
High Temperature
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with Oxyanions

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Preface

The origin of this book is the four monographs on the thermal decomposition of inorganic salts with oxyanions which the author wrote under the auspices of the Standard Reference Data Program between 1968 and 1972. The aim of that work was to provide a reference for scientists and engineers who need to use these compounds at high temperatures, but who do not know whether a particular compound even exists at a particular temperature. Since the original work is now out of print and more information has become available in the thirty years since the monographs were published, it seemed useful to prepare an updated version.

The aim is still to provide useful and critically evaluated information which the potential user may not have the time or inclination to find for himself. This information is useful in a variety of contexts, from questions of basic chemistry to technologically related questions involving the corrosion of metals in molten salts or the preparation of molten salt baths as heat-transfer media.

On the assumption that some information is better than none, both qualitative and quantitative material have been included. The latter includes thermodynamics of the decomposition reactions and their rates, as well as phase transitions and densities of the solid and liquid salts. Although some of the qualitative material may be quite old, it has been included if it is the only information available.

A discussion of the thermodynamics used in this book, which is essential for understanding the meaning of the tables, as well as a discussion of the kinetics of solid-state decomposition, is included in Chapter 1, which also includes a discussion of the sources of the data used.

Kurt H. Stern

The Author

Dr. Kurt H. Stern obtained his B.A. degree in chemistry from Drew University in Madison, NJ in 1948, his M.S. degree in physical chemistry from the University of Michigan in 1950, and a Ph.D. from Clark University under Prof. Arthur Martell in 1953. He then joined the faculty of the University of Arkansas, where he and his students carried out research in non-aqueous and molten salt electrochemistry. In 1959, while spending a sabbatical year at the National Bureau of Standards in Washington, he was asked to join the staff and to start a program in molten salt electrochemistry. While at NBS he became involved in the formation of the National Standards Reference Data Program under whose auspices he wrote the four monographs on which the present book is based. In 1969 he moved to the Naval Research Laboratory where he continued his research, most recently on the electrodeposition of refractory compounds, such as carbides and silicides, from molten salts. He has published approximately 100 research articles and monographs on his work. Concurrently with his research, he has served on the faculty of the National Institutes of Health Graduate School.

Since his retirement from active research in 1991, he has completed a book on protective metallurgical and ceramic coatings (Chapman and Hall, 1996).

Acknowledgments

I would like to thank my wife Faith for her great patience and perseverance in dealing with the problems of a semi-literate computer-competent husband and author, for rescuing me several times from semi-fatal computer errors, for developing the format for the tables, and for the artwork involved in the preparation of many of the figures.

Thanks also to my son Alan who several times managed to retrieve the manuscript from the electronic domain to which I had unintentionally consigned it by inadvertent key strokes.

Thanks to Dr. Irwin Singer of the Naval Research Laboratory for assistance with thermochemical software which greatly increased the speed of preparation of the many tables in the book.

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Finally, thanks to several librarians at both the Library of Congress and the Naval Research Laboratory, particularly Harriet Oxley at NRL who helped me with literature searches and copyright problems.

Any errors can be blamed on the author, who would be glad to hear of them from readers, so corrections can be made in possible future printings.

Contents

Chapter 1

Introduction

- 1.1 General
- 1.2 Equilibrium Calculations
- 1.3 Phase Transitions
- 1.4 Density
- 1.5 Kinetics of Thermal Decomposition
 - 1.5.1 General
 - 1.5.2 Mechanism of Endothermic Solid State Decomposition
 - 1.5.2.1 Kinetic Equations
 - 1.5.2.1.1 Nucleus Formation
 - 1.5.2.1.2 Growth of Nuclei
 - 1.5.2.2 Surface Area Changes during Decomposition
 - 1.5.3 The Effect of Pressure on Rate.
 - 1.5.4 Activation Energy
 - 1.5.5 The Effect of Preparation Method on Rate
 - 1.5.6 The Effect of Heat Transfer on Rate
 - 1.5.7 The Influence of Crystal Defect Structure on Decomposition Rate.

References

Chapter 2

Carbonates

- 2.1 Introduction
 - 2.1.1 Structure of the Carbonate Ion
 - 2.1.2 General Features of Carbonate Decomposition
 - 2.1.3 Phase Transitions
 - 2.1.4 Density
- 2.2 CO, CO₂, and O₂
- 2.3 The Individual Carbonates
 - 2.3.1 Barium
 - 2.3.2 Beryllium
 - 2.3.3 Cadmium
 - 2.3.4 Calcium
 - 2.3.5 Cesium
 - 2.3.6 Cobalt
 - 2.3.7 Copper .
 - 2.3.8 Iron
 - 2.3.9 Lead
 - 2.3.10 Lithium
 - 2.3.11 Magnesium
 - 2.3.12 Manganese.
 - 2.3.13 Mercury
 - 2.3.13.1 HgCO₃
 - 2.3.13.2 Hg₂CO₃

- 2.3.14 Nickel
- 2.3.15 Potassium
- 2.3.16 Rare Earths
- 2.3.17 Rubidium
- 2.3.18 Silver
- 2.3.19 Sodium
- 2.3.20 Strontium
- 2.3.21 Thallium
- 2.3.22 Zinc

References

Chapter 3

Sulfites

- 3.1 General
- 3.2 Individual Sulfites
 - 3.2.1 Barium
 - 3.2.2 Cadmium
 - 3.2.3 Calcium
 - 3.2.4 Cesium
 - 3.2.5 Cobalt
 - 3.2.6 Iron
 - 3.2.7 Lead
 - 3.2.8 Lithium
 - 3.2.9 Magnesium
 - 3.2.10 Manganese
 - 3.2.11 Potassium
 - 3.2.12 Rare Earths
 - 3.2.13 Silver
 - 3.2.14 Sodium
 - 3.2.15 Strontium
 - 3.2.16 Zinc

References

Chapter 4

Sulfates

- 4.1 General
- 4.2 Decomposition Equilibria
- 4.3 Individual Sulfates
 - 4.3.1 Aluminum
 - 4.3.2 Antimony
 - 4.3.3 Barium
 - 4.3.4 Beryllium
 - 4.3.5 Bismuth
 - 4.3.6 Cadmium
 - 4.3.7 Calcium
 - 4.3.8 Cesium
 - 4.3.9 Chromium
 - 4.3.10 Cobalt
 - 4.3.11 Copper

- 4.3.12 Gallium
- 4.3.13 Hafnium
- 4.3.14 Indium
- 4.3.15 Iron
- 4.3.16 Lead
- 4.3.17 Lithium
- 4.3.18 Magnesium
- 4.3.19 Manganese
- 4.3.20 Mercury
- 4.3.21 Nickel
- 4.3.22 Potassium
- 4.3.23 Radium
- Rare Earths
- 4.3.24 Cerium
- 4.3.25 Dysprosium
- 4.3.26 Erbium
- 4.3.27 Europium
- 4.3.28 Gadolinium
- 4.3.29 Holmium
- 4.3.30 Lanthanum
- 4.3.31 Neodymium
- 4.3.32 Praesodymium
- 4.3.33 Samarium
- 4.3.34 Terbium
- 4.3.35 Thulium
- 4.3.36 Ytterbium
- 4.3.37 Rhodium
- 4.3.38 Rubidium
- 4.3.39 Scandium
- 4.3.40 Silver
- 4.3.41 Sodium
- 4.3.42 Strontium
- 4.3.43 Tantalum
- 4.3.44 Thallium
- 4.3.45 Thorium
- 4.3.46 Tin
- 4.3.47 Titanium
- 4.3.48 Uranium
- 4.3.49 Vanadium
- 4.3.50 Zinc
- 4.3.51 Zirconium

References

Chapter 5

Nitrites and Nitrates

- 5.1 Gaseous Equilibria in the N–O System
- 5.2 The Nitrites
- 5.3 The Nitrates
 - 5.3.1 General
 - 5.3.2 Decomposition Equilibria

5.4 Individual Nitrites and Nitrates

- 5.4.1 Aluminum
- 5.4.2 Barium
 - 5.4.2.1 $\text{Ba}(\text{NO}_2)_2$
 - 5.4.2.2 $\text{Ba}(\text{NO}_3)_2$
- 5.4.3 Beryllium
- 5.4.4 Bismuth
- 5.4.5 Cadmium
 - 5.4.5.1 $\text{Cd}(\text{NO}_2)_2$
 - 5.4.5.2 $\text{Cd}(\text{NO}_3)_2$
- 5.4.6 Calcium
 - 5.4.6.1 $\text{Ca}(\text{NO}_2)_2$
 - 5.4.6.2 $\text{Ca}(\text{NO}_3)_2$
- 5.4.7 Cesium
 - 5.4.7.1 CsNO_2
 - 5.4.7.2 CsNO_3
- 5.4.8 Chromium
- 5.4.9 Cobalt
 - 5.4.9.1 $\text{Co}(\text{NO}_2)_2$
 - 5.4.9.2 $\text{Co}(\text{NO}_3)_2$
- 5.4.10 Copper
 - 5.4.10.1 $\text{Cu}(\text{NO}_2)_2$
 - 5.4.10.2 $\text{Cu}(\text{NO}_3)_2$
- 5.4.11 Gallium
- 5.4.12 Gold
- 5.4.13 Hafnium
- 5.4.14 Indium
- 5.4.15 Iron
- 5.4.16 Lead
 - 5.4.16.1 $\text{Pb}(\text{NO}_2)_2$
 - 5.4.16.2 $\text{Pb}(\text{NO}_3)_2$
- 5.4.17 Lithium
 - 5.4.17.1 LiNO_2
 - 5.4.17.2 LiNO_3
- 5.4.18 Magnesium
- 5.4.19 Manganese
- 5.4.20 Mercury
 - 5.4.20.1 $\text{Hg}(\text{NO}_2)_2$
 - 5.4.20.2 HgNO_3
 - 5.4.20.3 $\text{Hg}(\text{NO}_3)_2$
- 5.4.21 Nickel
 - 5.4.21.1 $\text{Ni}(\text{NO}_2)_2$
 - 5.4.21.2 $\text{Ni}(\text{NO}_3)_2$
- 5.4.22 Palladium
 - 5.4.22.1 $\text{Pd}(\text{NO}_2)_2$
 - 5.4.22.2 $\text{Pd}(\text{NO}_3)_2$
- 5.4.23 Potassium
 - 5.4.23.1 KNO_2
 - 5.4.23.2 KNO_3
- 5.4.24 Radium
- 5.4.25 Rare Earths
 - 5.4.25.1 Nitrites

- 5.4.25.2 Nitrates
- 5.4.26 Rubidium
 - 5.4.26.1 RbNO_2
 - 5.4.26.2 RbNO_3
- 5.4.27 Scandium
- 5.4.28 Silver
 - 5.4.28.1 AgNO_2
 - 5.4.28.2 AgNO_3
- 5.4.29 Sodium
 - 5.4.29.1 NaNO_2
 - 5.4.29.2 NaNO_3
- 5.4.30 Strontium
 - 5.4.30.1 $\text{Sr}(\text{NO}_2)_2$
 - 5.4.30.2 $\text{Sr}(\text{NO}_3)_2$
- 5.4.31 Thallium
 - 5.4.31.1 TlNO_2
 - 5.4.31.2 TlNO_3
- 5.4.32 Thorium
- 5.4.33 Tin
- 5.4.34 Titanium
- 5.4.35 Zinc
- 5.4.36 Zirconium

References

Chapter 6

Oxysalts of the Halogens

- 6.1 General
- 6.2 Phase Transitions
- 6.3 Density
- 6.4 Chemistry of the Halogen Oxysalts

References

Chapter 7

Oxysalts of Chlorine

- 7.1 General
- 7.2 Classes of Oxychlorine Salts
 - 7.2.1 Chlorites
 - 7.2.2 Chlorates
 - 7.2.3 Perchlorates
- 7.3 Individual Salts
 - 7.3.1 Aluminum
 - 7.3.2 Barium
 - 7.3.2.1 $\text{Ba}(\text{ClO}_2)_2$
 - 7.3.2.2 $\text{Ba}(\text{ClO}_3)_2$
 - 7.3.2.3 $\text{Ba}(\text{ClO}_4)_2$
 - Cadmium
 - 7.3.3.1 $\text{Cd}(\text{ClO}_3)_2$
 - 7.3.3.2 $\text{Cd}(\text{ClO}_4)_2 \cdot$
 - 7.3.4 Calcium
 - 7.3.4.1 $\text{Ca}(\text{ClO})_2$

- 7.3.4.2 $\text{Ca}(\text{ClO}_2)_2$
- 7.3.4.3 $\text{Ca}(\text{ClO}_3)_2$
- 7.3.4.4 $\text{Ca}(\text{ClO}_4)_2$
- 7.3.5 Cesium
 - 7.3.5.1 CsClO_2
 - 7.3.5.2 CsClO_3
 - 7.3.5.3 CsClO_4
- 7.3.6 Cobalt
- 7.3.7 Copper
 - 7.3.7.1 $\text{Cu}(\text{ClO}_2)_2$
 - 7.3.7.2 CuClO_4
 - 7.3.7.3 $\text{Cu}(\text{ClO}_4)_2$
- 7.3.8 Iron
 - 7.3.8.1 $\text{Fe}(\text{ClO}_4)$
- 7.3.9 Lead
 - 7.3.9.1 $\text{Pb}(\text{ClO}_2)_2$
 - 7.3.9.2 $\text{Pb}(\text{ClO}_3)_2$
 - 7.3.9.3 $\text{Pb}(\text{ClO}_4)_2$
- 7.3.10 Lithium
 - 7.3.10.1 LiClO
 - 7.3.10.2 LiClO_2
 - 7.3.10.3 LiClO_3
 - 7.3.10.4 LiClO_4
- 7.3.11 Magnesium
 - 7.3.11.1 $\text{Mg}(\text{ClO}_2)_2$
 - 7.3.11.2 $\text{Mg}(\text{ClO}_3)_2$
 - 7.3.11.3 $\text{Mg}(\text{ClO}_4)_2$
- 7.3.12 Manganese
- 7.3.13 Mercury
 - 7.3.13.1 $\text{Hg}_2(\text{ClO}_2)_2$
 - 7.3.13.2 $\text{Hg}(\text{ClO}_2)_2$
 - 7.3.13.3 $\text{Hg}(\text{ClO}_3)_2$
 - 7.3.13.4 $\text{Hg}_2(\text{ClO}_4)_2$
- 7.3.14 Nickel
 - 7.3.14.1 $\text{Ni}(\text{ClO}_3)_2$
 - 7.3.14.2 $\text{Ni}(\text{ClO}_4)_2$
- 7.3.15 Potassium
 - 7.3.15.1 KClO_2
 - 7.3.15.2 KClO_3
 - 7.3.15.3 KClO_4
- 7.3.16 Rare Earths
 - 7.3.16.1 Chlorites
 - 7.3.16.2 Chlorates
 - 7.3.16.3 Perchlorates
- 7.3.17 Rubidium
 - 7.3.17.1 RbClO_2
 - 7.3.17.2 RbClO_3
 - 7.3.17.3 RbClO_4
- 7.3.18 Scandium
- 7.3.19 Silver
 - 7.3.19.1 AgClO_2
 - 7.3.19.2 AgClO_3

- 7.3.19.3 AgClO_4
- 7.3.20 **Sodium**
 - 7.3.20.1 NaClO_2
 - 7.3.20.2 NaClO_3
 - 7.3.20.3 NaClO_4
- 7.3.21 **Strontium**
 - 7.3.21.1 $\text{Sr}(\text{ClO}_2)_2$
 - 7.3.21.2 $\text{Sr}(\text{ClO}_3)_2$
 - 7.3.21.3 $\text{Sr}(\text{ClO}_4)_2$
- 7.3.22 **Thallium**
 - 7.3.22.1 TlClO_2
 - 7.3.22.2 TlClO_3
 - 7.3.22.3 TlClO_4
- 7.3.23 **Thorium**
 - 7.3.23.1 $\text{Th}(\text{ClO}_4)_4$
- 7.3.24 **Tin**
 - 7.3.24.1 Perchlorates
- 7.3.25 **Yttrium**
 - 7.3.25.1 $\text{Y}(\text{ClO}_4)_2$
- 7.3.26 **Zinc**
 - 7.3.26.1 $\text{Zn}(\text{ClO}_3)_2$
 - 7.3.26.2 $\text{Zn}(\text{ClO}_4)_2$

References

Chapter 8

Oxysalts of Bromine

- 8.1 **General**
- 8.2 **Classes of Oxybromine Salts**
 - 8.2.1 **Bromites**
 - 8.2.2 **Bromates**
 - 8.2.3 **Perbromates**
- 8.3 **Individual Bromine Oxysalts**
 - 8.3.1 **Barium**
 - 8.3.1.1 $\text{Ba}(\text{BrO}_2)_2$
 - 8.3.1.2 $\text{Ba}(\text{BrO}_3)_2$
 - 8.3.1.3 $\text{Ba}(\text{BrO}_4)_2$
 - 8.3.2 **Cadmium**
 - 8.3.2.1 $\text{Cd}(\text{BrO}_3)_2$
 - 8.3.3 **Calcium**
 - 8.3.3.1 $\text{Ca}(\text{BrO}_3)_2$
 - 8.3.3.2 $\text{Ca}(\text{BrO}_4)_2$
 - 8.3.4 **Cesium**
 - 8.3.4.1 CsBrO_3
 - 8.3.4.2 CsBrO_4
 - 8.3.5 **Copper**
 - 8.3.5.1 $\text{Cu}(\text{BrO}_3)_2$
 - 8.3.6 **Lead**
 - 8.3.6.1 $\text{Pb}(\text{BrO}_3)_2$
 - 8.3.7 **Lithium**
 - 8.3.7.1 LiBrO_2

- 8.3.7.2 LiBrO_3
- 8.3.7.3 LiBrO_4
- 8.3.8 **Magnesium**
 - 8.3.8.1 $\text{Mg}(\text{BrO}_3)_2$
 - 8.3.8.2 $\text{Mg}(\text{BrO}_4)_2$
- 8.3.9 **Mercury**
 - 8.3.9.1 HgBrO_3
 - 8.3.9.2 $\text{Hg}(\text{BrO}_3)_2$
- 8.3.10 **Nickel**
 - 8.3.10.1 $\text{Ni}(\text{BrO}_3)_2$
- 8.3.11 **Potassium**
 - 8.3.11.1 KBrO_3
 - 8.3.11.2 KBrO_4
- 8.3.12 **Rare Earths**
 - 8.3.12.1 **Bromates**
- 8.3.13 **Rubidium**
 - 8.3.13.1 RbBrO_3
 - 8.3.13.2 RbBrO_4
- 8.3.14 **Silver**
 - 8.3.14.1 AgBrO_3
- 8.3.15 **Sodium**
 - 8.3.15.1 NaBrO_3
 - 8.3.15.2 NaBrO_4
- 8.3.16 **Strontium**
 - 8.3.16.1 $\text{Sr}(\text{BrO}_3)_2$
 - 8.3.16.2 $\text{Sr}(\text{BrO}_4)_2$
- 8.3.17 **Thallium**
 - 8.3.17.1 TlBrO_3
- 8.3.18 **Zinc**

References

Chapter 9

Oxysalts of Iodine

- 9.1 **General**
- 9.2 **Classes of Oxyiodine Salts**
 - 9.2.1 **Iodites**
 - 9.2.2 **Iodates**
 - 9.2.3 **Periodates**
- 9.3 **Individual Salts**
 - 9.3.1 **Aluminum**
 - 9.3.1.1 $\text{Al}(\text{IO}_3)_3$
 - 9.3.2 **Barium**
 - 9.3.2.1 $\text{Ba}(\text{IO}_3)_2$
 - 9.3.2.2 $\text{Ba}(\text{IO}_4)_2$
 - 9.3.2.3 $\text{Ba}_5(\text{IO}_6)_2$
 - 9.3.3 **Bismuth**
 - 9.3.4 **Cadmium**
 - 9.3.4.1 $\text{Cd}(\text{IO}_3)_2$
 - 9.3.4.2 $\text{Cd}_3(\text{IO}_5)_2$
 - 9.3.4.3 $\text{Cd}_5(\text{IO}_6)_2$
 - 9.3.4.4 $\text{Cd}_2\text{I}_2\text{O}_9$

- 9.3.5 Calcium
 - 9.3.5.1 $\text{Ca}(\text{IO}_3)_2$, $\text{Ca}_5(\text{IO}_6)_2$
 - 9.3.5.2 CaI_2O_9
- 9.3.6 Cesium
 - 9.3.6.1 CsIO_3
 - 9.3.6.2 CsIO_4
- 9.3.7 Chromium
 - 9.3.7.1 $\text{Cr}(\text{IO}_3)_3$
- 9.3.8 Cobalt
 - 9.3.8.1 $\text{Co}(\text{IO}_3)_2$
- 9.3.9 Copper
 - 9.3.9.1 $\text{Cu}(\text{IO}_3)_2$
- 9.3.10 Indium
 - 9.3.10.1 $\text{In}(\text{IO}_3)_3$
 - 9.3.10.2 InIO_5
- 9.3.11 Iron
 - 9.3.11.1 $\text{Fe}(\text{IO}_3)_3$
 - 9.3.11.2 $\text{Fe}_5(\text{IO}_6)_2$
 - 9.3.11.3 $\text{Fe}(\text{IO}_4)_3$
 - 9.3.11.4 $\text{Fe}_5(\text{IO}_6)_3$
- 9.3.12 Lead
 - 9.3.12.1 $\text{Pb}(\text{IO}_3)_2$
 - 9.3.12.2 $\text{Pb}(\text{IO}_3)_4$
 - 9.3.12.3 $\text{Pb}(\text{IO}_4)_2$
 - 9.3.12.4 $\text{Pb}_3(\text{IO}_5)_2$
- 9.3.13 Lithium
 - 9.3.13.1 LiIO_3
 - 9.3.13.2 Li_2IO_4
 - 9.3.13.3 Li_5IO_6
- 9.3.14 Magnesium
 - 9.3.14.1 $\text{Mg}(\text{IO}_3)_2$
 - 9.3.14.2 $\text{Mg}(\text{IO}_4)_2$
 - 9.3.14.3 $\text{Mg}_2\text{I}_2\text{O}_9$
- 9.3.15 Manganese
 - 9.3.15.1 $\text{Mn}(\text{IO}_3)_2$
 - 9.3.15.2 $\text{Mn}_3(\text{IO}_5)_2$
- 9.3.16 Mercury
 - 9.3.16.1 $\text{Hg}_2(\text{IO}_3)_2$
 - 9.3.16.2 $\text{Hg}(\text{IO}_3)_2$
 - 9.3.16.3 $\text{Hg}_2(\text{IO}_4)_2$
 - 9.3.16.4 $\text{Hg}_5(\text{IO}_6)_2$
 - 9.3.16.5 $\text{Hg}_4\text{I}_2\text{O}_9$
- 9.3.17 Nickel
 - 9.3.17.1 $\text{Ni}(\text{IO}_3)_2$
 - 9.3.17.2 $\text{Ni}_3(\text{IO}_5)_2$
 - 9.3.17.3 $\text{Ni}_2\text{I}_2\text{O}_4$
- 9.3.18 Plutonium
 - 9.3.18.1 $\text{Pu}(\text{IO}_3)_4$
- 9.3.19 Potassium
 - 9.3.19.1 KIO_3
 - 9.3.19.1.1 Periodates

- 9.3.19.2 KIO_4
- 9.3.19.3 $\text{K}_4\text{I}_2\text{O}_9$ (2 $\text{K}_2\text{O} \cdot \text{I}_2\text{O}_7$)
- 9.3.19.4 K_3IO_5 (3 $\text{K}_2\text{O} \cdot \text{I}_2\text{O}_7$)
- 9.3.19.5 K_5IO_6 (5 $\text{K}_2\text{O} \cdot \text{I}_2\text{O}_7$)
- 9.3.20 Radium
 - 9.3.20.1 $\text{Ra}(\text{IO}_3)_2$
- 9.3.21 Rare Earths
 - 9.3.21.1 Iodates
 - 9.3.21.2 Periodates
- 9.3.22 Rubidium
 - 9.3.22.1 RbIO_3
 - 9.3.22.2 RbIO_4
- 9.3.23 Silver
 - 9.3.23.1 AgIO_3
 - 9.3.23.2 AgIO_4
 - 9.3.23.3 AgIO_5
 - 9.3.23.4 Ag_5IO_6
 - 9.3.23.5 $\text{Ag}_4\text{I}_2\text{O}_9$
- 9.3.24 Sodium
 - 9.3.24.1 NaIO_2
 - 9.3.24.2 NaIO_3
 - 9.3.24.3 Na_2IO_4
 - 9.3.24.4 NaIO_4
 - 9.3.24.5 Na_5IO_6
- 9.3.25 Strontium
 - 9.3.25.1 $\text{Sr}(\text{IO}_3)_2$
 - 9.3.25.2 $\text{Sr}_5(\text{IO}_6)_2$
 - 9.3.25.3 SrI_2O_9
- 9.3.26 Thallium
 - 9.3.26.1 $\text{Tl}(\text{IO}_3)_3$
 - 9.3.26.2 Tl_5IO_6
- 9.3.27 Thorium
 - 9.3.27.1 $\text{Th}(\text{IO}_3)_4$
- 9.3.28 Titanium
 - 9.3.28.1 $\text{Ti}(\text{IO}_3)_4$
- 9.3.29 Yttrium
 - 9.3.29.1 $\text{Y}(\text{IO}_3)_3$
 - 9.3.29.2 YIO_5
- 9.3.30 Zinc
 - 9.3.30.1 $\text{Zn}(\text{IO}_3)_2$
 - 9.3.30.2 $\text{Zn}(\text{IO}_5)_2$
- 9.3.31 Zirconium
 - 9.3.31.1 $\text{Zr}(\text{IO}_3)_4$

References

1 Introduction

1.1 GENERAL

In many areas of chemistry and chemical technology there exists a need to know the properties of salts at high temperatures. These areas include chemical synthesis, metallurgy, corrosion by salts, and catalysis.

Questions often relate to the thermal stability of the salt, usually phrased in terms of the following questions: Up to what temperature is the salt stable? What happens to it above that temperature — does it melt or decompose in either the solid or liquid state? What are its decomposition products? If it is placed in a closed container, how much will the pressure build up?

This is true whether one needs to know the properties of a particular salt, or whether one wishes to select salts fitting particular criteria, such as melting points or decomposition pressures.

The kind of information desired proceeds from the qualitative — congruent melting point or decomposition products to the quantitative — melting points, decomposition pressures, and rates of decomposition, i.e., thermodynamics and kinetics.

The topics covered in this book include the above kinds of information for oxyanions of the elements which form discrete anions: carbon, sulfur, nitrogen, and the halogens including:

Carbon: carbonates

Sulfur: sulfites, sulfates

Nitrogen: nitrites, nitrates

Chlorine: chlorites, chlorates, perchlorates

Bromine: bromites, bromates, perbromates

Iodine: iodates, periodates

In order to avoid complicating factors (the subject is already complicated enough) coverage has been restricted to anhydrous salts and monatomic cations, e.g., no ammonium and acid salts are included. Even with these restrictions, nearly 300 salts fit these criteria.

There is also a large body of literature dealing with additives, such as catalysts, the effect of radiation and mechanical treatment, which affects both the surface and internal structure of crystals, which are not treated in detail in this book.

Between 1968 and 1972 the author published four monographs covering this subject under the auspices of the National Standard Reference Data Program (NSRDS) (see below). This material is no longer readily available and needs revision and updating.

This book generally follows the format of the monographs. Each class of salts, e.g., sulfates, is treated in a separate chapter. Since a major question is always “Does this salt exist?” each section includes a periodic table which provides this information. A blank space does not mean the salt does not (or cannot) exist, but only that nothing is known of its existence, perhaps because no one has tried to synthesize it.

The discussion of each salt includes both qualitative and quantitative information, what is known of its behavior above ambient temperature, and quantitative data: phase transitions, densities, and thermodynamic properties. When possible, high temperature properties, enthalpies and entropies at 298.15 K and above, are listed. When these are available, they are used to calculate equilibrium constants and partial pressures of the component gases. (For a discussion of this topic

see Chapter 1.2). Kinetic data for decomposition reactions, such as rates and activation energies, are also included, but this information is inherently less reliable since these parameters depend not only on the nature of the material, but also on its physical state, e.g., particle size and defect structure. This topic is also discussed in a separate section.

1.2 EQUILIBRIUM CALCULATIONS

The main method for deciding what happens to substances when they are heated is thermodynamic calculations. Before they can be carried out, however, the relevant decomposition reaction(s) must be known. For some substances this is straightforward; for example, the decomposition of a carbonate always results in the formation of a metal oxide, nearly always in the solid state, and CO_2 . For other classes of salts the problem is more difficult. For sulfates the gaseous decomposition products may be SO_3 , or mixtures of this gas, SO_2 , and O_2 , depending on the equilibrium $\text{SO}_3 = \text{SO}_2 + 1/2\text{O}_2$ at the temperature of interest. Some oxyhalogens decompose to halides, others to oxides, and some to a mixture of both. Correspondingly, the gaseous products will also be different in the two cases. Thus it is essential to decide first what the reactions are for which calculations are to be performed. In most of these cases, where simultaneous equilibria obtain, calculations of partial pressures usually require the solution of simultaneous equations. Examples will be given in the appropriate sections.

In order to calculate the equilibrium constant for a particular reaction, thermodynamic functions of reactants and products as a function of temperature must be known. The calculation of these functions is discussed in detail in the work of Wagman et al. cited below.

The ΔG of the reaction is then calculated in one of two ways: (1) the appropriate addition and subtraction of ΔG_f for reactants and products, or (2) the calculation of Gibbs energy functions for reactants and products from enthalpy and entropy increments

$$gef = \frac{G_T^0 - H_{298}^0}{T} = \frac{H_T^0 - H_{298}^0}{T} - (S_T^0 - S_{298}^0) - S_{298}^0 \quad (1.1)$$

Finally, the equilibrium constant is calculated from

$$G_T = T\Delta gef + \Delta H_{298}^0 \quad \text{and} \quad (1.2)$$

$$\Delta G = RT \ln K \quad (1.3)$$

These methods were used in this work when necessary. However, in many cases the equilibrium constants could be calculated by a computer program developed by Outukompu Research, which uses data stored in their program. These data are usually the most recent available. References used in this program are listed below. When data above 298 K were not available, data at 298 K are given. These are taken from Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; and Nuttall, R. L., *The NBS tables of chemical thermodynamic properties*, *J. Phys. Chem. Reference Data* 11, Suppl. 2, 1982

HSC Chemistry for Windows

This program stores data for approximately 7800 compounds. Data come from a variety of sources. Those chiefly used for calculations in this work include

Barin, I., *Thermochemical Data of Pure Substances*, VCH Verlagsgesellschaft, Weinheim, 1989 and 1993.

Barin, I., Knacke, O., and Kubaschewski, O., *Thermodynamic Properties of Inorganic Substances*, Springer-Verlag, Berlin, 1973, Supplement 1977.

Chase, M. W., Davis, C. A., Downey, J. R., Frurip, D. J., McDonald, R. A., and Syverud, A. N., JANAF thermochemical tables, *J. Phys. Chem. Reference Data*, 14, Supplement 1, 1985.

Knacke, O., Kubaschewski, O., and Hesselman, K., *Thermochemical Properties of Inorganic Substances*, Springer Verlag, Berlin, 1991.

In addition, some tables come from a 1997 edition of HSC. References for these tables appear at the end of each chapter.

Previous work by the present author is given in the following monographs:

High Temperature Properties and Decomposition of Inorganic Salts

Part 1. Sulfates, Stern, K. H. and Weise, E. L., NSRDS – NBS, 1966.

Part 2. Carbonates, Stern, K. H. and Weise, E. L., NSRDS – NBS, 1969.

Part 3. Nitrates and Nitrites, Stern, K. H., *J. Phys. Chem. Ref. Data*, 1, 3, 1972.

Part 4. Oxysalts of the Halogens, Stern, K. H., *J. Phys. Chem. Ref. Data*, 3, 2, 1974.

When data from the HSC program were used, ΔH_f° , ΔG_f° , and S° have been listed for reactants and products as a function of temperature. Gaseous equilibria are listed in separate tables in each section, e.g., $\text{SO}_2 + 1/2 \text{O}_2 = \text{SO}_3$ for sulfates. In many cases the equilibrium constants for the decomposition reactions can be calculated directly from data in the program. When this was not possible, other methods, using the equations given above, were used.

When the equilibrium constants are known, the partial pressures of the individual gases can be calculated under certain restrictive conditions, e.g., closed system, pressures of some gases are fixed, etc. For example, if one starts with a closed system that is initially pumped out and the salt allowed to decompose so that pressure builds until equilibrium is reached, it is possible to calculate the partial pressures of the gases in the system. Thus, for carbonates, the pressure of CO_2 equals the equilibrium constant. For other classes of salts the calculations can be much more complicated. Appropriate methods are discussed in the individual chapters.

1.3 PHASE TRANSITIONS

Solid–solid phase transitions have been much studied and are generally reliable if they were carried out appropriately, e.g., if equilibrium was approached from above and below.

Melting points are usually obtained by rapid heating of the salt to minimize decomposition, but this cannot always be avoided. The lower values should therefore be regarded as lower limits. Above the melting point most salts decompose so rapidly that boiling points cannot be measured. When more recent or reliable data were not available, phase transitions were taken from the following NBS publication: Rossini, F. D., Wagman, D. D., Evans, W. H., Levine, S., and Jaffe, I. *Selected Values of Chemical Thermodynamic Properties*, NBS Circular 500, U.S. Govt. Printing Office, Washington, D.C. 1952.

1.4 DENSITY

The densities of solid salts are generally determined directly by pycnometry, or are calculated from crystallographic (X-ray diffraction) data. In the latter method atomic packing must be assumed. Since no allowance is made for crystal imperfections, calculated densities are generally higher than experimental values by as much as 10%. Since most crystallographers do not indicate the temperature for which the density is calculated, in this work the experimental values have been given when they were available. However, in some cases the experimental values seem to depend on the method of preparation, perhaps because of variations in the defect density. Thus, although the density of a given sample can certainly be determined to four or five significant figures, not too

much significance should be attached to figures beyond the third. This is particularly true because the units of the reported density values are frequently in doubt. In some cases they are not stated at all; in others it is not clear whether the units are g/cm³ or g/ml; in still others they are specific gravity values and may be referred to water at 4°C or at some other temperature. The difference between cubic centimeters and milliliters is so small (the ratio is 1.000028) as to be negligible. However, the difference in the density of water between 4 and 20° is in the third significant figure and is no longer negligible for better measurements.

In this work the units reported by the original authors are given. When no units are given it can generally be assumed that g/ml is meant.

There are some density data for solid salts above ambient temperature which are given in the form of thermal expansion coefficients. These have been listed when they seemed reliable. Above the melting point, density data are scarce. Most are available for alkali halides but those available for salts are taken from the critically evaluated compilation: Janz, G.J., Thermodynamics and transport properties for molten salts. correlation equations for critically evaluated density, surface tension, electrical conductance, and viscosity data, *J. Phys. Chem. Reference Data*, 17, Suppl. 2, 1988.

1.5 KINETICS OF THERMAL DECOMPOSITION

1.5.1 GENERAL

In contrast to the thermodynamics of decomposition, where a few parameters permit the calculation of the equilibrium properties of the system, the determination of decomposition rates is largely an experimental problem, i.e., there are no standard kinetic data from which these rates can be calculated. This is particularly true for the decomposition reactions of solids which are "topochemical," i.e., where the rate depends on structural factors. One reason for this situation is that it does not yet seem possible to prepare duplicate samples of any solid inorganic salt that are identical in all the properties that may determine the rate of decomposition, e.g., the dislocation density of the crystals.

Nevertheless, the kinetics of decomposition are of sufficient interest, for both theoretical and practical reasons, that it seems worthwhile to include the results of at least the more carefully done studies. In this section we summarize features common to all decompositions and the factors affecting decomposition rates. The discussion is essentially limited to solids, since most experimental and theoretical work has been done in this area. It should be pointed out that many of the theoretical foundations were laid several decades ago, and that newer developments deal mostly with refinements. Kinetics of the individual compounds are treated in their respective sections.

1.5.2 MECHANISM OF ENDOTHERMIC SOLID-STATE DECOMPOSITION

Many authors have derived equations for the rate of decomposition from theoretical models. The aim of these studies is to find functional relations between some measurable quantities of the system, such as weight and time, which can be tested against experimental results. Although the usual caveat against taking agreement between the predictions of the model and experimental results as evidence for the correctness of the model applies, nevertheless such agreement, together with other experimental evidence, e.g., microscopic examination, is frequently very helpful in at least narrowing the possibilities.

In this section some of the models which have been proposed are briefly summarized. Greater detail can be found in books by Garner,¹ Young,² and Tompkins³ and in the original references.

Most models try to account for the shape of the experimental α (= fraction decomposed) vs. time(*t*) curves. These are generally S-shaped, with a relatively slow induction period, a steep portion during which the bulk of the material decomposes, and a slow final section. Experimentally

determined curves differ primarily in the relative length of the induction period. This induction period is commonly identified with the formation of nuclei of the new phase B imbedded in A; these nuclei grow, by spreading both over the surface and into the bulk of the decomposing particle. After the surface is covered by B, this phase grows into the bulk of the decomposing particle. Decomposition thus occurs only at the reactant/product phase boundary, as has been argued by Langmuir from phase rule considerations.⁴ There seems to be general agreement that the evolution of gas C during endothermic solid decomposition is not a rate-limiting step in the process because the product B is sufficiently porous to permit C to escape readily. However, if the gas is generated in the bulk of the crystal, e.g., by ionizing radiation, and must diffuse along grain boundaries, the rate of decomposition may depend markedly on the diffusion constant of the gas. This case has been discussed by Gafner.⁵

Although the measured decomposition rates are not rate-limited by diffusion of gas out of the crystal, it is clear that in the case of readily reversible decompositions, such as those of the carbonates, the measured rate will depend on the difference between the equilibrium pressure p_e and the actual pressure p at the reaction interface. Thus, although the functional dependence of α on t may be independent of $p_e - p$, the actual rates are not. It is largely for this reason that it is not possible to tabulate “standard reference data” rate constants, since the pressure p is not usually known. Instead, one finds decompositions carried out in streams of various “sweep gases,” which may or may not remove product gases from the reaction interface, or in a vacuum. In the latter case, the question as to whether the manometrically measured pressure equals the pressure at the interface needs to be answered. Small sample size and a porous oxide favor this condition.

1.5.2.1 Kinetic Equations

The most complete classification of solid decompositions has been worked out by Jacobs and Tompkins.⁶ When the decomposition begins at some points on the A lattice where the energy is most favorable, small fragments of B are imbedded in A. These may at first retain the lattice parameters of A and will therefore possess some strain energy as a result of this deformation. Jacobs and Tompkins show that the Gibbs energy accompanying the formation of a fragment of B containing m molecules is

$$\Delta G = am^{2/3} - bm$$

where a is proportional to the strain energy and b is the negative of the bulk Gibbs energy per molecule. ΔG passes through a maximum at $m = m^*$ when a fragment has the critical size to be in equilibrium with its surroundings. Smaller fragments are unstable and revert to A; larger fragments are stable nuclei and grow. Whether decomposition proceeds from the growth of a few nuclei or whether many small nuclei are formed depends on the relative magnitudes of the activation energies for nucleus formation (ΔG_1^\ddagger) and the growth stage ΔG_2^\ddagger . If $\Delta G_2^\ddagger < \Delta G_1^\ddagger$, growth of existing nuclei predominates over formation of new ones. If $\Delta G_2^\ddagger = \Delta G_1^\ddagger$, many small nuclei are formed, none of which grow to visible size. In that case the induction period is much reduced. The whole surface then nucleates rapidly and the kinetics of the remainder of the reaction depends on the rate at which the interface progresses into the crystal.

We next consider various mechanisms for each of the stages in the decomposition.

1.5.2.1.1 Nucleus Formation

Jacobs and Tompkins⁶ consider only structure-sensitive nucleation, which occurs at definite sites in the lattice where the activation energy is least, such as lattice defects and dislocations. The rate of nucleus formation thus depends on both the defect density and on the activation energy.

Jacobs and Tompkins distinguish two cases:

- a. The decomposition of a single molecule leads to the formation of a nucleus. The probability of this unimolecular decomposition is

$$k_1 = \Gamma \exp(\Delta G_1^\ddagger / RT) \quad (1.4)$$

where Γ is the frequency of lattice vibrations and ΔG_1^\ddagger is the activation Gibbs energy for nucleus formation. The rate of nucleus formation at time t then is

$$dN/dt = k_1 N_0 \exp(-k_1 t) \quad (1.5)$$

or

$$N = N_0 [1 - \exp(-k_1 t)]$$

where N_0 is the total number of potential nucleus-forming sites. The possible loss of nucleus-forming sites through their ingestion by growing nuclei is neglected. In the early stages of the reaction and especially for large ΔG_1^\ddagger and consequently small k_1

$$N \cong k_1 N_0 t \quad (1.6)$$

so that the number of nuclei increases linearly with time.

- b. A power law results from two possible mechanisms: (1) a stable nucleus is formed in a bimolecular combination of two active intermediates, and (2) several decompositions are required to form a stable nucleus. The first of these possibilities may require the surface migration of several B molecules until they coalesce into a stable nucleus. Some aspects of this phenomenon have been discussed by MacDonald.⁷

1.5.2.2 Growth of Nuclei

As each nucleus is formed, it grows, generally hemispherically, i.e., it spreads across the surface of the crystal and into its interior. Since the laws for the formation of nuclei are different from those for their growth, the overall decomposition rate is likely to be complicated if the two rates are of comparable magnitude. This is particularly true if the complications resulting from overlapping nuclei are taken into account. As nuclei grow, they ingest or overlap sites which would otherwise yield nuclei. Also, as nuclei grow, they impinge on one another and cease to grow along the line of contact. Both of these effects result in rates different from those predicted from models without these refinements.

The simplest decomposition kinetics, commonly observed for carbonates, result from a model in which nucleation and subsequent surface growth are extremely rapid. The rate of decomposition is then determined by the progression of the reaction interface into the crystal. Rate laws have been derived for various geometries, but the ones for spherical particles are most useful and have been given in several equivalent forms by various authors. In this derivation it is assumed that the reaction interface proceeds at a constant velocity into the crystal; i.e., for a constant interfacial area, the rate of decomposition is a constant. For a spherical particle, the reaction proceeds along a constantly diminishing interface. For such particles of initial radius R_0 , the fraction decomposed at time t is

$$\frac{4/3\pi R_0^3 - 4/3\pi(R_0 - k_2 t)^3}{4/3\pi R_0^3} = 1 - \left(1 - \frac{k_2 t}{R_0}\right)^3 = \frac{3k_2 t}{R_0} - \frac{3k_2^2 t^2}{R_0^2} + \frac{k_2^3 t^3}{R_0^3} \quad (1.7)$$

and

$$\frac{d\alpha}{dt} = \frac{3k_2}{R_0} - \frac{6k_2^3 t}{R_1^2} + \frac{3k_2^3 t^3}{R_0^3} \quad (1.8)$$

These equations were first derived by Hume and Colvin.⁸

The same, but superficially different, equation was derived by Fischbeck and Schnaidt⁹ in a form now frequently used:

$$d\alpha/dt = k_1 A \quad (1.9)$$

where A is the total area of the reacting interface. For a spherical particle $A = k'_2 (1 - \alpha)^{2/3}$, where k'_2 depends on R_0 , and hence

$$\frac{d\alpha}{dt} = k'_2 (1 - \alpha)^{2/3} \quad (1.10)$$

In this form the equation is frequently referred to as the 2/3 power law. In terms of mass change it can be written as¹⁹

$$-\frac{dm}{dt} = k''_2 m^{2/3} \quad (1.11)$$

where k''_2 again depends on R_0 . Equation 1.10 is usually given in integrated form

$$k'_2 t = 1 - (1 - \alpha)^{1/3} \quad (1.12)$$

The dependence of rate on particle size can be included by substitution $k_2 = k'_2/R_0$.

The second limiting case arises when the rate of linear propagation of the reacting interface is so great that each particle decomposes as soon as it has a nucleus. For this case, Hume and Colvin give

$$\text{Rate} = k_0 N_t$$

i.e.,

$$dN/dt = k_0 N_t \quad (1.13)$$

where N_t is the number of particles at time t . Integration from N_0 to N_t gives

$$\ln(N_t/N_0) = k_0 t \quad (1.14)$$

a first-order reaction. This behavior is most likely to be approached by very small particles.

In general, the kinetics of decomposition is more complex than in the two limiting cases just outlined. Thus, if nucleation is not extremely rapid, the number of nuclei will increase in time. Each of these nuclei will then begin to grow at a different time. Some of them will spread over sites at which nucleation would have occurred at some future time. These sites are referred to as “phantom nuclei” by Jacobs and Tompkins.⁶ This problem has been studied in great detail by

Mampel.¹⁰ Both Jacobs and Tompkins and Mampel assume the rate of nuclei formation to be first order,

$$dN/dt = k_1 N_0 \exp(-k_1 t) \quad (1.15)$$

where N_0 is the total number of possible sites. For the induction period, Mampel finds a t^4 law for α , a relation derived by Jacobs and Tompkins for random nucleation and short times, and by Fischbeck and Spingler¹¹ for the case of no overlap, a constant rate of nuclei formation, and a large total number of nuclei.

For large radii ($R > k_2 t$) Mampel finds

$$\frac{k_2 t}{R} \approx 1 - (1 - \alpha)^{1/3} \quad (1.16)$$

an equation (1.12) previously given for the contracting sphere case. For small radii the fraction decomposed is

$$X = 1 - c e^{-kt} \quad (1.17)$$

where c is independent of t , but does depend on R in a rather complicated way. The rates are dependent on particle size and both small and large radii give lower rates than intermediate radii.

A generalized equation has been derived by Erofeev¹² in terms of probability theory. In his treatment,

$$\alpha = 1 - \left(- \int_0^t p \, dt \right) \quad (1.18)$$

where p is the probability that a molecule will react in the time interval dt .

The general solution of (1.18) for thermal decomposition is

$$\alpha = 1 - \exp(-k t^n) \quad (1.19)$$

where the constant n depends on the shape of the nucleus and the number of electrons necessary for the formation of a stable nucleus. For example, cylindrical nuclei (the centers of formation are edges or surface cracks) give $n = 3$, flat nuclei give $n = 4$. Thus the evaluation of n , most easily carried out by transforming (1.19) into

$$\ln [-\ln(1 - \alpha)] = \ln k + n \ln t \quad (1.20)$$

and plotting the left side of (1.20) vs. $\ln t$, gives some information about the nucleation mechanism.

1.5.2.3 Surface Area Changes Decomposition

Since the molar volume of the product oxides is less than that of the corresponding salts, decomposition results in a porous structure through which the product gases readily escape. Although not directly related to decomposition kinetics, the resulting increase in surface area during decomposition is of some interest in the production of “active solids” and has been treated by several authors. Accordingly, we briefly review it here.

The oxide is first formed at sites on the salt lattice and is therefore in a strained state. Gregg¹³ has described these as small crystallites or micelles. The strained pseudo-lattice will tend to recrystallize into a stable oxide lattice with a resulting decrease in surface area. Three mechanisms for this recrystallization are generally recognized. At temperatures $T/T_m < 0.2$, where T_m is the melting point of the oxide, adhesion predominates. This mechanism results from contact between parts of the micelles which are atomically contiguous. For $0.2 < T/T_m < 0.35$, surface diffusion predominates. Here mobile atoms or ions in the surface layer leave their position on the lattice to migrate to sites of lower energies, i.e., to stable oxide lattice positions. Above $T/T_m = 0.5$, sintering, i.e., lattice or bulk diffusion, is the most significant process leading to decreased surface area. Thus, as decomposition proceeds, there are basically two processes leading to changes in surface area: formation of the metastable oxide produces an increase in surface, and formation of stable oxide decreases the area. Consequently, the “surface area” vs. “fraction decomposed” plot exhibits a maximum before decomposition is complete. Nicholson¹⁴ has developed a mathematical model which agrees well with experimental observation. If the purpose of the decomposition is the preparation of an “active solid,” the reaction should not be carried to completion in order to achieve the desired maximum surface area.

