



CRYOCHEMISTRY

G. B. SERGEEV.
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Г.Б. СЕРГЕЕВ, В.А. БАТЮК

КРИОХИМИЯ

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FOREWORD TO THE RUSSIAN EDITION

The current trend in chemical kinetics today is the growing shift of emphasis from studies on reactions in the gas and liquid phases to those in solids and at low temperatures. Low temperatures open up unique potentialities for the researcher to learn more about the kinetics and mechanism of reactions involving unstable reactive species and the tunnelling of electrons and protons.

In recent years, a large number of publications dealing with chemical reactions at low temperatures have appeared both in and outside the Soviet Union. The present monograph is the first attempt by Soviet authors to examine systematically the kinetics of various low-temperature reactions. This approach to the subject lays a theoretical foundation for an important scientific discipline which will, in all probability, extend into the engineering field before long. A sizeable contribution to the emergence and establishment of this division of chemistry in the USSR has come from the present authors and their associates in research on low-temperature chemical synthesis carried out at the Moscow State University.

The Russian manuscript had already gone to press when a collected volume on cryochemistry (*Cryochemistry*, M. Moskovits and G.A. Ozin (Eds), John Wiley and Sons, New York, 1976) appeared in the United States. Taken together, the two books give an all-around picture of cryochemistry — a new division of chemistry.

June 1977

*Academician N. N. Semenov,
Nobel Prize Laureate*

PREFACE

Cryochemistry (from the Greek *kruos* for cold) is a new field of chemistry concerned with the behaviour of reactive substances at low temperatures and with phenomena which set apart low-temperature chemical reactions from those taking place at higher temperatures.

Obviously, the term "low temperatures" is a relative one, and its definition has been varying with advances in science and engineering. In physics, this term applies to temperatures around the boiling point of helium, that is, 4.2 K (-269°C). In chemistry, it goes for temperatures between 223 and 70 K, whereas the term "extremely low" applies to temperatures below 70 K.

Systematic studies on low-temperature chemical reactions began in the late 1950s when it was found that reactive atoms and radicals could be trapped at the boiling point of liquid helium. Trapping studies gave an impetus to further investigations in the field of cryochemistry. Sizeable contributions to cryochemistry on the world scale have been made by the Soviet scientists Semenov, Kargin, Voyevodsky, their disciples and followers.

This book is the first Soviet monograph on the subject, pooling together a wealth of data in the rapidly developing field of chemical reactions at low temperatures. A large variety of low-temperature reactions have been investigated in both the Soviet Union and other countries in the past 20 years. Unfortunately, the space available in a single volume is not sufficient for an appropriate coverage of all experimental data and all theoretical aspects of cryochemistry closely related to other divisions of chemistry and cryogenic engineering. Cryochemistry is drawing heavily on advances in solid-state physics and chemistry, polymer chemistry, photochemistry, radiation chemistry, cryophysics, and biochemistry. In turn, advances in cryochemistry stimulate work on many problems in the associated divisions of chemistry and physics.

Ample space in the monograph is devoted to studies by Soviet scientists who have actively contributed to advances in the most

important divisions of cryochemistry. The literature has been covered mainly up to 1975, although some references published in 1976 are also included.

The subject-matter presented in the book deals with reactions in gases and liquids, production and transformations of ions in frozen solids, and some kinetic models proposed to explain processes involving reactive species. The very fact that no generally accepted model for cryogenic reactions in solids has been developed yet is an indication of the complexity of the problems raised.

Ample space is given to the use of low temperatures in various fields of science and engineering, notably low-temperature polymerization, chain reactions, reactions involving molecular complexes, chemical and biochemical reactions in frozen multicomponent solutions. Naturally, the book also covers these authors' studies on the stimulation of chemical reactions by low temperatures, reactions with a negative temperature coefficient, and the effect of phase and structural inhomogeneity of the system on chemical processes at low temperatures.

We sincerely hope that this monograph will win more workers for this new and challenging field of chemistry.

*G.B. Sergeev
V.A. Batyuk*

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INTRODUCTION

Temperature is a decisive factor controlling chemical reactions. As a rule, the temperature dependence of the reaction rate is described by the Arrhenius equation which states that for most reactions the rate increases with rising temperature exponentially. This appears to have been the main reason why chemical reactions at low temperatures interested investigators so little until quite recently.

On the other hand, it has been found that some chemical reactions, contrary to traditional thought, would proceed at rates which increase with decreasing temperature. Indeed, some processes have been noted to change their path drastically if the reacting system was cooled to cryogenic temperatures. More and more of such low-temperature reactions are being discovered all the time. It has also been found that some reactions that would not proceed at room temperature will do so at low temperatures. Analysis and understanding of these seemingly anomalous events are important for both theory and practice.

