solid catalysts as zeolites, and the development of batteries and fuel cells using solid-state electrolytes are described.

Due to their theoretical and practical importance numerous investigations of reactions involving the motion of the building units of ionic solids have been carried out. It might therefore be of interest to briefly highlight some of the historical aspects of such investigations in relation to current research as well as to illustrate their industrial significance by a few examples.

In the early period dating from 1912 to about 1930 a variety of solid-state reaction systems were studied (¹). The pioneering work in this area has been carried out by J. A. Hedvall. Formation of solid solutions has been reported for such systems exhibiting complete miscibility as CoO–ZnO, CoO–MgO, CoO–MnO, CoO–NiO, NiO–MnO, NiO–MgO, CaO–CdO, BaO–SrO, and Fe₂O₃–Cr₂O₃ as well as for such systems of partial solubility as Al₂O₃–Cr₂O₃, Al₂O₃–Fe₂O₃, Fe₂O₃–Mn₂O₃, CdO–MnO, and MgO–MnO.

Many instances of actual compound formation have been described, as illustrated by the following cases. Acidic oxides react additively with basic oxides to form the corresponding salts. Table I shows examples of various interacting components, whereas Table II refers specifically to the formation of spinels by additive reactions. This type of reaction is of considerable practical interest, and, accordingly, has been extensively explored. The mechanism of some additive reactions (Fe₂O₃ + MgO, NiO, ZnO; Fe₂O₃ + Cd₂O₃) is discussed elsewhere in this volume (^{2,3}). Similarly reactions

TABLE I
Compound Formation
from Acidic and Basic Oxides

Acid	Base
SiO ₂	BaO
TiO ₂	BeO
ZrO ₂	CaO
WO ₃	CdO
MoO ₃	CuO
V ₂ O ₅	FeO
Sb ₂ O ₃	MgO
As ₂ O ₃	NiO
	PbO
	SrO
	ZnO

TABLE II
Additive Spinel Formation

Reaction	Temperature of first noticeable reaction (°C)
MgO + Al ₂ O ₃ → MgAl ₂ O ₄	800
MgO + Cr ₂ O ₃ → MgCr ₂ O ₄	600
MgO + Fe ₂ O ₃ → MgFe ₂ O ₄	500
CaO + Al ₂ O ₃ → CaAl ₂ O ₄	800
CaO + Fe ₂ O ₃ → CaFe ₂ O ₄	550
ZnO + Al ₂ O ₃ → ZnAl ₂ O ₄	700
ZnO + Cr ₂ O ₃ → ZnCr ₂ O ₄	400
ZnO + Fe ₂ O ₃ → ZnFe ₂ O ₄	500
CdO + Fe ₂ O ₃ → CdFe ₂ O ₄	800
NiO + Al ₂ O ₃ → NiAl ₂ O ₄	1000
NiO + Fe ₂ O ₃ → NiFe ₂ O ₄	500
CoO + Al ₂ O ₃ → CoAl ₂ O ₄	550
PbO + Fe ₂ O ₃ → PbFe ₂ O ₄	500
2MgO + SnO ₂ → SnMg ₂ O ₄	1400
2CaO + SnO ₂ → SnCa ₂ O ₄	900

occur between oxides and salts decomposable into a solid and a gas. Again, such reactions are of considerable practical utility. Table III shows the formation of spinels by this route. This variety of additive reactions is represented in this volume by chapters on the reaction between TiO₂ and SrCO₃ and between SiO₂ and CaCO₃^(4,5). In these modern studies experimental techniques have been employed which were not available to the earlier workers.

It is of interest to note that the initial kinetic studies investigated reactions

TABLE III
Additive Spinel Formation with Reactant Decomposition

Reaction	Temperature of first noticeable reaction (°C)
$\text{CaCO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{CaAl}_2\text{O}_4 + \text{CO}_2$	600
$\text{CaCO}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{CaFe}_2\text{O}_4 + \text{CO}_2$	600
$\text{SrCO}_3 + \text{Al}_2\text{O}_3 \rightarrow \text{SrAl}_2\text{O}_4 + \text{CO}_2$	900
$\text{BaCO}_3 + \text{Fe}_2\text{O}_3 \rightarrow \text{BaFe}_2\text{O}_4 + \text{CO}_2$	650
$\text{BaSO}_4 + \text{Al}_2\text{O}_3 \rightarrow \text{BaAl}_2\text{O}_4 + \text{SO}_2 + \frac{1}{2}\text{O}_2$	1200
$\text{CoCO}_3 + 2\text{Al}(\text{OH})_3 \rightarrow \text{CoAl}_2\text{O}_4 + \text{CO}_2 + 3\text{H}_2\text{O}$	840

of this kind—for example, the reaction between BaCO_3 and SiO_2 . For reaction in powder mixtures with diffusion-controlled rates the following rate expression was derived (⁶):

$$(1 - \sqrt[3]{1 - \alpha})^2 = (C/R^2)t$$

where α is the fraction of completion and R the grain radius of the minority component being surrounded by the excess component. A number of refinements of the kinetic expressions have been developed, many of which have been reviewed by Hulbert and Popowich (⁴). Subsequently expressions for the kinetics controlled by nucleation or phase boundary reactions have also been derived.