1.5.3 THE EFFECT OF PRESSURE ON RATE

Most of the work on this topic has been carried out on carbonates because only one gas is produced and the analysis is thus inherently simpler. For other salts, several gases are present. Although the principles are basically the same, the discussion has been given here in terms of carbonates.

When the pressure of CO_2 in a carbonate–oxide system is equal to the equilibrium pressure p_e , no net reaction occurs. When $p < p_e$, the thermodynamic driving force favors oxide formation; conversely, when $p > p_e$, carbonate formation is favored. In the actual system the favored reaction may not occur, however, because kinetic factors prevent it. Particularly when p is not far from p_e , the reaction may not proceed because some rate-limiting process, such as nucleus formation, is proceeding too slowly. The resulting spurious equilibria¹⁵ give rise to hysteresis effects, i.e., decomposition stops for some $p < p_e$, recombination stops for some $p > p_e$. It is for this reason that this work relies largely on thermodynamic methods for the calculation of equilibrium pressures.

When the carbonate and oxide are present as pure phases, the value of p_e is completely unambiguous, i.e., at a given temperature $p_e = K_p$, the equilibrium constant for the reaction $\text{MCO}_3 = \text{MO} + \text{CO}_2$. However, when the condensed phase consists of a solid or liquid solution, p_e no longer has a unique value since

$$K = (a_{\text{MO}} / a_{\text{MCO}_3}) p_e \quad (1.21)$$

and p_e now depends on the solution composition. Since the decomposition rate is generally some function of $p_e - p$, we consider only systems without solution formation. We have also omitted discussion of the effect of “foreign” gases, i.e., gases other than CO_2 , on the rate. Such gases, e.g., O_2 , H_2O , frequently function as catalysts or inhibitors, but these effects are difficult to relate to well-defined properties of the system.^{16–18} In order to study the dependence of the reaction rate on CO_2 pressure, it is necessary that the pressure remains fixed throughout the course of the decomposition while more CO_2 is evolving. Since the significant pressure is that at the reaction interface, it is possible that in a closed system where one depends on diffusion to remove the excess CO_2 , the pressure at the interface will exceed the nominal value, particularly if the sample size is large and the reaction is rapid. The effect of a pressure gradient has been investigated¹⁹ by the application of Fick’s law. For both slow and fast reactions the rate is proportional to $p_e - p_0$ where p_0 is the pressure at the reaction site but the proportionality constants differ in the two cases. One way to avoid the problem of pressure gradients is to use sweep gases made from a known mixture of CO_2

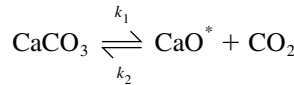
and some inert gas. Independence of decomposition rate from flow rate is generally taken as evidence that the reaction is not diffusion controlled, e.g.,²⁰ if the surface area is constant, the decomposition rate is proportional to $p_e - p_0$, i.e.,

$$v = k(p_0 - p) \quad (1.22)$$

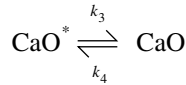
Such a relation was also found to hold for both cylindrical pellets of calcite and powdered CaCO_3 ,²¹ Cremer and Nitsch,²² in studying the decomposition of CaCO_3 , found that for samples which followed a 2/3 power rate law the pressure dependence of the rate (in $m^{1/3}t^{-1}$) was given by

$$v = k(1/p - 1/p_0) \quad (1.23)$$

A similar equation has been derived²⁰ from a two-step model in which the CaO is assumed to be formed first in some “active” state CaO^* which occupies a constant fraction of the surface. The reactions then are



$$1 - \Theta \quad \Theta \quad P$$



both of which are reversible. The rate

$$R = -dw/dt = \frac{k_0 k_1 k_3 - P k_0 k_2 k_4}{k_1 + k_3 + k_4 + k_2 P} \quad (1.24)$$

where the constant k_0 is introduced to convert the surface area to surface concentration in molecules per square centimeters, to account for the roughness factor, and the fact that only a portion of the total surface area may be potentially reactive. Equation 1.24 can be written as

$$R = \frac{1 - CP}{VP + D} \quad (1.25)$$

where $P = 0$, $R = R_0 = 1/D$, $P = P_e$, $R = R_0$, and $C = 1/P_e$
Hence

$$R = \frac{1 - P/P_e}{BP + 1/R_0} \quad (1.26)$$

When $1/R_0 \gg BP$,

$$R = 1/BP - 1/P_e$$

which is essentially the equation given by Cremer and Nitsch.²²

1.5.4 ACTIVATION ENERGY

The activation energy E^\ddagger , as defined by the usual Arrhenius equation

$$k = Ae^{-E^\ddagger/RT}$$

is usually at least as great as the thermodynamic enthalpy for the reaction, ΔH , though it is frequently greater. When $E^\ddagger = \Delta H$, the reaction is often described as occurring “without activation.” The question as to whether $E^\ddagger = \Delta H$ for the endothermic carbonate decomposition was first considered by Fischbeck and Schnaidt.²³ Shortly thereafter, Zawadzki and Bretsnajder¹⁵ showed that for a reversible reaction of the type $A(s) = B(s) + C(g)$, the experimental value of E^\ddagger for the forward reaction, as determined from the temperature dependence of k , must necessarily increase with rising pressure and will have its minimum value in the absence of the backward reaction, i.e., in a vacuum. This dependence was verified for the decomposition of CaCO_3 , CdCO_3 , and Ag_2CO_3 . In a vacuum the temperature dependence of k was the same as that of the equilibrium pressure p_e , i.e., $E = \Delta H$. The dependence of E^\ddagger on the pressure was reexamined by Pavlyuchenko and Prodan,²⁴ who distinguished two cases: (1) if E^\ddagger is determined from the temperature dependence of the rate, with the pressure p held constant at the various temperatures, then E^\ddagger increases as $p \rightarrow p_e$. (2) If, however, the ratio p/p_e is held constant as the temperature is changed, then E^\ddagger will be independent of the actual numerical value of the ratio and will have the same value as in a vacuum. This conclusion was reached by a theoretical argument and verified by data on the decomposition of CdCO_3 . Since condition (1) is the more usual experimentally, particularly in the older literature, it is not surprising that widely varying values of E^\ddagger for the same reaction have been reported²⁵ by authors who failed to recognize the dependence of E^\ddagger on pressure.

The atomic mechanism responsible for monomolecular reactions, including thermal decompositions, was first discussed by Polanyi and Wigner.²⁶ Their model assumes that decomposition occurs when, due to energy fluctuations in the bonds of the molecule, the bond strength is exceeded; or more precisely, the bond energy “resides in harmonic vibrations and that decomposition occurs when their amplitude is exceeded.” The resulting expression for the first-order Polanyi–Wigner rate constant is

$$k = \nu \exp(-E^\ddagger/RT) \quad (1.27)$$

where ν is the atomic frequency of vibration and E^\ddagger is the activation energy. Thus, a molecule having energy E^\ddagger would leave the surface.

Shannon²⁷ analyzed in some detail the theory as it applies to the thermal decomposition of solids. He found that of the 31 reactions for which he compared experimental rate constants with those calculated from the Polanyi–Wigner equation, only a third showed order-of-magnitude agreement. In Shannon’s view, the lack of agreement stems from neglecting rotational and other vibrational degrees of freedom.

Shannon calculated the rate constant for thermal decomposition of a solid from absolute reaction rate theory. The resulting equation is of the same form as Equation 1.27, but ν is replaced by a partition function ratio:

$$k = (kT/h)(Q^*/Q) \exp(-E/kT) \quad (1.28)$$

where Q^* is the complete partition function of the activated complex, excluding that for the reaction coordinate, and Q is the complete partition complex for the reactant. Detailed calculations of the partition functions were carried out for the decomposition of CaCO_3 and MgCO_3 , using known values of the rotational and vibrational partition functions and several models for the activated complex. The best agreement with experiment was obtained for a model in which the carbonate

ion in the lattice is free to rotate and the CO_2 molecule leaves directly from the surface of the solid, rather than from a mobile surface layer.

It should be noted that over the past 50 years studies of solid decomposition kinetics have progressed from the application of equations which were originally derived for gases to more and more detailed studies on molecular events occurring at the reactant-product interface. This point has been emphasized by Boldyrev²⁸ who, with his co-workers, has amassed a large body of evidence that shows the importance of defect structure on kinetics. This structure may be affected by radiation or by mechanical forces, such as grinding, which affect both the surface and the internal structure of crystals.

1.5.5 THE EFFECT OF PREPARATION METHOD ON RATE

Various authors have recognized that the rate of thermal decomposition may depend on the method of preparation and the thermal “history” of the sample, but systematic studies in this area are inherently difficult. However, there has been progress in this field, called “tribochemical decomposition.” Boldyrev²⁸ has distinguished between physical and chemical effects. The main process in the former is the introduction of defects by diminution, e.g., grinding. The latter arise from chemical processes at the contact points of solid particles. Boldyrev²⁸ has provided a framework for the analysis of these effects and tested his hypotheses with an experimental study of some nitrate and bromate decompositions. Additional problems arise if impurities present in the samples at very low concentrations, such as H_2O , catalyze the decomposition.²⁹ In that case, the resulting change in mechanism will affect not only the rate but also the activation energy.

If the carbonate is a single crystal, the reaction will propagate from the surface to the interior. For polycrystalline materials the reaction may additionally propagate along grain boundaries.³⁰

A systematic study of the effect of sample constitution on the decomposition rate was carried out by Cremer and Nitsch.²² They decomposed four calcite samples at 850°C and CO_2 pressures ranging from 120 to 220 torr. The CaO product exhibited increasing grain size with increasing pressure. The four CaO samples were then reacted with CO_2 at 850°C and 429 torr to produce four CaCO_3 samples with similarly increasing grain size. When these four samples were then decomposed under identical conditions (850° , 200 torr CO_2) the rate of decomposition increased in inverse order of crystal size. The disappearance of the induction period with decreasing crystal size was particularly noticeable. These results are explained in terms of more rapid nucleus formation at lower pressures, leading to smaller CaO crystals and consequently a larger number of active sites in the CaCO_3 formed subsequently.

It is evident from these results that the course of the decomposition is affected by the microstructure of the sample and that reproducible preparation and characterization of nominally identical materials are important prerequisites for understanding and systematizing decomposition kinetics.

1.5.6 THE EFFECT OF HEAT TRANSFER ON RATE

An endothermic solid-state decomposition proceeds as the product–reactant interface advances into the interior of the sample. The interface can, however, advance only if the necessary heat of reaction is applied to it. Since the source of heat is outside the sample, the rate of heat transfer to the interface may become rate-determining if the inherent rate of reaction exceeds the rate of heat transport. The rate of heat transport depends not only on the properties of the product through which heat must be transported, but also on the general experimental arrangement. It is for this reason that one expects and finds the literature to be conflicting.

For example, Narsimhan³⁰ derived an equation for the thermal decomposition rate based on the idea that the entire particle rapidly reaches the decomposition temperature, so there are no internal temperature gradients. All the heat reaching the reaction interface is used up in the decomposition, so the reaction rate depends on the rate of heat transport. For both spherical and cylindrical particles,

good agreement with some literature values is found. Under these conditions the chemical steps are no longer rate-determining. It can thus be seen that in any solid-state reaction whose enthalpy is appreciable, the establishment, maintenance, and measurement of the temperature at the reaction interface is a complicated problem. Thus, careful studies of the decomposition of PbCO_3 ³¹ and several other inorganic salts³² have shown that the induction period may disappear if the entire sample is rapidly brought to the reaction temperature. There is, therefore, some question now as to whether the commonly reported induction periods in the decomposition of so many substances are artifacts of the experimental arrangements. Considerable care in the experiment's design is certainly required to insure a constant and known temperature at the reaction interface throughout the course of the decomposition.

1.5.7 THE INFLUENCE OF CRYSTAL DEFECT STRUCTURE ON DECOMPOSITION RATE

The idea that the defect structure of a solid reactant affects the rate of decomposition seems to be generally accepted; but of all the factors influencing the kinetics, this is the one most difficult to characterize quantitatively. Boldyrev and his many co-workers²⁸ have made considerable progress in elucidating the factors which affect the decomposition rate of solids; however, at the level of detail required for the understanding of a particular reaction, it seems difficult to make connections to the standard kinetic equations derived by earlier workers.

Searcy and co-workers^{32–34} have addressed the problems that arise from the use of large and/or powdered samples by measuring decomposition from specific faces of small single crystals, using the Langmuir method in which weight loss in a vacuum is measured. The authors cite several advantages of this approach: (1) the possibility that intergranular diffusion may be slow enough to influence the measured rate is eliminated; (2) the area and morphology of the interface at which the reaction proceeds can be precisely measured as a function of time; (3) the ratio of the measured flux of gaseous reaction product which leaves the reactant surface to the maximum (equilibrium) flux which can be predicted from equilibrium data and the kinetic theory of gases, provides a potentially valuable parameter for describing and understanding reaction kinetics, just as it does for congruent vaporization.

The maximum flux is given by the Hertz—Knudsen—Langmuir (HKL) equation

$$J_{\max} = \frac{P_{eq}}{(2\pi MRT)^{1/2}} = \frac{\exp(-G_d^0/RT)}{(2\pi MRT)^{1/2}} \quad (1.29)$$

The ratio of the experimental flow J to J_{\max} , α_v , the decomposition coefficient, may be useful in assessing the decomposition mechanism. However, account must be taken of formation of the solid product in a metastable state. The formation of this material may be the rate-limiting step. Beruto and Searcy^{33,34} have carried out a study of CaCO_3 decomposition using these principles. They have also studied the nature of the CaO formed. Thus, the field of solid decomposition kinetics seems to be moving toward a detailed examination of the products formed, with less emphasis on the overall kinetic equations.

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2 Carbonates

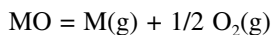
2.1 INTRODUCTION

2.1.1 STRUCTURE OF THE CARBONATE ION

The carbonate ion is a well-defined entity in which the three oxygens are arranged in the same plane as the carbon atom at a distance of 1.30 ± 0.01 Å with bond angles of 120° . This value of the C–O distance, calculated by Pauling¹ on the basis of the resonance structures shown in [Figure 2.1](#), is in good agreement with experimental measurements on calcite,^{2,3} ranging from 1.29 to 1.31 Å. The resonance energy is 176 kJ per mole.

2.1.2 GENERAL FEATURES OF CARBONATE DECOMPOSITION

All carbonates decompose with the evolution of CO_2 , the decomposition product being either the corresponding oxide or a basic carbonate, the latter decomposing with further evolution of CO_2 as the temperature is raised. The oxides of some metals are unstable in the same temperature range as the corresponding carbonates, so the decomposition occurs as simultaneous reactions



Consequently, the gas phase contains CO_2 , M, and O_2 . The oxide equilibria have not been calculated, but the text for particular elements indicates when they are important, such as for the higher atomic weight metals.

The melting points of pure carbonates are generally not measurable directly, though they may be estimated by extrapolation from phase diagrams or by rapid heating, particularly under high CO_2 pressures which minimizes decomposition.

The dissociation $\text{CO}_2 = \text{CO} + 1/2 \text{O}_2$ is too slight at temperatures relevant for carbonate decomposition, but a separate table for this reaction has been provided for up to 2400 K.

The thermal stability of a polyatomic anion decreases with increasing polarizing power of the associated cation, since polarization of the anion structure leads to the distortion and consequent weakening of the intra-ionic bonds. This topic has been discussed in detail elsewhere.⁴ Here we provide [Figure 2.2](#) which plots ΔHf_{298} , a measure of thermal stability, against $r^{1/2}/Z^*$, a measure of cation polarizing power, for the carbonates. It can be seen that the plot is approximately linear and thus can be used for predicting one parameter when the other is known. Similar plots can be constructed for the other anions in this book,⁴ but will not be reproduced.

The discussion of the high-temperature properties and thermal decomposition of carbonates in this chapter, a plan which will be followed for other classes of compounds in subsequent chapters, is given for each element. A brief discussion is followed by quantitative data on phase transitions, densities, and thermodynamic parameters for the carbonate, the corresponding oxide, and the decomposition reaction $\text{MCO}_3 = \text{MO} + \text{CO}_2$. If the carbonate and oxide are solids and form no solid solution, the equilibrium constant is the pressure of CO_2 which would be obtained if one begins with an evacuated container and lets the system come to equilibrium. In this case, the pressure is a unique function of the temperature. As pointed out in Chapter 1, this is no longer true

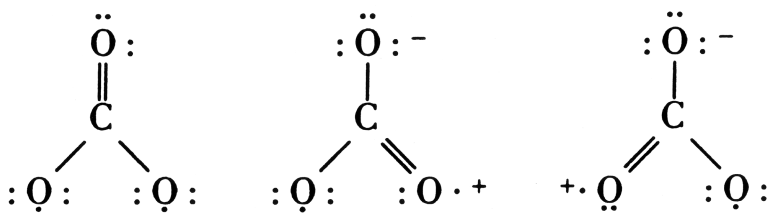


FIGURE 2.1 Structure of the carbonate (CO_3) ion. (From Pauling, L., *The Nature of the Chemical Bond*, 3rd ed., Cornell University Press, Ithaca, NY, 1960. With permission.)

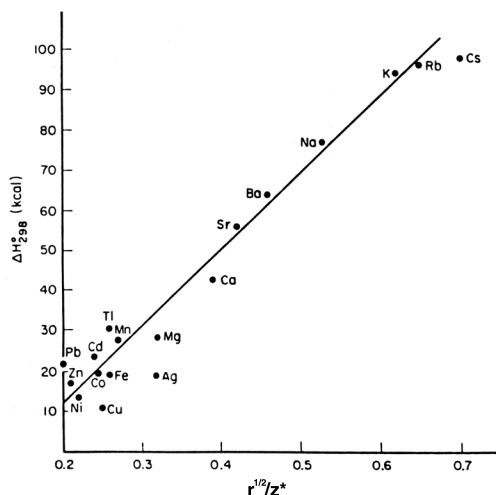


FIGURE 2.2 ΔH_{298}° vs. $r^{1/2}/Z^*$ for the carbonates.

if the oxide and carbonate form a solid or liquid solution. In that case, $K = (a_{\text{MO}} / a_{\text{MO}_3})$. P , and the pressure of CO_2 depends on the condensed phase composition.

One aspect of carbonate decomposition that should be kept in mind is the quality of the “anhydrous” starting materials. In many cases they were prepared by heating hydrates that were not completely dehydrated, and the residual water may affect the decomposition, particularly the kinetics.

2.1.3 PHASE TRANSITIONS

This topic was discussed in Chapter 1.3. Transitions of carbonates are listed under the individual salts. When they are taken from the NBS compilation given in Chapter 1, the reference is 1.3.

2.1.4 DENSITY

This topic was treated in detail in 1.4. Densities for individual carbonates are given for each salt.

2.2 CO , CO_2 , AND O_2

The CO_2 produced by the decomposition of a carbonate dissociates partly to CO and O_2 . However, at temperatures for which most of the carbonate equilibria have been calculated, the decomposition of CO_2 is very slight. Therefore, the decomposition equilibria for carbonates have been given in terms of CO_2 only. However, for those wishing to refine the calculations, thermodynamic functions for the three gases and the equilibrium constant for the reaction $\text{CO}_2 = \text{CO} + \text{O}_2$ have been listed

for up to 2400 K in [Tables 2.1 to 2.4](#). It should also be noted that if a carbonate is decomposed in air (0.21 atm O₂) the decomposition will be partially repressed.

2.3 THE INDIVIDUAL CARBONATES

The known carbonates are shown in [Figure 2.3](#).

2.3.1 BARIUM

The effect of the BaCO₃ transitions at 1079 and 1241 K on the calculated equilibrium pressure is virtually nil. The solid transitions ([Table 2.5](#)) of BaCO₃ exhibit pronounced hysteresis, i.e., different temperatures are obtained, depending on whether the transition is approached from above or from below.⁶ The melting point can only be measured under high CO₂ pressure. ΔH and ΔS for the transitions are taken from Chapter 1.3. Densities ([Table 2.6](#)) are only known for the solid. Thermodynamic functions for BaCO₃ and BaO and the equilibrium BaCO₃ = BaO + CO₂ are given in [Tables 2.7 to 2.9](#). The salt is evidently quite stable to 1200 K.

2.3.2 BERYLLIUM

Normal anhydrous BeCO₃ may not exist at ambient temperatures. Dehydration of the hydrate at elevated temperatures probably forms basic carbonates.¹⁰ The values of ΔH_f° for BeCO₃ are calculated from a measured value of ΔH for the reaction BeO + CO₂ = BeCO₃¹⁰ and the current value for BeO. The known thermodynamic values are summarized in [Table 2.10](#).

2.3.3 CADMIUM

The density ([Table 2.11](#)) must be regarded as very uncertain since there are no 20th century measurements, and De Schulten¹² reports a value of 4.960.

Thermodynamic data ([Tables 2.12 to 2.14](#)) indicate that the salt is unstable above 500 K.

The rate of decomposition has been measured as a function of CO₂ pressure by Centnerszwer and Brusz¹⁴ and Prodan and Pavlyuchenko.¹⁵ The decomposition yields CdO without the formation of intermediates. In vacuum the activation energy is 151 kJ. The rate of decomposition depends on the method of preparation. The kinetics follows the contracting sphere model.

2.3.4 CALCIUM

The aragonite–calcite transition has been studied as a function of temperature and pressure.^{16,17} At ambient pressure the transition occurs near 730 K.^{18,19} In addition, a transition from vaterite to calcite occurs in the range 620 to 670 K, with small impurity concentrations producing large changes in the transition temperature.¹⁹ This information is summarized in [Table 2.17](#). Thermodynamic data ([Tables 2.18 to 2.20](#)) indicate that CaCO₃ is stable to 1100–1200 K. The density is given in [Table 2.15](#), and the expansion coefficient of CaCO₃ in [Table 2.16](#).

2.3.5 CESIUM

The melting point of Cs₂CO₃ is 1065 K.²³ Transitions are listed in [Table 2.21](#). Very little is known of its decomposition, but the thermodynamic data ([Tables 2.22 to 2.24](#)) indicate considerable thermal stability.

2.3.6 COBALT

Experimental information on the thermal decomposition of CoCO₃ is scarce. A number of basic oxides have been reported,²⁴ but their existence cannot be regarded as proved. In a more recent

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | H | He | |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides **Ce Pr Nd** Pm **Sm Eu Gd** Tb Dy Ho Er Tm Yb Lu
Actinides Th Pa U Np **Pu** Am Cm Bk Cf Es Fm Md No Lw

FIGURE 2.3 The known carbonates: full square, existence known; half square, existence uncertain.

study²⁵ no intermediates were reported, but the decomposition pressure exhibited an unexplained break in the log p vs. 1/T plot.

In view of several density values in the 4.1 to 4.2 range (Table 2.25), the value of 2.818 for sferocobaltite given in [13] is probably in error.

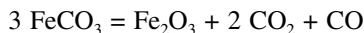
Thermodynamic data (Tables 2.26 to 2.28) indicate that CoCO_3 is unstable toward decomposition above 400 K.

2.3.7 COPPER

Little is known of CuCO_3 , but thermodynamic data have been published (Tables 2.29 to 2.31); however, they are based on extrapolations. The decomposition reaction (Table 2.31) is spontaneous from ambient temperature upward, but the salt may be stable for kinetic reasons.

2.3.8 IRON

Anhydrous FeCO_3 can be prepared by heating the 1/2 hydrate in CO_2 at high pressure (40 to 50 atm) to near 300°C. The thermal decomposition always leads to a higher-valent oxide, since the CO_2 liberated immediately oxidizes the FeO to Fe_2O_3 .²⁸ The reaction may also be written



The oxidation occurs so fast that even in vacuum no FeO is formed. Thermodynamic data that are available at 298 K are given in Table 2.34; density in Table 2.32. Data on the thermal expansion of FeCO_3 are given in Table 2.33.

2.3.9 LEAD

Several studies^{32–35} indicate that decomposition of PbCO_3 results in the formation of several oxycarbonates, but which ones are formed depends on the atmosphere — CO_2 and its pressure, air, or nitrogen — and temperature. The following intermediates have been reported: $\text{PbO} \cdot \text{PbCO}_3$, $3 \text{PbO} \cdot 5 \text{PbCO}_3$, $2 \text{PbO} \cdot \text{PbCO}_3$, and $3 \text{PbO} \cdot \text{PbCO}_3$.

Because of the variety of conditions employed, the reported equilibrium pressures and temperatures between the various oxycarbonates probably do not have much thermodynamic significance. Therefore, only thermodynamic parameters for decomposition to PbO have been listed (Tables 2.35

to 2.37). These thermodynamic results are consistent with experimental studies which indicate that decomposition occurs between 500 and 700 K.

Since there is so much disagreement about the intermediates formed, the kinetics measured by various workers can also not be considered reliable. Not only are the decomposition products not known reliably, but it has been reported that PbCO_3 specimens of different particle size decompose in different ways under identical conditions.

The density at ambient temperature has been reported as 6.533⁷ and 6.582.^{8a}

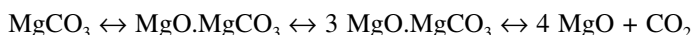
2.3.10 LITHIUM

The melting point of LiCO_3 is still uncertain. The measurements^{36,37} are considerably lower than the value of 1008 K given in Chapter 1.3, but differ from each other by 6 degrees. In both these studies the salt was protected from decomposition by being kept under a pressure of CO_2 high enough to prevent weight changes. ΔH_m given by Janz et al.³⁸ and Rolin and Recapet³⁹ differ by 7 kJ. These data are collected in Table 2.39. Density data are given in Table 2.38.

Equilibrium pressures of CO_2 above liquid Li_2CO_3 were measured by Janz and Lorenz,⁴⁰ using a dynamic method in which the temperature was varied until weight changes (losses on heating, gains on cooling) were noted. The resulting pressures were larger by several orders of magnitude than K values determined from thermodynamic data. This discrepancy can be accounted for by remembering that in a liquid decomposition P depends on liquid composition (see Chapter 1.2), and Li_2O certainly dissolves in the liquid salt. This also means that above the melting point, K values in Table 2.42 no longer equal partial pressures. Thermodynamic data are given in Tables 2.40 to 2.42.

2.3.11 MAGNESIUM

In vacuum, MgCO_3 decomposes to MgO at temperatures as low as 600 K, the solids exhibiting X-ray lines corresponding to MgCO_3 and MgO only.⁴¹ In an earlier work Centnerszwer and Bruzs⁴² reported the following equilibria:

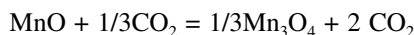


These equilibria are based entirely on pressure measurements and weight loss data. Until structural evidence for the existence of these compounds is produced, their existence must be regarded as doubtful.

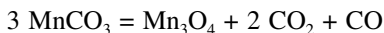
The decomposition follows “rapid nucleation and contracting sphere” kinetics with an activation energy of 150 kJ, somewhat higher than the enthalpy of decomposition.^{43–45} Densities are given in Table 2.43, thermal expansion coefficient in Table 2.44, and thermodynamic data in Tables 2.45 to 2.47. From data in Table 2.47, it is apparent that MgCO_3 is unstable above 700 K, in agreement with quoted experimental studies.

2.3.12 MANGANESE

The thermal decomposition of MnCO_3 is complicated by the easy interconvertability of the various manganese oxides. When MnCO_3 is decomposed in O_2 -containing atmospheres, the oxide formed depends on the temperature. In addition, a number of non-stoichiometric oxides are also formed,⁴⁶ the particular oxide formed depending primarily on the temperature and partial pressure of oxygen. In the absence of oxygen, the decomposition product is MnO , at least up to 600–700 K.⁴⁷ Above this temperature range MnO may be oxidized by the CO_2 formed according to Mahanty and Ray⁴⁸



The decomposition can thus also be thought of as



The actual temperature at which such transformations occur depends, therefore, on the efficiency of CO_2 removal and on the partial pressure of CO_2 . The thermodynamics of many reactions involving manganese compounds have been given by Mah.⁴⁹ The predominant mode of decomposition of MnCO_3 is $\text{MnCO}_3 = \text{MnO} + \text{CO}_2$. We have, therefore, given equilibrium constants for this reaction and for the reaction $3 \text{ MnCO}_3 = \text{Mn}_3\text{O}_4 + 2 \text{ CO}_2 + \text{CO}$. Thermodynamic functions for other oxides are listed in Mah and Coughlin.^{49,50} There are many studies of MnCO_3 decomposition, e.g., Lamure and Iltis and Mu and Perlmutter,^{52,53} but the results seem to depend largely on experimental conditions: atmosphere, temperature, and the condition of the carbonate. We have, therefore, included only the calculated thermodynamic results (Tables 2.49 to 2.51). For both reactions the calculated results show that decomposition becomes significant in the 700 to 800 K range, in agreement with experimental results. The kinetics follows the contracting sphere model.

The density at 294 K has been given as 3.125¹³ and 3.633²⁹ (Table 2.48).

2.3.13 MERCURY

2.3.13.1 HgCO_3

Most authors indicate that the compound does not exist, but contrary evidence has been presented by Erdoes⁸⁷ who gives dissociation pressures for the reaction



Thermodynamic data for the salt are given in Table 2.53, and for decomposition in Table 2.54. These indicate decomposition above 500 K.

2.3.13.2 Hg_2CO_3

This compound has been reported to be very sensitive to light and to decompose near 100°C.⁸⁸ Thermodynamic data for the salt are given in Table 2.55. Data for the decomposition (Table 2.56) are in approximate agreement with this.

2.3.14 NICKEL

Yellow and green forms of NiCO_3 have been reported, with densities of 4.36 and 4.395, but they may be identical. The salt decomposes directly to NiO , decomposition being complete at 300 K (Tables 2.57 to 2.59).⁵³

2.3.15 POTASSIUM

Transitions are listed in Table 2.61, densities in Table 2.60, and thermodynamic functions in Tables 2.63 to 2.65. The equilibrium calculations have been carried out for $\text{K}_2\text{CO}_3 = \text{K}_2\text{O}(\text{s}) + \text{CO}_2(\text{g})$, although both $\text{K}_2\text{O}(\text{g})$ and $\text{KO}(\text{g})$ have been reported to be minor constituents above decomposing K_2CO_3 .⁵⁴

2.3.16 RARE EARTHS

Although hydrates of rare earth carbonates at ambient temperature are well-known, their dehydration most likely leads to a series of basic carbonates. However, anhydrous carbonates of La, Ce, Pr, Nd, Sm, Eu, and Gd have been reported by Head and Holley,⁸⁹ who carefully decomposed the hydrates by TGA and removed the theoretical amounts of water.

2.3.17 RUBIDIUM

Very little information, aside from thermodynamic data, is available. These (Tables 2.65 to 2.67) indicate that the salt is stable even to 1500 K. The melting point is 1143 K.⁵⁶

2.3.18 SILVER

The thermal decomposition of Ag_2CO_3 is complicated by the fact that the decomposition product, Ag_2O , decomposes further ($\text{Ag}_2\text{O} = 2 \text{Ag} + 1/2 \text{O}_2$; for thermodynamic data see Otto⁵⁷). Therefore, weight loss experiments can only be carried out in a rather narrow temperature range, $< 520 \text{ K}$, where Ag_2CO_3 decomposes but Ag_2O does not. Alternatively, at higher temperatures the reaction can be followed by absorbing CO_2 and O_2 in separate traps and measuring their respective weight changes.

The kinetics are most consistent with a model of rapid nucleation followed by contracting sphere kinetics.⁵⁸ However, the actual rates are extremely dependent on the method of preparation. Kadlets and Dubinin³⁵ studied this effect by preparing Ag_2CO_3 using two different methods: one by precipitation from concentrated solutions which precipitated rapidly, the other by precipitation from very dilute solution so the salt first formed as a supersaturated solution. Although both preparations exhibited the same X-ray diffraction pattern, the second preparation decomposes much more rapidly than the first, an effect which the authors attribute to a higher defect density. Direct evidence is lacking, however. We have given data both for the decomposition of Ag_2CO_3 and of Ag_2O (Tables 2.68 to 2.71).

The density of the salt at ambient temperature has been reported as 6.077¹³ and 6.131⁵⁹ by X-ray diffraction.

2.3.19 SODIUM

The literature on the phase transitions of Na_2CO_3 is somewhat contradictory. The transitions at 629 and 759 K, but not the one at 891 K, were observed by Reisman,³⁷ as was the melting point. Two other transitions, at 593 and 723 K, were observed by Ginzburg⁶⁰ and Popov,⁶¹ and very similar values also by Jaffray and Martin.⁶² ΔH_m values of Janz et al.,⁵⁵ and Rolin and Recarpet³⁹ differ by 5 kJ; the average value has been listed in Table 2.73, as has all other information on transitions. According to Khlapova⁶³ who studied the polymorphism of Na_2CO_3 by DTA, the actual transition temperature will vary somewhat, depending on sample preparation and treatment, in some cases by 10 or 15 degrees. If this is so, solid–solid transitions would require careful reinvestigation.

Because the salt is stable well into the liquid range, reliable density values could be measured. These are listed in Table 2.72.

Decomposition pressures were measured by Janz and Lorenz,³⁶ but the same comments apply to them as were made for Li_2CO_3 . The difficulties encountered in measuring equilibrium pressures above the liquid salt by the effusion method have been described in great detail by Motzfeld.⁶⁴ He showed that above the melting point, CO_2 , Na(g) , and O_2 vaporize from the melt, but the activation energy for evaporation of CO_2 is quite high. Consequently, both the observed pressure and the steady-state composition of the melt depend on the size of the effusion orifice. In this work the pressures of these three gases have not been given, but they can be calculated from the data for the dissociation of the oxide given in Chase et al.⁶⁵ and the tables in this work. All of the thermodynamic data pertaining to the dissociation of Na_2CO_3 are given in Tables 2.74 to 2.76.

2.3.20 STRONTIUM

The decomposition of SrCO_3 resembles that of BaCO_3 . Wanmaker and Radielovic⁶⁶ studied the decomposition in air gravimetrically and reported that it commenced at 1120 K and ended at 1450 K. Up to 1220 K the decomposition rate was constant; at higher temperatures a change from zero-order to first-order kinetics occurred as the reaction proceeded beyond $\alpha = 0.5$. A kinetic study of

the effect of processing parameters between 1170 and 1270 K shows that the slow step is the diffusion of the reaction components to the product layer.⁶⁹

The density of the salt as strontianite at 298 K was reported as 3.736,⁵¹ and for the precipitated salt as 3.585.⁶⁷

Phase changes are given in Table 2.77, and thermodynamic data related to decomposition in Tables 2.78 to 2.80.

2.3.21 THALLIUM

There seem to be no high-temperature thermodynamic data for Tl_2CO_3 . Data for 298.15 K are given in Table 2.82

Transitions are listed in Table 2.81. The density at 298 K has been given as 7.11¹³ and as 7.23 from X-ray diffraction.⁷³

2.3.22 ZINC

The decomposition of ZnCO_3 has been studied by several authors. Huttig, Meller, and Lehman⁷⁵ used natural ZnCO_3 , smithsonite. Bretsnajder and Cibor⁷⁶ used synthetic material. In neither case was the material pure ZnCO_3 . There is also some indication that the decomposition is not entirely reversible.^{77,78} It is generally agreed that for most of the concentration range contracting sphere kinetics are followed, but the details of the induction period are not certain. Gedalla⁷⁹ analyzed the kinetics of heating curves obtained in air in terms of mechanism, but could not reach a definite conclusion. Various values have been reported for the activation energy, but it is not certain whether the value at zero pressure equals the reaction enthalpy. Thermodynamic data related to the decomposition are given in Tables 2.83 to 2.85.

Ambient temperature densities have been reported as 4.4,¹³ 4.348,⁷ and 4.333^{8a} for X-ray diffraction.

TABLE 2.1
Thermodynamic Data for $\text{CO}_2(\text{g})$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|---|------------|
| 298.15 | -393.51 | 213.77 | -457.24 | Barin 1993 |
| 400.00 | -389.45 | 225.44 | -479.62 | Barin 1993 |
| 500.00 | -385.03 | 235.28 | -502.67 | Barin 1993 |
| 600.00 | -380.35 | 243.81 | -526.63 | Barin 1993 |
| 700.00 | -375.46 | 251.34 | -551.40 | Barin 1993 |
| 800.00 | -370.41 | 258.08 | -576.88 | Barin 1993 |
| 900.00 | -365.23 | 264.19 | -602.99 | Barin 1993 |
| 1000.00 | -359.91 | 269.78 | -629.70 | Barin 1993 |
| 1100.00 | -354.49 | 274.95 | -656.94 | Barin 1993 |
| 1200.00 | -348.97 | 279.76 | -684.67 | Barin 1993 |
| 1300.00 | -343.35 | 284.25 | -712.88 | Barin 1993 |
| 1400.00 | -337.65 | 288.47 | -741.51 | Barin 1993 |
| 1500.00 | -331.88 | 292.46 | -770.56 | Barin 1993 |
| 1600.00 | -326.04 | 296.23 | -800.00 | Barin 1993 |
| 1700.00 | -320.13 | 299.81 | -829.80 | Barin 1993 |
| 1800.00 | -314.17 | 303.21 | -859.95 | Barin 1993 |
| 1900.00 | -308.16 | 306.46 | -890.44 | Barin 1993 |
| 2000.00 | -302.10 | 309.57 | -921.24 | Barin 1993 |
| 2100.00 | -296.01 | 312.54 | -952.35 | Barin 1993 |
| 2200.00 | -289.89 | 315.39 | -983.74 | Barin 1993 |
| 2300.00 | -283.75 | 318.12 | -1015.42 | Barin 1993 |
| 2400.00 | -277.58 | 320.74 | -1047.37 | Barin 1993 |

TABLE 2.2
Thermodynamic Data of CO(g)

| T K | ΔH_f° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔG_f° kJ mol⁻¹ | Reference |
|----------------------|--|---|--|------------------|
| 298.15 | -110.54 | 197.66 | -169.47 | Barin 1989 |
| 400.00 | -107.55 | 206.28 | -190.07 | Barin 1989 |
| 500.00 | -104.59 | 212.90 | -211.04 | Barin 1989 |
| 600.00 | -101.57 | 218.40 | -232.61 | Barin 1989 |
| 700.00 | -98.50 | 223.14 | -254.69 | Barin 1989 |
| 800.00 | -95.37 | 227.31 | -277.22 | Barin 1989 |
| 900.00 | -92.19 | 231.06 | -300.14 | Barin 1989 |
| 1000.00 | -88.95 | 234.47 | -323.42 | Barin 1989 |
| 1100.00 | -85.66 | 237.60 | -347.02 | Barin 1989 |
| 1200.00 | -82.33 | 240.51 | -370.91 | Barin 1989 |
| 1300.00 | -78.94 | 243.21 | -395.12 | Barin 1989 |
| 1400.00 | -75.52 | 245.75 | -419.57 | Barin 1989 |
| 1500.00 | -72.05 | 248.14 | -444.26 | Barin 1989 |
| 1600.00 | -68.55 | 250.40 | -469.19 | Barin 1989 |
| 1700.00 | -65.01 | 252.55 | -494.34 | Barin 1989 |
| 1800.00 | -61.44 | 254.59 | -519.70 | Barin 1989 |
| 1900.00 | -57.83 | 256.54 | -545.26 | Barin 1989 |
| 2000.00 | -54.21 | 258.40 | -571.00 | Barin 1989 |
| 2100.00 | -50.56 | 260.18 | -596.93 | Barin 1989 |
| 2200.00 | -46.88 | 261.89 | -623.04 | Barin 1989 |
| 2300.00 | -43.19 | 263.53 | -649.31 | Barin 1989 |
| 2400.00 | -39.49 | 265.11 | -675.74 | Barin 1989 |

TABLE 2.3
Thermodynamic Data of O₂(g)

| T K | ΔHf° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔGf° kJ mol⁻¹ | Reference |
|----------------------|---|---|---------------------------------|------------------|
| 298.15 | 0.00 | 205.15 | -61.17 | Barin 1993 |
| 400.00 | 3.06 | 213.96 | -82.53 | Barin 1993 |
| 500.00 | 6.21 | 220.96 | -104.28 | Barin 1993 |
| 600.00 | 9.44 | 226.87 | -126.68 | Barin 1993 |
| 700.00 | 12.74 | 231.95 | -149.63 | Barin 1993 |
| 800.00 | 16.09 | 236.42 | -173.05 | Barin 1993 |
| 900.00 | 19.45 | 240.42 | -196.90 | Barin 1993 |
| 1000.00 | 22.92 | 244.04 | -221.12 | Barin 1993 |
| 1100.00 | 26.39 | 247.35 | -245.70 | Barin 1993 |
| 1200.00 | 29.91 | 250.41 | -270.59 | Barin 1993 |
| 1300.00 | 33.45 | 253.25 | -295.77 | Barin 1993 |
| 1400.00 | 37.03 | 255.90 | -321.23 | Barin 1993 |
| 1500.00 | 40.65 | 258.39 | -346.95 | Barin 1993 |
| 1600.00 | 44.29 | 260.74 | -372.90 | Barin 1993 |
| 1700.00 | 47.96 | 262.97 | -399.09 | Barin 1993 |
| 1800.00 | 51.66 | 265.09 | -425.49 | Barin 1993 |
| 1900.00 | 55.39 | 267.10 | -452.10 | Barin 1993 |
| 2000.00 | 59.15 | 269.03 | -478.91 | Barin 1993 |
| 2100.00 | 62.93 | 270.87 | -505.91 | Barin 1993 |
| 2200.00 | 66.74 | 272.65 | -533.08 | Barin 1993 |
| 2300.00 | 70.56 | 274.35 | -560.43 | Barin 1993 |
| 2400.00 | 74.42 | 275.99 | -587.95 | Barin 1993 |

TABLE 2.4
 $\text{CO}_2(\text{g}) = \text{CO}(\text{g}) + \frac{1}{2} \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 282.96 | 86.47 | 257.18 | 8.682E – 046 |
| 400.00 | 283.42 | 87.82 | 248.29 | 3.745E – 033 |
| 500.00 | 283.55 | 88.11 | 239.49 | 9.513E – 026 |
| 600.00 | 283.50 | 88.02 | 230.68 | 8.233E – 021 |
| 700.00 | 283.33 | 87.77 | 221.89 | 2.759E – 017 |
| 800.00 | 283.09 | 87.45 | 213.13 | 1.210E – 014 |
| 900.00 | 282.78 | 87.08 | 204.41 | 1.367E – 012 |
| 1000.00 | 282.42 | 86.71 | 195.72 | 5.971E – 011 |
| 1100.00 | 282.03 | 86.33 | 187.06 | 1.307E – 009 |
| 1200.00 | 281.60 | 85.96 | 178.45 | 1.705E – 008 |
| 1300.00 | 281.14 | 85.59 | 169.87 | 1.492E – 007 |
| 1400.00 | 280.65 | 85.23 | 161.33 | 9.554E – 007 |
| 1500.00 | 280.15 | 84.88 | 152.83 | 4.761E – 006 |
| 1600.00 | 279.63 | 84.55 | 144.35 | 1.936E – 005 |
| 1700.00 | 279.10 | 84.23 | 135.92 | 6.660E – 005 |
| 1800.00 | 278.56 | 83.92 | 127.51 | 1.993E – 004 |
| 1900.00 | 278.02 | 83.63 | 119.13 | 5.304E – 004 |
| 2000.00 | 277.47 | 83.34 | 110.78 | 1.278E – 003 |
| 2100.00 | 276.92 | 83.08 | 102.46 | 2.826E – 003 |
| 2200.00 | 276.38 | 82.82 | 94.17 | 5.808E – 003 |
| 2300.00 | 275.84 | 82.58 | 85.90 | 1.120E – 002 |
| 2400.00 | 275.30 | 82.36 | 77.65 | 2.041E – 002 |

TABLE 2.5
Transitions of BaCO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--|------|-------------------|----------------------|-----------|
| c, orthorhombic(γ) → | 1076 | 14.9 | 13.7 | 1.3 |
| c, hexagonal(β) ← c, ortho- rhombic | 1023 | | | 6 |
| c, hexagonal → c, cubic(α) | 1249 | 3.0 | | 6 |
| c, hexagonal(β) ← c, cubic | 1229 | | | |
| c(α) → l | 1653 | | | 1.3 |

TABLE 2.6
Density of BaCO₃

| Phase | T(K) | d | Reference |
|---------------|------|---------------|-----------|
| c | 293 | 4.287 | 7 |
| c (witherite) | 299 | 4.308 (X-ray) | 8a |
| c (cubic) | 1348 | 3.889 (X-ray) | 8c |

TABLE 2.7
Thermodynamic Data of BaCO₃

| T K | ΔHf° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔGf° kJ mol⁻¹ | Reference |
|----------------------|---|---|---------------------------------|------------------|
| 298.15 | -1216.29 | 112.13 | -1249.72 | Barin 1993 |
| 400.00 | -1206.89 | 139.15 | -1262.55 | Barin 1989 |
| 500.00 | -1196.66 | 161.96 | -1277.64 | Barin 1989 |
| 600.00 | -1185.65 | 182.00 | -1294.85 | Barin 1989 |
| 700.00 | -1173.99 | 199.97 | -1313.97 | Barin 1989 |
| 800.00 | -1161.71 | 216.36 | -1334.80 | Barin 1989 |
| 900.00 | -1148.85 | 231.50 | -1357.20 | Barin 1989 |
| 1000.00 | -1135.42 | 245.65 | -1381.06 | Barin 1989 |
| 1100.00 | -1103.60 | 275.49 | -1406.64 | Barin 1989 |
| 1200.00 | -1088.12 | 288.96 | -1434.88 | Barin 1989 |
| 1300.00 | -1069.02 | 304.26 | -1464.56 | Barin 1989 |
| 1400.00 | -1052.70 | 316.36 | -1495.60 | Barin 1989 |
| 1500.00 | -1036.38 | 327.61 | -1527.80 | Barin 1989 |

TABLE 2.8
Thermodynamic Data of BaO

| T K | ΔHf° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔGf° kJ mol⁻¹ | Reference |
|----------------------|---|---|---------------------------------|------------------|
| 298.15 | -553.54 | 70.29 | -574.50 | Barin 1993 |
| 400.00 | -548.57 | 84.62 | -582.42 | Barin 1993 |
| 500.00 | -543.47 | 96.00 | -591.47 | Barin 1993 |
| 600.00 | -538.21 | 105.58 | -601.56 | Barin 1993 |
| 700.00 | -532.83 | 113.87 | -612.54 | Barin 1993 |
| 800.00 | -527.35 | 121.19 | -624.30 | Barin 1993 |
| 900.00 | -521.77 | 127.76 | -636.75 | Barin 1993 |
| 1000.00 | -516.11 | 133.72 | -649.83 | Barin 1993 |
| 1100.00 | -510.36 | 139.20 | -663.48 | Barin 1993 |
| 1200.00 | -504.53 | 144.28 | -677.66 | Barin 1993 |
| 1300.00 | -498.62 | 149.01 | -692.32 | Barin 1993 |
| 1400.00 | -492.63 | 153.44 | -707.45 | Barin 1993 |
| 1500.00 | -486.56 | 157.62 | -723.00 | Barin 1993 |