As the reactive systems change from the gaseous to the liquid and finally the solid state, weak intermolecular interactions play an increasingly important role. Owing to them, investigators have been able to isolate and analyze the otherwise unstable molecular complexes at cryogenic temperatures. Various physical effects can be utilized to process frozen substances so as to generate and trap radicals and ions. At low temperatures or during the subsequent warm-up, the reactive intermediates may enter into various reactions. Chemical transformations taking place in the solid phase at low temperatures markedly widen our knowledge of elementary chemical events and open up a road towards the synthesis of chemical species unattainable by alternate routes.

Thus, cooling the reactive species to cryogenic temperatures stimulates interactions which are responsible for the formation of complexes, brings about changes in the phase and structure of the system, and enables chemical processes to be conducted under unorthodox extremal conditions.

Cryogenic temperatures affect chemical processes differing in activation energy likewise differently. The probability of occurrence in the circumstances is the highest for a reaction having the lowest activation energy. Thus, cryogenic temperatures put to work a kind of selection in terms of energy, promoting a particular reaction from among the several reactions proceeding in parallel, which may well serve as the basis for a novel chemical technology. In particular, cryogenic temperatures make it possible to isolate extremely pure substances free from any impurities or by-products.

Of late, interest in cryochemistry has been growing not only among chemists. To them may be added, and in an ever growing number at that, biologists, medical research workers, food specialists, geologists, and people in many other fields of science and industry. This interest is stimulated by development work in permafrost localities, the use of low temperatures for the preservation of food, blood, medicines and biological preparations, etc.

Cryogenic temperatures, however, have another facet as regards their effect on chemical reactions. By promoting some reactions and inhibiting others, they may lead to the formation of an unwanted end product. To avoid this and to exercise proper control over such processes in general, it is essential to have a working knowledge of their nature, notably kinetic characteristics, and the effects that cooling may have on the structure and phase of the systems involved.

For many substances, chemical reactions at low temperatures usually entail a change from the gaseous or liquid state to the solid state. This is accompanied by radical changes in the physico-chemical properties and reactivity of the species. As often as not, such changes cannot be predicted or extrapolated from the macroscopic characteristics of the reactive systems at room temperature — what is needed is a detailed study into the properties of the reactive species at cryogenic temperatures, and this calls in turn for the development and use of appropriate techniques and procedures.

Knowledge of the behaviour of structured systems at cryogenic temperatures is a goal of paramount importance to present-day chemical kinetics. This knowledge will permit deeper insight into the mechanisms of reactions in solids and into general matters of reactivity.

For proper control over the behaviour of chemical species at low temperatures, it is essential to know their physico-chemical properties and understand the factors governing their reactivity. It is these matters, along with studies into the specific aspects of reactions at cryogenic temperatures, that constitute the subject of cryochemistry — a new division of chemistry.

CHAPTER ONE

HOMOGENEOUS AND HETEROGENEOUS LOW-TEMPERATURE REACTIONS INVOLVING GASES AND LIQUIDS

Early attempts to investigate the chemical reactions that take place at low temperatures date back to the 19th century. They were made by Dewar who was looking for ways and means to liquefy air and other gases. Dewar and his co-workers observed the interactions of alkali metals, hydrogen sulphide, hydrogen iodide, and some others with liquid oxygen. Their studies were not carried to completion, and today they are of purely historical interest.

A systematic effort as regards low-temperature chemical reactions began in the late 1950s. The publications that have appeared since then are reviewed in detail in [1], [2], and [3]. We shall dwell in brief only on the most important work carried out by the mid-1950s, placing emphasis on the studies that, in our opinion, have contributed most to establishing cryochemistry as a new division of chemical physics.

1.1. NONINITIATED SPONTANEOUS REACTIONS

A relatively small number of chemical reactions are known to be capable of proceeding at cryogenic temperatures as the reactive species are simply mixed together. For the first time, reactions occurring in the absence of any initiating agent were observed at the beginning of this century. Those were reactions between liquid hydrogen and fluorine. At normal temperature, mixtures of hydrogen and fluorine were observed to self-ignite and remain stable only at 90 K [4]. Experiments with the low-temperature reactions of hydrogen and fluorine in the gaseous phase had led to the discovery of a new class of ramified chain processes [5, 6].

Experiments at the beginning of this century also included reactions involving liquid fluorine. It was found that fluorine can react with many substances, including metals [3].