In the important case of reactions between powders conditions are unavoidably nonisothermal, due to the exothermic nature of solid-state reactions and due to the low heat conductivity of the components involved. Hence these conditions affect the kinetics, as already recognized by Jander (⁶) in his second equation:

$$X^2 = 2 k_i t \exp(-C'X)$$

where X is the thickness of the product layer and k_i the rate constant at initiation temperature.

Another class of reaction which had been thoroughly explored in the early period is represented by base exchange of the type $\text{Me}'\text{O} + \text{MeXO}_n$. Table IV lists base exchange reactions of BaO , SrO , and CaO with various salts, and Table V shows that this type of reaction may also lead to the formation of spinels. The reactions with the alkaline earth oxides (Table IV) exhibited certain regularities. Carbonates, sulfates, phosphates, and silicates react with BaO around 350–370°C, with SrO about 100°C higher and with CaO between about 520–540°C. The method used for defining initiation temperatures was thermal analysis, which could also be utilized to determine the

TABLE IV
Reaction Temperatures of Exchange Reactions between Alkaline Earth
Oxides and Salts of Oxygen-Containing Acids

Salt component	$T(^{\circ}\text{C})$ with BaO*	Reaction products	$T(^{\circ}\text{C})$ with SrO*	Reaction products	$T(^{\circ}\text{C})$ with CaO*	Reaction products
Carbonates:						
SrCO ₃	395	BaCO ₃ + SrO				
CaCO ₃	345	BaCO ₃ + CaO	465	SrCO ₃ + CaO		
MgCO ₃	345	BaCO ₃ + MgO	455	SrCO ₃ + MgO	525	CaCO ₃ + MgO
Sulfates:						
SrSO ₄	370	BaSO ₄ + SrO				
CaSO ₄	370	BaSO ₄ + CaO	450	SrSO ₄ + CaO		
MgSO ₄	370	BaSO ₄ + MgO	440	SrSO ₄ + MgO	540	CaSO ₄ + MgO
ZnSO ₄	340	BaSO ₄ + ZnO	425	SrSO ₄ + ZnO	520	CaSO ₄ + ZnO
CuSO ₄	345	BaSO ₄ + CuO	420	SrSO ₄ + CuO	515	CaSO ₄ + CuO
Phosphates:						
Sr ₃ (PO ₄) ₂	350	Ba ₃ (PO ₄) ₂ + SrO				
Ca ₃ (PO ₄) ₂	340	Ba ₃ (PO ₄) ₂ + CaO	450	Sr ₃ (PO ₄) ₂ + CaO		
Pb ₃ (PO ₄) ₂	335	Ba ₃ (PO ₄) ₂ + PbO	455	Sr ₃ (PO ₄) ₂ + PbO	525	Ca ₃ (PO ₄) ₂ + PbO
Co ₃ (PO ₄) ₂	355	Ba ₃ (PO ₄) ₂ + CoO	465	Sr ₃ (PO ₄) ₂ + CoO	520	Ca ₃ (PO ₄) ₂ + CoO
CrPO ₄	340	Ba ₃ (PO ₄) ₂ + Cr ₂ O ₃	465	Sr ₃ (PO ₄) ₂ + Cr ₂ O ₃	515	Ca ₃ (PO ₄) ₂ + Cr ₂ O ₃
Ag ₄ P ₂ O ₇	330	Ba ₃ (PO ₄) ₂ + Ag ₂ O†	450	Sr ₃ (PO ₄) ₂ + Ag ₂ O†	510	Ca ₃ (PO ₄) ₂ + Ag ₂ O†
Silicates:						
CaSiO ₃ (Wollastonite)	355	Barium silicate + CaO	455	Strontium silicate + CaO		
MgSiO ₃ (Enstatite)	355	Barium silicate + MgO	455	Strontium silicate + MgO	560	Calcium silicate + MgO
MnSiO ₃ (Rhodonite)	355	Barium silicate + MnO	465	Strontium silicate + MnO	565	Calcium silicate + MnO
Al ₂ SiO ₃ (Sillimanite)	355	Barium silicate + Al ₂ O ₃	430	Strontium silicate + Al ₂ O ₃	530	Calcium silicate + Al ₂ O ₃

* T = reaction temperature.

†Dissociates subsequently into Ag + O₂.