TABLE 2.9



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 269.24 | 171.93 | 217.98 | 6.421E – 039 |
| 400.00 | 268.88 | 170.91 | 200.51 | 6.506E – 027 |
| 500.00 | 268.16 | 169.32 | 183.50 | 6.734E – 020 |
| 600.00 | 267.10 | 167.39 | 166.66 | 3.087E – 015 |
| 700.00 | 265.69 | 165.23 | 150.03 | 6.364E – 012 |
| 800.00 | 263.95 | 162.90 | 133.62 | 1.882E – 009 |
| 900.00 | 261.85 | 160.44 | 117.45 | 1.523E – 007 |
| 1000.00 | 259.40 | 157.86 | 101.54 | 4.963E – 006 |
| 1100.00 | 238.76 | 138.66 | 86.23 | 8.035E – 005 |
| 1200.00 | 234.63 | 135.07 | 72.55 | 6.949E – 004 |
| 1300.00 | 227.05 | 128.99 | 59.36 | 4.118E – 003 |
| 1400.00 | 222.42 | 125.56 | 46.64 | 1.819E – 002 |
| 1500.00 | 217.93 | 122.46 | 34.24 | 6.422E – 002 |

TABLE 2.10

Thermodynamic Data of BeCO₃

| | ΔH (kJ mol ⁻¹) | Reference | ΔS (J mol ⁻¹ deg ⁻¹) | Reference |
|-------------------|------------------------------------|-----------|---|-----------|
| BeCO ₃ | -102.5 | 1.2 | — | |
| BeO | -606.09 | 1.2 | 14.15 | 1.2 |

TABLE 2.11

Density of CdCO₃

| Phase | T(K) | d | Reference |
|-------|------|--------------------------|-----------|
| c | 293 | 4.259 g ml ⁻¹ | 13 |

TABLE 2.12

Thermodynamic Data of CdCO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|---|-------------------|
| 298.15 | -751.87 | 92.47 | -779.43 | Barin et al. 1977 |
| 400.00 | -742.79 | 118.55 | -790.21 | Barin et al. 1977 |
| 500.00 | -732.55 | 141.35 | -803.23 | Barin et al. 1977 |
| 600.00 | -720.99 | 162.39 | -818.42 | Barin et al. 1977 |
| 700.00 | -708.11 | 182.21 | -835.66 | Barin et al. 1977 |
| 800.00 | -693.92 | 201.14 | -854.84 | Barin et al. 1977 |
| 900.00 | -678.41 | 219.40 | -875.87 | Barin et al. 1977 |
| 1000.00 | -661.58 | 237.12 | -898.70 | Barin et al. 1977 |

TABLE 2.13
Thermodynamic Data of CdO

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|---|-------------------|
| 298.15 | -258.99 | 54.81 | -275.33 | Barin et al. 1977 |
| 400.00 | -254.37 | 68.12 | -281.62 | Barin et al. 1977 |
| 500.00 | -249.60 | 78.75 | -288.98 | Barin et al. 1977 |
| 600.00 | -244.69 | 87.70 | -297.31 | Barin et al. 1977 |
| 700.00 | -239.67 | 95.46 | -306.48 | Barin et al. 1977 |
| 800.00 | -234.55 | 102.28 | -316.37 | Barin et al. 1977 |
| 900.00 | -229.35 | 108.40 | -326.91 | Barin et al. 1977 |
| 1000.00 | -224.08 | 113.96 | -338.03 | Barin et al. 1977 |

TABLE 2.14
CdCO₃ = CdO + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 99.37 | 176.11 | 46.86 | 6.156E - 009 |
| 400.00 | 98.97 | 175.00 | 28.97 | 1.645E - 004 |
| 500.00 | 97.92 | 176.68 | 11.58 | 6.172E - 002 |
| 600.00 | 95.96 | 169.13 | -5.52 | 3.025E + 002 |
| 700.00 | 92.99 | 164.57 | -22.21 | 4.548E + 001 |
| 800.00 | 88.96 | 159.21 | -38.41 | 3.222E + 002 |
| 900.00 | 83.83 | 153.19 | -54.03 | 1.369E + 003 |
| 1000.00 | 77.59 | 146.62 | -69.03 | 4.036E + 003 |

TABLE 2.15
Density of CaCO₃

| Phase | T(K) | d | Reference |
|--------------|------|--------------------------|-----------|
| c, calcite | 273 | 2.771 g ml ⁻¹ | 13 |
| c, calcite | 298 | 2.713 | 7 |
| c, calcite | 299 | 2.711 (X-ray) | 8 |
| c, aragonite | 297 | 2.930 | 7 |

TABLE 2.16
Thermal Expansion Coefficient of CaCO₃

| | |
|-----------|--|
| Calcite | $\alpha(2^\circ \text{ to } 81^\circ) = 25.1353 + 0.0118c \text{ opt. axis}$ and $-5.5782t + 0.00138t \perp \text{ opt. axis}$ $\alpha^{40} = 26.21 + 0.160(t - 40)$ opt. axis; and = -5.40 $0.0087(t - 40), \perp \text{ opt. axis}$ $\alpha(50^\circ \text{ to } 60^\circ) = 1.447$ |
| Aragonite | $\alpha^1 = 34.60 + 0.0337t$ $20^\circ - 70^\circ \alpha_2 = 17.19 + 0.0368t$ $\alpha_3 = 10.16 + 0.0064t$ |

TABLE 2.17
Transitions of CaCO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|-----------------------------|---------|-------------------|----------------------|-----------|
| c (aragonite) → c (calcite) | 728 | | | 18 |
| c (vaterite) → c (calcite) | 623–673 | | | 19 |

TABLE 2.18
Thermodynamic Data of CaCO₃ (calcite)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|---|------------|
| 298.15 | -1206.92 | 92.90 | -1234.62 | Barin 1993 |
| 400.00 | -1197.65 | 119.55 | -1245.47 | Barin 1993 |
| 500.00 | -104.55 | 142.07 | -1258.58 | Barin 1993 |
| 600.00 | -1176.82 | 161.62 | -1273.79 | Barin 1993 |
| 700.00 | -1165.61 | 178.88 | -1290.83 | Barin 1993 |
| 800.00 | -1154.01 | 194.37 | -1309.50 | Barin 1993 |
| 900.00 | -1142.05 | 208.46 | -1329.66 | Barin 1993 |
| 1000.00 | -1129.76 | 221.49 | -1351.16 | Barin 1993 |
| 1100.00 | -1117.15 | 233.41 | -1373.91 | Barin 1993 |
| 1200.00 | -1104.25 | 244.64 | -1397.81 | Barin 1993 |
| 1300.00 | -1091.05 | 255.20 | -1422.81 | Barin 1993 |
| 1400.00 | -1077.56 | 265.20 | -1448.83 | Barin 1993 |
| 1500.00 | -1063.79 | 274.70 | -1475.83 | Barin 1993 |

TABLE 2.19
Thermodynamic Data of CaO

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|---|------------|
| 298.15 | -635.09 | 38.07 | -646.44 | Barin 1993 |
| 400.00 | -630.47 | 51.38 | -651.02 | Barin 1993 |
| 500.00 | -625.65 | 62.12 | -656.71 | Barin 1993 |
| 600.00 | -620.67 | 71.20 | -663.39 | Barin 1993 |
| 700.00 | -615.58 | 79.04 | -670.91 | Barin 1993 |
| 800.00 | -610.40 | 85.96 | -679.17 | Barin 1993 |
| 900.00 | -605.15 | 92.14 | -688.08 | Barin 1993 |
| 1000.00 | -599.84 | 97.74 | -697.58 | Barin 1993 |
| 1100.00 | -594.47 | 102.86 | -707.61 | Barin 1993 |
| 1200.00 | -589.04 | 107.58 | -718.13 | Barin 1993 |
| 1300.00 | -583.55 | 111.97 | -729.11 | Barin 1993 |
| 1400.00 | -578.20 | 116.07 | -740.52 | Barin 1993 |
| 1500.00 | -572.43 | 119.92 | -752.32 | Barin 1993 |

TABLE 2.20
CaCO₃ = CaO + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|--------|-------------------------|--------|--------------|
| 298.15 | 178.33 | 158.94 | 130.94 | 1.143E – 023 |
| 400.00 | 177.74 | 157.27 | 114.83 | 1.008E – 015 |
| 500.00 | 176.87 | 155.33 | 99.20 | 4.323E – 011 |
| 600.00 | 175.80 | 153.39 | 83.76 | 5.095E – 008 |
| 700.00 | 174.57 | 151.50 | 68.52 | 7.701E – 006 |
| 800.00 | 173.19 | 149.66 | 53.46 | 3.228E – 004 |
| 900.00 | 171.67 | 147.87 | 38.59 | 5.759E – 003 |
| 1000.00 | 170.01 | 146.12 | 23.89 | 5.651E – 002 |
| 1100.00 | 168.20 | 144.40 | 9.36 | 3.593E – 001 |
| 1200.00 | 166.25 | 142.70 | –4.99 | 1.65E + 000 |
| 1300.00 | 164.15 | 141.02 | –19.18 | 5.898E + 000 |
| 1400.00 | 161.89 | 139.35 | –33.20 | 1.733E + 001 |
| 1500.00 | 159.47 | 137.68 | –47.05 | 4.350E + 000 |

TABLE 2.21
Transitions of Cs₂CO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------|------|-----------|--------------|-----------|
| c → l | 1065 | | | 23 |

TABLE 2.22
Thermodynamic Data of Cs₂CO₃

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|------------------------------|---|---------------------------|-------------------|
| 298.15 | –1147.25 | 204.47 | –1208.22 | Barin et al. 1977 |
| 400.00 | –1133.97 | 242.72 | –1231.05 | Barin et al. 1977 |
| 500.00 | –1119.85 | 274.18 | –1256.94 | Barin et al. 1977 |
| 600.00 | –1104.86 | 301.48 | –1285.75 | Barin et al. 1977 |
| 700.00 | –1089.07 | 325.81 | –1317.14 | Barin et al. 1977 |
| 800.00 | –1072.52 | 347.89 | –1350.84 | Barin et al. 1977 |
| 900.00 | –1055.24 | 368.24 | –1386.66 | Barin et al. 1977 |
| 1000.00 | –1037.23 | 387.21 | –1424.44 | Barin et al. 1977 |
| 1100.00 | –1018.51 | 405.05 | –1464.06 | Barin et al. 1977 |
| 1200.00 | –999.07 | 421.95 | –1505.41 | Barin et al. 1977 |
| 1300.00 | –978.94 | 438.07 | –1548.43 | Barin et al. 1977 |
| 1400.00 | –958.09 | 453.51 | –1593.01 | Barin et al. 1977 |
| 1500.00 | –936.55 | 468.38 | –1639.11 | Barin et al. 1977 |

TABLE 2.23
Thermodynamic Data of Cs₂O

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -345.98 | 146.86 | -389.76 | Knacke et al. 1991 |
| 400.00 | -338.06 | 169.67 | -405.93 | Knacke et al. 1991 |
| 500.00 | -329.95 | 187.75 | -423.83 | Knacke et al. 1991 |
| 600.00 | -321.51 | 203.14 | -443.39 | Knacke et al. 1991 |
| 700.00 | -312.73 | 216.66 | -464.39 | Knacke et al. 1991 |
| 800.00 | -303.63 | 228.81 | -486.68 | Knacke et al. 1991 |
| 900.00 | -294.19 | 239.92 | -510.12 | Knacke et al. 1991 |
| 1000.00 | -284.42 | 250.21 | -534.63 | Knacke et al. 1991 |
| 1100.00 | -274.33 | 259.83 | -560.14 | Knacke et al. 1991 |
| 1200.00 | -263.90 | 268.90 | -586.58 | Knacke et al. 1991 |
| 1300.00 | -253.15 | 277.51 | -613.90 | Knacke et al. 1991 |
| 1400.00 | -242.06 | 285.72 | -642.07 | Knacke et al. 1991 |
| 1500.00 | -230.64 | 285.72 | -671.04 | Knacke et al. 1991 |

TABLE 2.24
Cs₂CO₃ = Cs₂O + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | -407.77 | 156.16 | -361.22 | 5.144E - 064 |
| 400.00 | -406.46 | 152.39 | -345.50 | 7.553E - 046 |
| 500.00 | -404.87 | 148.85 | -330.44 | 2.992E - 035 |
| 600.00 | -403.01 | 145.46 | -315.73 | 3.245E - 028 |
| 700.00 | -400.88 | 142.19 | -301.35 | 3.246E - 023 |
| 800.00 | -398.48 | 139.00 | -287.29 | 1.740E - 019 |
| 900.00 | -395.82 | 135.87 | -273.55 | 1.326E - 016 |
| 1000.00 | -392.89 | 132.78 | -260.11 | 2.582E - 014 |
| 1100.00 | -389.69 | 129.73 | -246.99 | 1.865E - 012 |
| 1200.00 | -386.21 | 126.70 | -234.17 | 6.400E - 011 |
| 1300.00 | -382.44 | 123.69 | -221.65 | 1.240E - 009 |
| 1400.00 | -378.38 | 120.68 | -209.43 | 1.533E - 008 |
| 1500.00 | -374.03 | 117.68 | -197.51 | 1.323E - 007 |

TABLE 2.25
Density of CoCO₃

| Phase | T(K) | d | Reference |
|---------------------|------|---------------|-----------|
| c | | 4.07 | 26 |
| c | | 4.24 (X-ray) | 27 |
| c (spherocobaltite) | 299 | 4.214 (X-ray) | 8 |

TABLE 2.26
Thermodynamic Data of CoCO_3

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------------|
| 298.15 | -713.00 | 87.86 | -739.29 | Barin et al. 1977 |
| 400.00 | -704.12 | 113.40 | -749.48 | Barin et al. 1977 |
| 500.00 | -694.40 | 135.06 | -761.93 | Barin et al. 1977 |
| 600.00 | -683.99 | 154.02 | -775.40 | Barin et al. 1977 |
| 700.00 | -673.02 | 170.92 | -792.66 | Barin et al. 1977 |
| 800.00 | -661.55 | 186.23 | -810.53 | Barin et al. 1977 |
| 900.00 | -649.62 | 200.27 | -829.86 | Barin et al. 1977 |
| 1000.00 | -637.26 | 213.30 | -850.55 | Barin et al. 1977 |
| 1100.00 | -624.46 | 225.48 | -872.50 | Barin et al. 1977 |
| 1200.00 | -611.25 | 236.97 | -895.62 | Barin et al. 1977 |

TABLE 2.27
Thermodynamic Data of CoO

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -237.94 | 52.97 | -253.74 | Barin 1989 |
| 400.00 | -232.42 | 68.93 | -259.99 | Barin 1989 |
| 500.00 | -227.04 | 80.92 | -267.50 | Barin 1989 |
| 600.00 | -221.67 | 90.71 | -276.10 | Barin 1989 |
| 700.00 | -216.27 | 99.04 | -285.60 | Barin 1989 |
| 800.00 | -210.82 | 106.31 | -295.87 | Barin 1989 |
| 900.00 | -205.31 | 112.80 | -306.83 | Barin 1989 |
| 1000.00 | -199.73 | 116.68 | -318.41 | Barin 1989 |
| 1100.00 | -194.07 | 124.08 | -330.55 | Barin 1989 |
| 1200.00 | -188.31 | 129.09 | -343.21 | Barin 1989 |

TABLE 2.28
 $\text{CoCO}_3 = \text{CoO} + \text{CO}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 81.55 | 178.87 | 28.22 | 1.137E - 005 |
| 400.00 | 82.26 | 180.97 | 9.87 | 5.143E - 002 |
| 500.00 | 82.323 | 181.14 | -8.25 | 7.271E + 000 |
| 600.00 | 81.97 | 180.51 | -26.33 | 1.962E + 002 |
| 700.00 | 81.28 | 179.46 | -44.33 | 2.035E + 003 |
| 800.00 | 80.31 | 178.16 | -62.22 | 1.155E + 004 |
| 900.00 | 79.08 | 176.72 | -79.96 | 4.377E + 004 |
| 1000.00 | 77.61 | 175.17 | -97.56 | 1.248E + 005 |
| 1100.00 | 75.91 | 173.54 | -114.99 | 2.890E + 005 |
| 1200.00 | 73.98 | 171.87 | -132.26 | 5.724E + 005 |

TABLE 2.29
Thermodynamic Data of CuCO₃

| T K | Hf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|--------------------------|---|------------------------------|-------------------|
| 298.15 | -596.22 | 87.86 | -622.42 | Barin et al. 1977 |
| 400.00 | -587.00 | 114.38 | -632.75 | Barin et al. 1977 |
| 500.00 | -576.94 | 136.79 | -645.34 | Barin et al. 1977 |
| 600.00 | -566.20 | 156.36 | -660.01 | Barin et al. 1977 |
| 700.00 | -554.89 | 173.78 | -676.54 | Barin et al. 1977 |
| 800.00 | -543.09 | 189.53 | -694.71 | Barin et al. 1977 |
| 900.00 | -530.83 | 203.97 | -714.40 | Barin et al. 1977 |
| 1000.00 | -518.13 | 217.35 | -735.47 | Barin et al. 1977 |

TABLE 2.30
Thermodynamic Data of CuO

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|------------------------------|---|------------------------------|--------------------|
| 298.15 | -156.06 | 42.59 | -168.76 | Knacke et al. 1991 |
| 400.00 | -151.50 | 55.73 | -173.79 | Knacke et al. 1991 |
| 500.00 | -146.69 | 66.46 | -179.92 | Knacke et al. 1991 |
| 600.00 | -141.67 | 75.59 | -187.03 | Knacke et al. 1991 |
| 700.00 | -136.51 | 83.55 | -195.00 | Knacke et al. 1991 |
| 800.00 | -131.23 | 90.60 | -203.71 | Knacke et al. 1991 |
| 900.00 | -125.85 | 96.94 | -213.09 | Knacke et al. 1991 |
| 1000.00 | -120.37 | 102.72 | -223.08 | Knacke et al. 1991 |

TABLE 2.31
CuCO₃ = Cu + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|--------|-------------------------|---------|--------------|
| 298.15 | 46.65 | 168.50 | -3.59 | 4.249E + 000 |
| 400.00 | 46.05 | 166.79 | -20.66 | 4.994E + 002 |
| 500.00 | 45.22 | 164.95 | -37.25 | 7.794E + 003 |
| 600.00 | 44.18 | 163.04 | -53.65 | 4.688E + 004 |
| 700.00 | 42.92 | 161.11 | -69.86 | 1.634E + 005 |
| 800.00 | 41.45 | 159.14 | -85.87 | 4.048E + 005 |
| 900.00 | 39.76 | 157.16 | -101.69 | 7.983E + 005 |
| 1000.00 | 37.85 | 155.15 | -117.30 | 1.342E + 006 |

TABLE 2.32
Density of FeCO₃

| Phase | T(K) | d | Reference |
|-------------|-------|-------|-----------|
| c, siderite | 293.9 | 0.851 | 29 |

TABLE 2.33
Thermal Expansion Coefficient of FeCO₃

| | | Reference |
|------------------------------|--|-----------|
| FeCO ₃ , siderite | $\alpha^{40} = 19.2$ with $\Delta(20^\circ - 70^\circ) = 25.5$ and $\alpha^{40} = 6.05$ with 13 $\Delta(20^\circ - 70^\circ) = 917\text{L}$ | 13 |

TABLE 2.34
Thermodynamic Data of FeCO₃ (298.15K)

| | $\Delta H_f^\circ \text{ kJ mol}^{-1}$ | Reference | $S^\circ \text{ J mol}^{-1} \text{ deg}^{-1}$ | Reference |
|--------------------------------|--|-----------|---|-----------|
| FeCO ₃ | -740.6 | 1.2 | 92.9 | 30 |
| FeO | -266.5 | 1.2 | 57.49 | 31 |
| Fe ₃ O ₄ | -1117. | 30 | 146.4 | 31 |
| Fe ₂ O ₃ | -822.1 | 30 | 87.4 | 31 |

TABLE 2.35
Thermodynamic Data of PbCO₃

| T K | ΔH_f° kJ mol ⁻¹ | $S^\circ \text{ J mol}^{-1}$ deg ⁻¹ | $\Delta G_f^\circ \text{ kJ mol}^{-1}$ | Reference |
|---------|--|---|--|------------|
| 298.15 | -699.10 | 131.00 | -738.16 | Barin 1993 |
| 400.00 | -689.58 | 158.39 | -752.93 | Barin 1993 |
| 500.00 | -679.02 | 181.90 | -769.97 | Barin 1993 |
| 600.00 | -667.27 | 203.29 | -789.24 | Barin 1993 |
| 700.00 | 654.32 | 223.23 | -810.58 | Barin 1993 |
| 800.00 | 640.17 | 242.11 | -833.85 | Barin 1993 |
| 900.00 | 624.83 | 260.16 | -858.97 | Barin 1993 |
| 1000.00 | 608.29 | 277.58 | -885.87 | Barin 1993 |

TABLE 2.36
Thermodynamic Data of PbO

| T K | ΔH_f° kJ mol ⁻¹ | $S^\circ \text{ J mol}^{-1}$ deg ⁻¹ | $\Delta G_f^\circ \text{ kJ mol}^{-1}$ | Reference |
|---------|--|---|--|------------|
| 298.15 | -218.06 | 68.70 | -238.55 | Barin 1993 |
| 400.00 | -213.25 | 82.57 | -246.28 | Barin 1993 |
| 500.00 | -208.30 | 93.61 | -255.10 | Barin 1993 |
| 600.00 | -203.17 | 102.96 | -264.94 | Barin 1993 |
| 700.00 | -197.88 | 111.10 | -275.65 | Barin 1993 |
| 800.00 | -192.45 | 118.36 | -287.13 | Barin 1993 |
| 900.00 | -186.88 | 124.92 | -299.30 | Barin 1993 |
| 1000.00 | -181.17 | 130.93 | -312.10 | Barin 1993 |

TABLE 2.37
PbCO₃ = PbO + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|--------|-------------------------|--------|--------------|
| 298.15 | 87.53 | 151.47 | 42.37 | 3.766E – 008 |
| 400.00 | 86.88 | 149.62 | 27.04 | 2.946E – 004 |
| 500.00 | 85.69 | 146.99 | 12.20 | 5.316E – 002 |
| 600.00 | 83.75 | 143.48 | –2.332 | 1.596E + 000 |
| 700.00 | 80.98 | 139.21 | –16.47 | 1.695E + 001 |
| 800.00 | 77.31 | 134.35 | –30.15 | 9.311E + 001 |
| 900.00 | 72.73 | 128.94 | –43.32 | 3.270E + 002 |
| 1000.00 | 67.21 | 123.13 | –55.93 | 8.349E + 002 |

TABLE 2.38
Density of LiCO₃

| Phase | T(K) | d | Reference |
|-------|--------|--------|-----------|
| c | 290.7 | 2.111 | 13 |
| l | 1012.2 | 1.8246 | 40 |
| | 1027.4 | 1.8189 | |
| | 1029.7 | 1.8190 | |
| | 1052.1 | 1.8119 | |
| | 1069.7 | 1.8036 | |
| | 1082.7 | 1.7987 | |
| | 1105.1 | 1.9710 | |
| | 1120.1 | 1.7843 | |

TABLE 2.39
Transitions of LiCO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol°K) | Reference |
|--------------|------|-----------|--------------|-----------|
| c → l | 993 | | | 13 |
| | 999 | 42 | | 40 |
| | 1008 | | | 13 |

TABLE 2.40
Thermodynamic Data of Li_2CO_3

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1216.04 | 90.17 | -1242.92 | Barin 1989 |
| 400.00 | -1205.41 | 120.71 | -1253.70 | Barin 1989 |
| 500.00 | -1193.38 | 147.49 | -1267.13 | Barin 1989 |
| 600.00 | -1179.50 | 172.74 | -1283.15 | Barin 1989 |
| 700.00 | -1162.89 | 198.123 | -1301.65 | Barin 1989 |
| 800.00 | -1147.90 | 218.22 | -1322.48 | Barin 1989 |
| 900.00 | -1131.10 | 237.99 | -1345.29 | Barin 1989 |
| 1000.00 | -1067.79 | 302.59 | -1370.78 | Barin 1989 |
| 1100.00 | -1049.24 | 320.27 | -1401.54 | Barin 1989 |
| 1200.00 | -1030.70 | 336.40 | -1434.38 | Barin 1993 |
| 1300.00 | -1012.16 | 351.25 | -1468.78 | Barin 1989 |
| 1400.00 | -993.61 | 364.99 | -1504.60 | Barin 1989 |
| 1500.00 | -975.07 | 377.78 | -1541.74 | Barin 1989 |

TABLE 2.41
Thermodynamic Data of Li_2O

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -598.73 | 37.89 | -610.03 | Barin 1993 |
| 400.00 | -592.64 | 55.40 | -614.79 | Barin 1993 |
| 500.00 | -585.83 | 70.57 | -621.11 | Barin 1993 |
| 600.00 | -578.52 | 83.87 | -628.84 | Barin 1993 |
| 700.00 | -570.85 | 95.68 | -637.83 | Barin 1993 |
| 800.00 | -562.90 | 106.31 | -647.94 | Barin 1993 |
| 900.00 | -554.69 | 115.97 | -659.06 | Barin 1993 |
| 1000.00 | -546.24 | 124.87 | -671.11 | Barin 1993 |
| 1100.00 | -537.58 | 133.12 | -684.02 | Barin 1993 |
| 1200.00 | -528.72 | 140.83 | -697.72 | Barin 1993 |
| 1300.00 | -519.65 | 148.09 | -712.17 | Barin 1993 |
| 1400.00 | -510.38 | 154.96 | -727.32 | Barin 1993 |
| 1500.00 | -500.93 | 161.48 | -743.15 | Barin 1993 |

TABLE 2.42
 $\text{Li}_2\text{CO}_3 = \text{Li}_2\text{O} + \text{CO}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 223.80 | 161.49 | 175.66 | 1.673E – 031 |
| 400.00 | 223.33 | 160.12 | 159.28 | 1.578E – 021 |
| 500.00 | 222.52 | 158.35 | 143.35 | 1.055E – 015 |
| 600.00 | 220.63 | 154.94 | 127.67 | 7.667E – 012 |
| 700.00 | 216.58 | 148.80 | 112.42 | 4.077E – 009 |
| 800.00 | 214.59 | 146.16 | 97.66 | 4.197E – 007 |
| 900.00 | 211.19 | 142.17 | 83.23 | 1.475E – 005 |
| 1000.00 | 161.63 | 92.06 | 69.58 | 2.320E – 004 |
| 1100.00 | 157.17 | 87.80 | 60.59 | 1.326E – 003 |
| 1200.00 | 153. 02 | 84.19 | 51.99 | 5.452E – 003 |
| 1300.00 | 149.16 | 81.09 | 43.73 | 1.748E – 002 |
| 1400.00 | 145.58 | 78.44 | 35.76 | 4.630E – 002 |
| 1500.00 | 142.26 | 76.15 | 28.04 | 1.056E – 001 |

TABLE 2.43
Density of MgCO_3

| Phase | T(K) | d | Reference |
|-------|-------|---------------|-----------|
| c | 294.6 | 2.980 | 29 |
| c | 298.0 | 3.037 | 13 |
| c | 298.0 | 3.009 (X-ray) | 86 |

TABLE 2.44
Thermal Expansion Coefficient of MgCO_3

| | |
|-----------------------------|--|
| MgCO_3 , magnesite | $\alpha^{40} = 21.3$ with $\Delta(20^\circ - 70^\circ)$ $= 33.9 $ and $\alpha^{40} = 5.99$ with $\Delta(20^\circ - 70^\circ) = 24.3\perp$ |
|-----------------------------|--|

TABLE 2.45
Thermodynamic Data of MgCO_3

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | 1095.80 | 65.70 | –1115.39 | Knacke et al. 1991 |
| 400.00 | –1087.30 | 90.13 | –1123.35 | Knacke et al. 1991 |
| 500.00 | –1077.78 | 111.33 | –1133.44 | Knacke et al. 1991 |
| 600.00 | –1067.39 | 130.24 | –1145.54 | Knacke et al. 1991 |
| 700.00 | –1056.26 | 147.38 | –1159.43 | Knacke et al. 1991 |
| 800.00 | –1044.45 | 163.14 | –1174.97 | Knacke et al. 1991 |
| 900.00 | –1032.00 | 177.81 | –1192.02 | Knacke et al. 1991 |
| 1000.00 | –1018.91 | 191.58 | –1210.50 | Knacke et al. 1991 |

TABLE 2.46
Thermodynamic Data of MgO (periclase)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -601.24 | 26.92 | -609.27 | Knacke et al. 1991 |
| 400.00 | -597.13 | 38.73 | -612.63 | Knacke et al. 1991 |
| 500.00 | -592.69 | 48.64 | -617.01 | Knacke et al. 1991 |
| 600.00 | -588.02 | 57.15 | -622.31 | Knacke et al. 1991 |
| 700.00 | -583.21 | 64.57 | -628.40 | Knacke et al. 1991 |
| 800.00 | -578.29 | 71.14 | -635.19 | Knacke et al. 1991 |
| 900.00 | -573.28 | 77.03 | -642.61 | Knacke et al. 1991 |
| 1000.00 | -568.20 | 82.38 | -650.58 | Knacke et al. 1991 |

TABLE 2.47
MgCO₃ = MgO + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 101.05 | 174.99 | 48.88 | 2.729E - 009 |
| 400.00 | 100.72 | 174.05 | 31.10 | 8.682E - 005 |
| 500.00 | 100.06 | 172.59 | 13.76 | 3.648E - 002 |
| 600.00 | 99.02 | 170.72 | -3.41 | 1.979E + 000 |
| 700.00 | 97.60 | 168.52 | -20.37 | 3.312E + 001 |
| 800.00 | 95.76 | 166.07 | -37.10 | 2.646E + 002 |
| 900.00 | 93.49 | 163.41 | -53.58 | 1.288E + 003 |
| 1000.00 | 90.80 | 160.58 | -69.78 | 4.417E + 003 |

TABLE 2.48
Density of MnCO₃

| Phase | T(K) | d | Reference |
|------------------|-------|-------------------------|-----------|
| c | 293 | 3.125 gml ⁻¹ | 13 |
| c, rhodochrosite | 294.3 | 3.633 | 51 |

TABLE 2.49
Thermodynamic Data of MnCO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|------------|
| 298.15 | -894.10 | 85.80 | -219.68 | Barin 1989 |
| 400.00 | -885.03 | 111.89 | -929.80 | Barin 1989 |
| 500.00 | -875.05 | 134.11 | -942.11 | Barin 1989 |
| 600.00 | -864.37 | 153.58 | -956.51 | Barin 1989 |
| 700.00 | -853.10 | 170.93 | -972.75 | Barin 1989 |

TABLE 2.50
Thermodynamic Data of MnO (manganosite)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|------------|
| 298.15 | -385.22 | 59.71 | -403.02 | Barin 1993 |
| 400.00 | -380.51 | 73.28 | -409.82 | Barin 1993 |
| 500.00 | -375.68 | 84.05 | -417.71 | Barin 1993 |
| 600.00 | -370.71 | 93.11 | -426.58 | Barin 1993 |
| 700.00 | -365.62 | 100.95 | -436.29 | Barin 1993 |

TABLE 2.51
MnCO₃ = MnO + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 115.37 | 187.68 | 59.42 | 3.885E - 011 |
| 400.00 | 115.06 | 186.82 | 40.34 | 5.399E - 006 |
| 500.00 | 114.34 | 185.21 | 21.73 | 5.366E - 003 |
| 600.00 | 113.31 | 183.34 | 3.30 | 5.159E - 001 |
| 700.00 | 112.02 | 181.36 | -14.93 | 1.302E + 001 |

TABLE 2.52
3 MnCO₃ = Mn₃O₄ + 2CO₂(g) + CO(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 396.95 | 523.39 | 240.90 | 6.149E - 043 |
| 400.00 | 395.92 | 520.52 | 187.71 | 3.062E - 025 |
| 500.00 | 393.73 | 515.69 | 135.89 | 6.349E - 015 |
| 600.00 | 390.78 | 510.33 | 84.59 | 4.321E - 008 |
| 700.00 | 387.22 | 504.84 | 33.83 | 2.990E - 003 |
| 800.00 | 383.11 | 499.37 | -16.38 | 1.174E + 001 |

TABLE 2.53
Thermodynamic Data of HgCO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|------------|
| 298.15 | -553.29 | 184.10 | -608.18 | Karapet 70 |
| 400.00 | -553.29 | 184.10 | -626.93 | Karapet 70 |
| 500.00 | -553.29 | 184.10 | -645.34 | Karapet 70 |
| 600.00 | -553.29 | 184.10 | -663.75 | Karapet 70 |

TABLE 2.54
HgCO₃ = HgO + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|--------|-------------------------|--------|--------------|
| 298.15 | 69.00 | 99.94 | 39.20 | 1.354E – 007 |
| 400.00 | 77.77 | 125.19 | 27.70 | 2.414E – 004 |
| 500.00 | 87.19 | 146.18 | 14.10 | 3.363E – 002 |
| 600.00 | 97.17 | 164.36 | –1.45 | 1.336E + 000 |

TABLE 2.55
Thermodynamic Data of Hg₂CO₃

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|--------|------------------------------|---|------------------------------|-----------|
| 298.15 | –553.50 | 180.00 | –607.17 | CRC 94 |
| 400.00 | –542.98 | 210.37 | –627.12 | CRC 94 |
| 500.00 | –532.64 | 233.43 | –649.36 | CRC 94 |

TABLE 2.56
Hg₂CO₃ = Hg₂O + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|--------|-------------------------|--------|--------------|
| 298.15 | 68.76 | 165.15 | 19.55 | 3.761E – 004 |
| 400.00 | 65.72 | 156.27 | 3.22 | 3.800E – 001 |
| 500.00 | 63.27 | 150.77 | –12.12 | 1.844E + 001 |

TABLE 2.57
Thermodynamic Data of NiCO₃ (zaraitite)

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|--------|------------------------------|---|------------------------------|------------|
| 298.15 | –694.19 | 86.19 | –720.24 | Barin 1989 |
| 400.00 | –685.20 | 113.07 | –730.43 | Barin 1989 |
| 500.00 | –675.22 | 135.31 | –742.88 | Barin 1989 |
| 600.00 | –664.65 | 154.58 | –757.39 | Barin 1989 |
| 700.00 | –653.56 | 171.66 | –773.72 | Barin 1989 |

TABLE 2.58
Thermodynamic Data of NiO

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|--------|------------------------------|---|------------------------------|------------|
| 298.15 | –239.70 | 37.99 | –251.03 | Barin 1989 |
| 400.00 | –234.79 | 52.11 | –255.64 | Barin 1989 |
| 500.00 | –229.08 | 64.80 | –261.48 | Barin 1989 |
| 600.00 | –223.17 | 75.61 | –268.54 | Barin 1989 |
| 700.00 | –217.88 | 83.78 | –276.52 | Barin 1989 |

TABLE 2.59
 $\text{NiCO}_3 = \text{NiO} + \text{CO}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 61.34 | 165.57 | 11.97 | 7.983E – 003 |
| 400.00 | 60.97 | 164.48 | –4.83 | 4.269E + 000 |
| 500.00 | 61.11 | 164.76 | –21.27 | 1.668E + 002 |
| 600.00 | 61.12 | 164.84 | –37.78 | 1.947E + 003 |
| 700.00 | 60.22 | 163.46 | –54.20 | 1.109E + 004 |

TABLE 2.60
Density of K_2CO_3

| Phase | T(K) | d | Reference |
|-------|--------|--------------------------|--------------|
| c | 293 | 2.330 | 13, Vol. III |
| l | 1180.8 | 1.8922 gcm ⁻¹ | 40 |
| | 1185.3 | 1.8904 | |
| | 1193.9 | 1.8864 | |
| | 1195.9 | 1.8848 | |
| | 1206.6 | 1.8824 | |
| | 1213.5 | 1.8778 | |
| | 1220.0 | 1.8749 | |
| | 1223.6 | 1.8739 | |
| | 1234.1 | 1.8684 | |
| | 1245.3 | 1.8640 | |
| | 1257.4 | 1.8584 | |
| | 1270.0 | 1.8527 | |
| | 1283.3 | 1.8467 | |

TABLE 2.61
Transitions of K_2CO_3

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol°K) | Reference |
|--------------|------|-------------------|----------------------|------------|
| c,IV → c,III | 523 | | | 1,2 |
| c,III → c,II | 791 | | | 40 |
| c,II → c,I | 895 | | | 40 |
| c,I → l | 1171 | | | 23, 39, 55 |

TABLE 2.62**Thermodynamic Data of K_2CO_3**

| T K | ΔH_f° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔG_f° kJ mol⁻¹ | Reference |
|----------------|--|---|--|--------------------|
| 298.15 | -1150.18 | 155.52 | -1196.55 | Knacke et al. 1991 |
| 400.00 | -1137.78 | 191.20 | -1214.26 | Knacke et al. 1991 |
| 500.00 | -1124.34 | 221.14 | -1234.91 | Knacke et al. 1991 |
| 600.00 | -1109.81 | 247.60 | -1258.37 | Knacke et al. 1991 |
| 700.00 | -1094.27 | 271.54 | -1284.35 | Knacke et al. 1991 |
| 800.00 | -1077.04 | 293.59 | -1312.62 | Knacke et al. 1991 |
| 900.00 | -1060.27 | 314.17 | -1343.02 | Knacke et al. 1991 |
| 1000.00 | -1041.84 | 333.58 | -1375.41 | Knacke et al. 1991 |
| 1100.00 | -1022.47 | 352.03 | -1409.70 | Knacke et al. 1991 |
| 1200.00 | -974.48 | 393.27 | -1446.40 | Knacke et al. 1991 |
| 1300.00 | -953.56 | 419.02 | -1486.58 | Knacke et al. 1991 |
| 1400.00 | -932.64 | 425.52 | -1528.37 | Knacke et al. 1991 |
| 1500.00 | -911.72 | 439.96 | -1571.65 | Knacke et al. 1991 |

TABLE 2.63**Thermodynamic Data of K_2O**

| T K | ΔH_f° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔG_f° kJ mol⁻¹ | Reference |
|----------------|--|---|--|------------------|
| 298.15 | -361.50 | 102.01 | -391.91 | Barin 1989 |
| 400.00 | -353.66 | 124.59 | -403.50 | Barin 1989 |
| 500.00 | -345.59 | 142.59 | -416.88 | Barin 1989 |
| 600.00 | -337.25 | 157.79 | -431.92 | Barin 1989 |
| 700.00 | -328.68 | 170.99 | -448.37 | Barin 1989 |
| 800.00 | -319.90 | 182.71 | -466.07 | Barin 1989 |
| 900.00 | -310.93 | 193.27 | -484.88 | Barin 1989 |
| 1000.00 | -301.78 | 202.92 | -504.69 | Barin 1989 |
| 1100.00 | -264.06 | 239.78 | -527.82 | Barin 1989 |
| 1200.00 | -253.36 | 249.09 | -552.27 | Barin 1989 |
| 1300.00 | -242.66 | 257.65 | -577.61 | Barin 1989 |
| 1400.00 | -231.96 | 265.58 | -603.78 | Barin 1989 |
| 1500.00 | -221.26 | 272.97 | -630.71 | Barin 1989 |

TABLE 2.64

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 395.18 | 160.36 | 347.40 | 1.356E – 061 |
| 400.00 | 394.68 | 158.83 | 331.14 | 5.670E – 044 |
| 500.00 | 393.72 | 156.72 | 315.36 | 1.127E – 033 |
| 600.00 | 392.22 | 154.00 | 299.82 | 7.875E – 027 |
| 700.00 | 390.13 | 150.79 | 284.58 | 5.793E – 022 |
| 800.00 | 387.43 | 147.20 | 269.67 | 2.458E – 018 |
| 900.00 | 384.11 | 143.29 | 255.15 | 1.550E – 015 |
| 1000.00 | 380.15 | 139.12 | 241.03 | 2.565E – 013 |
| 1100.00 | 403.91 | 162.70 | 224.94 | 2.077E – 011 |
| 1200.00 | 372.15 | 135.57 | 209.46 | 7.615E – 010 |
| 1300.00 | 367.54 | 131.88 | 196.09 | 1.319E – 008 |
| 1400.00 | 363.02 | 128.53 | 183.07 | 1.475E – 007 |
| 1500.00 | 358.57 | 125.47 | 170.38 | 1.166E – 006 |

TABLE 2.65**Thermodynamic Data of Rb_2CO_3**

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | –1136.00 | 181.33 | –1190.07 | Barin 1993 |
| 400.00 | –1123.30 | 217.89 | –1210.45 | Barin 1993 |
| 500.00 | –1109.66 | 248.28 | –1233.80 | Barin 1993 |
| 600.00 | –1093.78 | 277.10 | –1260.04 | Barin 1993 |
| 700.00 | –1078.25 | 301.02 | –1288.96 | Barin 1993 |
| 800.00 | –1061.85 | 322.90 | –1320.17 | Barin 1993 |
| 900.00 | –1044.60 | 343.21 | –1353.49 | Barin 1993 |
| 1000.00 | –1026.51 | 362.26 | –1388.77 | Barin 1993 |
| 1100.00 | –1007.60 | 380.28 | –1425.91 | Barin 1993 |
| 1200.00 | –962.90 | 426.23 | –1474.38 | Barin 1993 |
| 1300.00 | –944.07 | 441.30 | –1517.76 | Barin 1993 |
| 1400.00 | –925.25 | 455.25 | –1562.60 | Barin 1993 |
| 1500.00 | –906.42 | 468.24 | –1608.78 | Barin 1993 |

TABLE 2.66
Thermodynamic Data of Rb₂O

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -339.00 | 125.52 | -376.42 | Barin 1993 |
| 400.00 | -331.28 | 147.76 | -390.39 | Barin 1993 |
| 500.00 | -323.37 | 165.41 | -406.07 | Barin 1993 |
| 600.00 | -314.28 | 181.98 | -423.47 | Barin 1993 |
| 700.00 | -301.52 | 202.03 | -442.94 | Barin 1993 |
| 800.00 | -271.64 | 240.86 | -464.33 | Barin 1993 |
| 900.00 | -262.44 | 251.70 | -488.97 | Barin 1993 |
| 1000.00 | -253.23 | 261.40 | -514.64 | Barin 1993 |
| 1100.00 | -244.03 | 270.18 | -541.22 | Barin 1993 |
| 1200.00 | -234.83 | 278.19 | -568.65 | Barin 1993 |
| 1300.00 | -225.62 | 285.55 | -596.84 | Barin 1993 |
| 1400.00 | -216.42 | 292.37 | -625.74 | Barin 1993 |
| 1500.00 | -207.21 | 298.73 | -655.30 | Barin 1993 |

TABLE 2.67
Rb₂CO₃ = Rb₂O + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 403.50 | 157.96 | 356.40 | 3.587E - 063 |
| 400.00 | 402.57 | 155.31 | 340.44 | 3.458E - 045 |
| 500.00 | 401.26 | 152.40 | 325.06 | 1.093E - 034 |
| 600.00 | 399.15 | 148.69 | 309.93 | 1.037E - 027 |
| 700.00 | 401.27 | 152.35 | 294.63 | 1.030E - 022 |
| 800.00 | 419.79 | 176.04 | 278.97 | 6.081E - 019 |
| 900.00 | 416.94 | 172.68 | 261.53 | 6.610E - 016 |
| 1000.00 | 413.37 | 168.93 | 244.44 | 1.701E - 013 |
| 1100.00 | 409.08 | 164.85 | 227.75 | 1.528E - 011 |
| 1200.00 | 379.11 | 131.71 | 221.06 | 2.381E - 010 |
| 1300.00 | 375.10 | 128.50 | 208.05 | 4.363E - 009 |
| 1400.00 | 371.18 | 125.59 | 195.35 | 5.139E - 008 |
| 1500.00 | 367.33 | 122.94 | 182.92 | 4.261E - 007 |

TABLE 2.68
Thermodynamic Data of Ag₂CO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|-------------------|
| 298.15 | -505.80 | 167.40 | -555.71 | Barin et al. 1977 |
| 400.00 | -493.87 | 201.74 | -574.57 | Barin et al. 1977 |
| 500.00 | -481.07 | 230.27 | -596.20 | Barin et al. 1977 |
| 600.00 | -467.18 | 255.56 | -620.51 | Barin et al. 1977 |
| 700.00 | -452.21 | 278.61 | -647.24 | Barin et al. 1977 |
| 800.00 | -436.17 | 300.02 | -676.18 | Barin et al. 1977 |

TABLE 2.69
Thermodynamic Data of Ag₂O

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|--------------------|
| 298.15 | -31.05 | 121.30 | -67.214 | Knacke et al. 1991 |
| 400.00 | -24.01 | 141.57 | -80.64 | Knacke et al. 1991 |
| 500.00 | -16.54 | 158.21 | -95.65 | Knacke et al. 1991 |

TABLE 2.70
Ag₂CO₃ = Ag₂O + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 81.25 | 167.67 | 31.26 | 3.338E - 006 |
| 400.00 | 80.42 | 165.27 | 14.31 | 1.352E - 002 |
| 500.00 | 79.49 | 163.22 | -2.12 | 1.663E + 000 |
| 600.00 | 78.24 | 160.94 | -18.33 | 3.940E + 001 |
| 700.00 | 76.55 | 158.35 | -34.29 | 3.623E + 002 |

TABLE 2.71
Ag₂O = 2Ag + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 31.05 | 66.63 | 11.19 | 1.098E - 002 |
| 400.00 | 30.75 | 65.81 | 4.43 | 2.639E - 001 |
| 500.00 | 30.08 | 64.32 | -2.08 | 1.649E + 000 |
| 600.00 | 29.08 | 62.50 | -8.42 | 5.411E + 000 |
| 700.00 | 27.78 | 60.50 | -14.57 | 1.223E + 001 |
| 800.00 | 26.21 | 58.41 | -20.52 | 2.187E + 001 |
| 900.00 | 24.38 | 56.25 | -26.25 | 3.341E + 001 |
| 1000.00 | 22.30 | 54.07 | -31.77 | 4.567E + 001 |

TABLE 2.72
Density of Na₂CO₃

| Phase | T(K) | d | Reference |
|-------|--------|--------------------------|-----------|
| c | 293 | 2.533 gml ⁻¹ | 13 |
| l | 1137.9 | 1.9685 gcm ⁻³ | 36 |
| | 1146.2 | 1.9666 | |
| | 1165.5 | 1.9576 | |
| | 1178.8 | 1.9508 | |
| | 1184.7 | 1.9477 | |
| | 1223.3 | 1.9288 | |
| | 1233.2 | 1.9264 | |
| | 1244.8 | 1.9211 | |
| | 1260.3 | 1.9142 | |
| | 1277.0 | 1.9080 | |

TABLE 2.73
Transitions of Na₂CO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------|------|-------------------|----------------------|------------|
| c,IV → c,III | 629 | | | 1,3 |
| c,III → c,II | 759 | | | |
| c,II → c,I | 891 | | | |
| c,I → l | 1129 | 31 | | 36, 38, 39 |

TABLE 2.74
Thermodynamic Data of Na₂CO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -1130.77 | 138.78 | -1172.15 | Knacke et al. 1991 |
| 400.00 | -1118.78 | 175.27 | -1188.09 | Knacke et al. 1991 |
| 500.00 | -142.35 | 202.97 | -1206.92 | Knacke et al. 1991 |
| 600.00 | -1090.19 | 230.71 | -1238.61 | Knacke et al. 1991 |
| 700.00 | -1072.68 | 257.66 | -1253.04 | Knacke et al. 1991 |
| 800.00 | -1056.18 | 279.78 | -1280.01 | Knacke et al. 1991 |
| 900.00 | -1040.20 | 298.59 | -1308.93 | Knacke et al. 1991 |
| 1000.00 | -1022.93 | 316.77 | -1339.70 | Knacke et al. 1991 |
| 1100.00 | -1004.37 | 334.75 | -1372.27 | Knacke et al. 1991 |
| 1200.00 | -955.66 | 377.44 | -1408.59 | Knacke et al. 1991 |
| 1300.00 | -936.71 | 392.61 | -1447.10 | Knacke et al. 1991 |
| 1400.00 | -917.75 | 406.66 | -1487.07 | Knacke et al. 1991 |
| 1500.00 | -898.80 | 419.74 | -1528.40 | Knacke et al. 1991 |

