Kevin C. de Berg

# The Iron(III) **Thiocyanate** Reaction Research History and Role in Chemical Analysis



## SpringerBriefs in Molecular Science

History of Chemistry

#### **Series Editor**

Seth C. Rasmussen, Department of Chemistry and Biochemistry, North Dakota State University, Fargo, ND, USA

Springer Briefs in Molecular Science: History of Chemistry presents concise summaries of historical topics covering all aspects of chemistry, alchemy, and chemical technology. The aim of the series is to provide volumes that are of broad interest to the chemical community, while still retaining a high level of historical scholarship such that they are of interest to both chemists and science historians.

Featuring compact volumes of 50 to 125 pages, the series acts as a venue between articles published in the historical journals and full historical monographs or books.

Typical topics might include:

- An overview or review of an important historical topic of broad interest
- Biographies of prominent scientists, alchemists, or chemical practitioners
- New historical research of interest to the chemical community

Briefs allow authors to present their ideas and readers to absorb them with minimal time investment. Briefs are published as part of Springer's eBook collection, with millions of users worldwide. In addition, Briefs are available for individual print and electronic purchase. Briefs are characterized by fast, global electronic dissemination, standard publishing contracts, easy-to-use manuscript preparation and formatting guidelines, and expedited production schedules. Both solicited and unsolicited manuscripts are considered for publication in this series.

More information about this subseries at http://www.springer.com/series/10127

## The Iron(III) Thiocyanate Reaction

Research History and Role in Chemical Analysis



Kevin C. de Berg Avondale College of Higher Education Cooranbong, NSW, Australia

ISSN 2191-5407 ISSN 2191-5415 (electronic)
SpringerBriefs in Molecular Science
ISSN 2212-991X
SpringerBriefs in History of Chemistry
ISBN 978-3-030-27315-6 ISBN 978-3-030-27316-3 (eBook)
https://doi.org/10.1007/978-3-030-27316-3

© The Author(s), under exclusive license to Springer Nature Switzerland AG 2019

This work is subject to copyright. All rights are solely and exclusively licensed by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

The publisher, the authors and the editors are safe to assume that the advice and information in this book are believed to be true and accurate at the date of publication. Neither the publisher nor the authors or the editors give a warranty, expressed or implied, with respect to the material contained herein or for any errors or omissions that may have been made. The publisher remains neutral with regard to jurisdictional claims in published maps and institutional affiliations.

This Springer imprint is published by the registered company Springer Nature Switzerland AG The registered company address is: Gewerbestrasse 11, 6330 Cham, Switzerland

#### **Preface**

Histories of chemistry and histories of science commonly focus on the historical development of ideas, themes, concepts and the personalities involved in these historical developments. Some histories will focus on a particular chemist giving insight into their family background, academic life and contributions made to chemistry or more broadly, scientific endeavour. Some examples that come to mind have been those written about Robert Boyle, Joseph Priestley, Antoine Lavoisier, Fritz Haber, Ernest Rutherford and Madame Curie just to name a few. It is less common to write a history about a chemical reaction but I have discovered that such a history will involve personalities, controversial ideas and applications to the broad landscape of science. By its very nature, a history of a chemical reaction will involve addressing some detailed chemistry, probably more than one might expect in a history focussed on a personality or a particular scientific idea. In the eighteenth century, chemists were disappointed that their discipline lacked the rigour that mathematics had brought to physics. It proved much easier to apply mathematics to visible objects like planets, projectiles and inclined planes than to the invisible constituents of matter undergoing chemical change. The development of calculus and its application to the thermodynamics and kinetics of chemical reactions proved an important turning point for chemistry. To demonstrate this often forgotten legacy, I do make use of mathematics in this book, but a level of mathematics not beyond that of a typical chemistry graduate. Some of the basic principles are revisited for the benefit of the reader where derivations are given. However, my challenge in a book series like this is to provide enough detail that will satisfy the historian and the chemist and I trust I will have been at least partly successful in achieving this.

My interest in history began in the mid-1980s when I completed a master's thesis on the history of the gas laws. What provoked my interest was the question: 'How did we come to express gas laws in the form used in modern chemistry'? This interest coincided with the establishment of the International History and Philosophy of Science and Science Teaching Group (IHPST) in 1989 and the opportunity to make subsequent contributions to its journal, *Science & Education-Contributions from History*, *Philosophy and Sociology of Science*, as an

vi Preface

author and reviewer. In 2014, I contributed a chapter on the role of the history of chemistry in the teaching and learning of chemistry for the *International Handbook of Research in History, Philosophy and Science Teaching*.

The iron(III) thiocyanate reaction, where an intense blood-red colour is produced by mixing solutions of ferric ions and thiocyanate ions, has captured my interest since high school days. The reaction was used in my first-year university chemistry laboratory days as a test for the presence of ferric ions and when I was given the opportunity to teach senior high school chemistry for a time, the reaction was used as the centrepiece for equilibrium study in what was then known in the 1970s as the CHEM STUDY syllabus. More recently, I was given the opportunity to study the reaction in the laboratory of Professor Marcel Maeder at the University of Newcastle since there were still some unresolved issues with the reaction. Two papers, published in *Inorganica Chimica Acta*, have resulted from this collaboration to date.