TABLE V
Spinel Formation by Exchange Reaction

Reaction	"Takeoff" temperatures (°C)
$\text{CaO} + \text{CuAl}_2\text{O}_4 \rightarrow \text{CaAl}_2\text{O}_4 + \text{CuO}$	760
$\text{CaO} + \text{Fe}_3\text{O}_4 \rightarrow \text{CaFe}_2\text{O}_4 + \text{FeO}$	525
$\text{SrO} + \text{CuAl}_2\text{O}_4 \rightarrow \text{SrAl}_2\text{O}_4 + \text{CuO}$	420
$\text{SrO} + \text{ZnAl}_2\text{O}_4 \rightarrow \text{SrAl}_2\text{O}_4 + \text{ZnO}$	427
$\text{SrO} + \text{FeCr}_2\text{O}_4 \rightarrow \text{SrCr}_2\text{O}_4 + \text{FeO}$	403
$\text{SrO} + \text{CoCr}_2\text{O}_4 \rightarrow \text{SrCr}_2\text{O}_4 + \text{CoO}$	403
$\text{SrO} + \text{CoAl}_2\text{O}_4 \rightarrow \text{SrAl}_2\text{O}_4 + \text{CoO}$	435
$\text{BaO} + \text{ZnAl}_2\text{O}_4 \rightarrow \text{BaAl}_2\text{O}_4 + \text{ZnO}$	345
$\text{BaO} + \text{FeCr}_2\text{O}_4 \rightarrow \text{BaCr}_2\text{O}_4 + \text{FeO}$	347
$\text{BaO} + \text{CoCr}_2\text{O}_4 \rightarrow \text{BaCr}_2\text{O}_4 + \text{CoO}$	331
$\text{BaO} + \text{CoAl}_2\text{O}_4 \rightarrow \text{BaAl}_2\text{O}_4 + \text{CoO}$	350

degree of completion based on the extent of heat liberation and as a rough measure of reaction rate. This principle of analysis as applied to solid-state reactions has been expanded to furnish more exact data in the chapter by Campbell in this volume⁽⁷⁾.

Although it was found nearly 45 years ago that the initiation temperatures depended essentially on the nature of the reacting basic oxide, there is still today no clearcut interpretation of the reaction mechanism. Some more recent investigations indicate that the motion of larger neutral groups, e.g., P_2O_5 , along grain boundaries may be involved, but more research of these interesting systems is required. It had already been observed by Hedvall that these reaction temperature regularities did not apply when the salt component was undergoing a crystallographic transition at a temperature below the normal reaction temperature. An example is given in Table VI. Silver nitrate,

TABLE VI
Induction of Reaction by Crystallographic Transition

Basic oxide	Reactant			
	AgNO_3		Ag_2SO_4	
	Transition temperature (°C)	Reaction temperature (°C)	Transition temperature (°C)	Reaction temperature (°C)
BaO	160	170	411	342
SrO	160	172	411	422
CaO	160	164	411	422

which has a transition at 160°C, reacts with the alkaline earth oxides BaO, SrO, and CaO at approximately that temperature, whereas silver sulfate, with a transition temperature of 411°C, reacts with barium oxide at the regular reaction temperature of 340°C. With strontium oxide and calcium oxide reaction occurs near the transition temperature. The reaction does not only occur at the transition temperature, but reaction rates are exceptionally high and result in a yield maximum, a feature which has been shown for a number of reactions. (See also the maximum of the self-diffusion coefficient in connection with crystallographic transition cited in the chapter in this volume by Hedvall.) This phenomenon, that a lattice becomes more reactive during the occurrence of a transformation, has been designated Hedvall's rule, and also applies to other changes of the lattice such as thermal decomposition or any other mode of forming a new lattice. The reactivity of freshly formed phases is of considerable practical interest, for instance, for the promotion of sintering or of reaction.

In the middle 1920's Hedvall observed the first evidence that reactions may be carried out by the motion of lattice ions. This was concluded from the fact that reaction commenced to take place at about the same temperatures at which ionic conductivity becomes noticeable. These conditions are shown in Table VII for the reaction between barium oxide and copper halides.

Among the important developments of this period was the well-known interpretation by Wagner of the formal rate expressions in terms of the gradient of chemical potential, mobility of ionic particles in solids, and of the lattice disorder models as postulated primarily by Frenkel and by Schottky. This early work provided the foundation of our present knowledge.

In this volume discussions are presented on a variety of aspects of ionic solid systems: kinetics of reaction, of diffusion and sintering, of crystallization, of nucleation and crystal growth, of precipitation, and of the destruction of crystals by evaporation or by thermal decomposition of a solution. Unquestionably such studies will provide valuable aid in furthering the practical utilization of reactions in ionic systems. However, as pointed out in the chapter by Stringer *et al.*⁽⁸⁾, theoretical models are still, in general, inadequate for

TABLE VII
BaO + 2CuX → BaX₂ + Cu₂O

Halide	Starting temperatures (°C)	
	Reaction	Conductivity
CuCl	270	260
CuBr	310	290
CuI	340	350