TABLE 2.75
Thermodynamic Data of Na₂O

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -417.98 | 75.04 | -440.36 | Barin 1989 |
| 400.00 | -410.55 | 96.43 | -449.12 | Barin 1989 |
| 500.00 | -402.65 | 114.05 | -459.67 | Barin 1989 |
| 600.00 | -394.31 | 129.23 | -471.85 | Barin 1989 |
| 700.00 | -385.63 | 142.61 | -485.46 | Barin 1989 |
| 800.00 | -376.66 | 154.59 | -500.33 | Barin 1989 |
| 900.00 | -367.44 | 165.44 | -516.34 | Barin 1989 |
| 1000.00 | -358.01 | 175.37 | -533.38 | Barin 1989 |
| 1100.00 | -346.66 | 186.24 | -551.52 | Barin 1989 |
| 1200.00 | -336.92 | 194.71 | -570.57 | Barin 1989 |
| 1300.00 | -315.14 | 212.19 | -590.98 | Barin 1989 |
| 1400.00 | -305.21 | 219.54 | -612.57 | Barin 1989 |
| 1500.00 | -247.08 | 260.68 | -638.10 | Barin 1989 |

TABLE 2.76
 $\text{Na}_2\text{CO}_3 = \text{Na}_2\text{O} + \text{CO}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 319.28 | 150.03 | 274.55 | 7.868E – 049 |
| 400.00 | 318.78 | 148.60 | 259.35 | 1.350E – 034 |
| 500.00 | 317.76 | 146.35 | 244.59 | 2.794E – 026 |
| 600.00 | 315.53 | 142.33 | 230.13 | 9.191E – 021 |
| 700.00 | 311.59 | 136.29 | 216.19 | 7.357E – 017 |
| 800.00 | 309.11 | 132.89 | 202.80 | 5.717E – 014 |
| 900.00 | 307.54 | 131.04 | 189.60 | 9.885E – 012 |
| 1000.00 | 305.01 | 128.39 | 176.62 | 5.935E – 012 |
| 1100.00 | 303.22 | 126.74 | 163.82 | 1.661E – 008 |
| 1200.00 | 269.78 | 97.03 | 153.35 | 2.111E – 007 |
| 1300.00 | 278.21 | 103.82 | 143.25 | 1.753E – 006 |
| 1400.00 | 274.89 | 101.36 | 132.99 | 1.091E – 005 |
| 1500.00 | 319.84 | 133.40 | 119.74 | 6.761E – 005 |

TABLE 2.77
Transitions of SrCO_3

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol°K) | Reference |
|--------------------------------|------|-------------------|----------------------|-----------|
| c, orthorhombic → c, hexagonal | 1198 | 17 | | 1, 6, 65 |
| c, hexagonal → c, cubic | 1770 | | | 65 |
| c → l | 1770 | | | 1, 1.3 |

TABLE 2.78
Thermodynamic Data of SrCO_3

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -1219.85 | 97.07 | -1248.79 | Barin et al. 1977 |
| 400.00 | -1210.66 | 123.50 | -1260.06 | Barin et al. 1977 |
| 500.00 | -1200.79 | 145.48 | -1273.54 | Barin et al. 1977 |
| 600.00 | -1190.34 | 164.54 | -1289.06 | Barin et al. 1977 |
| 700.00 | -1179.38 | 181.41 | -1306.37 | Barin et al. 1977 |
| 800.00 | -1167.99 | 196.62 | -1325.28 | Barin et al. 1977 |
| 900.00 | -1156.18 | 210.52 | -1345.65 | Barin et al. 1977 |
| 1000.00 | -1143.97 | 223.38 | -1367.35 | Barin et al. 1977 |
| 1100.00 | -1131.38 | 235.38 | -1390.30 | Barin et al. 1977 |
| 1200.00 | -1098.71 | 263.12 | -1415.46 | Knacke et al. 1991 |
| 1300.00 | -1084.48 | 274.51 | -1441.35 | Knacke et al. 1991 |
| 1400.00 | -1070.26 | 285.05 | -1469.33 | Knacke et al. 1991 |
| 1500.00 | -1056.03 | 294.87 | -1498.33 | Knacke et al. 1991 |

TABLE 2.79
Thermodynamic Data of SrO

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -592.04 | 55.52 | -608.59 | Barin 1989 |
| 400.00 | -587.24 | 69.34 | -614.98 | Barin 1989 |
| 500.00 | -582.28 | 80.40 | -622.48 | Barin 1989 |
| 600.00 | -577.15 | 89.74 | -631.00 | Barin 1989 |
| 700.00 | -571.89 | 97.86 | -640.39 | Barin 1989 |
| 800.00 | -566.51 | 105.04 | -650.54 | Barin 1989 |
| 900.00 | -561.03 | 111.49 | -661.37 | Barin 1989 |
| 1000.00 | -555.46 | 117.36 | -672.82 | Barin 1989 |
| 1100.00 | -549.81 | 122.74 | -684.83 | Barin 1989 |
| 1200.00 | -544.09 | 127.72 | -697.35 | Barin 1989 |
| 1300.00 | -538.29 | 132.37 | -710.36 | Barin 1989 |
| 1400.00 | -532.41 | 136.72 | -723.82 | Barin 1989 |
| 1500.00 | -526.47 | 140.82 | -737.70 | Barin 1989 |

TABLE 2.80
SrCO₃ = SrO + CO₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 234.30 | 172.22 | 182.96 | 8.795E - 033 |
| 400.00 | 233.97 | 171.28 | 165.46 | 2.462E - 022 |
| 500.00 | 233.48 | 170.19 | 148.39 | 3.140E - 016 |
| 600.00 | 232.84 | 169.02 | 131.43 | 3.609E - 012 |
| 700.00 | 232.04 | 167.79 | 114.59 | 2.811E - 009 |
| 800.00 | 231.07 | 166.50 | 97.87 | 4.066E - 007 |
| 900.00 | 229.93 | 165.16 | 81.29 | 1.914E - 005 |
| 1000.00 | 228.60 | 163.76 | 64.84 | 4.100E - 004 |
| 1100.00 | 227.08 | 162.31 | 48.54 | 4.955E - 003 |
| 1200.00 | 205.66 | 144.36 | 32.43 | 3.875E - 002 |
| 1300.00 | 202.85 | 142.11 | 18.11 | 1.872E - 001 |
| 1400.00 | 200.19 | 140.14 | 4.00 | 7.092E - 001 |
| 1500.00 | 197.69 | 138.41 | -9.926 | 2.217E + 000 |

TABLE 2.81
Transitions of Tl₂CO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------|------|-------------------|----------------------|-----------|
| c,II → c,I | 591 | | | 74 |
| c,I → I | 546 | 18 | 36 | 1 |
| | 536 | | | 73 |

TABLE 2.82
Thermodynamic Data (298.15 K) of Ti_2CO_3

| | ΔHf° kJ mol^{-1} | $\text{S}^\circ \text{ J mol}^{-1}$ deg^{-1} | Reference |
|--------------------------|---|--|-----------|
| Ti_2CO_3 | -700.0 | -155.2 | 1,3 |
| Ti_2O | -178.7 | -126. | |

TABLE 2.83
Thermodynamic Data of ZnCO_3

| T K | ΔHf° kJ mol^{-1} | $\text{S}^\circ \text{ J mol}^{-1}$ deg^{-1} | $\Delta\text{Gf}^\circ \text{ kJ}$ mol^{-1} | Reference |
|--------|---|--|---|------------|
| 298.15 | -812.78 | 82.40 | -837.35 | Barin 1993 |
| 400.00 | -803.91 | 107.90 | -847.35 | Barin 1993 |
| 500.00 | -793.80 | 130.39 | -859.00 | Barin 1993 |
| 600.00 | -782.32 | 151.29 | -873.09 | Barin 1993 |
| 700.00 | -769.45 | 171.09 | -889.22 | Barin 1993 |

TABLE 2.84
Thermodynamic Data of ZnO (zincite)

| T K | ΔHf° kJ mol^{-1} | $\text{S}^\circ \text{ J mol}^{-1}$ deg^{-1} | $\Delta\text{Gf}^\circ \text{ kJ}$ mol^{-1} | Reference |
|--------|---|--|---|------------|
| 298.15 | -350.46 | 43.64 | -363.47 | Barin 1993 |
| 400.00 | -346.07 | 56.28 | -368.58 | Barin 1993 |
| 500.00 | -341.50 | 66.48 | -374.74 | Barin 1993 |
| 600.00 | -336.75 | 75.13 | -381.83 | Barin 1993 |
| 700.00 | -331.88 | 82.63 | -389.72 | Barin 1993 |

TABLE 2.85
 $\text{ZnCO}_3 = \text{ZnO} + \text{CO}_2(\text{g})$

| T K | $\Delta\text{H}^\circ \text{ kJ}$ | $\Delta\text{S}^\circ \text{ J deg}^{-1}$ | $\Delta\text{G}^\circ \text{ kJ}$ | K |
|--------|-----------------------------------|---|-----------------------------------|--------------|
| 298.15 | 68.82 | 175.01 | 16.64 | 1.217E - 003 |
| 400.00 | 68.39 | 173.82 | -1.14 | 1.407E + 000 |
| 500.00 | 67.28 | 171.37 | -18.41 | 8.378E + 001 |
| 600.00 | 65.22 | 167.65 | -35.37 | 1.200E + 003 |
| 700.00 | 62.11 | 162.88 | -51.90 | 7.469E + 003 |

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3 Sulfites

3.1 GENERAL

In contrast to the many sulfates (see Chapter 4), there are very few anhydrous sulfites about which much is known. (See [Figure 3.1.](#)) They are usually prepared by the dehydration of hydrates and thus may not be entirely water-free. This may affect the decomposition reactions, since in some instances water and SO_2 evolve simultaneously.

High temperature thermodynamic data are available only for three sulfites: calcium, potassium, and sodium. Most sulfites are fairly unstable, decomposing at relatively low temperatures. The decomposition reactions are not always exactly known, with diverse decomposition products, including sulfur, being reported. There are two major decomposition reactions: (1) decomposition to the oxide and SO_2 , and (2) oxidation-reduction (disproportionation) to the sulfate and oxide and SO_2 , i.e.,



This reaction generally occurs at higher temperatures. Details of these two reactions are discussed under the individual elements.

The sulfite anion is pyramidal, with the three oxygens arranged around the sulfur apex. In Na_2SO_3 the O–S distance is 1.39 Å. Detailed bonding information has been discussed in a review of sulfite spectroscopy by Verma¹ which also classifies sulfites according to bonding: ionic or covalent.

In this chapter information on the various sulfites is summarized. Much of it comes from older literature which can be found in the relevant volumes of Gmelin.² This multivolume compilation which has been added to for many decades and is still a work “in progress,” is a valuable source of references for all inorganic compounds, but has not been critically evaluated.

Thermodynamic data at 298.15 K were mostly taken from Wagman et al.³ High temperature data for the above-mentioned three sulfites were taken from the HSC database referred to in Chapter 1.1. No thermodynamic data for oxides are included, since they were already given in Chapter 2, and sulfates, which may also be decomposition products, are described in Chapter 4. Therefore, when only minimal data are available, they are given in the text rather than in individual tables.

3.2 INDIVIDUAL SULFITES

3.2.1 BARIUM

The sulfite decomposes, beginning at 653 K.² Decomposition is complete at 1173 K. The decomposition reaction is most likely



$$\Delta \text{Hf}^\circ \text{ at } 298.15 \text{ K} = -1179.5 \text{ kJ mol}^{-1},^3$$

| | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

Lanthanides **Ce** Pr **Nd** Pm **Sm** **Eu** Gd Tb Dy Ho **Er** Tm Yb Lu
Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

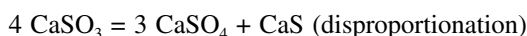
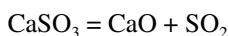
FIGURE 3.1

3.2.2 CADMIUM

Lutz and El Suradi⁴ found that CdSO_3 exists in two modifications, α and β , the latter resulting from the decomposition of the hydrate above 300°C . Above this temperature, decomposition of α - CdSO_4 forms CdO and $2 \text{ CdO} \cdot \text{CdSO}_4$. Between 375 and 450°C SO_2 evolves.

3.2.3 CALCIUM

Decomposition of CaSO_3 has been studied by several workers, using a variety of methods, usually DTA, TGA, and X-ray diffraction of the products.⁴⁻⁷ There is general agreement that there are two decomposition reactions:



but the temperature range in which each occurs depends on the gas phase.

Cubicciotti et al.⁵ used a torsion-effusion method to determine decomposition pressures in the range 723 to 767 K and found only SO_2 in the vapor. They surmised that the salt is in metastable equilibrium with respect to disproportionation below 775 K .

Thermodynamic data are given in [Table 3.1](#).

3.2.4 CESIUM

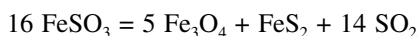
The preparation of the salt has been reported, but not its properties. ΔH_f° at $298.15 \text{ K} = -1134.7 \text{ kJ mol}^{-1}$.³

3.2.5 COBALT

The preparation of anhydrous CoSO_3 was tried in non-aqueous solution,⁸ but a truly anhydrous compound may not exist.

3.2.6 IRON

The decomposition by TGA was studied.⁹ In an inert atmosphere it occurs in two steps: an endothermic decomposition in the range 200 to 310°C ,



for which $\Delta H^\circ = 1117 \text{ kJ}$, and an exothermic decomposition above 320°C :

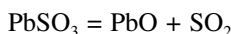


for which $\Delta H^\circ = -1192 \text{ kJ}$.

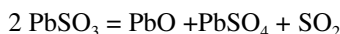
Since FeSO_4 decomposes simultaneously, the stoichiometries of the decompositions are doubtful.

3.2.7 LEAD

Depending on conditions, the dissociation between 300 and 500°C occurs either as⁴



or



The first reaction was also studied by Vishnyakov et al.¹⁰ who list dissociation pressures in the range 328 to 375°C . Above these temperatures they also find disproportionation occurs. ΔH_f° at $298.15\text{K} = -669.9 \text{ kJ mol}^{-1}$.³

3.2.8 LITHIUM

Decomposition of Li_2SO_3 has been studied in dry nitrogen.¹¹ It apparently occurs by disproportionation at 650 to 850°C , but the results are sketchy.

3.2.9 MAGNESIUM

Decomposition has been reported above 400°C ,^{12,13} MgO and MgSO_4 being formed as products. At 298.15 K , $\Delta H_f^\circ = -1008.3 \text{ kJ mol}^{-1}$, $S^\circ = 87.9 \text{ J mol}^{-1}\text{deg}^{-1}$.³

3.2.10 MANGANESE

$\text{MnSO}_3 \cdot 3 \text{ H}_2\text{O}$ loses water in steps up to 260° . Above this temperature (280 to 540°C) the decomposition occurs in two steps. In both, MnSO_4 is formed, but the other products, MnO and MnS , depend on conditions.^{13,14}

3.2.11 POTASSIUM

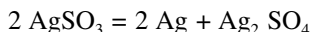
Most information on decomposition predates 1900 . Thermodynamic data are given in [Table 3.2](#).

3.2.12 RARE EARTHS

The rare earth sulfites have potential applications in thermochemical cycles and as starting materials for the preparation of sulfides which can be formed by the reduction of sulfites, e.g., by CO .^{15,16} One problem is that the anhydrous sulfites apparently cannot be synthesized directly, but only by the dehydration of hydrates. Thus, great care must be taken to avoid decomposing the salt while water is removed, frequently by removal of SO_2 . The decomposition product is frequently an oxysulfate, or sulfite-sulfate, e.g., $\text{Ce}_2(\text{SO}_3)_2\text{SO}_4$ and $\text{Ce}_2\text{SO}_3(\text{SO}_4)_4$. Listed are several references which will provide the reader with entry into the field, many by workers at Helsinki University.¹⁶⁻¹⁹

3.2.13 SILVER

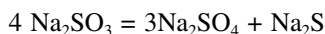
Above 100°C decomposition in a vacuum or under nitrogen gas proceeds according to^{20,21}



The density is 5.4 g cm⁻³.²² Thermodynamic data at 298.15 K are: $\Delta H_f^\circ = -490.8 \text{ kJ mol}^{-1}$, $S^\circ = 158.2 \text{ J mol}^{-1} \text{ deg}^{-1}$.³

3.2.14 SODIUM

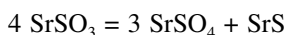
Decomposition has been studied in an inert atmosphere by Foerster and Kubel²³ and in air by Sack.²⁴ Both find disproportionation to be the predominant reaction above 700°C.



Thermodynamic data for Na₂SO₃ are given in [Table 3.3](#).

3.2.15 STRONTIUM

Decomposition probably occurs according to Gmelin² as



ΔH_f° at 298.15 K = -1177.0 kJ.³

3.2.16 ZINC

Decomposition of ZnSO₃ has been studied, but only with a hydrate as the starting material.^{25,26} Heating results in the simultaneous loss of water and SO₂; thus the results are suspect with respect to temperature range and the nature of the decomposition reaction.

TABLE 3.1
Thermodynamic Data of CaSO₃

| T K | ΔH^{fo} kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔG^{fo} kJ mol⁻¹ | Reference |
|----------------------|--|---|--|------------------|
| 298.15 | -1159.4 | 101.4 | -1189.6 | Barin 1993 |
| 400.00 | -1149.8 | 128.9 | -1201.4 | Barin 1993 |
| 500.00 | -1139.9 | 151.0 | -1215.4 | Barin 1993 |
| 600.00 | -1129.6 | 169.9 | -1231.5 | Barin 1993 |
| 700.00 | -1118.7 | 186.6 | -1249.3 | Barin 1993 |
| 800.00 | -1107.4 | 201.7 | -1268.8 | Barin 1993 |
| 900.00 | -1095.6 | 215.6 | -1289.6 | Barin 1993 |
| 1000.00 | -1083.2 | 228.6 | -1311.9 | Barin 1993 |

TABLE 3.2
Thermodynamic Data of K₂SO₃

| T K | ΔH^{fo} kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔG^{fo} kJ mol⁻¹ | Reference |
|----------------------|--|---|--|------------------|
| 298.15 | -1126.8 | 171.5 | -1177.9 | Barin 1989 |
| 400.00 | -1113.8 | 209.0 | -1197.4 | Barin 1989 |
| 500.00 | -1100.2 | 239.3 | -1219.8 | Barin 1989 |
| 600.00 | -1085.7 | 265.6 | -1245.1 | Barin 1989 |
| 700.00 | -1070.5 | 289.1 | -1272.8 | Barin 1989 |
| 800.00 | -1054.4 | 310.6 | -1302.8 | Barin 1989 |
| 900.00 | -1031.5 | 330.5 | -1334.9 | Barin 1989 |
| 1000.00 | -1019.7 | 349.2 | -1368.9 | Barin 1989 |

TABLE 3.3
Thermodynamic Data of Na₂SO₃

| T K | ΔH^{fo} kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔG^{fo} kJ mol⁻¹ | Reference |
|----------------------|--|---|--|------------------|
| 298.15 | -1089.4 | 146.0 | -1133.0 | Barin 1993 |
| 400.00 | -1077.0 | 182.0 | -1149.7 | Barin 1993 |
| 500.00 | -1064.3 | 210.3 | -1169.4 | Barin 1993 |
| 600.00 | -1051.2 | 234.2 | -1191.7 | Barin 1993 |
| 700.00 | -1037.6 | 255.1 | -1216.1 | Barin 1993 |
| 800.00 | -1023.6 | 273.7 | -1242.6 | Barin 1993 |
| 900.00 | -1009.2 | 290.7 | -1270.8 | Barin 1993 |
| 1000.00 | -994.3 | 306.4 | -1300.7 | Barin 1993 |

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4 Sulfates

4.1 GENERAL

The sulfates constitute one of the largest classes of inorganic oxyanion salts. (See Figure 4.1.) Because they are generally stable, they are used extensively in many areas of chemical technology. As can be seen in this chapter, many of their properties have been measured and their decomposition is well characterized.

The sulfate ion is tetrahedral, but both the S–O bond length and angle vary considerably from salt to salt, the S–O distance from 1.4 to 1.8 Å, the O–S–O angle from 95 to 120°. A Hückel molecular calculation of these features has been published.¹

The thermal stability of the sulfate anion varies with the cation, as was described for the carbonates, i.e., stability decreases with increasing polarizing power of the cation. Thus small cationic size and high charge promote decomposition. The primary decomposition is to the oxide and SO₃, accompanied by decomposition of that gas to SO₂ and O₂. Thus in a closed system there will also be two simultaneous equilibria:



Equilibrium data for the second reaction are given in separate tables (see below).

As in the preceding chapters, data for densities and phase transitions are also provided. The discussion of these properties in Chapter 1 applies here also.

4.2 DECOMPOSITION EQUILIBRIA

The following data relevant to the thermal decomposition of each sulfate have been listed: ΔH° , S° , and ΔG° for each sulfate from 298.15 K to as high a temperature as is available; similar data for the corresponding oxides which were not given in Chapter 2, and separate tables for ΔH° , ΔS° , and ΔG° for the decomposition to (a) the oxide and SO₃, and (b) the oxide and SO₂ and O₂; and the equilibrium constant for these reactions. All of these parameters were calculated using a computer program.² The source of the data used in these calculations is given in the same manner as in Chapter 2.

Partial pressures of the three gases can be calculated if the initial conditions are known. For example, if the decomposition is carried out in air, $p(\text{O}_2) = 0.21$. If it is carried out in a closed, originally evacuated container in which the only source of the gases is the decomposing sulfate, partial pressures can be calculated from the simultaneous solution of Equations 4.3 and 4.4, corresponding to Equations 4.1 and 4.2

$$K_1 = p(\text{SO}_3) \quad (4.3)$$

$$K_2 = p(\text{SO}_2) \cdot p^{1/2}(\text{O}_2) / p(\text{SO}_3) \quad (4.4)$$

As a good approximation $p(\text{SO}_3) = K_1$, $p(\text{O}_2) \approx 1/2 p(\text{SO}_2)$ and the pressures of these two gases can be calculated since $p(\text{SO}_3) \ll p(\text{SO}_2)$. Exact calculations require the simultaneous solutions of 4.3 and 4.4, but this is somewhat complicated.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides **Ce Pr Nd** Pm **Sm Eu Gd Tb Dy Ho Er Tm Yb Lu**
Actinides **Th** Pa **U** Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 4.1 The known sulfates.

Thermodynamic data for SO_3 , SO_2 , and for the equilibrium 4.2 are given in [Tables 4.1 to 4.3](#). As can be seen from Table 4.3, the equilibrium shifts to the right with increasing temperature.

4.3 INDIVIDUAL SULFATES

4.3.1 ALUMINUM

$\text{Al}_2(\text{SO}_4)_3$ decomposes directly to Al_2O_3 without the formation of an intermediate.³ However, different researchers have obtained Al_2O_3 in different states. Knutsen and Searcy found it to be amorphous,⁴ whereas Ingraham obtained $\gamma\text{-Al}_2\text{O}_3$.⁵

Since the volume of Al_2O_3 is much less than that of the sulfate, it is not surprising that the product is porous and that the kinetics follows the contracting sphere model.⁶

No solid–solid transitions are known and the solid decomposes without melting. Ambient temperature density is 2.71.⁷ Thermodynamic data are given in [Tables 4.4 to 4.7](#).

4.3.2 ANTIMONY

On heating, $\text{Sb}_2(\text{SO}_4)_3$ decomposes with partial oxidation. Oxysulfates exist about which little is known. From the thermodynamic data of the sulfate one surmises that it is stable to 1000 K, but since the course of the decomposition is unknown, only the thermodynamic data of the sulfate and the oxides have been listed ([Tables 4.8 to 4.12](#)).

4.3.3 BARIUM

BaSO_4 melts without obvious decomposition. The density of c, II is given as 4.499 at 288 K.⁸ Phase transitions are listed in [Table 4.13](#), and thermodynamic data in [Tables 4.14 to 4.16](#).

4.3.4 BERYLLIUM

Thermodynamic calculations ([Tables 4.18 to 4.21](#)) indicate that BeSO_4 is unstable above 1000 K. Kinetics of the decomposition have been studied by Johnson and Gallagher.¹¹ The authors use their data to study various kinetic models and find the contracting sphere model most satisfactory.

The density is given in [Table 4.17](#).

4.3.5 BISMUTH

Thermodynamic calculations (Tables 4.22 to 4.25) indicate that $\text{Bi}_2(\text{SO}_4)_3$ should be stable to above 1200 K, but an experimental study¹³ reports that decomposition proceeds through several oxysulfates, beginning at 700 K. One complication is the low melting point of Bi_2O_3 , 1090 K.¹⁰

The density is 5.08 at 288 K.¹⁴

4.3.6 CADMIUM

Solid-phase transitions and decomposition products of CdSO_4 have been studied by two groups of researchers,^{15,16} both of whom review the confused earlier literature. On heating, the salt undergoes at least one, possibly two, transformations, but the transition temperature is not certain. The highest temperature form melts near 1300 K. However, slow decomposition to $2\text{CdO} \cdot \text{CdSO}_4$ is observed well below this temperature. The final decomposition product is CdO . No thermodynamic data for the double salt are available, and therefore only data relevant for the decomposition to CdO are given (Tables 4.28 to 4.30). Data for CdO are given in Table 2.13.

There exist three high-temperature modifications of CdSO_4 whose structure was determined by X-ray diffraction.¹⁸

Densities are listed in Table 4.26, transitions in Table 4.27.

4.3.7 CALCIUM

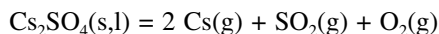
CaSO_4 decomposes directly to CaO . The supposed existence of an intermediate oxysulfate and discrepant values for the melting point of CaSO_4 are explained²⁰ by a eutectic between CaO and CaSO_4 near 1638 K, with less than 20% CaO .

Kinetic studies of the decomposition are not strictly comparable, since one was carried out in a vacuum²¹ and another in air,²² but both agree that the rate-determining step occurs at the CaSO_4 - CaO boundary.

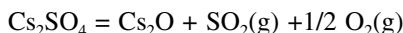
The density is 4.691.⁸ Transitions are in Table 4.31, and thermodynamic data in Tables 4.32 to 4.34. Data for CaO are in Table 2.19.

4.3.8 CESIUM

Very careful work by Lau et al.²³ has established that the main mode of vaporization of Cs_2SO_4 is sublimation, by which 95% of the material reaches the vapor state, ΔH_{sub} at 298.15 K being $320.1 \pm 2.0 \text{ kJ mol}^{-1}$. Five percent is accounted for by the congruent decomposition



A thermodynamic table for this reaction has been included, but it shows that it is minor compared to decomposition to the oxide:

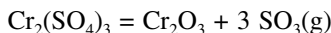
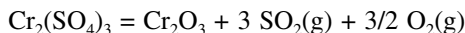


The density of the solid and liquid salt is given in Table 4.35, transitions in Table 4.36. Thermodynamic data are given in Tables 4.37 to 4.41. Data for Cs_2O are in Table 2.23.

4.3.9 CHROMIUM

$\text{Cr}(\text{II})$. CrSO_4 is known only in solution and as hydrates, and double salts, all easily oxidized by air. The monohydrate yields Cr_2O_3 on heating.

Cr(III). $\text{Cr}_2(\text{SO}_4)_3$ is stable to 573 K, but decomposes not far above this temperature, ultimately to Cr_2O_3 . The course of the decomposition is unknown, but we have included tables for the decomposition reactions



which indicate that decomposition is slight up to 1000 K. Thermodynamic data are given in Tables 4.42 to 4.45.

The density is 2.706 at 298 K.²⁷

4.3.10 COBALT

The decomposition of CoSO_4 has been studied by Pechkovsky²⁸ and Pechkovsky, Zvedin, and Beresneva²⁹ in a dynamic system at a flow rate of 3 l/hr between 1023 and 1223 K. Increase of SO_2 in the carrier gas inhibited decomposition. The decomposition is linear in time with no evidence of an oxysulfate, i.e., $\alpha = kt$. A linear function of $1/T$ between 1113 and 1133 K is $\ln k$, the slope yielding an activation energy of 319 kJ. This is also consistent with the work of Tagawa and Saijo.³⁰ The thermodynamic calculations (Tables 4.48 to 4.50) indicate that decomposition becomes appreciable above 1100 K. Data for CoO are in Table 2.27.

Densities are given in Table 4.46, and transitions in Table 4.47.

4.3.11 COPPER

Cu(I). Cu_2SO_4 oxidizes in air.

Cu(II). There is general agreement that the first product of the decomposition of CuSO_4 is an oxysulfate, $\text{CuO} \cdot \text{CuSO}_4$. In kinetic studies, the temperature range of this reaction has been reported as 1092 to 1133 K,³³ and 1053 to 1123 K,²⁹ possibly because of differences in the gas phase composition. The decomposition rate decreases with increasing oxygen content of the flow gas and increases with increasing SO_3 because these gases displace the $\text{SO}_3 = \text{SO}_3 + 1/2 \text{O}_2$ equilibrium in opposite directions.

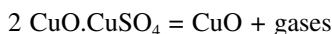
Decomposition of both sulfate and oxysulfate is zero-order. For the former, an Arrhenius activation energy of 212 kJ was obtained between 1053 and 1123 K, and for decomposition of the oxysulfate it was 346 kJ between 1133 and 1193 K. However, somewhat different values of 238 and 269 kJ for these reactions have also been reported,³⁴ and agree with those of Ingraham and Marier.³⁵

Although the values for sulfate decomposition agree fairly well, those for the oxysulfates are quite different, possibly because the Russian researchers ran this decomposition at a lower temperature, 1033 to 1073 K.

Two sets of measurements^{36,37} in fair agreement have been made of the equilibrium decomposition pressures, 948 to 1033 K, in the systems



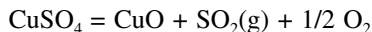
and



where the pressures in the first system are higher than in the second. Because of lack of data on the oxysulfate it is not yet possible to calculate these pressures thermodynamically. We have, however, calculated equilibrium constants for the reactions



and



which indicate appreciable reaction in the range found experimentally. These data are in [Tables 4.52 to 4.54](#). Densities are in [Table 4.51](#), and transitions in [Table 4.52](#). Data for CuO are in [Table 2.30](#).

4.3.12 GALLIUM

Ga_2SO_4 decomposes without melting to Ga_2O_3 . Marchal¹⁷ measured equilibrium pressures over the range 833 to 973 K, from which it appears that the salt is less stable than $\text{Al}_2(\text{SO}_4)_3$. Equilibrium constants cannot yet be calculated thermodynamically.

The density is 3.229 at 296 K.³⁹

4.3.13 HAFNIUM

Von Hevesy and Cremer⁴⁰ attempted to measure equilibrium pressures of $\text{Hf}(\text{SO}_4)_2$ in the range 823 to 923 K, but were not sure of obtaining true equilibrium. Decomposition was direct to HfO_2 , not through an intermediate oxysulfate, and the sulfate appears to be more stable than $\text{Zr}(\text{SO}_4)_2$. No thermodynamic data for the salt are available.

4.3.14 INDIUM

Seward⁴¹ measured equilibrium decomposition pressures of $\text{In}_2(\text{SO}_4)_3$ over the range 918 to 1093 K, from which it appeared to be more stable than $\text{Al}_2(\text{SO}_4)_3$. The product was In_2O_3 without an oxysulfate intermediate. Thermodynamic data for the decomposition are given in [Tables 4.55 to 4.58](#). These indicate that the salt is stable to 1100 K.

A kinetic study⁴² above 1073 K showed that the initial decomposition rate is nearly constant, but decreases with time. The degree of decomposition is given by

$$\alpha = 1 - \exp(-kt^n)$$

which can be written in logarithmic form as

$$\ln[-\ln(1 - \alpha)] = n \ln t + \ln k$$

From the linear plot of the left-hand side against $\ln t$, the constants n and k are obtained; n increases linearly from 1.0 at 1123 K to 1.6 at 1273 K, while k increases logarithmically from 0.021 to 0.410 between these temperatures. The values of n indicate that decomposition proceeds from nuclei in two dimensions.

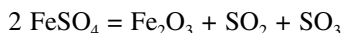
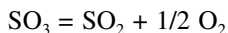
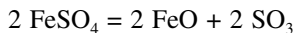
The density is 3.43 at 298 K.⁸

4.3.15 IRON

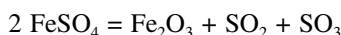
The sulfates of both Fe(II) and Fe(III) decompose without melting. Decomposition of $\text{Fe}_2(\text{SO}_4)_3$ to Fe_2O_3 is reversible, without the formation of an intermediate oxysulfate. FeSO_4 decomposes irreversibly, with oxidation, to Fe_2O_3 , through intermediates that have not been identified with certainty, though FeO is often assumed.

A number of researchers have measured equilibrium decomposition pressures,^{43–45} but these are no longer required for the calculation of thermodynamic functions that are now available and used for the calculations of equilibrium constants for the decomposition of both FeSO₄ and Fe₂(SO₄)₃ (Tables 4.59 to 4.62).

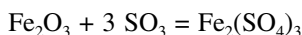
When FeSO₄ is heated above 823 K, the FeO formed is immediately oxidized by the oxygen or SO₃ liberated in the reaction.^{46–48} The reactions occurring are



corresponding to the net reaction



If the SO₃ remains in the system the following reaction may occur:



However, the reaction is slow and may be suppressed by removing the SO₃. As expected, an increase of O₂ in the sweep gas inhibits the decomposition.

When the weight loss was measured in air⁴⁹ between 953 and 1003 K, decomposition followed the Roginsky equation

$$1 - (1 - \alpha)^{2/3} = \alpha = kt$$

From the linear temperature dependence of ln k on 1/T an Arrhenius activation energy of 253 kJ was obtained. Since, at any temperature in the above range, the decomposition pressure of FeSO₄ is greater than that of Fe₂(SO₄)₃; the rate-determining step for decomposition of the former is decomposition of the ferric salt. Decomposition appears to occur exclusively on the surface of the original material, rather than in the interior of the grains.

Decomposition of Fe₂(SO₄)₃ is zero-order between 973 and 1073 K. Activation energies of 89 kJ⁵⁰ and 154 kJ⁵¹ for the reaction have been reported, the latter for vacuum, the former for a stream of dry N₂.

When the gas phase has a constant composition, the driving force for the reaction is the difference between the actual and equilibrium pressure of SO₃.

In air between 953 and 1053 K Roginsky's equation holds,⁴⁹ i.e., the degree of decomposition is a linear function of time. This implies that the decomposition is not autocatalytic, and that the new phase is instantaneously formed on the surface of the original material. During the later stages the rate is controlled by the diffusion of product gases through the solid oxide. The Arrhenius activation energy, calculated from the slope of ln k vs. 1/T is 289 kJ, quite different from the other values reported.

No explanation is evident for the wide range of reported activation energies reported by different authors, since one would not expect a radical change in mechanism to be produced by a change in experimental conditions.

Since the SO₂/SO₃ equilibrium is established relatively slowly, the rate-determining step is likely to involve the expulsion of an SO₃ molecule from the crystal lattice. All of the reported activation energies are much less than ΔH = 526 kJ, but ΔH per mole of SO₃ is 526/3 = 176 kJ which is at least in the right range.

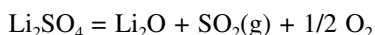
Thermodynamic data for the decomposition reactions are given in [Tables 4.59 to 4.64](#).

4.3.16 LEAD

Because PbSO_4 decomposes noticeably below the melting point, this value is difficult to determine reliably. The ultimate decomposition product is PbO . Various oxysulfates have been prepared in ways other than by pyrolysis of PbSO_4 . Some have congruent melting points and form eutectics with PbO or PbSO_4 ; for a summary and references, see Kelley⁵²; Rossini et al.⁹ lists $\text{PbO} \cdot \text{PbSO}_4$, m.p. 1243 K, $2 \text{ PbO} \cdot \text{PbSO}_4$, m.p. 1223 K. The former is the mineral lanarkite. Hoschek⁵³ found three intermediates before PbO in the pyrolysis of PbSO_4 , the two oxysulfates above and $4 \text{ PbO} \cdot \text{PbSO}_4$. Thermodynamic data are now available for all the above-mentioned oxysulfates, as well as $3 \text{ PbO} \cdot \text{PbSO}_4$, and these have been listed, permitting the user to calculate equilibria. However, only equilibria for decomposition of PbSO_4 to PbO have been given ([Tables 4.67 to 4.73](#)). Densities are listed in [Table 4.65](#) and transitions in [Table 4.66](#). Data for PbO are in [Table 2.37](#).

4.3.17 LITHIUM

A detailed study of Li_2SO_4 vaporization/decomposition²³ shows that decomposition occurs by the reaction



with Li_2O and Li_2SO_4 forming a solution. Sublimation of Li_2SO_4 accounts for about 0.3% of the pressure over the salt. The enthalpy of vaporization is 388.4 ± 4.1 kJ.

The density is given in [Table 4.74](#), thermodynamic data in [Tables 4.75 to 4.77](#). Data for Li_2O are in [Table 2.41](#).

4.3.18 MAGNESIUM

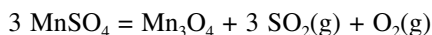
MgSO_4 begins to decompose below the melting point, directly to MgO without an oxysulfate intermediate. Melting points in the literature therefore vary widely. Thermodynamic calculations ([Tables 4.80 and 4.81](#)) indicate that decomposition probably becomes measurable above 1200 K. The initial decomposition temperature was observed to be near 1170 K, and was too rapid above 1450 K to be measurable.⁵⁶

The decomposition kinetics of MgSO_4 have been studied in a flow system in the range 1223 to 1323 K.⁵⁷ When N_2 flows over the salt at 3 l/hr, decomposition is linear in time. Under these conditions the product gases are continuously removed, and the SO_2/SO_3 equilibrium is not established. If these gases and O_2 flow over the salt, the reaction rate is nearly independent of oxygen, but the SO_3/SO_2 ratio decreases with decreasing O_2 content. The activation energy in the range 1293 to 1333 K is 661 kJ.⁴⁹

The density of MgSO_4 is given in [Table 4.78](#). Transitions are given in [Table 4.79](#), and thermodynamic data in [Tables 4.80 to 4.82](#). Data for MgO are in [Table 2.46](#).

4.3.19 MANGANESE

MnSO_4 decomposes before reaching its sometimes reported melting point of 973 K. The product usually observed on pyrolysis in air is Mn_3O_4 ,^{58,59} though Mn_2O_3 may appear mixed with it in the lower temperature range, complicating the kinetic picture.⁶⁰ Since Mn_3O_4 is the expected product we have provided thermodynamic functions for it and for the decomposition reaction



These data show that decomposition becomes appreciable above 1000 K. Data are given in [Tables 4.84 to 4.88](#). The density of MnSO_4 is in [Table 4.83](#). Data for MnO are in [Table 2.50](#).

4.3.20 MERCURY

Hg(I) . Pascal,⁶² using very old references, describes Hg_2SO_4 as unstable to light, disproportionating to Hg° and HgSO_4 , and melting with decomposition to Hg° , O_2 , and SO_2 .

Hg(II) . According to a study by Hoschek,¹⁵ HgSO_4 is unchanged after two hours at 673 K, but by 773 K decomposition occurs to $2 \text{HgO} \cdot \text{HgSO}_4$, identified through their X-ray spectra. All three compounds are volatile at elevated temperatures. The supposed next product, HgO , was not observed because it is even more volatile. If HgSO_4 is heated rapidly to 973 K, some Hg_2SO_4 appears along with the oxysulfates before volatilization is complete.

Since Hg_2SO_4 is so unstable, we have only listed thermodynamic functions for reactions involving HgSO_4 . However, functions for Hg_2O and Hg_2SO_4 have been listed ([Tables 4.89 to 4.92](#)). Note that data for both the divalent sulfate and oxide were extrapolated from 800 K.

The density of HgSO_4 is 6.50 at 298 K.⁶³

4.3.21 NICKEL

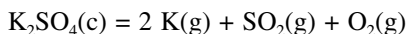
NiSO_4 decomposes, without melting, to NiO . TGA curves show no evidence of an oxysulfate intermediate.^{59,64–66} An experimental study⁵⁶ shows that the decomposition becomes noticeable at 900 K, and very rapid at 1223 K, consistent with thermodynamic data. These are listed in [Tables 4.93 to 4.95](#). Data for NiO are given in [Table 2.58](#).

A contracting sphere model applies, meaning that the reaction occurs at the oxide-sulfate boundary. Similar results were obtained by Tagawa and Saijo.³⁰

The specific gravity is 3.543.²⁷

4.3.22 POTASSIUM

The vaporization of K_2SO_4 was studied by the torsion-effusion method, and by mass spectrometry in the range 1180 to 1280 K.⁶¹ Sublimation contributes 63% of the flux, and decomposition



the rest. According to the authors, vaporization is kinetically hindered. Comparison with decomposition to $\text{K}_2\text{O} + \text{SO}_2 + \text{O}_2$ shows that because of the exponents involved, congruent decomposition is actually more significant. Thermodynamic data for both kinds of decomposition are given ([Tables 4.98 to 4.101](#)).

Densities are listed in [Table 4.96](#), and transitions in [Table 4.97](#). Data for K_2O are in [Table 2.63](#).

4.3.23 RADIUM

The density of RaSO_4 has been calculated as 5.77 g cm^{-3} from crystallographic data.¹⁰³ Thermodynamic data on RaSO_4 are given in [Table 4.102](#).

RARE EARTHS

Since relatively little is known about the high-temperature behavior of the rare-earth sulfates, a summary covering all of them is given first, followed by information about the individual salts.

On heating, all of the anhydrous sulfates of the trivalent rare-earth elements and yttrium, type formula $\text{R}_2(\text{SO}_4)_3$ decompose, without first melting, to basic salts (oxysulfates) of the type $\text{R}_2\text{O}_3 \cdot \text{SO}_3$, then to an oxide. The oxide final product is R_2O_3 for all the elements except cerium, praesodymium,

and terbium, which, in air at ambient pressure, form CeO₂, Pr₆O₁₁, and the somewhat variable oxide usually written as Tb₄O₇.



There have been three comprehensive studies which, taken together, reveal the trend in stability of the sulfates and oxysulfates within the rare-earth series. Woehler and Gruenzweig^{72,73} measured equilibrium decomposition pressures for reaction (a) for scandium, yttrium, and eight of the rare-earth elements in the range 973 to 1293 K. Nathans and Wenlandt⁷⁴ performed DTA and TGA, covering reactions (a) and (b) for yttrium and all the rare earths. Ivakin,⁷⁵ by a weight loss technique in a stream of dry N₂, working with yttrium and seven of the rare earths, investigated the kinetics of reaction (a) at 1223 and 1323 K and of reaction (b) at 1573 K. From these sources one may conclude that, with the exception of cerium, the stability of the sulfates in reaction (a) decreases from La to somewhere in the Sm Eu Gd group, and then increases to Lu, while the stability of the oxysulfates in reaction (b) decreases all the way from La to Lu. These conclusions hold for either kinetic or equilibrium definitions of “stability,” and they ignore a few reversals of order which are probably attributable to experimental errors, in view of the close similarity of adjacent members of the rare-earth series. Among the more stable sulfates the order of decreasing stability in reaction (a) is La to Y to Lu (or Yb) according to kinetics,⁷⁵ equilibrium pressures,⁷⁶ and DTA,⁷⁴ but not by TGA.⁷⁴ In reaction (b) Y falls near Ho and Er,^{74,75} in accordance with the crystal radii of R⁺³ and the lanthanide contraction.

By the equilibrium pressure criterion, Sc₂(SO₄)₃ is less stable than any of the rare-earth sulfates except cerium. However, unlike the rare earths, it seems to decompose directly to Sc₂O₃,⁷⁶ rather than through reactions (a) and (b).

Ce₂(SO₄)₃ is much less stable than the sulfates of the other rare earths,^{72,74,76} and less stable than Sc₂(SO₄)₃.⁷⁶ The product is CeO₂, rather than Ce₂O₃, but the mechanism is unknown. Least stable by far is Ce(SO₄)₃ which also yields CeO₂ ultimately. Woehler, Plueddemann, and Woehler⁴⁵ measured decomposition pressures in the range 634 to 755 K in what they believed to be the system 2 Ce(SO₄)₂ = Ce₂(SO₄)₃ + SO₂ + 1/2 O₂. Duval⁷⁷ found an intermediate 3 CeO₂·4SO₃ by TGA.

Ivakin's kinetic investigation⁷⁵ showed that the oxysulfates in reaction (b) decompose in accordance with a simple zero-order rate law, whereas reaction (a) is more complex kinetically. Thus a plot of the equation

$$1 - (1 - \alpha)^{1/3} = kt$$

is a line whose slope changes at one point from k₁ to k₂. This would suggest a compound intermediate between R₂(SO₄)₃ and R₂O₃·SO₃, but X-ray diffraction patterns were interpreted as showing that the only possible intermediate was a solid solution of variable composition.

The relative stabilities of the sulfates of Sc, Y, and the rare earths may be represented in the following order of decreasing stability:



This refers to decomposition of the normal anhydrous sulfate to its first decomposition product, oxysulfate or oxide as the case may be for each element. The dashed line preceding Gd represents the other rare earth elements. With increasing atomic number the stability first decreases in the order Pr - Nd - Sm - Eu and then increases in the order Tb - Dy - Ho - Er - Tm - Yb.

High-temperature behavior of the bivalent sulfates SmSO₄, EuSO₄, and YbSO₄ has not been investigated. They are expected to undergo self-oxidation, like FeSO₄, to ultimately yield R₂O₃.

4.3.24 CERIUM

$\text{Ce}_2(\text{SO}_4)_3$ melts at 1143 K. Thermodynamic data are listed in [Tables 4.103](#) to 4.106.

4.3.25 DYSPROSIUM

TGA and DTA curves indicate that $\text{Dy}_2(\text{SO}_4)_3$ decomposes to DyO_2SO_4 in the range 1183 to 1413 K and then to Dy_2O_3 up to 1593 K.⁷⁸

4.3.26 ERBIUM

TGA and DTA curves indicate that $\text{Er}_2(\text{SO}_4)_3$ decomposes to ErO_2SO_4 in the range 1213 to 1413 K, and then to Er_2O_3 from 1413 to 1543 K.⁷⁸

4.3.27 EUROPIUM

The dry salt is quite stable in air. Decomposition proceeds according to



and finally, Eu_2O_3 above 1173 K. Oxidation to Eu(III) occurs simultaneously.⁷⁹

4.3.28 GADOLINIUM

Decomposition to $\text{Gd}_2\text{O}_2\text{SO}_4$ occurs at 1300 K and to Gd_2O_3 at 1543 K.⁷⁸

4.3.29 HOLMIUM

Decomposition of $\text{Ho}_2(\text{SO}_4)_3$ to $\text{Ho}_2\text{O}_2\text{SO}_4$ occurs from 1203 to 1443 K, and to Ho_2O_3 from 1443 to 1583 K.⁷⁸

4.3.30 LANTHANUM

Thermodynamic functions of $\text{La}_2(\text{SO}_4)_3$ are given in [Table 4.107](#). Decomposition to $\text{La}_2\text{O}_2\text{SO}_4$ begins at 973 K and becomes appreciable at 1173 K. At 1513 K decomposition proceeds to La_2O_3 and the reaction is complete at 1593 K. Both reactions are kinetically first order.⁸⁰

4.3.31 NEODYMIUM

$\text{Nd}_2(\text{SO}_4)_3$ decomposes to $\text{Nd}_2\text{O}_2\text{SO}_4$ at ~1300 K and then, up to 1630 K, to Nd_2O_3 , consistent with the thermodynamic data in [Tables 4.108](#) to 4.111.