One is often asked the question, particularly by fellow chemists: 'What use is a study of history to the chemistry community or more broadly to the scientific community, or even more broadly to the general community'? My own reflections on an answer to this question have to do with the contribution of history to our broad understanding of how knowledge of our world has been built through many circuitous paths involving errors, controversies and clashes of culture. Even while giving specific detailed study to a particular chemical reaction like the iron(III) thiocyanate reaction, these reflections remain with me, even though occasionally sitting in the background. Hopefully, such a study will make us sympathetic to the role science plays in providing information on broader controversial topics like climate change.

Cooranbong, Australia

Kevin C. de Berg

#### Acknowledgements

I wish to acknowledge four sources that have had some influence on my embarking on the study of a chemical reaction from an historical perspective.

- 1. Associate Professor Michael Matthews, founding president of the IHPST group, provided an international platform upon which newcomers to history and philosophy of science research could receive helpful reviews of initial attempts at writing in this area from experts in the field. These reviews helped to hone one's skills at writing history while still being involved in the practice of a science discipline, which in my case, was chemistry.
- 2. Avondale College of Higher Education provided funding towards my travel and presentation of a paper on the iron(III) thiocyanate reaction at the 11th International Conference for the History of Chemistry in Trondheim, Norway, in 2017.
- 3. Professor Marcel Maeder from the University of Newcastle willingly gave me access to his laboratory facilities for conducting further research on the iron (III) thiocyanate reaction and from his chemometrics background was able to suggest procedures for addressing some difficulties which proved valuable in the final analysis.
- 4. Dr. Sarah Clifford from the University of Newcastle who willingly gave me practical assistance in learning how to operate the stopped-flow apparatus and its computer interface for recording large amounts of absorbance data.

### **Contents**

1	Intr	oduction	1
	1.1	Eighteenth Century Background	1
	1.2	Publication Summary of the Iron(III) Thiocyanate Reaction	
		Over 191 Years	5
	Refe	erences	15
2	The	Reaction and Chemical Analysis	19
	2.1	Qualitative Analysis	19
	2.2	Quantitative Analysis	20
	Refe	erences	23
3	The	Reaction and Its Nomenclature, Formulae, and Units	25
	3.1	Nomenclature and Formulae	25
	3.2	Units	27
	Refe	erences	29
4	The	Reaction: Chemical Affinity and Controversy	31
	4.1	Gladstone and 'Complete' or 'Incomplete Reaction'	31
	4.2	Identity of Species Responsible for the Blood-Red Colour	32
	4.3	Can One Verify 'Incompleteness' for the Iron(III) Thiocyanate	
		Reaction?	34
	4.4	Berthollet and Affinity	37
	Refe	erences	38
5	The Reaction: Chemical Affinity: Laws, Theories and Models 4		
	5.1	Geoffroy's Table of Affinity 1718	41
	5.2	Waage and Guldberg and the Law of Mass Action	43
	5.3	Law, Theory and Model	45
	5.4	The Role of Thermodynamics	46
	Dofe	aran cas	51

x Contents

6	The Reaction and Its Equilibrium Constants: The Role of Mathematics and Data Analysis			
	6.1	The Frank and Oswalt Technique	53	
	6.2	Approximations and Iterations	55	
	6.3	The Technique of Global Analysis	57	
	6.4	Instrumentation	62	
	6.5	The Potentiometric Method	63	
	Refe	erences	69	
7	The	Reaction and Its Kinetics	71	
	7.1	A Brief Historical Note	71	
	7.2	Reaction Rate Mechanism Proposed Since 1958	72	
	7.3	Hydrogen Ion Independent One-Step Mechanism	79	
	7.4	Hydrogen Ion Independent Two-Step Mechanism	81	
	7.5	Simple Mechanism for the Production of Two Iron(III)		
		Thiocyanate Complexes	83	
	Refe	erences	85	
8	The	Reaction in Secondary and Tertiary Education		
-		ricula	87	
	8.1	Course Work and Laboratory Work	87	
	8.2	The Use of Excel Spreadsheets at the Tertiary Level	90	
	8.3	Commercial Science Activity Packages	94	
	Refe	erences	94	
9	Conclusion			
	Refe	erences	99	

#### **About the Author**

**Kevin C. de Berg** completed his Ph.D. in physical chemistry in 1978 at the University of Queensland and his MAppSc in 1989 from Curtin University. His research thesis for the MAppSc degree examined the historical significance of the gas laws particularly for the education context. Interests in chemistry and history and philosophy of science led to an invitation to serve on the editorial committee of the journal: *Science & Education-Contributions from History, Philosophy, and Sociology of Science and Mathematics*; and to contribute a chapter titled: *The Place of the History of Chemistry in the Teaching and Learning of Chemistry*, for the International Handbook of Research in History, Philosophy and Science Teaching (2014). Kevin has spent 9 years as a High School Science and Mathematics Teacher and 36 years lecturing and researching in the area of physical and inorganic chemistry and history and philosophy of science. He is currently Conjoint Associate Professor at Avondale College of Higher Education.