4.3.32 PRAESODYMIUM

$\text{Pr}_2(\text{SO}_4)_3$ decomposes to $\text{Pr}_2\text{O}_2\text{SO}_4$ up to 1273 K. Between 1448 and 1658 K decomposition proceeds to Pr_2O_3 .⁷⁸

4.3.33 SAMARIUM

$\text{Sm}_2(\text{SO}_4)_3$ is stable up to 1073 K and then decomposes to $\text{Sm}_2\text{O}_2\text{SO}_4$. At 1500 K decomposition proceeds to Sm_2O_3 .

$$\Delta H^\circ_f(298) = -4473 \text{ kJ mol}^{-1}$$

$$\Delta G^\circ_f(298) = -3535 \text{ kJ mol}^{-1}$$

4.3.34 TERBIUM

$\text{Tb}_2(\text{SO}_4)_3$ decomposes to $\text{Tb}_2\text{O}_2\text{SO}_4$ in the range 1156 to 1363 K and to $\text{Tb}_2\text{O}_2\text{SO}_4$ at 1403 to 1590 K.⁷⁸

4.3.35 THULIUM

$\text{Tm}_2(\text{SO}_4)_3$ decomposes in the range 1213 to 1543 K, but the nature of the product is not certain.⁷⁸

4.3.36 YTTERBIUM

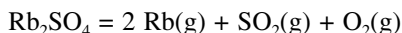
$\text{Yb}_2(\text{SO}_4)_3$ decomposes in the range 1173 to 1523 K, but the nature of the product is not clear.⁸⁰

4.3.37 RHODIUM

The compound $\text{Rh}_2(\text{SO}_4)_3$ is difficult to prepare in pure form. The reported density of 3.44 at 291 K⁸¹ needs confirmation.

4.3.38 RUBIDIUM

The vaporization/decomposition of Rb_2SO_4 has been studied by mass spectrometry and the torsion-effusion method.²³ Molecular vaporization accounts for 75% of the total, with the decomposition



accounting for the rest. The derived enthalpy of vaporization at 298 K is $340 \pm 2.8 \text{ kJ mol}^{-1}$. Thermodynamic functions for this reaction are given in [Tables 4.114 to 4.116](#). Data for Rb_2O are given in [Table 2.66](#). Densities are in [Table 4.112](#), phase changes in [Table 4.113](#).

4.3.39 SCANDIUM

$\text{Sc}_2(\text{SO}_4)_3$ is stable to 873 K and then decomposes directly to Sc_2O_3 .⁸² No high-temperature thermodynamic data for the salt are available, although they are known for the oxide.

4.3.40 SILVER

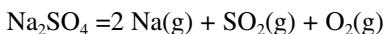
The salt exists in two crystalline modifications: a lower temperature rhombic and a higher temperature hexagonal. The measured transition temperature seems to depend somewhat on the heating (or cooling) rate.

Since Ag_2O is only stable over a narrow temperature range above ambient, the decomposition of Ag_2SO_4 may be thought of as proceeding directly to the oxide. The tables given, 4.118–4.120, permit carrying out the desired calculations. Data for Ag_2O are in [Tables 2.69 and 2.71](#). The density is 5.363 at 298 K,⁸³ and transitions are given in [Table 4.117](#).

4.3.41 SODIUM

Na_2SO_4 exists in several crystal modifications which are given in [Table 4.122](#). The nomenclature for the crystal forms is that of Kracek and Gibson.⁸⁴ The transition enthalpy between III and V is 3.1 kJ mol^{-1} from 298 to 450 K, whence ΔH°_f of III at 298.15 K is $-1381.4 \text{ kJ mol}^{-1}$.

A mass spectrometric and torsion effusion study²³ found that sublimation accounted for 37% of the mass loss and the decomposition



for the rest. The derived enthalpy of sublimation is 364.0 ± 1.3 kJ at 298.15 K. Other thermodynamic data are given in [Tables 4.123 to 4.125](#). Data for Na_2O are given in [Table 2.75](#). Densities are listed in [Table 4.121](#), transitions in [Table 4.122](#).

4.3.42 STRONTIUM

SrSO_4 exists in two crystalline modifications. SrSO_4 is the mineral stelestitute (stelestitute). The ambient temperature density is 3.91.⁸⁶ Transition data are given in [Table 4.126](#).

There are some discordant experimental decomposition studies [87], but the thermodynamic data ([Tables 4.127 to 4.129](#)) indicate stability to near 1500 K. Data for SrO are in [Table 2.79](#).

4.3.43 TANTALUM

The existence of anhydrous $\text{Ta}_2(\text{SO}_4)_3$ is uncertain.⁸⁸

4.3.44 THALLIUM

Tl(I) . According to most of the older literature,⁸⁹ Tl_2SO_4 may be heated as far as the melting point without noticeable decomposition or volatilization, after which it sublimes without decomposition. TGA studies have reported contradictory results. One has a plateau up to 628 K,⁹⁰ then a weight loss interpreted as formation of Tl_2O_3 , not quite complete by 1153 K. The other⁹¹ shows a plateau to 1000 K, followed by rapid volatilization.

Favorskaya and Ponomaryeva⁹² measured the vapor pressure of Tl_2SO_4 in the range 973 to 1233 K by a dynamic method, finding no evidence of decomposition. Thermodynamic calculations suggest the decomposition begins above 1200 K. Densities are given in [Tables 4.130](#), transitions in [Table 4.131](#), and thermodynamic data in [Tables 4.132 to 4.135](#).

Tl(III) . Little is known about $\text{Tl}_2(\text{SO}_4)_3$. It has been reported⁸⁹ to decompose readily to Tl_2SO_4 .

4.3.45 THORIUM

$\text{Th}(\text{SO}_4)_2$ is stable to at least 673 K, the temperature commonly used to prepare the anhydrous salt from the hydrates. However, the thermodynamic [Tables 4.136 to 4.139](#), indicate stability to near 1100 K. At higher temperatures, the salt decomposes to ThO_2 without melting or passing through an oxysulfate.

4.3.46 TIN

Sn(II) . At room temperature SnSO_4 is stable in air for several months, longer in vacuum in the dark, but on heating it undergoes self-oxidation to SnO_2 and SO_2 . Above 633 K in O_2 -free N_2 complete conversion has been found at 651 K, but there is little decomposition below this temperature.⁹⁵ Various other studies^{65,95} have obtained various contradictory results. Thermodynamic results ([Tables 4.140 to 4.147](#)) indicate stability to much higher temperatures, but these assume equilibrium rather than kinetic (vacuum or flowing gas) conditions.

Sn(IV) . Anhydrous $\text{Sn}(\text{SO}_4)_2$ is very hygroscopic, and becomes thermally unstable not far above 373 K.⁹⁶ However, TGA studies indicate decomposition in a vacuum becomes noticeable near 573 K, with complete conversion to SnO_2 at about 860 K.⁶⁵

4.3.47 TITANIUM

Ti(II) TiSO_4 , existence uncertain.

Ti(III) . $\text{Ti}_2(\text{SO}_4)_3$. Thermal properties unknown, except that it yields TiO_2 on ignition.

Ti(IV) . Anhydrous $\text{Ti}(\text{SO}_4)_2$ has been prepared.^{101,104} It decomposes in two steps,¹⁰¹ beginning at 423 K, ultimately yielding TiO_2 . Chuklantsev¹⁰⁴ heated the salt at $1.7^\circ/\text{min}$ in dry argon

by a procedure resembling TGA, and found decomposition beginning at 423 K to produce TiOSO_4 ; at 703 K this began decomposing to TiO_2 , and was complete by approximately 873 K. The decomposition pressures reported by Woehler et al.¹⁰⁵ for TiOSO_4 at 741 to 853 K are not trustworthy.

The density of TiSO_4 has been reported to be 2.47 gcm^{-3} at 293 K.¹⁰⁴ No thermodynamic data for TiSO_4 are known and therefore decomposition pressures cannot be calculated.

4.3.48 URANIUM

U(III). Difficult to isolate from solution; it is readily oxidized by H_2O .

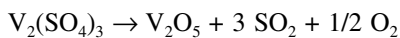
U(IV). Hydrates are well-known. Several methods for preparing anhydrous $\text{U}(\text{SO}_4)_2$ have been described.⁹⁷ Further heating produces UO_2SO_4 , even in the absence of air. Thermodynamic data for the decomposition are in [Tables 4.148 to 4.151](#).

U(VI). This occurs only in uranyl salts containing the UO_2^{2+} cation, which are outside the scope of this work.

4.3.49 VANADIUM

V(II). Only the hydrate $\text{VSO}_4 \cdot 7\text{H}_2\text{O}$ is known.

V(III). Rivenq⁹⁸ described the preparation and pyrolysis of anhydrous $\text{V}_2(\text{SO}_4)_3$. On heating in a vacuum the compound was stable to 598 K, but decomposed above 653 K. According to the author's interpretation of weight loss curves, the decomposition is complicated, its course dependent on temperature. The final product below 673 K was V_2O_3 , while above 681 K a mixture of V_2O_3 and V_2O_5 formed. Udupa⁹⁹ reported that the decomposition occurred in a single step



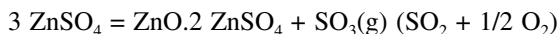
but in a higher temperature range, 723 to 893 K. Thermodynamic data are available for VOSO_4 , but not for $\text{V}_2(\text{SO}_4)_3$.

V(IV). Anhydrous VOSO_4 decomposes, without melting, above 673 K, with oxidation to V_2O_5 , SO_3 , and SO_2 . The reaction is reversible. Neumann and Sonntag¹⁰⁰ measured equilibrium decomposition pressures in the range 704 to 826 K.

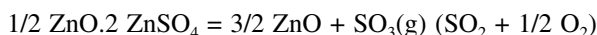
V(V). Anhydrous $\text{V}_2\text{O}_5 \cdot 2 \text{SO}_3$, $\text{V}_2\text{O}_5 \cdot 3 \text{SO}_3$, and $\text{V}_2\text{O}_5 \cdot 4 \text{SO}_3$ are known. The preparation of the last of these has been described by Hayek and Engelbrecht,¹⁰¹ who found it to be unstable above 373 to 473 K.

4.3.50 ZINC

The decomposition of ZnSO_4 proceeds through an intermediate oxysulfate $\text{ZnO} \cdot 2 \text{ZnSO}_4$. The decomposition can thus be characterized as



For the oxysulfate, the corresponding reaction is



Both reactions were studied by Brittain, Lau, Knittel, and Hildenbrand¹⁰² using a torsion-effusion method in the temperature range 800 to 900 K. They found the SO_3 pressure over both the sulfate and oxysulfate derived from extrapolation of steady-state pressures to the zero orifice area to be a factor of five lower than those calculated from established thermodynamic data. This indicates that the products are formed in a finely divided metastable state.

As for other sulfates, whether the product is SO_3 or $\text{SO}_2 + \text{O}_2$ seems to depend on experimental conditions which have somewhat different effects on different salts.

The kinetics was found to follow the contracting sphere model.⁵⁶

Two groups^{8,27} have reported different densities at 298 K: 3.74 and 3.546.

The $\alpha - \beta$ transition of ZnSO_4 was found at 1008 K,⁹ a temperature at which decomposition also becomes noticeable.

Thermodynamic data are given in Tables 4.152 to 4.154. Thermodynamic data for ZnO are given in Table 2.84.

4.3.51 ZIRCONIUM

The decomposition of $\text{Zr}(\text{SO}_4)_2$ results in the formation of ZrO_2 without the formation of an intermediate. There is considerable disagreement about a “decomposition temperature,” but is probably above 820 K.

Thermodynamic data are given in Tables 4.155 to 4.158.

TABLE 4.1
Thermodynamic Data of $\text{SO}_3(\text{g})$

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|---|---|---|------------|
| 298.15 | -395.77 | 256.77 | -472.32 | Barin 1989 |
| 400.00 | -390.25 | 272.64 | -499.30 | Barin 1989 |
| 500.00 | -384.20 | 286.11 | -527.26 | Barin 1989 |
| 600.00 | -377.66 | 298.02 | -556.47 | Barin 1989 |
| 700.00 | -370.75 | 308.67 | -586.82 | Barin 1989 |
| 800.00 | -363.59 | 318.23 | -618.17 | Barin 1989 |
| 900.00 | -356.22 | 326.91 | -650.44 | Barin 1989 |
| 1000.00 | -348.70 | 334.83 | -683.53 | Barin 1989 |
| 1100.00 | -341.05 | 342.12 | -717.38 | Barin 1989 |
| 1200.00 | -333.31 | 348.85 | -751.93 | Barin 1989 |
| 1300.00 | -325.49 | 355.11 | -787.14 | Barin 1989 |
| 1400.00 | -317.60 | 360.96 | -822.94 | Barin 1989 |
| 1500.00 | -309.65 | 366.45 | -859.32 | Barin 1989 |
| 1600.00 | -301.65 | 371.60 | -896.22 | Barin 1989 |
| 1700.00 | -293.62 | 376.47 | -933.63 | Barin 1989 |
| 1800.00 | -285.66 | 381.08 | -971.51 | Barin 1989 |
| 1900.00 | -277.47 | 385.46 | -1009.84 | Barin 1989 |
| 2000.00 | -269.36 | 389.62 | -1048.59 | Barin 1989 |
| 2100.00 | -261.23 | 393.58 | -1087.75 | Barin 1989 |
| 2200.00 | -253.09 | 397.37 | -1127.30 | Barin 1989 |
| 2300.00 | -244.93 | 400.99 | -1167.22 | Barin 1989 |
| 2400.00 | -236.77 | 404.77 | -1207.50 | Barin 1989 |

TABLE 4.2
Thermodynamic Data of SO₂(g)

| T K | ΔHf° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔGf° kJ mol⁻¹ | Reference |
|----------------------|---|---|---|------------------|
| 298.15 | -296.81 | 248.22 | -370.82 | Barin 1993 |
| 400.00 | -292.57 | 260.42 | -396.75 | Barin 1993 |
| 500.00 | -288.07 | 270.46 | -423.30 | Barin 1993 |
| 600.00 | -283.27 | 279.20 | -450.79 | Barin 1993 |
| 700.00 | -278.26 | 286.93 | -479.11 | Barin 1993 |
| 800.00 | -273.08 | 293.84 | -508.15 | Barin 1993 |
| 900.00 | -267.78 | 300.08 | -537.85 | Barin 1993 |
| 1000.00 | -262.38 | 305.77 | -568.15 | Barin 1993 |
| 1100.00 | -256.90 | 310.99 | -598.99 | Barin 1993 |
| 1200.00 | -251.36 | 315.81 | -630.34 | Barin 1993 |
| 1300.00 | -245.76 | 320.30 | -662.14 | Barin 1993 |
| 1400.00 | -240.11 | 324.48 | -694.38 | Barin 1993 |
| 1500.00 | -234.43 | 328.40 | -727.03 | Barin 1993 |
| 1600.00 | -228.70 | 333.00 | -760.06 | Barin 1993 |
| 1700.00 | -222.95 | 335.58 | -793.44 | Barin 1993 |
| 1800.00 | -217.17 | 338.89 | -827.17 | Barin 1993 |
| 1900.00 | -211.38 | 342.02 | -861.21 | Barin 1993 |
| 2000.00 | -205.56 | 345.00 | -895.57 | Barin 1993 |
| 2100.00 | -199.73 | 347.85 | -930.21 | Barin 1993 |
| 2200.00 | -193.88 | 350.57 | -965.13 | Barin 1993 |
| 2300.00 | -188.02 | 353.18 | -1000.32 | Barin 1993 |
| 2400.00 | -182.14 | 355.66 | -1035.76 | Barin 1993 |

TABLE 4.3
 $\text{SO}_3(\text{g}) = \text{SO}_2 + 1/2 \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 98.95 | 94.02 | 70.92 | 3.752E – 013 |
| 400.00 | 99.20 | 94.76 | 61.39 | 9.880E – 009 |
| 500.00 | 99.24 | 94.85 | 51.81 | 3.861E – 006 |
| 600.00 | 99.11 | 94.61 | 42.34 | 2.060E – 004 |
| 700.00 | 98.86 | 94.24 | 32.90 | 3.509E – 003 |
| 800.00 | 98.55 | 93.82 | 23.49 | 2.924E – 002 |
| 900.00 | 98.18 | 93.38 | 14.13 | 1.513E – 001 |
| 1000.00 | 97.77 | 92.96 | 4.82 | 5.603E – 001 |
| 1100.00 | 97.35 | 92.55 | –4.46 | 1.628E + 000 |
| 1200.00 | 96.90 | 92.17 | –13.70 | 3.946E + 000 |
| 1300.00 | 96.45 | 91.81 | –22.89 | 8.317E + 000 |
| 1400.00 | 96.00 | 91.47 | –32.06 | 1.571E + 001 |
| 1500.00 | 95.54 | 91.16 | –41.19 | 2.719E + 001 |
| 1600.00 | 95.09 | 90.86 | –50.29 | 4.384E + 001 |
| 1700.00 | 94.65 | 90.59 | –59.36 | 6.670E + 001 |
| 1800.00 | 94.21 | 90.34 | –68.41 | 9.667E + 001 |
| 1900.00 | 93.79 | 90.11 | –77.43 | 1.346E + 002 |
| 2000.00 | 93.37 | 89.90 | –86.43 | 1.809E + 002 |
| 2100.00 | 92.97 | 89.71 | –95.41 | 2.363E + 002 |
| 2200.00 | 92.58 | 89.52 | –104.37 | 3.008E + 002 |
| 2300.00 | 92.20 | 89.36 | –113.32 | 3.747E + 002 |
| 2400.00 | 91.84 | 89.20 | –122.24 | 4.579E + 002 |

TABLE 4.4
Thermodynamic Data of $\text{Al}_2(\text{SO}_4)_3$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | –3440.75 | 239.30 | –3512.10 | Knacke et al. 1991 |
| 400.00 | –3410.75 | 325.42 | –3540.92 | Knacke et al. 1991 |
| 500.00 | –3376.89 | 400.86 | –3577.32 | Knacke et al. 1991 |
| 600.00 | –3340.54 | 467.08 | –3620.78 | Knacke et al. 1991 |
| 700.00 | –3302.49 | 525.69 | –3670.48 | Knacke et al. 1991 |
| 800.00 | –3263.16 | 578.20 | –3725.72 | Knacke et al. 1991 |
| 900.00 | –3222.76 | 625.77 | –3785.96 | Knacke et al. 1991 |
| 1000.00 | –3181.42 | 669.32 | –3850.74 | Knacke et al. 1991 |
| 1100.00 | –3139.24 | 709.52 | –3919.71 | Knacke et al. 1991 |
| 1200.00 | –3096.35 | 746.92 | –3992.55 | Knacke et al. 1991 |
| 1300.00 | –3052.51 | 781.92 | –4069.01 | Knacke et al. 1991 |
| 1400.00 | –3008.04 | 814.87 | –4148.87 | Knacke et al. 1991 |
| 1500.00 | –2962.87 | 846.04 | –4231.93 | Knacke et al. 1991 |

TABLE 4.5
Thermodynamic Data of Al_2O_3

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------------|
| 298.15 | -1675.27 | 50.94 | -1690.46 | Barin et al. 1977 |
| 400.00 | -1666.25 | 76.86 | -1696.99 | Barin et al. 1977 |
| 500.00 | -1656.13 | 99.39 | -1705.83 | Barin et al. 1977 |
| 600.00 | -1645.27 | 119.17 | -1716.78 | Barin et al. 1977 |
| 700.00 | -1633.88 | 136.73 | -1729.59 | Barin et al. 1977 |
| 800.00 | -1622.04 | 152.53 | -1744.06 | Barin et al. 1977 |
| 900.00 | -1609.08 | 166.85 | -1760.04 | Barin et al. 1977 |
| 1000.00 | -1597.49 | 179.90 | -1777.39 | Barin et al. 1977 |
| 1100.00 | -1584.91 | 191.89 | -1795.99 | Barin et al. 1977 |
| 1200.00 | -1572.17 | 202.97 | -1815.74 | Barin et al. 1977 |
| 1300.00 | -1559.28 | 213.29 | -1836.56 | Barin et al. 1977 |
| 1400.00 | -1546.25 | 222.94 | -1858.38 | Barin et al. 1977 |
| 1500.00 | -1533.15 | 232.02 | -1881.13 | Barin et al. 1977 |

TABLE 4.6
 $\text{Al}_2(\text{SO}_4)_3 = \text{Al}_2\text{O}_3 + 3 \text{SO}_3(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 578.19 | 581.95 | 404.68 | 1.248E - 071 |
| 400.00 | 573.77 | 569.37 | 346.02 | 6.470E - 046 |
| 500.00 | 568.14 | 556.84 | 289.72 | 5.377E - 031 |
| 600.00 | 562.28 | 546.16 | 234.59 | 3.765E - 021 |
| 700.00 | 556.36 | 537.03 | 180.44 | 3.423E - 014 |
| 800.00 | 550.36 | 529.04 | 127.14 | 4.985E - 009 |
| 900.00 | 544.23 | 521.80 | 74.61 | 4.673E - 005 |
| 1000.00 | 537.85 | 515.08 | 22.77 | 6.467E - 002 |
| 1100.00 | 531.17 | 508.72 | -28.42 | 2.237E + 001 |

TABLE 4.7
 $\text{Al}_2(\text{SO}_4)_3 = \text{Al}_2\text{O}_3 + 3 \text{SO}_2(\text{g}) + 3/2 \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 875.04 | 864.02 | 617.43 | 6.594E - 109 |
| 400.00 | 871.37 | 853.66 | 529.91 | 6.240E - 070 |
| 500.00 | 865.85 | 841.38 | 445.16 | 3.095E - 047 |
| 600.00 | 859.60 | 829.99 | 361.60 | 3.290E - 032 |
| 700.00 | 852.95 | 819.75 | 279.12 | 1.479E - 021 |
| 800.00 | 846.00 | 810.47 | 197.62 | 1.246E - 013 |
| 900.00 | 838.76 | 801.95 | 117.00 | 1.617E - 007 |
| 1000.00 | 831.16 | 793.95 | 37.21 | 1.138E - 002 |
| 1100.00 | 823.20 | 786.37 | -41.80 | 9.662E + 001 |

TABLE 4.8
Thermodynamic Data of $\text{Sb}_2(\text{SO}_4)_3$

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|---|---|---|-------------------|
| 298.15 | -2402.50 | 291.21 | -2489.32 | Barin et al. 1977 |
| 400.00 | -2373.48 | 374.80 | -2523.40 | Barin et al. 1977 |
| 500.00 | -2343.11 | 442.49 | -2564.36 | Barin et al. 1977 |
| 600.00 | -2310.89 | 501.19 | -2611.60 | Barin et al. 1977 |
| 700.00 | -2276.80 | 553.69 | -2664.39 | Barin et al. 1977 |
| 800.00 | -2240.86 | 601.66 | -2722.19 | Barin et al. 1977 |
| 900.00 | -2203.07 | 646.15 | -2784.60 | Barin et al. 1977 |
| 1000.00 | -2163.41 | 687.92 | -2851.33 | Barin et al. 1977 |
| 1100.00 | -2121.90 | 727.47 | -2922.11 | Barin et al. 1977 |
| 1200.00 | 2078.52 | 765.20 | -2996.76 | Barin et al. 1977 |

TABLE 4.9
Thermodynamic Data of Sb_4O_6 , Valentinite

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|---|---|---|--------------------|
| 298.15 | -1417.54 | 246.02 | -1490.89 | Knacke et al. 1991 |
| 400.00 | -1396.02 | 308.01 | -1519.22 | Knacke et al. 1991 |
| 500.00 | -1373.81 | 357.53 | -1552.58 | Knacke et al. 1991 |
| 600.00 | -1350.99 | 399.13 | -1590.46 | Knacke et al. 1991 |
| 700.00 | -1327.74 | 434.96 | -1632.21 | Knacke et al. 1991 |
| 800.00 | -1304.17 | 466.43 | -1677.31 | Knacke et al. 1991 |
| 900.00 | -1280.33 | 494.51 | -1725.38 | Knacke et al. 1991 |
| 1000.00 | -1256.24 | 519.88 | -1776.12 | Knacke et al. 1991 |
| 1100.00 | -1231.94 | 543.04 | -1829.29 | Knacke et al. 1991 |
| 1200.00 | -1207.42 | 564.37 | -1884.67 | Knacke et al. 1991 |

TABLE 4.10
Thermodynamic Data of Sb_2O_5

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|---|---|---|------------|
| 298.15 | -971.90 | 125.10 | -1009.2 | Barin 1989 |
| 400.00 | -959.36 | 161.23 | -1023.85 | Barin 1989 |
| 500.00 | -946.40 | 190.13 | -1041.46 | Barin 1989 |
| 600.00 | -933.14 | 214.29 | -1061.72 | Barin 1989 |
| 700.00 | -919.73 | 234.96 | -1084.20 | Barin 1989 |
| 800.00 | -906.24 | 252.98 | -1108.62 | Barin 1989 |
| 900.00 | -892.70 | 268.92 | -1134.73 | Barin 1989 |
| 1000.00 | -879.15 | 283.20 | -1162.35 | Barin 1989 |
| 1100.00 | -865.59 | 296.13 | -1191.33 | Barin 1989 |
| 1200.00 | -852.04 | 307.92 | -1221.54 | Barin 1989 |

TABLE 4.11
Thermodynamic Data of Sb_2O_4 , Cervantite

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -907.51 | 126.98 | -945.37 | Barin 1993 |
| 400.00 | -895.32 | 162.09 | -960.16 | Barin 1993 |
| 500.00 | -882.72 | 190.19 | -977.82 | Barin 1993 |
| 600.00 | -869.77 | 213.79 | -998.05 | Barin 1993 |
| 700.00 | -856.60 | 234.08 | -1020.46 | Barin 1993 |
| 800.00 | -843.27 | 251.89 | -1044.78 | Barin 1993 |
| 900.00 | -829.80 | 267.75 | -1070.78 | Barin 1993 |
| 1000.00 | -816.22 | 282.06 | -1098.28 | Barin 1993 |
| 1100.00 | -802.54 | 296.00 | -1127.15 | Barin 1993 |
| 1200.00 | -788.76 | 307.08 | -1157.36 | Barin 1993 |

TABLE 4.12
Thermodynamic Data of Sb_2O_3 , Senarmontite

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -720.31 | 110.45 | -753.24 | Barin 1993 |
| 400.00 | -708.58 | 144.23 | -766.27 | Barin 1993 |
| 500.00 | -696.40 | 171.38 | -782.09 | Barin 1993 |
| 600.00 | -683.56 | 194.78 | -800.43 | Barin 1993 |
| 700.00 | -670.06 | 215.58 | -820.96 | Barin 1993 |
| 800.00 | -655.90 | 234.48 | -843.48 | Barin 1993 |
| 900.00 | -635.03 | 258.81 | -867.96 | Barin 1993 |
| 1000.00 | -565.35 | 333.50 | -898.85 | Barin 1993 |
| 1100.00 | -549.66 | 348.45 | -932.96 | Barin 1993 |
| 1200.00 | -533.97 | 362.11 | -968.50 | Barin 1993 |

TABLE 4.13
Transitions of BaSO_4

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol*K) | Reference |
|------------------------|------|-------------------|----------------------|-----------|
| c,II \rightarrow c,I | 1422 | | | 9,10 |
| c,I \rightarrow l | 1620 | 40.6 | 25 | 5,10 |

TABLE 4.14
Thermodynamic Data of BaSO₄, Barite

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|---|--|------------|
| 298.15 | -1473.20 | 132.20 | -1512.62 | Barin 1989 |
| 400.00 | -1461.81 | 164.94 | -1527.79 | Barin 1989 |
| 500.00 | -1449.43 | 192.53 | -1545.70 | Barin 1989 |
| 600.00 | -1436.46 | 216.16 | -1566.16 | Barin 1989 |
| 700.00 | -1423.16 | 236.66 | -1588.82 | Barin 1989 |
| 800.00 | -1409.65 | 254.70 | -1613.41 | Barin 1989 |
| 900.00 | -1396.00 | 270.78 | -1639.70 | Barin 1989 |
| 1000.00 | -1382.25 | 285.27 | -1667.51 | Barin 1989 |
| 1100.00 | -1368.43 | 298.44 | -1696.71 | Barin 1989 |
| 1200.00 | -1354.55 | 310.51 | -1727.16 | Barin 1989 |

TABLE 4.15
BaSO₄ = BaO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 523.89 | 194.86 | 465.79 | 2.444E - 082 |
| 400.00 | 522.99 | 192.31 | 446.06 | 5.562E - 059 |
| 500.00 | 521.76 | 189.57 | 426.97 | 2.459E - 045 |
| 600.00 | 520.59 | 187.44 | 408.13 | 2.926E - 036 |
| 700.00 | 519.58 | 185.87 | 389.47 | 8.615E - 030 |
| 800.00 | 518.71 | 184.72 | 370.94 | 5.999E - 025 |
| 900.00 | 518.01 | 183.88 | 352.51 | 3.459E - 021 |
| 1000.00 | 517.45 | 183.29 | 334.16 | 3.500E - 018 |
| 1100.00 | 517.02 | 182.88 | 315.85 | 1.001E - 015 |
| 1200.00 | 516.72 | 182.62 | 297.57 | 1.111E - 013 |

TABLE 4.16
BaSO₄ = BaO + SO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 622.84 | 288.88 | 536.71 | 9.171E - 095 |
| 400.00 | 622.19 | 287.08 | 507.36 | 5.495E - 067 |
| 500.00 | 621.00 | 284.42 | 478.79 | 9.492E - 051 |
| 600.00 | 619.70 | 282.05 | 450.47 | 6.028E - 040 |
| 700.00 | 618.44 | 280.11 | 422.36 | 3.023E - 032 |
| 800.00 | 617.26 | 278.53 | 394.53 | 1.754E - 026 |
| 900.00 | 616.18 | 277.26 | 366.65 | 5.233E - 022 |
| 1000.00 | 615.22 | 276.25 | 338.97 | 1.961E - 018 |
| 1100.00 | 614.36 | 275.43 | 311.39 | 1.630E - 015 |
| 1200.00 | 613.62 | 274.78 | 283.88 | 4.386E - 013 |

TABLE 4.17
Density of BeSO₄

| Phase | T(K) | d | Reference |
|-------|---------|---|-----------|
| c | ambient | 2.54 gcm ⁻³ , crystallographic | 12 |
| c | 298 | 2.44 | 8 |

TABLE 4.18
Thermodynamic Data of BeSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1200.81 | 77.97 | -1224.05 | Barin 1989 |
| 400.00 | -1191.13 | 105.77 | -1233.44 | Barin 1989 |
| 500.00 | -1180.15 | 130.21 | -1245.26 | Barin 1989 |
| 600.00 | -1167.95 | 152.43 | -1259.41 | Barin 1989 |
| 700.00 | -1154.62 | 172.95 | -1275.69 | Barin 1989 |
| 800.00 | -1140.21 | 192.18 | -1293.95 | Barin 1989 |
| 900.00 | -1123.56 | 211.76 | -1314.14 | Barin 1989 |
| 1000.00 | -1087.14 | 251.05 | -1338.19 | Barin 1989 |
| 1100.00 | -1069.24 | 268.11 | -1364.15 | Barin 1989 |
| 1200.00 | -1050.60 | 284.32 | -1391.78 | Barin 1989 |

TABLE 4.19
Thermodynamic Data of BeO, Bromellite

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -608.35 | 13.77 | -612.46 | Barin 1989 |
| 400.00 | -605.31 | 22.51 | -614.31 | Barin 1989 |
| 500.00 | -601.68 | 30.59 | -616.97 | Barin 1989 |
| 600.00 | -597.61 | 37.98 | -620.40 | Barin 1989 |
| 700.00 | -593.24 | 44.72 | -624.54 | Barin 1989 |
| 800.00 | -588.62 | 50.88 | -629.33 | Barin 1989 |
| 900.00 | -583.85 | 56.50 | -634.70 | Barin 1989 |
| 1000.00 | -578.97 | 61.64 | -640.61 | Barin 1989 |
| 1100.00 | -574.03 | 66.35 | -647.01 | Barin 1989 |
| 1200.00 | -569.02 | 70.71 | -653.87 | Barin 1989 |

TABLE 4.20
BeSO₄ = BeO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|-----------|----------------------------|-----------|--------------|
| 298.15 | 196.69 | 192.57 | 139.27 | 3.960E – 025 |
| 400.00 | 195.58 | 189.38 | 119.83 | 2.244E – 016 |
| 500.00 | 194.28 | 186.48 | 101.04 | 2.780E – 011 |
| 600.00 | 192.68 | 183.58 | 82.53 | 6.523E – 008 |
| 700.00 | 190.63 | 180.44 | 64.33 | 1.583E – 005 |
| 800.00 | 188.00 | 176.93 | 46.46 | 9.258E – 004 |
| 900.00 | 183.49 | 171.65 | 29.00 | 2.073E – 002 |
| 1000.00 | 159.47 | 145.42 | 14.05 | 1.845E – 001 |
| 1100.00 | 154.15 | 140.36 | -0.241 | 1.027E + 000 |
| 1200.00 | 148.27 | 135.25 | -14.020 | 4.077E + 000 |

TABLE 4.21
BeSO₄ = BeO + SO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|-----------|----------------------------|-----------|--------------|
| 298.15 | 295.64 | 286.60 | 210.19 | 1.486E – 037 |
| 400.00 | 294.78 | 284.14 | 181.12 | 2.217E – 024 |
| 500.00 | 293.51 | 281.33 | 152.85 | 1.073E – 016 |
| 600.00 | 291.78 | 278.19 | 124.87 | 1.344E – 011 |
| 700.00 | 289.50 | 274.68 | 97.22 | 5.554E – 011 |
| 800.00 | 286.55 | 270.75 | 69.95 | 2.707E – 005 |
| 900.00 | 281.67 | 265.03 | 43.13 | 3.136E – 003 |
| 1000.00 | 257.25 | 238.38 | 18.87 | 1.034E – 001 |
| 1100.00 | 251.50 | 232.91 | -4.70 | 1.672E + 000 |
| 1200.00 | 245.18 | 227.41 | -27.71 | 1.609E + 001 |

TABLE 4.22
Thermodynamic Data of Bi₂(SO₄)₃

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|------------------------------|---|------------------------------|-------------------|
| 298.15 | -2544.30 | 312.55 | -2637.48 | Barin et al. 1977 |
| 400.00 | -2512.02 | 396.89 | -2673.78 | Barin et al. 1977 |
| 500.00 | -2484.57 | 464.77 | -2716.96 | Barin et al. 1977 |
| 600.00 | -2452.43 | 523.33 | -2766.43 | Barin et al. 1977 |
| 700.00 | -2418.60 | 575.45 | -2821.41 | Barin et al. 1977 |
| 800.00 | -2383.08 | 622.85 | -2881.36 | Barin et al. 1977 |
| 900.00 | -2345.86 | 666.66 | -2945.86 | Barin et al. 1977 |
| 1000.00 | -2396.96 | 707.64 | -3014.60 | Barin et al. 1977 |
| 1100.00 | -2266.37 | 746.31 | -3087.31 | Barin et al. 1977 |
| 1200.00 | -2224.08 | 783.10 | -3163.80 | Barin et al. 1977 |

TABLE 4.23
Thermodynamic Data of Bi₂O₃

| T K | ΔH° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -573.88 | 151.50 | -619.05 | Barin 1993 |
| 400.00 | -562.15 | 185.33 | -636.28 | Barin 1993 |
| 500.00 | -550.29 | 211.77 | -656.17 | Barin 1993 |
| 600.00 | -538.10 | 233.99 | -678.49 | Barin 1993 |
| 700.00 | -525.57 | 253.30 | -702.88 | Barin 1993 |
| 800.00 | -512.71 | 270.46 | -729.08 | Barin 1993 |
| 900.00 | -499.51 | 286.00 | -756.92 | Barin 1993 |
| 1000.00 | -485.98 | 300.26 | -786.24 | Barin 1993 |
| 1100.00 | -423.73 | 360.26 | -820.02 | Barin 1993 |
| 1200.00 | -405.74 | 375.91 | -856.84 | Barin 1993 |

TABLE 4.24
Bi₂(SO₄)₃ = Bi₂O₃ + 3 SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 783.13 | 609.28 | 601.56 | 3.526E - 106 |
| 400.00 | 782.13 | 606.36 | 539.59 | 3.398E - 071 |
| 500.00 | 781.67 | 605.31 | 479.01 | 8.990E - 051 |
| 600.00 | 781.35 | 604.73 | 418.51 | 3.651E - 037 |
| 700.00 | 780.77 | 603.84 | 358.08 | 1.896E - 027 |
| 800.00 | 779.61 | 602.30 | 297.76 | 3.601E - 020 |
| 900.00 | 777.70 | 600.06 | 237.64 | 1.609E - 014 |
| 1000.00 | 774.89 | 597.12 | 177.78 | 5.167E - 10 |
| 1100.00 | 819.48 | 640.30 | 115.16 | 3.398E - 006 |
| 1200.00 | 818.42 | 639.38 | 51.16 | 5.925E - 003 |

TABLE 4.25
Bi₂(SO₄)₃ = Bi₂O₃ + 3 SO₂(g) + 3/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 1079.98 | 891.34 | 814.23 | 2.183E - 143 |
| 400.00 | 1079.74 | 890.65 | 723.48 | 3.277E - 095 |
| 500.00 | 1079.38 | 889.85 | 634.45 | 5.174E - 067 |
| 600.00 | 1078.67 | 888.57 | 545.53 | 3.191E - 048 |
| 700.00 | 1077.35 | 886.56 | 456.76 | 8.188E - 035 |
| 800.00 | 1075.24 | 883.75 | 368.24 | 9.003E - 025 |
| 900.00 | 1072.22 | 880.21 | 280.04 | 5.569E - 017 |
| 1000.00 | 1068.21 | 875.98 | 192.22 | 9.090E - 011 |
| 1100.00 | 1111.00 | 917.94 | 101.78 | 1.467E - 005 |
| 1200.00 | 1109.13 | 915.87 | 10.08 | 3.641E - 001 |

TABLE 4.26
Density of CdSO₄

| Phase | T(K) | d | Reference |
|-------|------|--------------|-----------|
| c | 293 | 4.692 (20/4) | 19 |
| c | 297 | 4.691 | 8 |

TABLE 4.27
Transitions of CdSO₄

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol*K) | Reference |
|-------------------|------|-------------------|----------------------|-----------|
| c \rightarrow c | — | | | |
| c \rightarrow l | 1273 | | | |

TABLE 4.28
Thermodynamic Data of CdSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -933.28 | 123.04 | -969.96 | Barin 1993 |
| 400.00 | -922.73 | 153.42 | -984.10 | Barin 1993 |
| 500.00 | -911.59 | 178.24 | -1000.71 | Barin 1993 |
| 600.00 | -899.68 | 199.93 | -1019.64 | Barin 1993 |
| 700.00 | -887.00 | 219.47 | -1040.63 | Barin 1993 |
| 800.00 | -873.54 | 237.43 | -1063.48 | Barin 1993 |
| 900.00 | -859.30 | 254.19 | -1088.07 | Barin 1993 |
| 1000.00 | -844.30 | 269.99 | -1114.29 | Barin 1993 |
| 1100.00 | -822.28 | 290.88 | -1142.25 | Barin 1993 |
| 1200.00 | -795.90 | 313.97 | -1172.66 | Barin 1993 |

TABLE 4.29
CdSO₄ = CdO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 278.52 | 188.54 | 222.31 | 1.119E - 039 |
| 400.00 | 278.12 | 187.35 | 203.18 | 2.922E - 027 |
| 500.00 | 277.79 | 186.62 | 184.49 | 5.322E - 020 |
| 600.00 | 277.33 | 185.80 | 165.86 | 3.629E - 015 |
| 700.00 | 276.58 | 184.64 | 147.33 | 1.012E - 011 |
| 800.00 | 275.40 | 183.07 | 128.94 | 3.804E - 009 |
| 900.00 | 273.73 | 181.12 | 110.73 | 3.740E - 007 |
| 1000.00 | 271.53 | 178.79 | 92.73 | 1.432E - 005 |
| 1100.00 | 262.50 | 170.29 | 75.19 | 2.688E - 004 |
| 1200.00 | 249.29 | 158.66 | 58.90 | 2.728E - 003 |

TABLE 4.30
 $\text{CdSO}_4 = \text{CdO} + \text{SO}_2(\text{g}) + 1/2\text{O}_2$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 377.48 | 282.57 | 293.23 | 4.200E – 052 |
| 400.00 | 377.32 | 282.11 | 264.47 | 2.887E – 035 |
| 500.00 | 377.02 | 281.47 | 236.29 | 2.055E – 025 |
| 600.00 | 376.44 | 280.41 | 208.19 | 7.475E – 019 |
| 700.00 | 375.44 | 278.88 | 180.23 | 3.550E – 014 |
| 800.00 | 373.95 | 276.89 | 152.43 | 1.112E – 010 |
| 900.00 | 371.91 | 274.50 | 124.86 | 5.658E – 008 |
| 1000.00 | 369.30 | 271.75 | 97.55 | 8.022E – 006 |
| 1100.00 | 359.85 | 262.84 | 70.73 | 4.377E – 004 |
| 1200.00 | 346.19 | 250.82 | 45.21 | 1.077E – 002 |

TABLE 4.31
Transitions of CaSO_4

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol°K) | Reference |
|--------------|----------|-------------------|----------------------|-----------|
| c,II → c,I | 1453 | 21 | 14. ₂ | 10 |
| c,I → l | See text | | | |

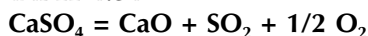
Note: c,II or α is the mineral anhydrite.

TABLE 4.32
Thermodynamic Data of CaSO_4

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------------|
| 298.15 | –1434.11 | 106.69 | –1465.92 | Barin et al. 1977 |
| 400.00 | –1423.45 | 137.38 | –1478.40 | Barin et al. 1977 |
| 500.00 | –1411.98 | 162.92 | –1493.44 | Barin et al. 1977 |
| 600.00 | –1399.53 | 185.60 | –1510.89 | Barin et al. 1977 |
| 700.00 | –1386.09 | 206.29 | –1530.50 | Barin et al. 1977 |
| 800.00 | –1371.67 | 225.54 | –1552.10 | Barin et al. 1977 |
| 900.00 | –1356.25 | 243.69 | –1575.57 | Barin et al. 1977 |
| 1000.00 | –1339.85 | 260.96 | –1600.81 | Barin et al. 1977 |
| 1100.00 | –1322.46 | 277.52 | –1627.74 | Barin et al. 1977 |
| 1200.00 | –1304.09 | 293.51 | –1656.29 | Barin et al. 1977 |
| 1300.00 | –1286.09 | 307.91 | –1686.37 | Barin 1993 |
| 1400.00 | –1268.10 | 321.24 | –1717.84 | Barin 1993 |
| 1500.00 | –1250.11 | 333.65 | –1750.59 | Barin 1993 |
| 1600.00 | –1232.12 | 345.26 | –1784.54 | Barin 1993 |

TABLE 4.33

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 403.25 | 188.15 | 347.16 | 1.495E – 061 |
| 400.00 | 402.73 | 186.64 | 328.08 | 1.427E – 043 |
| 500.00 | 402.13 | 185.31 | 309.48 | 4.642E – 033 |
| 600.00 | 401.20 | 183.63 | 291.03 | 4.592E – 026 |
| 700.00 | 399.76 | 181.42 | 272.77 | 4.407E – 021 |
| 800.00 | 397.68 | 178.64 | 254.76 | 2.315E – 017 |
| 900.00 | 394.88 | 175.36 | 237.06 | 1.740E – 014 |
| 1000.00 | 391.32 | 171.61 | 219.70 | 3.333E – 012 |
| 1100.00 | 386.95 | 167.45 | 202.75 | 2.352E – 010 |
| 1200.00 | 381.74 | 162.93 | 186.23 | 7.819E – 009 |
| 1300.00 | 377.06 | 159.18 | 170.12 | 1.458E – 007 |
| 1400.00 | 372.49 | 155.79 | 154.38 | 1.736E – 006 |
| 1500.00 | 368.03 | 152.72 | 138.96 | 1.448E – 005 |
| 1600.00 | 363.67 | 149.90 | 123.83 | 9.061E – 005 |

TABLE 4.34

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 502.21 | 282.18 | 418.08 | 5.609E – 074 |
| 400.00 | 501.94 | 281.41 | 389.37 | 1.409E – 051 |
| 500.00 | 501.36 | 280.15 | 361.29 | 1.792E – 038 |
| 600.00 | 500.31 | 278.24 | 333.36 | 9.455E – 030 |
| 700.00 | 498.62 | 275.65 | 305.66 | 1.546E – 023 |
| 800.00 | 496.22 | 272.46 | 278.25 | 6.767E – 019 |
| 900.00 | 493.06 | 268.74 | 251.19 | 2.631E – 015 |
| 1000.00 | 489.09 | 264.57 | 224.52 | 1.868E – 012 |
| 1100.00 | 484.29 | 260.00 | 198.29 | 3.831E – 010 |
| 1200.00 | 478.64 | 255.09 | 172.53 | 3.085E – 008 |
| 1300.00 | 473.51 | 250.98 | 147.23 | 1.213E – 006 |
| 1400.00 | 468.49 | 247.26 | 122.32 | 2.727E – 005 |
| 1500.00 | 463.58 | 243.87 | 97.77 | 3.937E – 004 |
| 1600.00 | 458.76 | 240.76 | 73.54 | 3.972E – 003 |

TABLE 4.35
Density of Cs₂SO₄

| Phase | T(K) | d | Reference |
|--------|------|-------|-----------|
| Solid | 293 | 4.246 | 24 |
| | 298 | 4.243 | 8 |
| | 333 | 4.222 | 25 |
| Liquid | 1309 | 3.037 | 26 |
| | 1336 | 3.018 | 26 |
| | 1378 | 2.988 | 26 |
| | 1438 | 2.937 | 26 |
| | 1494 | 2.889 | 26 |
| | 1547 | 2.841 | 26 |
| | 1604 | 2.787 | 26 |
| | 1645 | 2.743 | 26 |
| | 1696 | 2.690 | 26 |
| | 1743 | 2.636 | 26 |
| | 1803 | 2.566 | 26 |

TABLE 4.36
Transitions of Cs₂SO₄

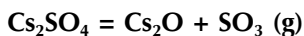
| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|------------------------|------|-------------------|----------------------|-----------|
| c,II \rightarrow c,I | 933 | | | 10 |
| c,I \rightarrow l | 1277 | 40. ₂ | 31. ₄ | 10 |

TABLE 4.37
Thermodynamic Data of Cs₂SO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|---|--|------------|
| 298.15 | -1443.02 | 211.92 | -1506.20 | Barin 1993 |
| 400.00 | -1428.50 | 253.73 | -1529.99 | Barin 1993 |
| 500.00 | -1412.86 | 288.56 | -1557.14 | Barin 1993 |
| 600.00 | -1395.80 | 319.62 | -1587.57 | Barin 1993 |
| 700.00 | -1377.22 | 348.24 | -1620.98 | Barin 1993 |
| 800.00 | -1356.98 | 375.24 | -1657.17 | Barin 1993 |
| 900.00 | -1334.95 | 401.16 | -1695.99 | Barin 1993 |
| 1000.00 | -1309.93 | 427.62 | -1737.55 | Barin 1993 |
| 1100.00 | -1289.74 | 446.85 | -1781.28 | Barin 1993 |
| 1200.00 | -1268.00 | 465.76 | -1826.91 | Barin 1993 |
| 1300.00 | -1209.73 | 511.77 | -1875.03 | Barin 1993 |
| 1400.00 | -1189.06 | 527.09 | -1926.98 | Barin 1993 |
| 1500.00 | -1168.39 | 541.35 | -1980.41 | Barin 1993 |
| 1600.00 | -1147.72 | 554.69 | -2035.22 | Barin 1993 |
| 1700.00 | -1127.05 | 567.22 | -2091.32 | Barin 1993 |
| 1800.00 | -1106.38 | 579.03 | -2148.64 | Barin 1993 |
| 1900.00 | -1085.72 | 590.21 | -2207.19 | Barin 1993 |
| 2000.00 | -1065.05 | 600.81 | -2266.66 | Barin 1993 |
| 2100.00 | | | | |
| 2200.00 | | | | |
| 2300.00 | | | | |
| 2400.00 | | | | |

TABLE 4.38
Thermodynamic Data of Cs₂SO₄ (g)

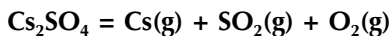
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|---|--|------------|
| 298.15 | -1122.60 | 406.50 | -1243.80 | JANAF 1985 |
| 400.00 | -1110.69 | 440.77 | -1287.00 | JANAF 1985 |
| 500.00 | -1097.90 | 469.28 | -1332.54 | JANAF 1985 |
| 600.00 | -1084.36 | 493.94 | -1380.73 | JANAF 1985 |
| 700.00 | -1070.32 | 515.57 | -1431.22 | JANAF 1985 |
| 800.00 | -1055.91 | 534.81 | -1483.76 | JANAF 1985 |
| 900.00 | -1041.22 | 552.12 | -1538.12 | JANAF 1985 |
| 1000.00 | -1026.32 | 567.81 | -1594.13 | JANAF 1985 |
| 1100.00 | -1011.28 | 582.15 | -1651.64 | JANAF 1985 |
| 1200.00 | -996.12 | 595.33 | -1710.52 | JANAF 1985 |
| 1300.00 | -980.87 | 607.54 | -1770.67 | JANAF 1985 |
| 1400.00 | -965.54 | 618.90 | -1832.00 | JANAF 1985 |
| 1500.00 | -950.15 | 629.52 | -1894.43 | JANAF 1985 |

TABLE 4.39

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 701.28 | 191.71 | 644.12 | 1.390E – 113 |
| 400.00 | 700.19 | 188.59 | 624.75 | 2.563E – 082 |
| 500.00 | 698.71 | 185.30 | 606.06 | 4.791E – 064 |
| 600.00 | 696.63 | 181.54 | 587.71 | 6.777E – 052 |
| 700.00 | 693.73 | 177.09 | 569.77 | 3.017E – 043 |
| 800.00 | 689.77 | 171.81 | 552.32 | 8.593E – 037 |
| 900.00 | 684.55 | 165.67 | 535.44 | 8.343E – 032 |
| 1000.00 | 676.81 | 157.42 | 519.39 | 7.372E – 028 |
| 1100.00 | 674.36 | 155.09 | 503.76 | 1.193E – 024 |
| 1200.00 | 670.79 | 151.99 | 488.40 | 5.481E – 022 |
| 1300.00 | 631.10 | 120.85 | 474.00 | 8.981E – 020 |
| 1400.00 | 629.41 | 119.60 | 461.97 | 5.785E – 018 |
| 1500.00 | 628.10 | 118.70 | 450.06 | 2.120E – 016 |
| 1600.00 | 627.17 | 118.09 | 438.22 | 4.935E – 015 |

TABLE 4.40

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 800.23 | 285.73 | 715.04 | 5.217E – 126 |
| 400.00 | 799.39 | 283.35 | 686.05 | 2.532E – 090 |
| 500.00 | 797.94 | 280.15 | 657.87 | 1.850E – 069 |
| 600.00 | 795.74 | 276.15 | 630.05 | 1.396E – 055 |
| 700.00 | 792.59 | 271.32 | 602.67 | 1.058E – 045 |
| 800.00 | 788.31 | 265.62 | 575.81 | 2.513E – 038 |
| 900.00 | 782.72 | 259.06 | 549.57 | 1.262E – 032 |
| 1000.00 | 774.58 | 250.38 | 524.21 | 4.131E – 028 |
| 1100.00 | 771.79 | 247.64 | 499.30 | 1.943E – 024 |
| 1200.00 | 767.69 | 244.16 | 474.70 | 2.163E – 021 |
| 1300.00 | 727.55 | 212.66 | 451.10 | 7.469E – 019 |
| 1400.00 | 725.40 | 211.07 | 429.91 | 9.088E – 017 |
| 1500.00 | 723.64 | 209.85 | 408.87 | 5.764E – 015 |
| 1600.00 | 722.26 | 208.96 | 387.93 | 2.159E – 013 |

TABLE 4.41

| T K | ΔH° kJ | ΔS° J deg⁻¹ | ΔG° kJ | K |
|----------------------|---|---|---|--------------|
| 298.15 | 1299.21 | 592.64 | 1122.51 | 2.111E – 197 |
| 400.00 | 1296.22 | 584.08 | 1062.59 | 1.694E – 139 |
| 500.00 | 1292.39 | 575.57 | 1004.60 | 1.100E – 105 |
| 600.00 | 1287.51 | 566.72 | 947.48 | 3.216E – 083 |
| 700.00 | 1281.40 | 557.32 | 891.28 | 3.066E – 067 |
| 800.00 | 1273.84 | 547.25 | 836.04 | 2.555E – 055 |
| 900.00 | 1264.67 | 536.47 | 781.85 | 4.157E – 046 |
| 1000.00 | 1252.65 | 523.70 | 728.95 | 8.327E – 039 |
| 1100.00 | 1245.57 | 516.96 | 676.91 | 7.138E – 033 |
| 1200.00 | 1237.04 | 509.55 | 625.57 | 5.848E – 028 |
| 1300.00 | 1192.06 | 474.18 | 575.63 | 7.398E – 024 |
| 1400.00 | 1184.78 | 468.78 | 528.48 | 1.907E – 020 |
| 1500.00 | 1177.57 | 463.81 | 481.86 | 1.655E – 017 |

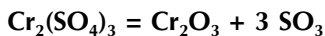
TABLE 4.42

| T K | ΔHf° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔGf° kJ mol⁻¹ | Reference |
|----------------------|---|--|---|------------------|
| 298.15 | –2942.72 | 258.78 | –3026.88 | Barin 1993 |
| 400.00 | –2919.24 | 346.44 | –3057.82 | Barin 1993 |
| 500.00 | –2884.91 | 422.85 | –3096.34 | Barin 1993 |
| 600.00 | –2846.39 | 493.15 | –3142.19 | Barin 1993 |
| 700.00 | –2804.41 | 557.67 | –3194.78 | Barin 1993 |
| 800.00 | –2760.58 | 616.17 | –3253.52 | Barin 1993 |
| 900.00 | –2716.32 | 668.31 | –3386.96 | Barin 1993 |
| 1000.00 | –2632.84 | 713.76 | –3386.96 | Barin 1993 |

TABLE 4.43

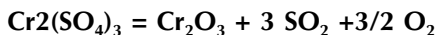
| T K | ΔHf° kJ mol⁻¹ | S° J mol⁻¹ deg⁻¹ | ΔGf° kJ mol⁻¹ | Reference |
|----------------------|---|--|---|------------------|
| 298.15 | –1139.70 | 81.20 | –1163.91 | Barin 1989 |
| 400.00 | –1127.61 | 116.10 | –1174.05 | Barin 1989 |
| 500.00 | –1115.78 | 142.51 | –1187.03 | Barin 1989 |
| 600.00 | –1103.86 | 164.22 | –1202.40 | Barin 1989 |
| 700.00 | –1091.82 | 182.78 | –1219.77 | Barin 1989 |
| 800.00 | –1079.64 | 199.05 | –1238.88 | Barin 1989 |
| 900.00 | –1067.30 | 213.58 | –1259.52 | Barin 1989 |
| 1000.00 | –1054.81 | 226.74 | –1281.55 | Barin 1989 |

TABLE 4.44



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 622.73 | 592.74 | 446.00 | 7.176E – 079 |
| 400.00 | 620.90 | 587.60 | 385.86 | 4.056E – 051 |
| 500.00 | 616.53 | 577.97 | 327.54 | 6.010E – 035 |
| 600.00 | 609.45 | 565.14 | 270.37 | 2.885E – 024 |
| 700.00 | 600.33 | 551.10 | 214.56 | 9.734E – 017 |
| 800.00 | 590.19 | 537.57 | 160.13 | 3.495E – 011 |
| 900.00 | 580.37 | 525.99 | 106.98 | 6.176E – 007 |
| 1000.00 | 572.31 | 517.48 | 54.83 | 1.366E – 003 |

TABLE 4.45



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 622.73 | 592.74 | 446.00 | 7.176E – 079 |
| 400.00 | 620.90 | 587.60 | 385.86 | 4.056E – 051 |
| 500.00 | 616.53 | 577.97 | 327.54 | 6.010E – 035 |
| 600.00 | 609.45 | 565.14 | 270.37 | 2.885E – 024 |
| 700.00 | 600.33 | 551.10 | 214.56 | 9.734E – 017 |
| 800.00 | 590.19 | 537.57 | 160.13 | 3.495E – 011 |
| 900.00 | 580.37 | 525.99 | 106.98 | 6.176E – 007 |
| 1000.00 | 572.31 | 517.48 | 54.83 | 1.366E – 003 |

TABLE 4.46

Density of CoSO₄

| Phase | T(K) | d | References |
|-------|------|-------------------------|------------|
| α | 298 | 3.86 gcm ⁻³ | 31 |
| β | 298 | 3.770 gcm ⁻³ | 32 |

Materials used may be impure

Densities are crystallographic

TABLE 4.47

Transitions of CoSO₄

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------|---------|-------------------|----------------------|-----------|
| α → β | 705 ± 8 | 6.8 ± 0.6 | 9.6 ± 0.8 | 32 |

TABLE 4.48
Thermodynamic Data of CoSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -888.26 | 117.36 | -923.25 | Knacke et al. 1991 |
| 400.00 | -876.88 | 150.12 | -936.32 | Knacke et al. 1991 |
| 500.00 | -864.31 | 178.10 | -953.36 | Knacke et al. 1991 |
| 600.00 | -850.69 | 202.90 | -972.43 | Knacke et al. 1991 |
| 700.00 | -836.28 | 225.10 | -993.85 | Knacke et al. 1991 |
| 800.00 | -821.28 | 245.12 | -1017.38 | Knacke et al. 1991 |
| 900.00 | -805.90 | 263.23 | -1042.81 | Knacke et al. 1991 |
| 1000.00 | -788.14 | 281.91 | -1070.05 | Knacke et al. 1991 |
| 1100.00 | -772.21 | 297.09 | -1099.01 | Knacke et al. 1991 |
| 1200.00 | -756.07 | 311.13 | -1129.43 | Knacke et al. 1991 |

TABLE 4.49
CoSO₄ = CoO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 254.55 | 192.38 | 197.20 | 2.813E - 035 |
| 400.00 | 254.21 | 191.47 | 177.63 | 6.348E - 024 |
| 500.00 | 253.06 | 188.92 | 158.60 | 2.692E - 017 |
| 600.00 | 251.36 | 185.84 | 139.86 | 6.658E - 013 |
| 700.00 | 249.26 | 182.69 | 121.44 | 8.663E - 010 |
| 800.00 | 246.87 | 179.42 | 103.34 | 1.788E - 007 |
| 900.00 | 244.37 | 176.48 | 85.54 | 1.083E - 005 |
| 1000.00 | 239.71 | 171.61 | 68.11 | 2.767E - 004 |
| 1100.00 | 237.09 | 169.11 | 51.08 | 3.754E - 003 |
| 1200.00 | 234.45 | 166.81 | 34.28 | 3.219E - 002 |

TABLE 4.50
CoSO₄ = CoO + SO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 353.51 | 286.40 | 268.12 | 1.055E - 047 |
| 400.00 | 353.42 | 286.24 | 238.92 | 6.272E - 032 |
| 500.00 | 352.30 | 283.77 | 210.41 | 1.039E - 022 |
| 600.00 | 350.47 | 280.45 | 182.20 | 1.371E - 016 |
| 700.00 | 348.12 | 276.84 | 154.33 | 3.039E - 012 |
| 800.00 | 345.42 | 273.24 | 126.83 | 5.228E - 009 |
| 900.00 | 342.55 | 269.86 | 99.68 | 1.639E - 006 |
| 1000.00 | 337.49 | 264.56 | 72.93 | 1.551E - 004 |
| 1100.00 | 334.44 | 261.66 | 46.62 | 6.113E - 003 |
| 1200.00 | 331.35 | 258.97 | 20.59 | 1.270E - 001 |

TABLE 4.51
Density of CuSO₄

| Phase | T(K) | d | Reference |
|-------|------|-------------------------|-----------|
| ? | 298 | 3.542 (pycnometric) | 27 |
| α | 298 | 4.113 gcm ⁻³ | 38 |
| β | 453 | 3.923 | 38 |

TABLE 4.52
Thermodynamic Data of CuSO₄

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|------------------------------|---|------------------------------|------------|
| 298.15 | -771.36 | 109.00 | -803.86 | Barin 1993 |
| 400.00 | -760.39 | 140.52 | -816.60 | Barin 1993 |
| 500.00 | -748.25 | 167.58 | -832.04 | Barin 1993 |
| 600.00 | -735.08 | 191.56 | -850.02 | Barin 1993 |
| 700.00 | -721.13 | 213.05 | -870.26 | Barin 1993 |
| 800.00 | -706.58 | 232.48 | -892.56 | Barin 1993 |
| 900.00 | -691.59 | 250.12 | -916.70 | Barin 1993 |
| 1000.00 | -676.33 | 266.20 | -942.53 | Barin 1993 |
| 1100.00 | -660.95 | 280.85 | -969.89 | Barin 1993 |
| 1200.00 | -645.60 | 294.21 | -998.66 | Barin 1993 |

TABLE 4.53
CuSO₄ = CuO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|-----------|----------------------------|-----------|--------------|
| 298.15 | 219.53 | 190.36 | 162.77 | 3.022E - 029 |
| 400.00 | 218.65 | 187.85 | 143.51 | 1.813E - 019 |
| 500.00 | 217.36 | 184.98 | 124.86 | 9.005E - 014 |
| 600.00 | 215.75 | 182.06 | 106.51 | 5.328E - 010 |
| 700.00 | 213.86 | 179.16 | 88.45 | 2.507E - 007 |
| 800.00 | 211.76 | 176.35 | 70.68 | 2.426E - 005 |
| 900.00 | 209.53 | 173.73 | 53.18 | 8.195E - 004 |
| 1000.00 | 207.27 | 171.35 | 35.92 | 1.329E - 002 |
| 1100.00 | 205.11 | 169.28 | 18.90 | 1.267E - 001 |
| 1200.00 | 203.15 | 167.58 | 2.05 | 8.139E - 001 |

TABLE 4.54

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 318.48 | 284.39 | 233.69 | 1.134E – 041 |
| 400.00 | 317.85 | 282.61 | 204.80 | 1.791E – 027 |
| 500.00 | 316.59 | 279.83 | 176.68 | 3.477E – 019 |
| 600.00 | 314.85 | 276.67 | 148.85 | 1.097E – 013 |
| 700.00 | 312.73 | 273.40 | 121.35 | 8.796E – 010 |
| 800.00 | 310.30 | 270.17 | 94.17 | 7.094E – 007 |
| 900.00 | 307.70 | 267.11 | 67.31 | 1.240E – 004 |
| 1000.00 | 305.04 | 264.31 | 40.74 | 7.445E – 003 |
| 1100.00 | 302.45 | 261.83 | 14.44 | 2.063E – 001 |
| 1200.00 | 300.06 | 259.75 | –11.64 | 3.213E + 000 |

TABLE 4.55

Thermodynamic Data of $\text{In}_2(\text{SO}_4)_3$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | –2787.00 | 272.00 | –2868.10 | Barin 1993 |
| 400.00 | –2757.18 | 357.86 | –2900.32 | Barin 1993 |
| 500.00 | –330.68 | 428.74 | –2939.74 | Barin 1993 |
| 600.00 | –355.78 | 491.25 | –2985.79 | Barin 1993 |
| 700.00 | –2654.21 | 547.98 | –3037.80 | Barin 1993 |
| 800.00 | –2614.87 | 600.47 | –3095.25 | Barin 1993 |
| 900.00 | –2573.02 | 649.74 | –3157.78 | Barin 1993 |
| 1000.00 | –2528.65 | 696.46 | –3225.11 | Barin 1993 |
| 1100.00 | –2481.78 | 741.12 | –3297.01 | Barin 1993 |
| 1200.00 | –2432.39 | 784.07 | –3373.28 | Barin 1993 |

TABLE 4.56

Thermodynamic Data of In_2O_3

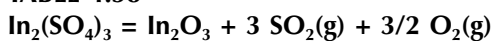
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | –925.79 | 104.20 | –956.86 | Knacke et al. 1991 |
| 400.00 | –914.88 | 135.59 | –969.12 | Knacke et al. 1991 |
| 500.00 | –903.34 | 161.31 | –984.00 | Knacke et al. 1991 |
| 600.00 | –891.36 | 183.15 | –1001.25 | Knacke et al. 1991 |
| 700.00 | –879.09 | 202.06 | –1020.53 | Knacke et al. 1991 |
| 800.00 | –866.60 | 218.73 | –1041.59 | Knacke et al. 1991 |
| 900.00 | –853.95 | 233.63 | –1064.22 | Knacke et al. 1991 |
| 1000.00 | –128.59 | 247.11 | –1088.27 | Knacke et al. 1991 |
| 1100.00 | –828.24 | 259.42 | –1113.60 | Knacke et al. 1991 |
| 1200.00 | –815.20 | 270.76 | –1140.12 | Knacke et al. 1991 |

TABLE 4.57



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 673.92 | 602.51 | 494.28 | 2.496E – 087 |
| 400.00 | 671.56 | 595.66 | 433.39 | 2.587E – 057 |
| 500.00 | 669.42 | 590.88 | 373.97 | 8.475E – 040 |
| 600.00 | 666.70 | 585.97 | 315.12 | 3.662E – 028 |
| 700.00 | 662.87 | 580.08 | 256.81 | 6.837E – 020 |
| 800.00 | 657.51 | 572.95 | 199.15 | 9.902E – 014 |
| 900.00 | 650.41 | 564.61 | 142.26 | 5.528E – 009 |
| 1000.00 | 641.41 | 555.15 | 86.27 | 3.116E – 005 |
| 1100.00 | 630.39 | 544.65 | 31.27 | 3.274E – 002 |
| 1200.00 | 617.26 | 533.25 | –22.63 | 9.668E + 000 |

TABLE 4.58



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 970.77 | 884.58 | 707.04 | 1.319E – 124 |
| 400.00 | 969.17 | 879.95 | 617.19 | 2.497E – 081 |
| 500.00 | 967.12 | 875.42 | 529.41 | 4.880E – 056 |
| 600.00 | 964.02 | 869.80 | 442.14 | 3.202E – 039 |
| 700.00 | 959.45 | 862.79 | 355.50 | 2.954E – 027 |
| 800.00 | 953.14 | 854.40 | 269.63 | 2.476E – 018 |
| 900.00 | 944.94 | 844.76 | 184.66 | 1.913E – 011 |
| 1000.00 | 934.73 | 834.01 | 100.71 | 5.482E – 006 |
| 1100.00 | 922.42 | 822.30 | 17.89 | 1.414E – 001 |
| 1200.00 | 907.97 | 809.74 | –63.72 | 5.941E + 002 |

TABLE 4.59

Thermodynamic Data of FeSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | –928.85 | 120.96 | –964.91 | Knacke et al. 1991 |
| 400.00 | –917.69 | 153.04 | –978.90 | Knacke et al. 1991 |
| 500.00 | –905.34 | 180.56 | –995.61 | Knacke et al. 1991 |
| 600.00 | –891.99 | 204.86 | –1014.91 | Knacke et al. 1991 |
| 700.00 | –877.89 | 226.58 | –1036.50 | Knacke et al. 1991 |
| 800.00 | –863.21 | 246.18 | –1060.15 | Knacke et al. 1991 |
| 900.00 | –848.09 | 263.99 | –1085.68 | Knacke et al. 1991 |
| 1000.00 | –832.68 | 280.22 | –1112.90 | Knacke et al. 1991 |
| 1100.00 | –817.10 | 295.07 | –1141.67 | Knacke et al. 1991 |
| 1200.00 | –801.49 | 308.65 | –1171.87 | Knacke et al. 1991 |

TABLE 4.60
Thermodynamic Data of $\text{Fe}_2(\text{SO}_4)_3$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -2582.99 | 307.52 | -2674.68 | Barin 1989 |
| 400.00 | -2553.49 | 392.30 | -2710.41 | Barin 1989 |
| 500.00 | -2520.77 | 465.20 | -2753.37 | Barin 1989 |
| 600.00 | -2485.61 | 529.24 | -2803.15 | Barin 1989 |
| 700.00 | -2448.64 | 586.20 | -2858.98 | Barin 1989 |
| 800.00 | -2410.22 | 636.48 | -2920.20 | Barin 1989 |
| 900.00 | -2370.61 | 684.12 | -2986.32 | Barin 1989 |
| 1000.00 | -2330.03 | 726.86 | -3058.90 | Barin 1989 |
| 1100.00 | -2288.66 | 766.29 | -3131.58 | Barin 1989 |
| 1200.00 | -2246.65 | 802.84 | -3210.06 | Barin 1989 |

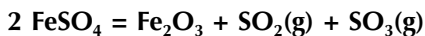
TABLE 4.61
Thermodynamic Data of FeO (wuestite)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -272.04 | 60.75 | -290.16 | Barin 1993 |
| 400.00 | -266.85 | 75.73 | -297.14 | Barin 1993 |
| 500.00 | -261.54 | 87.56 | -305.32 | Barin 1993 |
| 600.00 | -256.10 | 97.48 | -314.59 | Barin 1993 |
| 700.00 | -250.54 | 106.05 | -324.77 | Barin 1993 |
| 800.00 | -244.87 | 113.62 | -335.76 | Barin 1993 |
| 900.00 | -239.11 | 120.41 | -347.47 | Barin 1993 |
| 1000.00 | -233.24 | 126.58 | -359.82 | Barin 1993 |
| 1100.00 | -227.29 | 132.26 | -372.77 | Barin 1993 |
| 1200.00 | -221.24 | 137.52 | -386.26 | Barin 1993 |

TABLE 4.62
Thermodynamic Data of Fe_2O_3 (hematite)

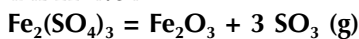
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -824.25 | 87.40 | -850.31 | Barin 1993 |
| 400.00 | -812.74 | 120.50 | -860.94 | Barin 1993 |
| 500.00 | -800.15 | 148.54 | -874.42 | Barin 1993 |
| 600.00 | -786.54 | 173.34 | -890.54 | Barin 1993 |
| 700.00 | -772.01 | 195.72 | -909.01 | Barin 1993 |
| 800.00 | -756.61 | 216.27 | -929.62 | Barin 1993 |
| 900.00 | -740.37 | 235.39 | -952.22 | Barin 1993 |
| 1000.00 | -723.85 | 252.81 | -976.65 | Barin 1993 |
| 1100.00 | -709.05 | 266.92 | -1002.66 | Barin 1993 |
| 1200.00 | -695.06 | 279.10 | -1029.97 | Barin 1993 |

TABLE 4.63



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 340.87 | 350.48 | 236.38 | 3.842E – 042 |
| 400.00 | 339.81 | 347.48 | 200.82 | 5.938E – 027 |
| 500.00 | 338.25 | 344.00 | 166.25 | 4.276E – 018 |
| 600.00 | 336.51 | 340.84 | 132.01 | 3.212E – 012 |
| 700.00 | 334.77 | 338.15 | 98.06 | 4.809E – 008 |
| 800.00 | 331.14 | 335.97 | 64.36 | 6.272E – 002 |
| 900.00 | 331.81 | 334.40 | 30.85 | 1.620E – 002 |
| 1000.00 | 330.43 | 332.96 | –2.53 | 1.356E + 000 |
| 1100.00 | 327.19 | 329.89 | –35.68 | 4.950E + 001 |
| 1200.00 | 323.25 | 326.46 | –68.50 | 9.594E + 002 |

TABLE 4.64



| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | K |
|---------|--|--|--|--------------|
| 298.15 | 571.45 | 550.20 | 407.41 | 4.146E – 072 |
| 400.00 | 570.01 | 546.13 | 351.56 | 1.224E – 046 |
| 500.00 | 568.01 | 541.66 | 297.17 | 8.951E – 032 |
| 600.00 | 566.09 | 538.17 | 243.19 | 6.709E – 022 |
| 700.00 | 564.37 | 535.52 | 189.51 | 7.199E – 015 |
| 800.00 | 562.85 | 533.48 | 136.07 | 1.303E – 009 |
| 900.00 | 561.59 | 531.99 | 82.80 | 1.564E – 005 |
| 1000.00 | 560.10 | 530.44 | 29.66 | 2.821E – 002 |
| 1100.00 | 556.45 | 526.98 | –23.22 | 1.267E + 001 |
| 1200.00 | 551.66 | 522.81 | –75.71 | 1.976E + 003 |

TABLE 4.65

Density of PbSO₄

| Phase | T(K) | d | Reference |
|-------|------|--------|-----------|
| c,II | 288 | 6.2907 | 54 |
| | 298 | 6.2866 | |
| | 308 | 6.2824 | |
| | 318 | 6.2780 | |

TABLE 4.66

Transitions of PbSO₄

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------|------|-------------------|----------------------|-----------|
| c,II → c,I | 1139 | 17.0 | 14.9 | 9.10 |
| c,I → I | 1360 | 40 | 29.7 | |

TABLE 4.67
Thermodynamic Data of PbSO₄ (anglesite)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -923.14 | 148.49 | -967.41 | Barin 1993 |
| 400.00 | -912.36 | 179.54 | -984.18 | Barin 1993 |
| 500.00 | -901.07 | 204.71 | -1003.42 | Barin 1993 |
| 600.00 | -888.77 | 227.10 | -1025.03 | Barin 1993 |
| 700.00 | -875.35 | 247.77 | -1048.79 | Barin 1993 |
| 800.00 | -860.73 | 267.27 | -1074.55 | Barin 1993 |
| 900.00 | -844.88 | 285.92 | -1102.21 | Barin 1993 |
| 1000.00 | -827.79 | 303.92 | -1131.71 | Barin 1993 |
| 1100.00 | -809.43 | 321.41 | -1162.98 | Barin 1993 |
| 1200.00 | -773.11 | 353.15 | -1196.88 | Barin 1993 |
| 1300.00 | -753.71 | 368.67 | -1232.98 | Barin 1993 |
| 1400.00 | -734.31 | 383.05 | -1270.58 | Barin 1993 |
| 1500.00 | -675.20 | 423.96 | -1311.14 | Barin 1993 |

TABLE 4.68
Thermodynamic Data of PbO.PbSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1157.45 | 223.32 | -1224.04 | Barin 1993 |
| 400.00 | -1141.89 | 268.16 | -1249.16 | Barin 1993 |
| 500.00 | -1125.68 | 304.30 | -1277.83 | Barin 1993 |
| 600.00 | -1108.29 | 335.98 | -1309.87 | Barin 1993 |
| 700.00 | -1089.62 | 364.73 | -1344.93 | Barin 1993 |
| 800.00 | -1069.62 | 391.41 | -1382.75 | Barin 1993 |
| 900.00 | -1048.26 | 416.55 | -1423.16 | Barin 1993 |
| 1000.00 | -1025.52 | 440.49 | -1466.02 | Barin 1993 |
| 1100.00 | -1001.40 | 463.48 | -1511.22 | Barin 1993 |
| 1200.00 | -975.87 | 485.68 | -1558.69 | Barin 1993 |
| 1300.00 | -948.95 | 597.22 | -1608.34 | Barin 1993 |
| 1400.00 | -920.61 | 528.22 | -1660.11 | Barin 1993 |
| 1500.00 | -890.86 | 548.74 | -1713.97 | Barin 1993 |

TABLE 4.69
Thermodynamic Data of 2 PbO.PbSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|---|--|------------|
| 298.15 | -1373.06 | 294.24 | -1460.79 | Barin 1989 |
| 400.00 | -1351.32 | 356.88 | -1494.08 | Barin 1989 |
| 500.00 | -1328.74 | 407.22 | -1532.35 | Barin 1989 |
| 600.00 | -1304.72 | 450.98 | -1575.30 | Barin 1989 |
| 700.00 | -1279.17 | 490.33 | -1622.40 | Barin 1989 |
| 800.00 | -1252.05 | 526.52 | -1673.26 | Barin 1989 |
| 900.00 | -1223.34 | 560.32 | -1727.62 | Barin 1989 |
| 1000.00 | -1193.02 | 592.25 | -1785.26 | Barin 1989 |
| 1100.00 | -1161.07 | 622.68 | -1848.02 | Barin 1989 |
| 1200.00 | -1157.51 | 651.88 | -1906.76 | Barin 1989 |
| 1300.00 | -1092.31 | 680.04 | -1976.36 | Barin 1989 |
| 1400.00 | -1055.49 | 707.32 | -2045.74 | Barin 1989 |
| 1500.00 | -1017.02 | 733.85 | -2117.80 | Barin 1989 |

TABLE 4.70
Thermodynamic Data of 3 PbO.PbSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|---|--|------------|
| 298.15 | -1623.74 | 340.58 | -1728.28 | Barin 1993 |
| 400.00 | -1601.25 | 413.99 | -1766.55 | Barin 1993 |
| 500.00 | -1574.49 | 473.64 | -1811.31 | Barin 1993 |
| 600.00 | -1546.16 | 525.25 | -1861.31 | Barin 1993 |
| 700.00 | -1516.32 | 571.22 | -1916.17 | Barin 1993 |
| 800.00 | -1485.01 | 613.01 | -1975.41 | Barin 1993 |
| 900.00 | -1452.22 | 651.60 | -2038.67 | Barin 1993 |
| 1000.00 | -1418.00 | 687.65 | -2105.65 | Barin 1993 |
| 1100.00 | -1382.33 | 721.64 | -2176.13 | Barin 1993 |
| 1200.00 | -1345.22 | 753.92 | -2249.92 | Barin 1993 |
| 1300.00 | -1306.67 | 784.76 | -2326.86 | Barin 1993 |
| 1400.00 | -1266.69 | 814.39 | -2406.83 | Barin 1993 |
| 1500.00 | -1225.28 | 842.95 | -2489.70 | Barin 1993 |

TABLE 4.71
Thermodynamic Data of 4 PbO.PbSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1828.94 | 424.59 | -1955.54 | Barin 1993 |
| 400.00 | -1798.24 | 513.07 | -2003.47 | Barin 1993 |
| 500.00 | -1766.44 | 583.97 | -2058.42 | Barin 1993 |
| 600.00 | -1732.90 | 645.06 | -2119.94 | Barin 1993 |
| 700.00 | -1697.59 | 699.46 | -2187.21 | Barin 1993 |
| 800.00 | -1660.48 | 748.98 | -2259.67 | Barin 1993 |
| 900.00 | -1621.57 | 794.79 | -2336.88 | Barin 1993 |
| 1000.00 | -1580.85 | 837.68 | -2418.53 | Barin 1993 |
| 1100.00 | -1538.31 | 878.21 | -2504.34 | Barin 1993 |
| 1200.00 | -1493.94 | 916.80 | -2594.11 | Barin 1993 |
| 1300.00 | -1447.76 | 953.76 | -2687.65 | Barin 1993 |
| 1400.00 | -1399.75 | 989.33 | -2784.81 | Barin 1993 |
| 1500.00 | -1349.92 | 1023.70 | -2885.47 | Barin 1993 |

TABLE 4.72
PbSO₄ = PbO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 309.31 | 176.98 | 256.54 | 1.124E - 045 |
| 400.00 | 308.87 | 175.66 | 238.60 | 6.907E - 032 |
| 500.00 | 308.57 | 175.01 | 221.07 | 8.007E - 024 |
| 600.00 | 307.95 | 173.89 | 203.61 | 1.872E - 018 |
| 700.00 | 306.71 | 172.00 | 186.31 | 1.247E - 014 |
| 800.00 | 304.69 | 169.32 | 169.24 | 8.886E - 012 |
| 900.00 | 301.79 | 165.90 | 152.48 | 1.412E - 009 |
| 1000.00 | 297.93 | 161.84 | 136.08 | 7.783E - 008 |
| 1100.00 | 293.06 | 157.21 | 120.13 | 1.973E - 006 |
| 1200.00 | 296.17 | 159.60 | 104.66 | 2.780E - 005 |
| 1300.00 | 291.10 | 155.53 | 88.91 | 2.676E - 004 |
| 1400.00 | 286.09 | 151.82 | 73.54 | 1.803E - 003 |
| 1500.00 | 241.42 | 120.88 | 60.11 | 8.065E - 002 |

TABLE 4.73

| T K | ΔH° kJ | ΔS° J deg⁻¹ | ΔG° kJ | K |
|----------------------|---|---|---|--------------|
| 298.15 | 408.26 | 271.00 | 327.46 | 4.219E – 058 |
| 400.00 | 408.07 | 270.43 | 299.90 | 6.825E – 040 |
| 500.00 | 407.81 | 269.86 | 272.88 | 3.092E – 029 |
| 600.00 | 407.05 | 268.50 | 245.95 | 3.855E – 022 |
| 700.00 | 405.57 | 266.24 | 219.21 | 4.376E – 017 |
| 800.00 | 403.24 | 263.13 | 192.73 | 2.598E – 013 |
| 900.00 | 399.96 | 259.29 | 166.61 | 2.136E – 010 |
| 1000.00 | 395.70 | 254.80 | 140.90 | 4.361E – 010 |
| 1100.00 | 390.40 | 249.76 | 115.67 | 3.214E – 006 |
| 1200.00 | 393.08 | 251.76 | 90.96 | 1.097E – 004 |
| 1300.00 | 387.55 | 247.34 | 66.01 | 2.225E – 003 |
| 1400.00 | 382.09 | 243.29 | 41.48 | 2.832E – 002 |
| 1500.00 | 336.97 | 212.03 | 18.92 | 2.193E – 001 |

TABLE 4.74**Density of Li_2SO_4**

| Phase | T(K) | d | Reference |
|--------------|-------------|----------|------------------|
| c,II | 298 | 2.221 | 8 |
| c,I | 883 | 2.07 | 55 |
| liquid | 1133 | 2.004 | 26 |
| | 1147 | 1.999 | |
| | 1170 | 1.989 | |
| | 1196 | 1.978 | |
| | 1236 | 1.962 | |
| | 1250 | 1.956 | |
| | 1274 | 1.947 | |
| | 1311 | 1.932 | |
| | 1330 | 1.924 | |
| | 1363 | 1.911 | |
| | 1385 | 1.901 | |
| | 1430 | 1.884 | |
| | 1457 | 1.873 | |
| | 1465 | 1.869 | |
| | 1487 | 1.860 | |

TABLE 4.75
Thermodynamic Data of Li₂SO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1436.49 | 115.10 | -1470.81 | Barin 1993 |
| 400.00 | -1423.39 | 152.78 | -1484.50 | Barin 1993 |
| 500.00 | -1409.03 | 184.78 | -1501.41 | Barin 1993 |
| 600.00 | -1393.16 | 213.66 | -1521.36 | Barin 1993 |
| 700.00 | -1375.80 | 240.39 | -1544.07 | Barin 1003 |
| 800.00 | -1356.95 | 265.54 | -1569.38 | Barin 1993 |
| 900.00 | -1307.82 | 323.42 | -1598.90 | Barin 1993 |
| 1000.00 | -1286.48 | 345.90 | -1632.38 | Barin 1993 |
| 1100.00 | -1265.14 | 366.24 | -1668.01 | Barin 1993 |
| 1200.00 | -1235.80 | 391.90 | -1706.07 | Barin 1993 |
| 1300.00 | -1215.30 | 408.31 | -1746.09 | Barin 1993 |
| 1400.00 | -1194.79 | 423.50 | -1787.69 | Barin 1993 |
| 1500.00 | -1174.29 | 437.64 | -1830.76 | Barin 1993 |

TABLE 4.76
Li₂SO₄ = Li₂O + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 441.99 | 179.56 | 388.46 | 8.670E - 069 |
| 400.00 | 440.51 | 175.26 | 370.41 | 4.224E - 049 |
| 500.00 | 439.00 | 171.90 | 353.05 | 1.301E - 037 |
| 600.00 | 436.98 | 168.24 | 336.04 | 5.531E - 030 |
| 700.00 | 434.20 | 163.96 | 319.42 | 1.454E - 024 |
| 800.00 | 430.47 | 159.00 | 303.27 | 1.574E - 020 |
| 900.00 | 396.92 | 119.46 | 289.40 | 1.593E - 017 |
| 1000.00 | 391.54 | 113.80 | 277.75 | 3.096E - 015 |
| 1100.00 | 386.51 | 109.00 | 266.61 | 2.181E - 013 |
| 1200.00 | 373.77 | 97.79 | 256.42 | 6.875E - 012 |
| 1300.00 | 370.16 | 94.90 | 246.79 | 1.210E - 010 |
| 1400.00 | 366.82 | 92.42 | 237.43 | 1.383E - 009 |
| 1500.00 | 363.72 | 90.28 | 228.30 | 1.120E - 008 |

TABLE 4.77



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 540.95 | 273.58 | 459.18 | 3.253E – 081 |
| 400.00 | 539.71 | 270.03 | 431.70 | 4.174E – 057 |
| 500.00 | 538.23 | 266.74 | 404.86 | 5.021E – 043 |
| 600.00 | 536.09 | 262.85 | 378.38 | 1.139E – 033 |
| 700.00 | 533.06 | 258.20 | 352.32 | 5.100E – 027 |
| 800.00 | 529.01 | 252.81 | 326.76 | 4.602E – 022 |
| 900.00 | 495.09 | 212.84 | 303.53 | 2.409E – 018 |
| 1000.00 | 489.32 | 206.75 | 282.56 | 1.735E – 015 |
| 1100.00 | 483.85 | 201.55 | 262.15 | 3.551E – 013 |
| 1200.00 | 470.68 | 189.96 | 242.73 | 2.713E – 011 |
| 1300.00 | 466.62 | 186.71 | 223.90 | 1.007E – 009 |
| 1400.00 | 462.81 | 183.89 | 205.37 | 2.172E – 008 |
| 1500.00 | 459.26 | 181.44 | 187.11 | 3.046E – 007 |

TABLE 4.78

Density of MgSO_4

| Phase | T(K) | d | Reference |
|-------|------|------|-----------|
| c,II | 288 | 2.71 | 57a |
| c,II | 298 | 2.66 | 8 |

TABLE 4.79

Transitions of MgSO_4

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol*K) | Reference |
|------------------------|------|-------------------|----------------------|-----------|
| c,II \rightarrow c,I | 1283 | — | — | 5 |
| c,I \rightarrow liq. | 1400 | 14.6 | 10.4 | 10 |

TABLE 4.80
Thermodynamic Data of MgSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1284.86 | 91.60 | -1312.18 | Barin 1993 |
| 400.00 | -1274.26 | 122.10 | -1323.10 | Barin 1993 |
| 500.00 | -1262.66 | 147.94 | -1336.63 | Barin 1993 |
| 600.00 | -1250.25 | 170.56 | -1352.58 | Barin 1993 |
| 700.00 | -1237.16 | 190.71 | -1370.66 | Barin 1993 |
| 800.00 | -1223.49 | 208.97 | -1390.66 | Barin 1993 |
| 900.00 | -1209.26 | 225.72 | -1412.41 | Barin 1993 |
| 1000.00 | -1179.24 | 241.26 | -1435.76 | Barin 1993 |
| 1100.00 | -1179.24 | 255.81 | -1460.62 | Barin 1993 |
| 1200.00 | -1163.47 | 269.52 | -1486.90 | Barin 1993 |
| 1300.00 | -1147.21 | 282.54 | -1514.51 | Barin 1993 |
| 1400.00 | -1130.46 | 294.95 | -1543.39 | Barin 1993 |
| 1500.00 | -1099.91 | 316.38 | -1574.48 | Barin 1993 |

TABLE 4.81
MgSO₄ = MgO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 287.86 | 192.10 | 230.59 | 3.966E - 041 |
| 400.00 | 286.88 | 189.27 | 211.17 | 2.642E - 028 |
| 500.00 | 285.77 | 186.80 | 192.37 | 7.975E - 021 |
| 600.00 | 284.57 | 184.61 | 173.80 | 7.382E - 016 |
| 700.00 | 283.21 | 182.52 | 155.44 | 2.510E - 012 |
| 800.00 | 281.62 | 180.40 | 137.30 | 1.083E - 009 |
| 900.00 | 279.76 | 178.22 | 119.37 | 1.179E - 007 |
| 1000.00 | 277.61 | 175.95 | 101.66 | 4.893E - 006 |
| 1100.00 | 275.12 | 173.59 | 84.18 | 1.006E - 004 |
| 1200.00 | 272.29 | 171.13 | 66.94 | 1.219E - 003 |
| 1300.00 | 269.10 | 168.58 | 49.96 | 9.831E - 003 |
| 1400.00 | 265.54 | 165.94 | 33.23 | 5.756E - 002 |
| 1500.00 | 248.29 | 153.68 | 17.77 | 2.405E - 001 |

TABLE 4.82



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 386.81 | 286.12 | 301.51 | 1.488E – 053 |
| 400.00 | 386.08 | 284.04 | 272.47 | 2.610E – 036 |
| 500.00 | 385.00 | 281.65 | 244.18 | 3.079E – 026 |
| 600.00 | 383.67 | 279.22 | 216.14 | 1.520E – 019 |
| 700.00 | 382.07 | 276.76 | 188.34 | 8.808E – 015 |
| 800.00 | 380.16 | 274.22 | 160.79 | 3.167E – 011 |
| 900.00 | 377.94 | 271.60 | 133.50 | 1.784E – 008 |
| 1000.00 | 375.38 | 268.91 | 106.47 | 2.742E – 006 |
| 1100.00 | 372.47 | 266.14 | 79.72 | 1.637E – 004 |
| 1200.00 | 369.20 | 263.29 | 53.29 | 4.809E – 003 |
| 1300.00 | 365.56 | 260.38 | 27.06 | 6.176E – 002 |
| 1400.00 | 361.54 | 257.40 | 1.17 | 9.042E – 001 |
| 1500.00 | 343.83 | 244.83 | –23.41 | 6.538E + 000 |

TABLE 4.83

Density of Manganese Sulfates

| Phase | T(K) | d | Reference |
|---|------|---------------------------|-----------|
| MnSO ₄ (c) | 298 | 3.181 (25/4) | 27 |
| Mn ₂ (SO ₄) ₃ | 288 | 3.24 (g/cm ³) | 61 |

TABLE 4.84

Thermodynamic Data of MnSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | –1065.25 | 112.10 | –1098.67 | Knacke et al. 1991 |
| 400.00 | –1054.00 | 144.44 | –1111.77 | Knacke et al. 1991 |
| 500.00 | –1041.57 | 172.12 | –1127.63 | Knacke et al. 1991 |
| 600.00 | –1028.28 | 196.33 | –1146.08 | Knacke et al. 1991 |
| 700.00 | –1014.34 | 217.81 | –1166.81 | Knacke et al. 1991 |
| 800.00 | –999.85 | 237.15 | –1189.57 | Knacke et al. 1991 |
| 900.00 | –984.87 | 254.79 | –1214.18 | Knacke et al. 1991 |
| 1000.00 | –969.44 | 271.05 | –1240.48 | Knacke et al. 1991 |
| 1100.00 | –953.57 | 286.17 | –1268.35 | Knacke et al. 1991 |
| 1200.00 | –937.28 | 300.33 | –1297.68 | Knacke et al. 1991 |
| 1300.00 | –920.59 | 313.69 | –1328.39 | Knacke et al. 1991 |
| 1400.00 | –903.50 | 326.36 | –1360.40 | Knacke et al. 1991 |
| 1500.00 | –886.01 | 338.42 | –1393.64 | Knacke et al. 1991 |

TABLE 4.85
Thermodynamic Data of Mn₃O₄

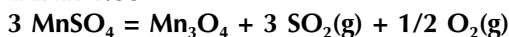
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1387.80 | 155.60 | -1434.19 | Barin 1993 |
| 400.00 | -1372.70 | 199.06 | -1452.33 | Barin 1993 |
| 500.00 | -1356.77 | 234.57 | -1474.06 | Barin 1993 |
| 600.00 | -1340.05 | 265.04 | -1499.07 | Barin 1993 |
| 700.00 | -1322.67 | 291.82 | -1526.94 | Barin 1993 |
| 800.00 | -1304.70 | 315.81 | -1557.34 | Barin 1993 |
| 900.00 | -1286.16 | 337.63 | -1590.03 | Barin 1993 |
| 1000.00 | -1267.10 | 357.71 | -1624.81 | Barin 1003 |
| 1100.00 | -1247.51 | 376.38 | -1661.53 | Barin 1993 |
| 1200.00 | -1227.41 | 393.86 | -1700.05 | Barin 1993 |
| 1300.00 | -1206.80 | 410.36 | -1740.27 | Barin 1993 |
| 1400.00 | -1185.69 | 426.00 | -1782.09 | Barin 1993 |
| 1500.00 | -1146.36 | 453.18 | -1826.13 | Barin 1993 |

TABLE 4.86
MnSO₄ = MnO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 284.27 | 204.38 | 223.33 | 7.422E - 040 |
| 400.00 | 283.24 | 201.48 | 202.65 | 3.428E - 027 |
| 500.00 | 281.69 | 198.03 | 182.67 | 8.223E - 020 |
| 600.00 | 279.91 | 194.81 | 163.03 | 6.394E - 015 |
| 700.00 | 277.97 | 191.81 | 143.70 | 1.888E - 011 |
| 800.00 | 275.84 | 188.96 | 124.66 | 7.238E - 009 |
| 900.00 | 273.51 | 186.23 | 105.91 | 7.127E - 007 |
| 1000.00 | 270.98 | 183.56 | 87.42 | 2.713E - 005 |
| 1100.00 | 268.22 | 180.93 | 69.19 | 5.177E - 004 |
| 1200.00 | 265.23 | 178.33 | 51.23 | 5.887E - 003 |
| 1300.00 | 262.00 | 175.75 | 33.52 | 4.496E - 002 |
| 1400.00 | 258.52 | 173.17 | 16.08 | 2.512E - 001 |
| 1500.00 | 254.79 | 170.60 | -1.11 | 1.093E + 000 |

TABLE 4.87

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 383.22 | 298.41 | 294.25 | 2.785E – 052 |
| 400.00 | 382.44 | 296.24 | 263.94 | 3.387E – 035 |
| 500.00 | 380.92 | 292.88 | 234.48 | 3.175E – 025 |
| 600.00 | 379.02 | 289.42 | 205.37 | 1.317E – 018 |
| 700.00 | 376.83 | 286.05 | 176.60 | 6.624E – 014 |
| 800.00 | 374.38 | 282.78 | 148.16 | 2.116E – 010 |
| 900.00 | 371.69 | 279.61 | 120.04 | 1.078E – 007 |
| 1000.00 | 368.75 | 276.52 | 92.23 | 1.520E – 005 |
| 1100.00 | 365.56 | 273.48 | 64.73 | 8.431E – 004 |
| 1200.00 | 362.13 | 270.50 | 37.53 | 2.323E – 002 |
| 1300.00 | 358.45 | 267.55 | 10.63 | 3.740E – 001 |
| 1400.00 | 354.52 | 264.64 | –15.98 | 3.947E + 000 |
| 1500.00 | 350.33 | 261.75 | –42.30 | 2.972E + 001 |

TABLE 4.88

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 917.52 | 769.12 | 688.20 | 2.628E – 121 |
| 400.00 | 914.62 | 760.98 | 610.23 | 2.019E – 080 |
| 500.00 | 909.94 | 750.58 | 534.65 | 1.382E – 056 |
| 600.00 | 904.42 | 740.53 | 460.10 | 8.733E – 041 |
| 700.00 | 898.32 | 731.13 | 386.53 | 1.428E – 029 |
| 800.00 | 891.69 | 722.30 | 313.86 | 3.202E – 021 |
| 900.00 | 884.58 | 713.93 | 242.05 | 8.925E – 015 |
| 1000.00 | 876.98 | 705.92 | 171.06 | 1.159E – 009 |
| 1100.00 | 868.88 | 698.20 | 100.86 | 1.623E – 005 |
| 1200.00 | 860.27 | 690.71 | 31.41 | 4.291E – 002 |

TABLE 4.89
Thermodynamic Data of Hg₂SO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------------|
| 298.15 | –743.12 | 200.83 | –803.00 | Barin et al. 1977 |
| 400.00 | –728.94 | 241.64 | –825.60 | Barin et al. 1977 |
| 500.00 | –713.59 | 275.84 | –851.51 | Barin et al. 1977 |
| 600.00 | –696.81 | 306.39 | –880.64 | Barin et al. 1977 |
| 700.00 | –678.61 | 334.41 | –912.70 | Barin et al. 1977 |
| 800.00 | –658.99 | 360.59 | –947.47 | Barin et al. 1977 |
| 900.00 | –637.95 | 385.36 | –984.77 | Barin et al. 1977 |
| 1000.00 | –615.49 | 409.02 | –1024.50 | Barin et al. 1977 |

TABLE 4.90
Thermodynamic Data of HgSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -707.50 | 140.16 | -749.29 | Barin 1989 |
| 400.00 | -696.33 | 172.29 | -765.25 | Barin 1989 |
| 500.00 | -683.88 | 200.01 | -783.89 | Barin 1989 |
| 600.00 | -669.97 | 225.33 | -805.17 | Barin 1989 |
| 700.00 | -654.59 | 249.01 | -828.90 | Barin 1989 |
| 800.00 | -637.75 | 271.47 | -854.93 | Barin 1989 |
| 900.00 | -619.45 | 293.01 | -883.16 | Barin 1989 |
| 1000.00 | -599.68 | 313.83 | -913.51 | Barin 1989 |

TABLE 4.91
HgSO₄ = HgO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 220.95 | 186.88 | 165.23 | 1.122E - 029 |
| 400.00 | 220.01 | 184.20 | 146.33 | 7.754E - 020 |
| 500.00 | 218.61 | 181.10 | 128.06 | 4.173E - 014 |
| 600.00 | 216.53 | 177.33 | 110.13 | 2.578E - 010 |
| 700.00 | 213.58 | 172.80 | 92.62 | 1.225E - 007 |
| 800.00 | 209.59 | 167.49 | 75.60 | 1.157E - 005 |
| 900.00 | 204.45 | 161.45 | 59.15 | 3.689E - 004 |
| 1000.00 | 198.07 | 154.73 | 43.33 | 5.450E - 003 |

TABLE 4.92
HgSO₄ = HgO + SO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 319.90 | 280.90 | 236.15 | 4.209E - 042 |
| 400.00 | 319.21 | 278.96 | 207.63 | 7.661E - 028 |
| 500.00 | 317.85 | 275.95 | 179.87 | 1.611E - 019 |
| 600.00 | 315.64 | 271.94 | 152.47 | 5.310E - 014 |
| 700.00 | 312.44 | 267.04 | 125.52 | 4.297E - 010 |
| 800.00 | 308.13 | 261.30 | 99.09 | 3.384E - 007 |
| 900.00 | 302.63 | 254.83 | 73.28 | 5.580E - 005 |
| 1000.00 | 295.84 | 247.69 | 48.15 | 3.054E - 003 |

TABLE 4.93
Thermodynamic Data of NiSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -872.91 | 92.00 | -900.34 | Barin 1989 |
| 400.00 | -858.64 | 133.15 | -911.90 | Barin 1989 |
| 500.00 | -844.21 | 165.33 | -926.87 | Barin 1989 |
| 600.00 | -829.36 | 192.38 | -944.79 | Barin 1989 |
| 700.00 | -814.10 | 215.90 | -965.23 | Barin 1989 |
| 800.00 | -798.43 | 236.83 | -987.89 | Barin 1989 |
| 900.00 | -782.34 | 255.77 | -1012.53 | Barin 1989 |
| 1000.00 | -765.83 | 273.16 | -1038.99 | Barin 1989 |
| 1100.00 | -748.91 | 289.28 | -1067.12 | Barin 1989 |
| 1200.00 | -731.57 | 304.36 | -1096.81 | Barin 1989 |

TABLE 4.94
NiSO₄ = NiO + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 237.44 | 202.76 | 176.99 | 9.764E - 032 |
| 400.00 | 233.60 | 191.61 | 156.96 | 3.175E - 021 |
| 500.00 | 230.93 | 185.58 | 138.14 | 3.697E - 015 |
| 600.00 | 228.53 | 181.25 | 119.78 | 3.729E - 011 |
| 700.00 | 225.47 | 176.55 | 101.89 | 2.490E - 008 |
| 800.00 | 222.22 | 172.20 | 84.45 | 3.056E - 006 |
| 900.00 | 218.79 | 168.17 | 67.44 | 1.218E - 004 |
| 1000.00 | 215.19 | 164.38 | 50.81 | 2.216E - 003 |
| 1100.00 | 211.40 | 160.77 | 34.56 | 2.285E - 002 |
| 1200.00 | 207.41 | 157.30 | 18.66 | 1.514E - 001 |

TABLE 4.95
NiSO₄ = NiO + SO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 336.39 | 296.78 | 247.91 | 3.664E - 044 |
| 400.00 | 332.80 | 286.37 | 218.25 | 3.137E - 029 |
| 500.00 | 330.16 | 280.42 | 189.94 | 1.427E - 020 |
| 600.00 | 327.63 | 275.86 | 162.12 | 7.682E - 015 |
| 700.00 | 324.33 | 270.78 | 134.79 | 8.737E - 011 |
| 800.00 | 320.76 | 266.02 | 107.95 | 8.936E - 008 |
| 900.00 | 316.97 | 261.55 | 81.57 | 1.842E - 005 |
| 1000.00 | 312.96 | 257.34 | 55.63 | 1.242E - 003 |
| 1100.00 | 308.75 | 253.32 | 30.10 | 3.721E - 002 |
| 1200.00 | 304.31 | 249.46 | 4.96 | 6.082E - 001 |

TABLE 4.96
Density of K₂SO₄

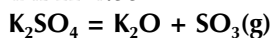
| Phase | T(K) | d | Reference |
|----------|------|-------|-----------|
| c,II (α) | 291 | 2.663 | 68 |
| c,II | 298 | 2.662 | 69 |
| c,I (β) | 298 | 2.621 | 70 |
| Liquid | 1343 | 1.888 | 26 |
| | 1376 | 1.870 | |
| | 1418 | 1.848 | |
| | 1472 | 1.818 | |
| | 1520 | 1.792 | |
| | 1579 | 1.760 | |
| | 1670 | 1.737 | |
| | 1713 | 1.687 | |
| | 1763 | 1.660 | |
| | 1803 | 1.637 | |
| | 1859 | 1.607 | |
| | 1929 | 1.569 | |

TABLE 4.97
Transitions of K₂SO₄

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------|------|-----------|--------------|-----------|
| c,II → c,I | 856 | 8.12 | 9.50 | 9,10,71 |
| c,I → l | 1342 | 36.6 | 27.3 | |

TABLE 4.98
Thermodynamic Data of K₂SO₄

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|------------------------------|---|------------------------------|------------|
| 298.15 | -1437.79 | 175.56 | -1490.13 | Barin 1993 |
| 400.00 | -1423.25 | 217.37 | -1510.20 | Barin 1993 |
| 500.00 | -1407.82 | 251.79 | -1533.71 | Barin 1993 |
| 600.00 | -1391.53 | 281.45 | -1560.40 | Barin 1993 |
| 700.00 | -1373.86 | 308.66 | -1589.92 | Barin 1993 |
| 800.00 | -1353.94 | 335.21 | -1622.11 | Barin 1993 |
| 900.00 | -1324.78 | 369.52 | -1657.35 | Barin 1993 |
| 1000.00 | -1305.62 | 389.70 | -1695.32 | Barin 1993 |
| 1100.00 | -1285.66 | 408.72 | -1735.25 | Barin 1993 |
| 1200.00 | -1264.88 | 426.80 | -1777.03 | Barin 1993 |
| 1300.00 | -1243.28 | 444.08 | -1820.58 | Barin 1993 |
| 1400.00 | -1187.89 | 485.28 | -1867.28 | Barin 1993 |
| 1500.00 | -1167.75 | 499.18 | -1916.51 | Barin 1993 |

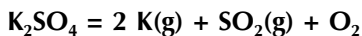
TABLE 4.99

| T K | ΔH° kJ | ΔS° J deg⁻¹ | ΔG° kJ | K |
|----------------------|---|---|---|--------------|
| 298.15 | 680.53 | 183.22 | 625.90 | 2.166E – 110 |
| 400.00 | 679.35 | 179.86 | 607.40 | 4.731E – 080 |
| 500.00 | 678.02 | 176.91 | 589.57 | 2.529E – 062 |
| 600.00 | 676.62 | 174.36 | 572.01 | 1.579E – 050 |
| 700.00 | 674.42 | 171.00 | 554.73 | 4.004E – 042 |
| 800.00 | 670.45 | 165.73 | 537.87 | 7.548E – 036 |
| 900.00 | 657.63 | 150.66 | 522.04 | 5.004E – 031 |
| 1000.00 | 655.15 | 148.05 | 507.10 | 3.234E – 027 |
| 1100.00 | 680.54 | 173.18 | 490.05 | 5.341E – 024 |
| 1200.00 | 678.20 | 171.15 | 472.83 | 2.610E – 021 |
| 1300.00 | 675.13 | 168.69 | 455.83 | 4.819E – 019 |
| 1400.00 | 638.33 | 141.27 | 440.56 | 3.641E – 017 |
| 1500.00 | 636.84 | 140.24 | 426.48 | 1.404E – 015 |

TABLE 4.100

| T K | ΔH° kJ | ΔS° J deg⁻¹ | ΔG° kJ | K |
|----------------------|---|---|---|--------------|
| 298.15 | 779.48 | 277.24 | 696.82 | 8.126E – 123 |
| 400.00 | 778.55 | 274.63 | 668.70 | 4.675E – 088 |
| 500.00 | 777.26 | 271.75 | 641.38 | 9.764E – 068 |
| 600.00 | 775.73 | 268.97 | 614.34 | 3.253E – 054 |
| 700.00 | 773.29 | 265.24 | 587.62 | 1.405E – 044 |
| 800.00 | 769.00 | 259.55 | 561.36 | 2.207E – 037 |
| 900.00 | 755.80 | 244.04 | 536.17 | 7.569E – 032 |
| 1000.00 | 752.92 | 241.01 | 511.91 | 1.812E – 027 |
| 1100.00 | 777.89 | 265.73 | 485.59 | 8.698E – 024 |
| 1200.00 | 775.11 | 263.31 | 459.13 | 1.030E – 020 |
| 1300.00 | 771.59 | 260.50 | 432.94 | 4.007E – 018 |
| 1400.00 | 734.33 | 232.74 | 408.50 | 5.720E – 016 |
| 1500.00 | 732.38 | 231.39 | 385.30 | 3.817E – 014 |

TABLE 4.101



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 1318.98 | 598.49 | 1140.54 | 1.465E – 200 |
| 400.00 | 1315.97 | 589.90 | 1080.01 | 8.991E – 142 |
| 500.00 | 1312.33 | 581.80 | 1021.43 | 1.918E – 107 |
| 600.00 | 1308.23 | 574.34 | 963.63 | 1,265E – 084 |
| 700.00 | 1303.02 | 566.35 | 906.58 | 2.210E – 068 |
| 800.00 | 1295.80 | 556.73 | 850.41 | 2.946E – 056 |
| 900.00 | 1279.49 | 537.56 | 795.68 | 6.545E – 047 |
| 1000.00 | 1273.33 | 531.08 | 742.25 | 1.681E – 039 |
| 1100.00 | 1266.48 | 524.55 | 689.47 | 1.808E – 033 |
| 1200.00 | 1258.92 | 517.98 | 637.34 | 1.798E – 028 |
| 1300.00 | 1250.64 | 511.35 | 585.88 | 2.866E – 024 |
| 1400.00 | 1208.64 | 480.08 | 536.53 | 9.553E – 021 |
| 1500.00 | 1201.96 | 475.47 | 488.76 | 9.519E – 018 |

TABLE 4.102

Thermodynamic Data of RaSO_4

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------|
| 298.15 | –1471.00 | 159.00 | –1518.40 | Phillips 88 |
| 400.00 | –1460.51 | 189.27 | –1536.22 | Phillips 88 |
| 500.00 | –1450.21 | 212.25 | –1556.33 | Phillips 88 |
| 600.00 | –1439.91 | 231.03 | –1578.53 | Phillips 88 |
| 700.00 | –1429.61 | 246.91 | –1602.44 | Phillips 88 |
| 800.00 | –1419.31 | 260.67 | –1627.84 | Phillips 88 |
| 900.00 | –1409.01 | 272.80 | –1654.52 | Phillips 88 |
| 1000.00 | –1398.71 | 283.65 | –1682.36 | Phillips 88 |

TABLE 4.103

Thermodynamic Data of $\text{Ce}_2(\text{SO}_4)_3$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------------|
| 298.15 | –3954.30 | 287.44 | –4040.00 | Barin et al. 1977 |
| 400.00 | –3954.30 | 287.44 | –4073.79 | Barin et al. 1977 |
| 500.00 | –3893.53 | 442.21 | –4114.63 | Barin et al. 1977 |
| 600.00 | –3860.42 | 502.51 | –4161.93 | Barin et al. 1977 |
| 700.00 | –3825.33 | 556.57 | –4214.93 | Barin et al. 1977 |
| 800.00 | –3788.25 | 606.05 | –4273.90 | Barin et al. 1977 |
| 900.00 | –3749.18 | 652.04 | –4336.02 | Barin et al. 1977 |
| 1000.00 | –3708.13 | 695.28 | –4403.41 | Barin et al. 1977 |
| 1100.00 | –3665.08 | 736.29 | –4475.00 | Barin et al. 1977 |
| 1200.00 | –3620.05 | 775.46 | –4550.60 | Barin et al. 1977 |
| 1300.00 | –3573.03 | 813.08 | –4630.04 | Barin et al. 1977 |
| 1400.00 | –3524.03 | 849.39 | –4713.18 | Barin et al. 1977 |
| 1500.00 | 3473.04 | 884.56 | –4799.88 | Barin et al. 1977 |

TABLE 4.104

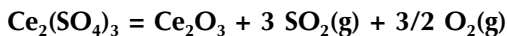
Thermodynamic Data of Ce_2O_3

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1796.19 | 150.58 | -1841.09 | Barin 1993 |
| 400.00 | -1783.61 | 186.79 | -1858.33 | Barin 1993 |
| 500.00 | -1770.48 | 216.07 | -1878.52 | Barin 1993 |
| 600.00 | -1756.87 | 240.89 | -1901.40 | Barin 1993 |
| 700.00 | -1742.89 | 262.42 | -1926.59 | Barin 1993 |
| 800.00 | -1728.62 | 281.48 | -1953.80 | Barin 1993 |
| 900.00 | -1714.08 | 298.60 | -1982.82 | Barin 1993 |
| 1000.00 | -1699.30 | 314.17 | -2013.47 | Barin 1993 |
| 1100.00 | -1684.29 | 328.48 | -2045.61 | Barin 1993 |
| 1200.00 | -1669.05 | 341.73 | -2079.13 | Barin 1993 |
| 1300.00 | -1653.60 | 354.10 | -2113.93 | Barin 1993 |
| 1400.00 | -1637.95 | 365.70 | -2149.92 | Barin 1993 |
| 1500.00 | -1622.08 | 376.65 | -2187.05 | Barin 1993 |

TABLE 4.105

$\text{Ce}_2(\text{SO}_4)_3 = \text{Ce}_2\text{O}_3 + 3 \text{SO}_3(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 970.81 | 633.46 | 781.95 | 9.874E - 138 |
| 400.00 | 970.29 | 631.87 | 717.54 | 1.953E - 094 |
| 500.00 | 970.44 | 632.18 | 654.34 | 4.319E - 069 |
| 600.00 | 970.58 | 632.44 | 591.11 | 3.429E - 052 |
| 700.00 | 970.18 | 631.85 | 527.89 | 4.032E - 040 |
| 800.00 | 968.87 | 630.12 | 464.78 | 4.474E - 031 |
| 900.00 | 966.45 | 627.28 | 401.90 | 4.705E - 024 |
| 1000.00 | 962.74 | 623.39 | 339.36 | 1.872E - 018 |
| 1100.00 | 957.64 | 618.54 | 277.25 | 6.812E - 014 |
| 1200.00 | 951.07 | 612.83 | 215.68 | 4.084E - 010 |
| 1300.00 | 942.97 | 606.36 | 154.71 | 6.069E - 007 |
| 1400.00 | 933.30 | 599.19 | 94.43 | 2.996E - 004 |
| 1500.00 | 922.02 | 591.42 | 34.89 | 6.093E - 002 |

TABLE 4.106

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 1267.67 | 915.53 | 994.71 | 5.216E – 175 |
| 400.00 | 1267.90 | 916.17 | 901.43 | 1.884E – 118 |
| 500.00 | 1268.14 | 916.72 | 809.78 | 2.486E – 085 |
| 600.00 | 1267.89 | 916.28 | 718.12 | 2.997E – 063 |
| 700.00 | 1266.77 | 914.57 | 626.57 | 1.741E – 047 |
| 800.00 | 1264.51 | 911.57 | 535.25 | 1.119E – 035 |
| 900.00 | 1260.98 | 907.43 | 444.29 | 1.628E – 028 |
| 1000.00 | 1256.06 | 902.56 | 353.80 | 3.294E – 019 |
| 1100.00 | 1249.68 | 896.19 | 263.87 | 2.942E – 013 |
| 1200.00 | 1241.78 | 889.32 | 174.59 | 2.510E – 008 |
| 1300.00 | 1232.33 | 881.77 | 86.03 | 3.491E – 004 |
| 1400.00 | 1221.30 | 873.60 | –1.74 | 1.161E + 000 |
| 1500.00 | 1208.65 | 864.88 | –88.67 | 1.225E + 003 |

TABLE 4.107
Thermodynamic Data of $\text{La}_2(\text{SO}_4)_3$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|-------------|
| 298.15 | –3941.30 | 280.33 | –4024.88 | Phillips 88 |
| 400.00 | –3912.79 | 362.58 | –4057.82 | Phillips 88 |
| 500.00 | –3884.80 | 425.04 | –4097.32 | Phillips 88 |
| 600.00 | –3856.81 | 476.08 | –4142.46 | Phillips 88 |
| 700.00 | –3828.83 | 519.23 | –4192.28 | Phillips 88 |

TABLE 4.108
Thermodynamic Data of $\text{Nd}_2(\text{SO}_4)_3$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------------|
| 298.15 | –3899.49 | 288.28 | –3985.44 | Barin et al. 1977 |
| 400.00 | –3870.69 | 371.23 | –4019.18 | Barin et al. 1977 |
| 500.00 | –3840.41 | 438.72 | –4059.77 | Barin et al. 1977 |
| 600.00 | –3808.14 | 497.49 | –4106.63 | Barin et al. 1977 |
| 700.00 | –3773.88 | 550.26 | –4159.06 | Barin et al. 1977 |
| 800.00 | –3737.64 | 598.63 | –4216.54 | Barin et al. 1977 |
| 900.00 | –3699.41 | 643.64 | –4278.68 | Barin et al. 1977 |
| 1000.00 | –3659.19 | 685.99 | –4345.18 | Barin et al. 1977 |
| 1100.00 | –3616.98 | 726.29 | –4415.81 | Barin et al. 1977 |
| 1200.00 | –3572.79 | 764.64 | –4490.36 | Barin et al. 1977 |
| 1300.00 | –3526.61 | 801.60 | –4568.69 | Barin et al. 1977 |
| 1400.00 | –3478.44 | 837.29 | –4650.64 | Barin et al. 1977 |
| 1500.00 | –3428.28 | 871.88 | –4736.11 | Barin et al. 1977 |

TABLE 4.109

Thermodynamic Data of Nd_2O_3

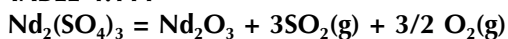
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -1807.91 | 158.57 | -1855.19 | Knacke et al. 1991 |
| 400.00 | -1796.07 | 192.66 | -1873.13 | Knacke et al. 1991 |
| 500.00 | -1783.75 | 220.13 | -1893.81 | Knacke et al. 1991 |
| 600.00 | -1770.94 | 243.48 | -1917.02 | Knacke et al. 1991 |
| 700.00 | -1757.71 | 263.86 | -1942.41 | Knacke et al. 1991 |
| 800.00 | -1744.12 | 282.00 | -1962.72 | Knacke et al. 1991 |
| 900.00 | -1730.18 | 298.42 | -1998.75 | Knacke et al. 1991 |
| 1000.00 | -1715.90 | 313.46 | -2029.36 | Knacke et al. 1991 |
| 1100.00 | -1701.30 | 327.37 | -2061.41 | Knacke et al. 1991 |
| 1200.00 | -1686.39 | 340.34 | -2094.80 | Knacke et al. 1991 |
| 1300.00 | -1671.16 | 352.53 | -2129.45 | Knacke et al. 1991 |
| 1400.00 | -1655.04 | 364.46 | -2165.29 | Knacke et al. 1991 |
| 1500.00 | -1639.74 | 375.20 | -2202.28 | Knacke et al. 1991 |

TABLE 4.110

 $\text{Nd}_2(\text{SO}_4)_3 = \text{Nd}_2\text{O}_3 + 3 \text{SO}_3(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 904.29 | 640.61 | 713.29 | 1.057E - 125 |
| 400.00 | 903.88 | 639.36 | 648.13 | 2.267E - 085 |
| 500.00 | 904.05 | 639.73 | 584.18 | 9.241E - 062 |
| 600.00 | 904.22 | 640.05 | 520.19 | 5.125E - 046 |
| 700.00 | 903.91 | 639.59 | 456.20 | 9.019E - 035 |
| 800.00 | 902.76 | 638.07 | 392.31 | 2.414E - 026 |
| 900.00 | 900.58 | 635.51 | 328.62 | 8.429E - 020 |
| 1000.00 | 897.20 | 631.96 | 265.24 | 1.394E - 014 |
| 1100.00 | 892.52 | 627.51 | 202.26 | 2.482E - 010 |
| 1200.00 | 886.47 | 622.26 | 139.76 | 8.237E - 007 |
| 1300.00 | 878.99 | 614.28 | 77.83 | 7.455E - 004 |
| 1400.00 | 870.62 | 610.06 | 16.53 | 2.417E - 001 |
| 1500.00 | 859.87 | 602.66 | -44.11 | 3.483E + 001 |

TABLE 4.111



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 1201.14 | 922.68 | 926.05 | 5.586E – 163 |
| 400.00 | 1201.49 | 923.65 | 832.02 | 2.187E – 109 |
| 500.00 | 1201.75 | 924.26 | 739.62 | 5.319E – 078 |
| 600.00 | 1201.54 | 923.89 | 647.20 | 4.479E – 057 |
| 700.00 | 1200.50 | 922.30 | 554.89 | 3.895E – 042 |
| 800.00 | 1198.40 | 919.52 | 462.78 | 6.036E – 031 |
| 900.00 | 1195.11 | 915.65 | 371.02 | 2.917E – 022 |
| 1000.00 | 1190.52 | 910.83 | 279.69 | 2.452E – 015 |
| 1100.00 | 1184.56 | 905.16 | 188.88 | 1.072E – 009 |
| 1200.00 | 1177.18 | 898.75 | 98.68 | 5.062E – 005 |
| 1300.00 | 1168.35 | 891.69 | 9.15 | 4.288E – 001 |
| 1400.00 | 1158.61 | 884.47 | –79.64 | 9.370E + 002 |
| 1500.00 | 1146.50 | 876.12 | –167.68 | 6.911E + 005 |

TABLE 4.112

Density of Rb₂SO₄

| Phase | T(K) | d | Reference |
|--------|------|-------|-----------|
| c,II | 293 | 3.614 | 25 |
| c,II | 298 | 3.613 | 8 |
| c,II | 333 | 3.594 | 25 |
| Liquid | 1359 | 2.538 | 26 |
| | 1385 | 2.521 | |
| | 1418 | 2.499 | |
| | 1468 | 2.466 | |
| | 1508 | 2.440 | |
| | 1562 | 2.403 | |
| | 1617 | 2.367 | |
| | 1670 | 2.331 | |
| | 1688 | 2.319 | |
| | 1755 | 2.275 | |
| | 1818 | 2.233 | |

TABLE 4.113

Transitions of Rb₂SO₄

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol*K) | Reference |
|--------------|------|-------------------|----------------------|-----------|
| c,II → c,I | 923 | | | 9 |
| c,I → liquid | 1347 | | | 9 |

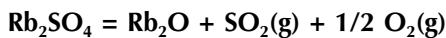
TABLE 4.114
Thermodynamic Data of Rb₂SO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1435.61 | 197.44 | -1494.48 | Barin 1989 |
| 400.00 | -1423.22 | 233.08 | -1516.45 | Barin 1989 |
| 500.00 | -1409.69 | 263.22 | -1541.30 | Barin 1989 |
| 600.00 | -1395.05 | 289.88 | -1568.98 | Barin 1989 |
| 700.00 | -1379.40 | 313.98 | -1599.19 | Barin 1989 |
| 800.00 | -1362.79 | 336.16 | -1631.71 | Barin 1989 |
| 900.00 | -1345.23 | 356.83 | -1666.37 | Barin 1989 |
| 1000.00 | -1321.20 | 382.22 | -1703.42 | Barin 1989 |
| 1100.00 | -1300.69 | 401.76 | -1742.63 | Barin 1989 |
| 1200.00 | -1280.19 | 419.60 | -1783.71 | Barin 1989 |
| 1300.00 | -1259.69 | 436.01 | -1826.50 | Barin 1989 |
| 1400.00 | -1200.54 | 479.98 | -1872.51 | Barin 1989 |
| 1500.00 | -1179.62 | 494.41 | -1921.23 | Barin 1989 |

TABLE 4.115
Rb₂SO₄ = Rb₂O + SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 700.85 | 184.85 | 645.73 | 7.262E - 114 |
| 400.00 | 701.69 | 187.32 | 626.76 | 1.403E - 082 |
| 500.00 | 702.12 | 188.29 | 607.97 | 3.023E - 064 |
| 600.00 | 703.11 | 190.12 | 589.04 | 5.196E - 052 |
| 700.00 | 707.13 | 196.71 | 560.44 | 3.196E - 043 |
| 800.00 | 727.56 | 222.94 | 549.21 | 1.373E - 036 |
| 900.00 | 726.57 | 221.78 | 526.96 | 2.590E - 031 |
| 1000.00 | 719.27 | 214.02 | 505.25 | 4.038E - 027 |
| 1100.00 | 715.61 | 210.53 | 484.03 | 1.032E - 023 |
| 1200.00 | 712.06 | 207.44 | 463.13 | 6.898E - 021 |
| 1300.00 | 708.59 | 204.66 | 442.53 | 1.650E - 018 |
| 1400.00 | 666.53 | 173.36 | 423.83 | 1.533E - 016 |
| 1500.00 | 662.76 | 170.76 | 406.62 | 6.902E - 015 |

TABLE 4.116



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 799.80 | 278.88 | 716.65 | 2.735E – 126 |
| 400.00 | 800.89 | 282.09 | 688.06 | 1.386E – 090 |
| 500.00 | 801.35 | 283.14 | 659.78 | 1.167E – 069 |
| 600.00 | 802.21 | 284.73 | 631.37 | 1.070E – 055 |
| 700.00 | 806.00 | 290.95 | 602.33 | 1.121E – 045 |
| 800.00 | 826.10 | 316.75 | 572.70 | 4.014E – 038 |
| 900.00 | 824.74 | 315.17 | 541.10 | 3.917E – 032 |
| 1000.00 | 817.04 | 306.97 | 510.07 | 2.263E – 027 |
| 1100.00 | 812.96 | 303.08 | 479.57 | 1.680E – 023 |
| 1200.00 | 808.96 | 299.60 | 449.43 | 2.722E – 020 |
| 1300.00 | 805.04 | 296.46 | 419.64 | 1.372E – 017 |
| 1400.00 | 762.53 | 264.83 | 391.77 | 2.408E – 015 |
| 1500.00 | 758.31 | 261.92 | 365.44 | 1.877E – 013 |

TABLE 4.117

Transitions of Ag_2SO_4

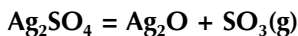
| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol*K) | Reference |
|--------------|------|-------------------|----------------------|-----------|
| c.II → c.I | 685 | 8.0 | 11.7 | 9, 10 |
| c.I → liquid | 933 | 17. | | |

TABLE 4.118

Thermodynamic Data of Ag_2SO_4

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -715.88 | 200.41 | -775.64 | Barin 1989 |
| 400.00 | -701.89 | 340.71 | -798.17 | Barin 1989 |
| 500.00 | -686.97 | 273.95 | -823.94 | Barin 1989 |
| 600.00 | -670.89 | 303.24 | -852.83 | Barin 1989 |
| 700.00 | -653.63 | 329.81 | -884.50 | Barin 1989 |
| 800.00 | -616.55 | 381.05 | -921.39 | Barin 1989 |
| 900.00 | -596.96 | 404.11 | -960.66 | Barin 1989 |
| 1000.00 | -558.60 | 444.85 | -1003.45 | Barin 1989 |

TABLE 4.119



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 289.07 | 177.66 | 236.13 | 4.048E – 042 |
| 400.00 | 287.63 | 173.51 | 218.23 | 3.160E – 029 |
| 500.00 | 286.23 | 170.37 | 201.04 | 9.901E – 022 |
| 600.00 | 284.63 | 167.47 | 184.15 | 9.270E – 017 |
| 700.00 | 282.68 | 164.47 | 167.55 | 3.134E – 013 |
| 800.00 | 261.59 | 134.57 | 153.93 | 8.883E – 011 |
| 900.00 | 258.62 | 131.08 | 140.65 | 6.862E – 009 |
| 1000.00 | 237.45 | 108.55 | 129.00 | 1.824E – 007 |

TABLE 4.120



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 388.02 | 271.68 | 307.02 | 1.611E – 054 |
| 400.00 | 417.59 | 334.08 | 283.96 | 8.238E – 038 |
| 500.00 | 415.54 | 329.53 | 250.77 | 6.305E – 027 |
| 600.00 | 412.81 | 324.58 | 218.07 | 1.033E – 019 |
| 700.00 | 409.32 | 319.21 | 185.87 | 1.346E – 014 |
| 800.00 | 386.34 | 286.80 | 156.90 | 5.682E – 011 |
| 900.00 | 381.17 | 280.72 | 128.52 | 3.468E – 008 |
| 1000.00 | 357.52 | 255.47 | 102.05 | 4.668E – 006 |

TABLE 4.121

Density of Na_2SO_4

| Phase | T(K) | d | Reference |
|--------|------|--------------|-----------|
| c,V | 298 | 2.664 | 84 |
| c,III | 298 | 2.697 | 84 |
| c,I | 993 | 2.64 (X-ray) | 85 |
| Liquid | 1173 | 2.061 | 26 |
| | 1218 | 2.039 | |
| | 1263 | 2.017 | |
| | 1305 | 1.997 | |
| | 1350 | 1.971 | |

TABLE 4.122

Transitions of Na_2SO_4

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------|------|-------------------|----------------------|-----------|
| c,V → c,III | 450 | 3.10 | 6.9 | 10 |
| c,III → c,I | 515 | 7.49 | 14.56 | 10 |
| c,I → liquid | 1157 | 23.85 | 20.63 | 10 |

TABLE 4.123

Thermodynamic Data of Na_2SO_4

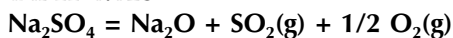
| T K | ΔH° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG° kJ mol ⁻¹ | Reference |
|---------|--|---|--|--------------------|
| 298.15 | -1387.82 | 149.60 | -1432.42 | Knacke et al. 1991 |
| 400.00 | -1373.86 | 189.73 | -1449.76 | Knacke et al. 1991 |
| 500.00 | -1358.39 | 224.18 | -1470.48 | Knacke et al. 1991 |
| 600.00 | -1330.38 | 276.56 | -1496.31 | Knacke et al. 1991 |
| 700.00 | -1312.57 | 304.01 | -1525.37 | Knacke et al. 1991 |
| 800.00 | -1294.14 | 328.59 | -1557.02 | Knacke et al. 1991 |
| 900.00 | -1275.09 | 351.03 | -1591.02 | Knacke et al. 1991 |
| 1000.00 | -1255.38 | 371.79 | -1627.17 | Knacke et al. 1991 |
| 1100.00 | -1235.03 | 391.18 | -1665.33 | Knacke et al. 1991 |
| 1200.00 | -1190.82 | 429.51 | -1706.24 | Knacke et al. 1991 |
| 1300.00 | -1171.12 | 445.28 | -1749.99 | Knacke et al. 1991 |
| 1400.00 | -1151.42 | 459.89 | -1795.26 | Knacke et al. 1991 |
| 1500.00 | -1131.71 | 473.48 | -1841.93 | Knacke et al. 1991 |
| 1600.00 | -1112.01 | 486.20 | -1889.92 | Knacke et al. 1991 |
| 1700.00 | -1092.31 | 498.14 | -1939.15 | Knacke et al. 1991 |
| 1800.00 | -1072.60 | 509.40 | -1989.53 | Knacke et al. 1991 |
| 1900.00 | -1052.90 | 520.06 | -2041.01 | Knacke et al. 1991 |
| 2000.00 | -1033.20 | 530.16 | -2093.52 | Knacke et al. 1991 |

TABLE 4.124

 $\text{Na}_2\text{SO}_4 = \text{Na}_2\text{O} + \text{SO}_3(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------------|---|------------------------------|--------------|
| 298.15 | 574.07 | 182.22 | 519.74 | 8.627E - 092 |
| 400.00 | 573.07 | 179.34 | 501.33 | 3.370E - 066 |
| 500.00 | 571.54 | 175.97 | 483.56 | 3.011E - 051 |
| 600.00 | 558.41 | 150.70 | 467.99 | 1.797E - 041 |
| 700.00 | 556.18 | 147.27 | 453.09 | 1.538E - 034 |
| 800.00 | 553.90 | 144.23 | 438.52 | 2.318E - 029 |
| 900.00 | 551.43 | 141.32 | 424.25 | 2.374E - 025 |
| 1000.00 | 548.68 | 138.42 | 410.26 | 3.703E - 022 |
| 1100.00 | 547.33 | 137.18 | 396.43 | 1.491E - 019 |
| 1200.00 | 520.60 | 114.05 | 383.74 | 1.972E - 017 |
| 1300.00 | 530.49 | 122.02 | 371.87 | 1.140E - 015 |
| 1400.00 | 528.61 | 120.62 | 359.74 | 3.773E - 014 |
| 1500.00 | 574.99 | 153.65 | 344.51 | 1.004E - 012 |
| 1600.00 | 573.74 | 152.84 | 329.19 | 1.787E - 011 |
| 1700.00 | 572.53 | 152.11 | 313.95 | 2.253E - 010 |
| 1800.00 | 571.35 | 151.43 | 298.77 | 2.134E - 009 |
| 1900.00 | 570.20 | 150.81 | 283.66 | 1.589E - 008 |
| 2000.00 | 569.06 | 150.23 | 268.61 | 9.642E - 008 |

TABLE 4.125



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 673.02 | 276.24 | 590.66 | 3.237E – 104 |
| 400.00 | 672.27 | 274.11 | 562.63 | 3.329E – 074 |
| 500.00 | 670.78 | 270.81 | 535.37 | 1.163E – 056 |
| 600.00 | 657.51 | 245.31 | 510.33 | 3.702E – 045 |
| 700.00 | 655.05 | 241.51 | 485.99 | 5.395E – 037 |
| 800.00 | 652.45 | 238.04 | 462.01 | 6.778E – 031 |
| 900.00 | 649.61 | 234.70 | 438.38 | 3.590E – 026 |
| 1000.00 | 646.45 | 231.38 | 415.07 | 2.075E – 022 |
| 1100.00 | 644.67 | 229.73 | 391.97 | 2.428E – 019 |
| 1200.00 | 617.50 | 206.22 | 370.04 | 7.783E – 017 |
| 1300.00 | 626.95 | 213.82 | 348.98 | 9.477E – 015 |
| 1400.00 | 624.61 | 212.09 | 327.69 | 5.928E – 013 |
| 1500.00 | 670.53 | 244.80 | 303.33 | 2.731E – 011 |
| 1600.00 | 668.83 | 243.71 | 278.90 | 7.834E – 010 |
| 1700.00 | 667.18 | 242.70 | 254.58 | 1.503E – 008 |
| 1800.00 | 665.66 | 241.78 | 230.36 | 2.063E – 007 |
| 1900.00 | 663.98 | 240.92 | 206.23 | 2.138E – 006 |
| 2000.00 | 662.43 | 240.13 | 182.17 | 1.745E – 005 |

TABLE 4.126

Transitions of SrSO₄

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol*K) | Reference |
|--------------|------|-------------------|----------------------|-----------|
| c,II → c,I | 1425 | | | 9 |
| c,I → liquid | 1878 | | | 9 |

TABLE 4.127

Thermodynamic Data of SrSO₄(celestite)

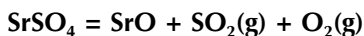
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1458.96 | 121.75 | -1495.26 | Barin 1993 |
| 400.00 | -1448.31 | 152.42 | -1509.28 | Barin 1993 |
| 500.00 | -1437.30 | 176.98 | -1529.79 | Barin 1993 |
| 600.00 | -118.47 | 198.05 | -1544.56 | Barin 1993 |
| 700.00 | -1413.61 | 216.73 | -1565.32 | Barin 1993 |
| 800.00 | -1400.93 | 233.66 | -1587.85 | Barin 1993 |
| 900.00 | -1387.69 | 249.24 | -1612.01 | Barin 1993 |
| 1000.00 | -1373.89 | 263.77 | -1637.67 | Barin 1993 |
| 1100.00 | -1359.54 | 277.45 | -1664.73 | Barin 1993 |
| 1200.00 | -1344.63 | 290.41 | -1693.13 | Barin 1993 |
| 1300.00 | -1329.16 | 302.79 | -1722.80 | Barin 1993 |
| 1400.00 | -1313.15 | 314.66 | -1753.67 | Barin 1993 |
| 1500.00 | -1286.28 | 333.29 | -1786.22 | Barin 1993 |

TABLE 4.128



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 471.16 | 190.54 | 414.35 | 2.524E – 073 |
| 400.00 | 470.83 | 189.56 | 395.00 | 2.591E – 052 |
| 500.00 | 470.82 | 189.53 | 376.05 | 5.137E – 040 |
| 600.00 | 470.92 | 189.72 | 357.09 | 8.126E – 032 |
| 700.00 | 470.97 | 189.79 | 338.11 | 5.855E – 026 |
| 800.00 | 470.83 | 189.62 | 319.14 | 1.447E – 021 |
| 900.00 | 470.44 | 189.16 | 300.20 | 3.762E – 018 |
| 1000.00 | 469.74 | 188.42 | 281.33 | 2.015E – 015 |
| 1100.00 | 468.68 | 187.41 | 262.53 | 3.409E – 013 |
| 1200.00 | 467.24 | 186.16 | 243.85 | 2.426E – 011 |
| 1300.00 | 465.40 | 184.69 | 225.30 | 8.842E – 010 |
| 1400.00 | 463.14 | 183.02 | 206.91 | 1.902E – 008 |
| 1500.00 | 450.17 | 173.97 | 189.21 | 2.574E – 007 |

TABLE 4.129



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 570.11 | 284.56 | 485.31 | 8.436 – 086 |
| 400.00 | 570.03 | 284.33 | 456.30 | 2.560E – 060 |
| 500.00 | 570.05 | 284.37 | 427.87 | 1.984E – 045 |
| 600.00 | 570.03 | 284.33 | 399.43 | 1.674E – 035 |
| 700.00 | 569.83 | 284.03 | 371.01 | 2.054E – 028 |
| 800.00 | 569.38 | 283.43 | 342.63 | 4.231E – 023 |
| 900.00 | 568.62 | 282.54 | 314.33 | 5.690E – 019 |
| 1000.00 | 567.51 | 281.37 | 286.14 | 1.129E – 015 |
| 1100.00 | 566.02 | 279.96 | 258.07 | 5.552E – 013 |
| 1200.00 | 564.14 | 278.33 | 230.15 | 9.572E – 011 |
| 1300.00 | 561.85 | 276.50 | 202.41 | 7.354E – 009 |
| 1400.00 | 559.14 | 274.49 | 174.86 | 2.989E – 007 |
| 1500.00 | 545.71 | 265.13 | 148.02 | 6.999E – 006 |

TABLE 4.130

Density of Ti_2SO_4

| Phase | T(K) | d | Reference |
|--|------|-------|-----------|
| $\text{Ti}_2\text{SO}_4(\text{c})$ | 298 | 6.77 | 93 |
| $\text{Ti}_2\text{SO}_4(\text{c})$ | 303 | 6.768 | 94 |
| $\text{Ti}_2(\text{SO}_4)_3(\text{c})$ | 288 | 5.22 | 14 |

TABLE 4.131
Transitions of Ti_2SO_4

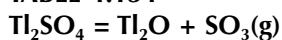
| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|------------------------|------|-------------------|----------------------|-----------|
| II \rightarrow I | 765 | | | 95 |
| I \rightarrow liquid | 905 | 23 | 25.5 | 9 |

TABLE 4.132
Thermodynamic Data of Ti_2SO_4

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -931.78 | 230.54 | -1000.51 | Barin 1989 |
| 400.00 | -917.09 | 272.83 | -1026.22 | Barin 1989 |
| 500.00 | -901.40 | 307.79 | -1055.29 | Barin 1989 |
| 600.00 | -175.73 | 338.65 | -1087.64 | Barin 1989 |
| 700.00 | -866.25 | 366.68 | -1122.93 | Barin 1989 |
| 800.00 | -846.80 | 392.64 | -1160.91 | Barin 1989 |
| 900.00 | -826.09 | 417.02 | -1201.41 | Barin 1989 |
| 1000.00 | -781.69 | 465.02 | -1246.71 | Barin 1989 |
| 1100.00 | -761.19 | 484.56 | -1294.21 | Barin 1989 |
| 1200.00 | -740.69 | 502.40 | -1343.57 | Barin 1989 |
| 1300.00 | -720.19 | 518.81 | -1394.64 | Barin 1989 |
| 1400.00 | -699.69 | 534.01 | -1447.29 | Barin 1989 |
| 1500.00 | -679.18 | 548.15 | -1501.41 | Barin 1989 |

TABLE 4.133
Thermodynamic Data of Ti_2O

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -169.03 | 145.19 | -212.32 | Knacke et al. 1991 |
| 400.00 | -160.83 | 168.84 | -228.36 | Knacke et al. 1991 |
| 500.00 | -152.49 | 187.44 | -246.21 | Knacke et al. 1991 |
| 600.00 | -143.91 | 203.08 | -265.75 | Knacke et al. 1991 |
| 700.00 | -135.10 | 216.65 | -286.75 | Knacke et al. 1991 |
| 800.00 | -126.07 | 228.70 | -309.03 | Knacke et al. 1991 |
| 900.00 | -85.48 | 276.34 | -334.19 | Knacke et al. 1991 |
| 1000.00 | -73.71 | 288.74 | -362.45 | Knacke et al. 1991 |
| 1100.00 | -61.94 | 299.96 | -391.90 | Knacke et al. 1991 |
| 1200.00 | -50.17 | 310.21 | -422.41 | Knacke et al. 1991 |
| 1300.00 | -38.39 | 319.63 | -453.91 | Knacke et al. 1991 |
| 1400.00 | -26.62 | 328.35 | -486.32 | Knacke et al. 1991 |
| 1500.00 | 14.85 | 336.47 | -519.56 | Knacke et al. 1991 |

TABLE 4.134

| T K | ΔH° kJ | ΔS° J deg⁻¹ | ΔG° kJ | K |
|----------------------|---|---|---|--------------|
| 298.15 | 366.98 | 171.42 | 315.87 | 4.532E – 056 |
| 400.00 | 366.01 | 168.65 | 298.55 | 1.023E – 039 |
| 500.00 | 364.71 | 165.75 | 281.83 | 3.590E – 030 |
| 600.00 | 362.89 | 162.45 | 265.42 | 7.792E – 024 |
| 700.00 | 360.40 | 158.63 | 249.36 | 2.462E – 019 |
| 800.00 | 357.14 | 154.29 | 233.71 | 5.486E – 016 |
| 900.00 | 384.39 | 186.23 | 216.78 | 2.613E – 013 |
| 1000.00 | 359.29 | 158.55 | 200.73 | 3.265E – 011 |
| 1100.00 | 358.20 | 157.52 | 184.93 | 1.650E – 009 |
| 1200.00 | 357.21 | 156.66 | 169.22 | 4.298E – 008 |
| 1300.00 | 356.31 | 155.93 | 153.60 | 6.729E – 007 |
| 1400.00 | 355.47 | 155.31 | 138.03 | 7.071E – 006 |
| 1500.00 | 354.68 | 154.77 | 122.53 | 5.404E – 005 |

TABLE 4.135

| T K | ΔH° kJ | ΔS° J deg⁻¹ | ΔG° kJ | K |
|----------------------|---|---|---|--------------|
| 298.15 | 366.98 | 171.42 | 315.87 | 4.532E – 056 |
| 400.00 | 366.01 | 168.65 | 298.55 | 1.023E – 039 |
| 500.00 | 364.71 | 165.75 | 281.83 | 3.590E – 030 |
| 600.00 | 362.89 | 162.45 | 265.42 | 7.792E – 024 |
| 700.00 | 360.40 | 158.63 | 249.36 | 2.462E – 019 |
| 800.00 | 357.14 | 154.29 | 233.71 | 5.486E – 016 |
| 900.00 | 384.39 | 186.23 | 216.78 | 2.613E – 013 |
| 1000.00 | 359.29 | 158.55 | 200.73 | 3.265E – 011 |
| 1100.00 | 358.20 | 157.52 | 184.93 | 1.650E – 009 |
| 1200.00 | 357.21 | 156.66 | 169.22 | 4.298E – 008 |
| 1300.00 | 356.31 | 155.93 | 153.60 | 6.729E – 007 |
| 1400.00 | 355.47 | 155.31 | 138.03 | 7.071E – 006 |
| 1500.00 | 354.68 | 154.77 | 122.53 | 5.494E – 005 |

TABLE 4.136
Thermodynamic Data of Th(SO₄)₂

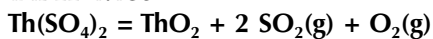
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -2542.46 | 159.00 | -2590.01 | Barin 1993 |
| 400.00 | -2523.74 | 213.26 | -2609.04 | Barin 1993 |
| 500.00 | -2502.88 | 259.70 | -2632.73 | Barin 1993 |
| 600.00 | -2479.72 | 301.87 | -2660.84 | Barin 1993 |
| 700.00 | -2454.25 | 341.08 | -2693.01 | Barin 1993 |
| 800.00 | -2426.47 | 378.15 | -2728.98 | Barin 1993 |
| 900.00 | -2396.37 | 413.56 | -2768.58 | Barin 1993 |
| 1000.00 | -2363.97 | 447.68 | -2811.65 | Barin 1993 |
| 1100.00 | -2329.26 | 480.75 | -2858.08 | Barin 1993 |
| 1200.00 | -2292.24 | 512.94 | -2907.77 | Barin 1993 |
| 1300.00 | -2252.91 | 544.41 | -2960.65 | Barin 1993 |
| 1400.00 | -2211.27 | 575.26 | -3016.63 | Barin 1993 |
| 1500.00 | -2167.33 | 605.57 | -3075.68 | Barin 1993 |

TABLE 4.137
Thermodynamic Data of ThO₂ (thorianite)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -1226.41 | 65.23 | -1245.86 | Knacke et al. 1991 |
| 400.00 | -1219.77 | 84.35 | -1253.51 | Knacke et al. 1991 |
| 500.00 | -1212.82 | 99.84 | -1262.74 | Knacke et al. 1991 |
| 600.00 | -1205.62 | 112.97 | -1273.40 | Knacke et al. 1991 |
| 700.00 | -1198.24 | 124.34 | -1285.28 | Knacke et al. 1991 |
| 800.00 | -1190.72 | 134.38 | -1298.23 | Knacke et al. 1991 |
| 900.00 | -1183.09 | 143.37 | -1312.12 | Knacke et al. 1991 |
| 1000.00 | -1175.35 | 151.52 | -1326.87 | Knacke et al. 1991 |
| 1100.00 | -1167.52 | 159.00 | -1342.40 | Knacke et al. 1991 |
| 1200.00 | -1159.59 | 165.89 | -1358.65 | Knacke et al. 1991 |
| 1300.00 | -1151.57 | 172.30 | -1375.56 | Knacke et al. 1991 |
| 1400.00 | -1143.47 | 178.30 | -1393.10 | Knacke et al. 1991 |
| 1500.00 | -1135.29 | 183.95 | -1411.21 | Knacke et al. 1991 |

TABLE 4.138

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 524.66 | 419.77 | 399.50 | 1.007E – 070 |
| 400.00 | 523.47 | 416.37 | 356.92 | 2.439E – 047 |
| 500.00 | 521.65 | 412.36 | 315.48 | 1.096E – 033 |
| 600.00 | 518.78 | 407.15 | 274.49 | 1.264E – 024 |
| 700.00 | 514.50 | 400.59 | 234.09 | 3.392E – 018 |
| 800.00 | 508.57 | 392.69 | 194.42 | 2.018E – 013 |
| 900.00 | 500.85 | 383.62 | 155.59 | 9.310E – 010 |
| 1000.00 | 491.23 | 373.51 | 117.73 | 7.081E – 007 |
| 1100.00 | 479.65 | 362.48 | 80.92 | 1.436E – 004 |
| 1200.00 | 466.04 | 350.65 | 45.26 | 1.071E – 002 |
| 1300.00 | 450.37 | 338.12 | 10.81 | 3.676E – 001 |
| 1400.00 | 432.62 | 324.97 | –22.35 | 6.820E + 000 |
| 1500.00 | 412.74 | 311.27 | –54.16 | 7.695E + 001 |

TABLE 4.139

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|---------------|
| 298.15 | 722.56 | 607.82 | 541.34 | 1.418E – 095 |
| 400.00 | 721.87 | 605.90 | 479.51 | 2.381E – 063 |
| 500.00 | 720.13 | 602.05 | 419.10 | 1.634E – 044 |
| 600.00 | 716.99 | 596.38 | 359.17 | 5.362E – 032 |
| 700.00 | 712.23 | 589.06 | 299.88 | 4.176E – 023 |
| 800.00 | 705.66 | 580.32 | 241.40 | 1.725E – 016 |
| 900.00 | 687.20 | 570.38 | 183.86 | 2.130E – 011 |
| 1000.00 | 688.78 | 559.42 | 227.36 | 2.223E – 007 |
| 1100.00 | 674.33 | 547.58 | 77.00 | 3.808E – 004 |
| 1200.00 | 659.84 | 534.98 | 17.87 | 1.668E – 0001 |
| 1300.00 | 643.27 | 521.73 | –34.97 | 2.543E + 001 |
| 1400.00 | 624.61 | 507.91 | –86.46 | 1.683E + 003 |
| 1500.00 | 603.83 | 493.58 | –136.54 | 5.689E + 004 |

TABLE 4.140
Thermodynamic Data of SnSO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1014.60 | 138.57 | -1055.92 | Barin 1993 |
| 400.00 | -1003.36 | 170.97 | -1071.75 | Barin 1993 |
| 500.00 | -991.61 | 197.15 | -1090.19 | Barin 1993 |
| 600.00 | -978.86 | 220.38 | -1111.08 | Barin 1993 |
| 700.00 | -964.97 | 241.76 | -1134.20 | Barin 1993 |
| 800.00 | -949.90 | 261.87 | -1159.39 | Barin 1993 |
| 900.00 | -933.59 | 281.06 | -1186.54 | Barin 1993 |
| 1000.00 | -916.04 | 299.54 | -1215.58 | Barin 1993 |
| 1100.00 | -897.23 | 317.46 | -1246.43 | Barin 1993 |
| 1200.00 | -877.14 | 334.93 | -1279.06 | Barin 1993 |
| 1300.00 | -855.78 | 352.02 | -1313.41 | Barin 1993 |
| 1400.00 | -833.14 | 368.79 | -1349.45 | Barin 1993 |
| 1500.00 | -809.22 | 385.29 | -1387.16 | Barin 1993 |

TABLE 4.141
Thermodynamic Data of Sn(SO₄)₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -1648.50 | 149.79 | -1693.16 | Barin 1993 |
| 400.00 | -1629.52 | 204.45 | -1711.30 | Barin 1993 |
| 500.00 | -1609.63 | 248.79 | -1734.02 | Barin 1993 |
| 600.00 | -1588.50 | 287.28 | -1760.86 | Barin 1993 |
| 700.00 | -1566.12 | 321.75 | -1791.34 | Barin 1993 |
| 800.00 | -1542.50 | 353.28 | -1825.12 | Barin 1993 |
| 900.00 | -1517.63 | 382.55 | -1861.92 | Barin 1993 |
| 1000.00 | -1491.52 | 410.05 | -1901.57 | Barin 1993 |
| 1100.00 | -1464.16 | 436.11 | -1943.89 | Barin 1993 |
| 1200.00 | -1435.56 | 460.99 | -1988.75 | Barin 1993 |
| 1300.00 | -1405.72 | 484.87 | -2036.05 | Barin 1993 |
| 1400.00 | -1374.63 | 507.90 | -2085.70 | Barin 1993 |
| 1500.00 | -1342.30 | 530.20 | -2137.61 | Barin 1993 |

TABLE 4.142
Thermodynamic Data of SnO

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -285.77 | 56.48 | -302.61 | Barin 1993 |
| 400.00 | -280.72 | 71.04 | -309.13 | Barin 1993 |
| 500.00 | -275.50 | 82.67 | -316.84 | Barin 1993 |
| 600.00 | -270.11 | 92.50 | -325.61 | Barin 1993 |
| 700.00 | -264.58 | 101.02 | -335.29 | Barin 1993 |
| 800.00 | -258.93 | 108.57 | -345.78 | Barin 1993 |
| 900.00 | -253.16 | 115.35 | -356.98 | Barin 1993 |
| 1000.00 | -247.30 | 121.53 | -368.83 | Barin 1993 |
| 1100.00 | -241.33 | 127.22 | -381.27 | Barin 1993 |
| 1200.00 | -235.26 | 132.50 | -394.26 | Barin 1993 |
| 1300.00 | -229.10 | 137.43 | -407.76 | Barin 1993 |
| 1400.00 | -222.84 | 142.07 | -421.74 | Barin 1993 |
| 1500.00 | -216.48 | 146.46 | -436.17 | Barin 1993 |

TABLE 4.143
Thermodynamic Data of SnO₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -580.28 | 52.34 | -595.89 | Barin 1989 |
| 400.00 | -574.38 | 69.29 | -602.10 | Barin 1989 |
| 500.00 | -567.79 | 83.98 | -609.78 | Barin 1989 |
| 600.00 | -560.68 | 96.92 | -618.84 | Barin 1989 |
| 700.00 | -553.20 | 108.45 | -629.12 | Barin 1989 |
| 800.00 | -545.42 | 118.83 | -640.49 | Barin 1989 |
| 900.00 | -537.41 | 128.27 | -652.85 | Barin 1989 |
| 1000.00 | -529.19 | 136.93 | -666.12 | Barin 1989 |
| 1100.00 | -520.81 | 144.92 | -680.21 | Barin 1989 |
| 1200.00 | -512.29 | 152.32 | -695.08 | Barin 1989 |
| 1300.00 | -503.68 | 159.22 | -710.66 | Barin 1989 |
| 1400.00 | -494.99 | 165.65 | -726.91 | Barin 1989 |
| 1500.00 | -486.26 | 171.68 | -743.78 | Barin 1989 |

TABLE 4.144

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 333.07 | 174.68 | 280.98 | 5.873E – 050 |
| 400.00 | 332.39 | 172.71 | 263.31 | 4.094E – 035 |
| 500.00 | 331.91 | 171.63 | 246.09 | 1.943E – 026 |
| 600.00 | 331.09 | 170.15 | 229.00 | 1.154E – 020 |
| 700.00 | 329.64 | 167.93 | 212.09 | 1.487E – 016 |
| 800.00 | 327.38 | 164.93 | 195.44 | 1.730E – 013 |
| 900.00 | 324.21 | 161.20 | 179.13 | 4.007E – 011 |
| 1000.00 | 320.05 | 156.83 | 163.22 | 2.975E – 009 |
| 1100.00 | 314.85 | 151.88 | 147.78 | 9.590E – 008 |
| 1200.00 | 308.57 | 146.42 | 132.86 | 1.645E – 006 |
| 1300.00 | 301.20 | 140.53 | 118.51 | 1.729E – 005 |
| 1400.00 | 292.71 | 134.24 | 104.77 | 1.232E – 004 |
| 1500.00 | 283.09 | 127.61 | 91.68 | 6.416E – 004 |

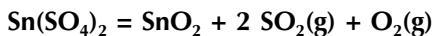
TABLE 4.145

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 432.02 | 268.70 | 351.90 | 2.204E – 062 |
| 400.00 | 431.60 | 267.47 | 324.61 | 4.045E – 043 |
| 500.00 | 431.13 | 266.47 | 297.91 | 7.503E – 032 |
| 600.00 | 430.19 | 264.76 | 271.34 | 2.376E – 024 |
| 700.00 | 428.50 | 262.17 | 244.99 | 5.218E – 019 |
| 800.00 | 425.93 | 258.24 | 218.93 | 5.058E – 015 |
| 900.00 | 422.39 | 254.58 | 193.26 | 6.061E – 012 |
| 1000.00 | 417.82 | 249.78 | 168.04 | 1.667E – 009 |
| 1100.00 | 412.19 | 244.42 | 143.32 | 1.562E – 007 |
| 1200.00 | 405.47 | 238.59 | 119.17 | 6.491E – 006 |
| 1300.00 | 397.65 | 232.33 | 95.62 | 1.438E – 004 |
| 1400.00 | 388.71 | 225.71 | 72.71 | 1.935E – 003 |
| 1500.00 | 378.63 | 218.76 | 50.49 | 1.745E – 002 |

TABLE 4.146

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|------------------------|---|------------------------|--------------|
| 298.15 | 137.50 | 161.99 | 89.21 | 2.345E – 016 |
| 400.00 | 136.40 | 158.74 | 72.91 | 3.012E – 010 |
| 500.00 | 135.75 | 157.29 | 57.11 | 1.080E – 006 |
| 600.00 | 134.90 | 155.75 | 41.45 | 2.461E – 004 |
| 700.00 | 133.51 | 153.62 | 25.98 | 1.152E – 002 |

TABLE 4.147



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|------------------------|---|------------------------|--------------|
| 298.15 | 474.59 | 604.14 | 294.46 | 2.554E – 052 |
| 400.00 | 473.05 | 599.65 | 233.19 | 3.519E – 031 |
| 500.00 | 471.91 | 597.10 | 173.36 | 7.728E – 019 |
| 600.00 | 470.70 | 594.91 | 113.76 | 1.247E – 010 |
| 700.00 | 469.13 | 592.50 | 54.38 | 8.742E – 005 |
| 800.00 | 466.99 | 589.65 | –4.73 | 2.036E + 000 |

TABLE 4.148

Thermodynamic Data of $\text{U}(\text{SO}_4)_2$

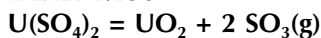
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | –2317.94 | 161.08 | –2365.96 | Barin 1989 |
| 400.00 | –2299.07 | 215.35 | –2385.21 | Barin 1989 |
| 500.00 | –2278.22 | 261.78 | –2409.11 | Barin 1989 |
| 600.00 | –2255.06 | 303.95 | –2437.43 | Barin 1989 |
| 700.00 | –2229.58 | 343.17 | –2469.80 | Barin 1989 |
| 800.00 | –2201.80 | 380.23 | –2505.99 | Barin 1989 |
| 900.00 | –2171.71 | 415.65 | –2545.79 | Barin 1989 |
| 1000.00 | –2131.31 | 449.76 | –2589.07 | Barin 1989 |
| 1100.00 | –2104.60 | 482.83 | –2635.71 | Barin 1989 |
| 1200.00 | –2067.58 | 515.03 | –2685.61 | Barin 1989 |
| 1300.00 | –2028.25 | 546.49 | –2738.69 | Barin 1989 |
| 1400.00 | –1986.61 | 577.34 | –2794.89 | Barin 1989 |
| 1500.00 | –1942.66 | 607.65 | –2854.14 | Barin 1989 |

TABLE 4.149

Thermodynamic Data of UO_2

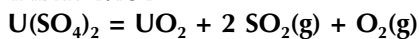
| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------------|
| 298.15 | –1064.91 | 77.82 | –1108.11 | Barin et al. 1977 |
| 400.00 | –1077.90 | 97.98 | –1117.09 | Barin et al. 1977 |
| 500.00 | –1070.39 | 114.72 | –1127.75 | Barin et al. 1977 |
| 600.00 | –1062.54 | 129.03 | –1139.96 | Barin et al. 1977 |
| 700.00 | –1054.46 | 141.48 | –1153.50 | Barin et al. 1977 |
| 800.00 | –1046.21 | 152.49 | –1168.21 | Barin et al. 1977 |
| 900.00 | –1037.84 | 162.36 | –1183.96 | Barin et al. 1977 |
| 1000.00 | –1029.34 | 171.30 | –1200.65 | Barin et al. 1977 |
| 1100.00 | –1020.75 | 179.49 | –1218.19 | Barin et al. 1977 |
| 1200.00 | –1012.06 | 187.05 | –1236.53 | Barin et al. 1977 |
| 1300.00 | –1003.29 | 194.08 | –1255.58 | Barin et al. 1977 |
| 1400.00 | –994.43 | 200.64 | –1275.32 | Barin et al. 1977 |
| 1500.00 | –985.49 | 206.81 | –1295.70 | Barin et al. 1977 |

TABLE 4.150



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 441.50 | 430.29 | 313.21 | 1.327E – 055 |
| 400.00 | 440.67 | 425.15 | 269.51 | 6.354E – 036 |
| 500.00 | 439.42 | 425.15 | 226.85 | 1.994E – 024 |
| 600.00 | 437.20 | 421.13 | 184.52 | 8.606E – 017 |
| 700.00 | 433.62 | 415.64 | 142.67 | 2.254E – 011 |
| 800.00 | 428.42 | 408.72 | 101.44 | 2.377E – 007 |
| 900.00 | 421.44 | 400.53 | 60.97 | 2.892E – 004 |
| 1000.00 | 412.58 | 391.20 | 21.37 | 7.648E – 002 |
| 1100.00 | 401.75 | 380.90 | –17.24 | 6.588E + 000 |
| 1200.00 | 388.90 | 369.73 | –54.78 | 2.425E + 002 |

TABLE 4.151



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 639.40 | 618.33 | 455.05 | 1.868E – 080 |
| 400.00 | 639.08 | 617.45 | 392.10 | 6.202E – 052 |
| 500.00 | 637.89 | 614.84 | 330.47 | 2.972E – 035 |
| 600.00 | 635.41 | 610.35 | 269.20 | 3.651E – 024 |
| 700.00 | 631.34 | 604.12 | 208.46 | 2.775E – 016 |
| 800.00 | 625.51 | 596.35 | 148.42 | 2.033E – 010 |
| 900.00 | 617.79 | 587.29 | 89.23 | 6.617E – 006 |
| 1000.00 | 608.12 | 577.12 | 31.00 | 2.401E – 002 |
| 1100.00 | 596.44 | 566.00 | –26.16 | 1.747E + 001 |
| 1200.00 | 582.71 | 554.06 | –82.17 | 3.776E + 003 |

TABLE 4.152

Thermodynamic Data of ZnSO₄ (zinkosite)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | –982.80 | 110.50 | –1015.75 | Barin 1993 |
| 400.00 | –972.32 | 140.69 | –1028.59 | Barin 1993 |
| 500.00 | –961.25 | 165.35 | –1043.93 | Barin 1993 |
| 600.00 | –949.43 | 186.88 | –1061.56 | Barin 1993 |
| 700.00 | –936.85 | 206.27 | –1081.23 | Barin 1993 |
| 800.00 | –923.50 | 224.08 | –1102.76 | Barin 1993 |
| 900.00 | –909.39 | 240.69 | –1126.01 | Barin 1993 |
| 1000.00 | –894.52 | 256.35 | –1150.87 | Barin 1993 |
| 1100.00 | –859.51 | 290.38 | –1178.92 | Barin 1993 |
| 1200.00 | –844.99 | 303.01 | –1208.60 | Barin 1993 |
| 1300.00 | –830.47 | 314.63 | –1239.49 | Barin 1993 |
| 1400.00 | –815.95 | 325.39 | –1271.50 | Barin 1993 |
| 1500.00 | –801.43 | 335.41 | –1304.55 | Barin 1993 |

TABLE 4.153



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 236.58 | 189.91 | 179.95 | 2.952E – 032 |
| 400.00 | 236.00 | 188.23 | 160.71 | 1.028E – 021 |
| 500.00 | 235.56 | 187.24 | 141.94 | 1.481E – 015 |
| 600.00 | 235.02 | 186.27 | 123.26 | 1.855E – 011 |
| 700.00 | 234.21 | 185.03 | 104.69 | 1.538E – 008 |
| 800.00 | 233.01 | 104.69 | 86.27 | 2.327E – 006 |
| 900.00 | 231.35 | 181.47 | 68.02 | 1.127E – 004 |
| 1000.00 | 229.16 | 179.18 | 49.98 | 2.449E – 003 |
| 1100.00 | 207.04 | 157.43 | 33.86 | 2.465E – 002 |
| 1200.00 | 205.59 | 156.17 | 18.19 | 1.616E – 001 |
| 1300.00 | 204.30 | 155.14 | 2.62 | 7.846E – 001 |
| 1400.00 | 203.16 | 154.29 | –12.85 | 3.016E + 000 |
| 1500.00 | 202.16 | 153.60 | –28.24 | 9.629E + 000 |

TABLE 4.154



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 335.53 | 283.94 | 250.87 | 1.108E – 044 |
| 400.00 | 335.20 | 282.99 | 222.01 | 1.015E – 029 |
| 500.00 | 334.79 | 282.08 | 193.75 | 5.720E – 021 |
| 600.00 | 334.13 | 280.88 | 165.60 | 3.821E – 015 |
| 700.00 | 333.08 | 279.27 | 137.59 | 5.398E – 011 |
| 800.00 | 331.56 | 277.25 | 109.76 | 6.806E – 008 |
| 900.00 | 329.52 | 274.86 | 82.15 | 1.705E – 005 |
| 1000.00 | 326.93 | 272.13 | 54.80 | 1.372E – 003 |
| 1100.00 | 304.38 | 249.98 | 29.40 | 4.014E – 002 |
| 1200.00 | 302.49 | 248.34 | 4.49 | 6.376E – 001 |
| 1300.00 | 300.76 | 246.95 | –20.27 | 6.525E + 000 |
| 1400.00 | 299.16 | 245.76 | –44.91 | 4.738E + 001 |
| 1500.00 | 297.70 | 244.75 | –69.43 | 2.618E + 002 |

TABLE 4.155



| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------|
| 298.15 | –2243.46 | 133.05 | –2283.13 | DeKock 1984 |
| 400.00 | –2224.34 | 187.87 | –2299.49 | DeKock 1984 |
| 500.00 | –2202.47 | 236.60 | –2320.77 | DeKock 1984 |
| 600.00 | –2179.57 | 278.34 | –2346.57 | DeKock 1984 |
| 700.00 | –2156.50 | 313.90 | –2376.23 | DeKock 1984 |
| 800.00 | –2133.71 | 344.34 | –2409.18 | DeKock 1984 |
| 900.00 | –2111.43 | 370.59 | –2444.96 | DeKock 1984 |
| 1000.00 | –2089.83 | 393.36 | –2483.18 | DeKock 1984 |

TABLE 4.156
Thermodynamic Data of ZrO₂ (Baddelite)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|---|--|------------|
| 298.15 | -1097.46 | 50.36 | -1112.48 | Barin 1993 |
| 400.00 | -1091.31 | 68.07 | -1118.53 | Barin 1993 |
| 500.00 | -1084.71 | 82.78 | -1126.10 | Barin 1993 |
| 600.00 | -1077.80 | 95.37 | -1135.02 | Barin 1993 |
| 700.00 | -1070.68 | 106.33 | -1145.12 | Barin 1993 |
| 800.00 | -1063.41 | 116.05 | -1156.24 | Barin 1993 |
| 900.00 | -1056.00 | 124.77 | -1168.29 | Barin 1993 |
| 1000.00 | -1048.48 | 132.69 | -1181.17 | Barin 1993 |

TABLE 4.157
Zr(SO₄)₂ = ZrO₂ + 2 SO₃(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 354.47 | 430.85 | 226.01 | 2.516E - 040 |
| 400.00 | 352.54 | 425.49 | 182.34 | 1.536E - 024 |
| 500.00 | 349.36 | 418.39 | 140.16 | 2.272E - 015 |
| 600.00 | 346.45 | 413.07 | 98.60 | 2.600E - 009 |
| 700.00 | 344.31 | 409.77 | 57.48 | 5.136E - 005 |
| 800.00 | 343.13 | 408.17 | 16.59 | 8.250E - 002 |
| 900.00 | 343.00 | 408.00 | -24.20 | 2.540E + 001 |
| 1000.00 | 343.96 | 409.00 | -65.05 | 2.500E + 003 |

TABLE 4.158
Zr(SO₄)₂ = ZrO₂ + 2 SO₂(g) + O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|------------------------|---|------------------------|--------------|
| 298.15 | 552.37 | 618.90 | 367.85 | 3.542E - 065 |
| 400.00 | 550.94 | 615.01 | 304.94 | 1.499E - 040 |
| 500.00 | 547.83 | 608.08 | 243.79 | 3.387E - 026 |
| 600.00 | 544.66 | 602.30 | 183.28 | 1.103E - 016 |
| 700.00 | 542.04 | 598.24 | 123.27 | 6.323E - 010 |
| 800.00 | 540.22 | 595.80 | 63.58 | 7.054E - 005 |
| 900.00 | 539.35 | 594.76 | 4.06 | 5.811E - 001 |
| 1000.00 | 539.50 | 594.92 | -55.41 | 7.848E + 002 |

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5 Nitrites and Nitrates

5.1 GASEOUS EQUILIBRIA IN THE N–O SYSTEM

When nitrites and nitrates are thermally decomposed, nitrogen, oxygen, and their compounds are produced. A literature survey produces the following list of substances which appear in one or another decomposition: O_2 , N_2 , NO , NO_2 , N_2O_3 , N_2O_4 , N_2O_5 . Which of these compounds are produced in any specific case depends on the salt, temperature, and experimental conditions. Since reactions between these compounds occur quite readily, thermodynamic functions for them have been listed (Tables 5.1 to 5.8). The matter of reactions between all these compounds is somewhat complicated, because several of them are thermodynamically quite unfavorable and thus do not need to be considered. On that basis the following conclusions can be drawn:

N_2O_5 is unstable with respect to dissociation to either N_2O_4 or N_2O_3 from 298 K up.

The equilibrium $N_2O_4 = 2 NO_2$ shifts markedly to the right with increasing temperature.

Above 400 K the concentration of N_2O_4 is negligible.

Although N_2O_3 has been reported as a product of nitrate decomposition, it is unstable with respect to dissociation into NO_2 and NO above 400 K; it could therefore exist in equilibrium mixtures only near ambient temperatures.

The equilibrium $NO + 1/2 O_2 = NO_2$ is very temperature dependent; up to 500 K, NO_2 predominates markedly; above that temperature both species are significant and must always be considered in the salt decomposition.

N_2 and O_2 are very stable with respect to both NO and NO_2 ; thus if N_2 is formed during salt decomposition, it will not react further; O_2 may react with NO and with nitrites.

If all equilibria were established quickly during decomposition of the salts, N_2 and O_2 would be the only gaseous components; however, the reaction $NO_2 = 1/2 N_2 + O_2$ is very slow below 1000 K; thus, if NO_2 is the primary decomposition product, it will not decompose appreciably by this reaction and only the equilibrium $NO + 1/2 O_2 = NO_2$ needs to be considered.

For similar reasons, the decomposition of NO to the elements can be neglected. The same conclusions were reached by Kelley¹ in examining the decomposition of a few nitrates. (The reader may investigate the thermodynamics of all the conceivable reactions in the N–O system by using the data in Tables 5.1 to 5.8).

5.2 THE NITRITES

Relatively little is known about anhydrous nitrites except the alkali metal and alkaline earth salts. (See Figure 5.1.) The nitrite ion is less stable than the nitrate, so the nitrites of magnesium and beryllium, small and highly charged cations, are quite unstable.

The nitrite ion is bent, with bond angles of 116° and 132° , and N–O distances of 1.13 and 1.23 Å having been reported.^{2,3} Cotton and Wilkinson⁴ describe the bent structure in terms of resonance or, in MO theory, by assuming that N forms three sp^2 hybrid orbitals, one housing an unshared pair, and the other two being used in σ bonding to the oxygens. The p_z orbitals of N and O are used for π bond formation.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides Ce **Pr Nd** Pm **Sm** Eu Gd **Tb Dy** Ho Er Tm **Yb** Lu
 Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 5.1 The known nitrites.

The coordination of the nitrite ion appears to differ with the salt. For example, in AgNO_3 , Ag^+ is closer to N than to O, whereas in NaNO_2 , Na^+ is closer to O than to N.² The periodic table existence chart (Figure 5.1) which lists the known nitrites omits bonding information.

Nitrites decompose at lower temperatures than the corresponding nitrates. The course of decomposition depends on the nature of the salt and the gas phase composition. Nitrites of the more electropositive elements decompose to form the oxide directly by reactions of the type $2\text{MNO}_2 = \text{M}_2\text{O} + \text{NO} + \text{NO}_2$, but if the gases are not immediately removed, the nitrite is easily oxidized to the nitrate by NO_2 , if the latter salt is stable at the decomposition temperature. In some cases, particularly the rare-earth nitrites, the first decomposition product is an oxynitrite. According to Addison and Sutton,⁵ simple nitrites will be stable only if a higher valent-state of the metal is not readily available. Otherwise, decomposition to oxynitrites will occur to achieve the more stable valence of the metal. This view is supported somewhat by the nonexistence of many nitrites of metals in the first two long periods of the periodic table.

5.3 THE NITRATES

5.3.1 GENERAL

Although anhydrous nitrates of the alkali and alkaline earth metals have been known and widely used for a long time, the anhydrous nitrates of many other metals have been prepared only relatively recently. (See Figure 5.2.) The existence of some is still in doubt. Methods for preparing these nitrates have been described by Addison and Logan.⁶ These authors, as well as Hardy and Field,⁸ have also written extensive reviews of nitrate chemistry. Since not much has changed since they were written, only a brief summary of factors relevant to thermal decomposition is provided here.

In the hydrated salts and in aqueous solution the nitrate ion is a distinct entity. This is also true for the anhydrous nitrates of the electropositive metals, but in many other salts the nitrate ion is bonded covalently to the metal. The distinction between ionic and covalent nitrates can most easily be made on the basis of their infrared spectra. Chasan and Norwitz⁹ prepared a listing of ionic and covalent salts based on an examination of the literature, and covalent nitrate complexes were reviewed by Addison and Sutton.⁵ Spectra of liquid nitrates were discussed by Wait and Janz.¹⁰ Figure 5.2 represents the author's evaluation of the literature with respect to the existence and bonding of anhydrous nitrates, but no attempt was made to classify the covalent nitrates with respect to the number of oxygens bonded to the metal atom. This topic, which is of great structural interest,

| | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn |
| Fr | Ra | Ac | | | | | | | | | | | | | | | |

Lanthanides Ce **Pr Nd** Pm Sm Eu Gd Tb **Dy** Ho Er Tm **Yb Lu**
Actinides **Th** Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 5.2 The known nitrates.

is discussed in the review by Addison and Logan.⁷ In some cases the type of bonding has not been clearly established. In others, which are discussed in this chapter, evidence for the existence of the compound is shaky.

The alkali and alkaline earth nitrates, except $\text{Be}(\text{NO}_3)_2$, are ionic, but otherwise there are no obvious criteria. For example, AgNO_3 and $\text{Cd}(\text{NO}_3)_2$ are ionic, but $\text{Cu}(\text{NO}_3)_2$ and $\text{Zn}(\text{NO}_3)_2$ are covalent. $\text{Co}(\text{NO}_3)_2$ exhibits characteristics of both ionic and covalent bonding.

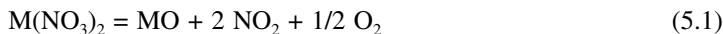
The ionic nitrates generally melt to liquids which are stable to various degrees above their melting points. These liquids can be distilled under reduced pressure.¹¹ The covalent nitrates are generally not stable as liquids. When heated, they first sublime, frequently giving molecular vapors, and then decompose. The cation influences the stability of the anion through its ability to distort its structure in the same manner as for carbonates and sulfates, as discussed in Chapters 2 and 4.

Since the nitrite of a given metal is generally much less stable than the nitrate, the former can appear only as an unstable intermediate in the decomposition of the nitrate. This is particularly true for covalent nitrates. In the case of ionic nitrates, however, both salts may be more or less equally unstable over some temperature range, so that the decomposition reactions can become quite complex. This is particularly so since the salts may be oxidized or reduced by the gaseous decomposition products. For example, NO_2 produced by the decomposition of the nitrate may oxidize the nitrite ion also formed back to the nitrate. Since the experimental arrangement usually determines the gas-phase composition, reports by different authors frequently conflict. In such cases the common features have been emphasized in this chapter. A consequence of the complexity of most nitrate decompositions is that kinetic studies have usually been restricted to identifying the reactions. Even when rate constants and activation energies are reported it is frequently not clear with which particular reactions they are identified.

5.3.2 DECOMPOSITION EQUILIBRIA

In contrast to the decomposition of carbonates, which yield only a single gaseous product, and of sulfates, for which useful generalizations about gas composition can be made (Chapter 4), the situation for nitrates is more complex. Partial pressures of the gaseous constituents must be calculated by a rather complicated method (see below) and, even so, some compromises are required. For example, although it is known that over some temperature ranges alkali metal and alkaline earth nitrates decompose to nitrites as a first step, no high- temperature thermo-

dynamic data for the latter salts are available. Therefore the following procedure has been adopted; when good quality experimental decomposition studies are available, they are discussed. When thermodynamic data are available, the decomposition is treated as if the oxide is the final product, analogous to the treatment of carbonates (Chapter 2) and sulfates (Chapter 4); e.g., for a divalent salt



and the gas equilibrium



The reasons for neglecting other gaseous species have already been discussed in Chapter 5.1. The approach is the one used previously by Kelley,¹ and in all cases where nitrates are not stable represents the best approximation to the physical situation. The equilibrium constants for Equations 5.1 and 5.2 are

$$K_1 = \frac{P_{NO_2}^2 P_{O_2}^{1/2} a_{MO}}{a_{M(NO_3)_2}} \quad (5.3)$$

$$K_2 = \frac{P_{NO_2}^2 P_{O_2}}{P_{NO}^2} \quad (5.4)$$

The partial pressures of the three gases can be calculated if the oxide and nitrate do not form solid solutions (unit activity of each) and if the only source of the gases is the salt. In addition to Equations 5.3 and 5.4, a third relation is derived from the fact that N and O must be liberated in a fixed atomic ratio. Thus

$$P_{O_2} = \frac{1}{4}(P_{NO_2} + P_{NO}) + \frac{1}{2}P_{NO} \quad (5.5)$$

or

$$4P_{O_2} = P_{NO_2} + 3P_{NO}$$

If the condensed phases are pure, a condition which can hold only if both the salt and the oxide are solids, the term $a(MO)/a(MNO_3)_2 = 1$ and appropriate substitution yields an equation in $P(O_2)$ alone:

$$\frac{K_1^{1/2}}{P_{O_2}^{1/4}} + \frac{3(K_1 K_2)^{1/2}}{P_{O_2}^{3/4}} = 4P_{O_2} \quad (5.6)$$

Making the substitution $X = P^{1/4}(O_2)$, this equation can be written in the form

$$X^7 - a X^2 - b = 0 \quad (5.7)$$

where $a = K_1^{1/2}$, $b = 3/4 (K_1.K_2)^{1/2}$. This equation has only one real positive root for positive values of a and b , but cannot be solved in closed form. Newton's method was used to solve it by iteration. After the solution for $P(O_2)$ had been obtained, $P(NO_2)$ and $P(NO)$ were calculated from the equations

$$P_{NO_2} = K_1^{1/2} / P_{O_2}^{1/4}$$

$$P_{NO} = (K_1 K_2)^{1/2} / P_{O_2}^{3/4}$$

The pressures thus obtained are those to be expected if the pure nitrate is initially placed into a closed container containing no other reactants, and the system is allowed to reach equilibrium.

Although the pressures in the real system may differ from those calculated by the above procedure, particularly if nitrites are formed, the values obtained are a useful guide to the stability of the salts.

All the partial pressures calculated from the equilibrium constants assume unit activity for the condensed-phase components. This assumption is good when they are solid. Above the melting points of the salts, however, continued decomposition of the salt will result in a solution containing dissolved oxide and the partial pressures will depend on the melt composition, and will therefore change as the decomposition proceeds. Because of the form of K_1 , the partial pressure calculation will be worst for small oxide concentrations. An examination of the various tables shows that O_2 and NO are the major products of nitrate decomposition, the concentration of NO_2 being rather minor. This results from the fact that the equilibrium $2 NO_2 = 2 NO + O_2$ lies to the right for low pressures.

5.4 INDIVIDUAL NITRITES AND NITRATES

5.4.1 ALUMINUM

$Al(NO_3)_3$ has been prepared in nearly pure form by vacuum sublimation of its adduct with N_2O_5 . It condensed as a white powder at -78° .¹² None of its properties have been measured. Its classification as a covalent was made on the basis of the spectrum of the N_2O_5 adduct.

5.4.2 BARIUM

5.4.2.1 $Ba(NO_2)_2$

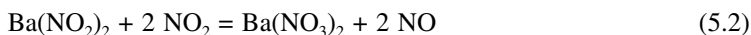
The melting point of the salt is very much in doubt. Centnerszwer and Piekelný¹³ give $262^\circ C$. Protsenko and Bordyushkova¹⁴ give $284^\circ C$. Neither paper describes any experimental detail. Similarly, solid transitions were reported¹⁵ at 203 and $230^\circ C$, but no details are available.

Decomposition of the salt has been studied by three groups of researchers^{13,16,17} at somewhat different temperatures and under various atmospheres. Although they differ in detail, they generally agree on the main features.

The primary decomposition reaction, which is reversible, is



The reaction begins as low as $250^\circ C$. In the temperature range in which $Ba(NO_3)_2$ is stable, the NO_2 formed oxidizes the nitrite¹⁸

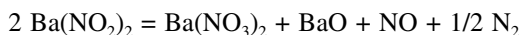


Above 400°C, BaO reacts with NO to form N₂.

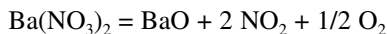


“Overall” reactions given by the various authors are obtained from various combinations of Reactions 5.1 to 5.3. The speed of the overall reaction and the distribution of products are evidently affected by the composition of the gas phase and the manner of its removal. For example, Protsenko and Bordyushkova¹⁷ observed that in the range 410 to 440°C the rate varied in the order air > vacuum > argon. The rate in air may be the greatest since O₂ can oxidize NO which may increase the rate of 5.2. In argon the Arrhenius activation energy for a first-order reaction is 65.3 kJ.

The effect of gas composition and pressure on the temperature range over which the decomposition reaction occurs can be seen by comparing the above results with a TGA study under vacuum.¹⁹ The first stage of the decomposition, corresponding to



occurs between 90 and 150°C. The second stage, beginning at 450°C and complete at 600°C, is the decomposition of the nitrate



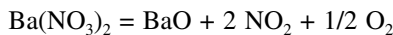
The melting point has been reported as 546 ± 11 K.^{13,17} The density as a function of temperature is given in [Table 5.9](#) and thermodynamic data in [Table 5.10](#).

5.4.2.2 Ba(NO₃)₂

Decomposition has been observed as low as 525°C, but it is still slow at 550°C.²⁰ In fact, even the liquid salt decomposes only slowly just above its melting point.^{21,22} The first stage of the reaction is the formation of the nitrite



but this salt is very unstable so that the overall decomposition is



As can be observed from the calculated dissociation pressures in [Table 5.12](#), the dissociation might be expected to be inhibited in air. This may account for the stability observed by Addison and Coldrey.²¹ The salt appears to have no solid-state transitions. Ambient temperature density is 3.23.⁵⁷

Thermodynamic data are given in [Tables 5.11](#) and 5.12.

5.4.3 BERYLLIUM

Be(NO₃)₂ is a white, hygroscopic solid. The bonding between the metal and the nitrate group is covalent. On being heated above 125°C it rapidly loses NO₂ with the formation of the oxide nitrate Be₄O(NO₃)₆.²⁴ Obviously, for that reason, there are no high-temperature thermodynamic data. Data at 298.15 K are shown in [Table 5.13](#).

5.4.4 BISMUTH

The preparation of $\text{Bi}(\text{NO}_3)_2$ has been reported. Bonding appears to be covalent.²⁷

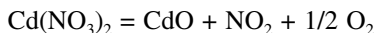
5.4.5 CADMIUM

5.4.5.1 $\text{Cd}(\text{NO}_2)_2$

The pure anhydrous salt has apparently never been prepared, although it has been reported in reaction mixtures.²⁸

5.4.5.2 $\text{Cd}(\text{NO}_3)_2$

The infrared spectrum²⁹ indicates the solid to be typically ionic. It decomposes rapidly above 573 K,³⁰ consistent with the thermodynamic data. The reported melting point is uncertain. The transition is given in [Table 5.14](#), and thermodynamic data in [Tables 5.15](#) to [5.17](#). Decomposition is reported to be reversible and to yield no intermediates:³¹

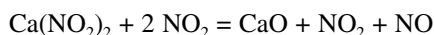


5.4.6 CALCIUM

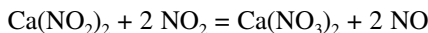
5.4.6.1 $\text{Ca}(\text{NO}_2)_2$

The solid-state transitions were obtained from heating curves ([Table 5.18](#)). The nature of the phases was not characterized.³²

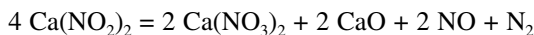
The decomposition reactions of $\text{Ca}(\text{NO}_2)_2$ are similar to those for the Ba and Sr salts. Centnerszwer and Piekelnny¹³ measured the decomposition pressure over the temperature range 540 to 588 K. In an inert atmosphere $\log P$ is linear in $1/T$; p varied from 0 at 540 K to 693 torr at 588 K. This suggests that a single reaction is responsible for the measured pressure, but it is not at all clear what this reaction is, since the enthalpy change calculated by the authors from the pressure data (147.7 kJ) differs considerably from ΔH° at 298 K for the reaction cited by the authors.



for which $\Delta H = 234.4$ kJ. The lack of high-temperature data for $\text{Ca}(\text{NO}_2)_2$ prevents a comparison of ΔH° at the experiment temperature. At somewhat higher temperatures only NO appears as the product, probably because NO_2 oxidizes the nitrite



The decomposition was also studied by Protsenko and Bordyushkova¹⁴ at somewhat higher temperatures, 693 and 723 K, which are still sufficiently low for the nitrate to be stable, or at least for its decomposition to be negligible compared to that of the nitrite. They noted that the rate of decomposition varied with the gas phase in the order: argon < air < vacuum. From an analysis of the gas phase and the weight loss of the sample, they conclude that in argon the main reaction is the formation of the nitrate with partial reduction of the NO to N_2 :



which is fairly consistent with the above reactions. These have also been found by Oza and Oza,³³ who find that they are reversible. Thus, since the nitrate is unstable in the presence of NO, the production of N₂ is inhibited and the above reaction will be minor unless the product gases are continually removed from the system.

Interpretation of the pressure measurements of Centnerszwer and Pieckiely would therefore need to take into account all the above reactions. In reaction schemes as complicated as the present one, equilibrium pressure measurements alone are likely to be of limited utility, particularly since the partial pressures of the component gases depend not only on the equilibrium constants of the reactions, but also on the composition of the condensed phases.

5.4.6.2 Ca(NO₃)₂

The salt exhibits no crystalline transitions.³⁴ Thermodynamic data are shown in Table 5.19. Its decomposition has not been studied in detail. Some indication of its stability may be gained from the thermodynamic data for the decomposition reaction (Table 5.20 and 5.21). Although the calculated dissociation pressures are substantial above 700 K, Addison and Coldrey³⁵ found the liquid to be clear at 828 K and small bubbles to form at 833 K, but both of these temperatures lie below the generally accepted melting point of 834 K. The behavior of the salt near the melting point evidently needs more careful study.

A kinetic study³⁶ carried out in the range 858 to 1000 K indicates the evolution of NO₂, with the initial formation of a supersaturated solution of CaO in Ca(NO₃)₂.

5.4.7 CESIUM

5.4.7.1 CsNO₂

The salt is stable to 450°C and decomposes to the oxide above that temperature if the product gases, NO and NO₂, are removed.³⁷ In their presence the oxide is partially oxidized to the nitrate.

Below 700 K, CsNO₂ evaporates without decomposition and the vapor contains both monomers and dimers. ΔH of sublimation is 161.5 kJ, and 208.8 kJ for the dimer, recalculated to 298 K. The enthalpy of dimerization is 477 kJ.³⁸

5.4.7.2 CsNO₃

The salt exhibits one solid–solid transition. The hysteresis, which is frequently exhibited by this transformation leads to some uncertainty in the enthalpy change. The problem is discussed in detail by Rao and Rao.³⁹

A semi-quantitative study⁴⁰ indicates that the salt decomposes only slowly up to 828 K, 0.05% nitrite appearing in the melt after heating for 10 min. A mass spectrometric study⁴¹ indicates that, although some decomposition occurs as low as 775 K, prolonged heating at 835 K does not permit detection of decomposition in the powder pattern of the residue. These results were extended by Bagaratian et al.³⁸ who also found decomposition to nitrites to be slight and who give sublimation enthalpies, calculated to 298 K, as 195 kJ for the monomer and 234 kJ for the dimer. The enthalpy of dimerization is –158 kJ.

Densities of CsNO₂ and CsNO₃ are given in Tables 5.22 and 5.23, transitions in Table 5.24, and thermodynamic data in Tables 5.25 to 5.29.

5.4.8 CHROMIUM

Anhydrous Cr(NO₃)₂ has been prepared. The compound is covalent. When the pale green powder is heated in a vacuum or an atmosphere of nitrogen, it begins to decompose rapidly at 60°C, and the decomposition rate is a maximum at 100°C. Decomposition may proceed through a series of

oxide nitrates, but none of these is stable enough to give a plateau on TGA. The first plateau is attained at 200°C and corresponds to Cr_3O_8 .⁴²

5.4.9 COBALT

5.4.9.1 $\text{Co}(\text{NO}_2)_2$

The existence of this salt has been reported,⁴³ but it must still be regarded as doubtful. It supposedly begins to evolve NO near 100°C.

5.4.9.2 $\text{Co}(\text{NO}_3)_2$

The salt decomposes to Co_3O_4 in a single step without formation of an intermediate.⁴⁴ The decomposition begins at 100 to 105°C,^{44,45} but there is some question as to the temperature at which decomposition is maximum. Both Addison and Sutton⁴⁴ and Addison and Logan⁴⁶ state that the rate is maximum at 270°C, but the experimental curve published by Addison and Sutton⁴⁴ shows this maximum approximately 100°C lower.

Thermodynamic data are given in [Tables 5.30](#) and [5.31](#).

5.4.10 COPPER

5.4.10.1 $\text{Cu}(\text{NO}_2)_2$

Reports about the existence of this salt are conflicting.⁴⁷ Its preparation is doubtful.

5.4.10.2 $\text{Cu}(\text{NO}_3)_2$

Below 500 K heating of the solid salt results primarily in the vaporization of the covalent molecule as a monomer. In this temperature range the only thermal decomposition, into NO_2 and O_2 , is exhibited by the solid. The vapor is more stable. The vapor pressure of $\text{Cu}(\text{NO}_3)_2$ was determined by Addison and Hathaway⁴⁸ by extrapolating pressure-time curves to zero time in order to subtract the pressures of NO_2 and O_2 . These vapor pressures increased from 0.32 torr at 430 K to 3.59 torr at 405 K. A plot of $\log P$ vs. $1/T$ is linear and yields a sublimation enthalpy of 67.0 kJ. Above 500 K both the solid and the vapor phase decompose to $\text{NO}_2 + \text{O}_2$.

No high-temperature thermodynamic data are available. Transitions are listed in [Table 5.32](#) and thermodynamic data at 298 K in [Table 5.33](#).

5.4.11 GALLIUM

$\text{Ga}(\text{NO}_3)_2$ was probably prepared by Dupre,⁵⁰ using vacuum dehydration of the hydrate at 40°C. A large fraction of the salt had decomposed to Ga_2O_3 when the temperature reached 200°C.

Thermodynamic data at 298 K are given in [Table 5.34](#).

5.4.12 GOLD

Evidence for the existence of $\text{Au}(\text{NO}_3)_3$ seems to be based on a report by Field and Hardy⁵² who treated hydrated gold nitrates successively with HNO_3 and N_2O_5 . Although the gold content corresponded to the trinitrate, no quantitative nitrate analysis was performed. Further information is lacking.

5.4.13 HAFNIUM

Although Addison and Logan⁴⁶ indicated the existence of an anhydrous nitrate in their periodic table, there is some question as to whether such a compound has actually been prepared. Field

and Hardy⁵² succeeded in preparing the addition compound $\text{Hf}(\text{NO}_3)_4 \cdot \text{N}_2\text{O}_5$, but this compound sublimed as such, rather than losing N_2O_5 . More recently, Tuseev, Izmailovich, and Komissarova⁵³ succeeded in preparing $\text{Hf}(\text{NO}_3)_4$ and studying its decomposition. Melting and decomposition occurred simultaneously at 383 to 403 K, followed by a two-stage decomposition leading first to the formation of an oxynitrate in the successive temperature ranges 443 to 448 and 483 to 488 K.

5.4.14 INDIUM

The infrared spectrum shows that $\text{In}(\text{NO}_3)_3$ is covalent and stable to at least 90°C, since this was the temperature of its preparation.⁵⁴ The thermodynamic data available at 298 K are listed in [Table 5.35](#).

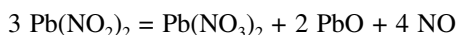
5.4.15 IRON

$\text{Fe}(\text{NO}_3)_3$ has only been prepared as the volatile adduct $\text{Fe}(\text{NO}_3)_3 \cdot \text{N}_2\text{O}_5$, although it is possible that $\text{Fe}(\text{NO}_3)_3$ exists in the vapor state.⁵⁵

5.4.16 LEAD

5.4.16.1 $\text{Pb}(\text{NO}_2)_2$

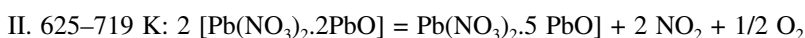
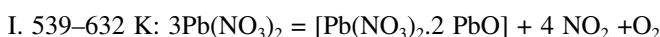
Very little is known about this salt. It has been prepared by treating the chloride with AgNO_2 and measuring decomposition by TGA.⁵⁶ It occurs in two stages, the first one beginning at about 110°C being consistent with the stoichiometry



The second stage is the decomposition of the nitrate. However, this occurs in the range 320 to 450°C and seems to proceed directly to PbO , a result which is inconsistent with other studies of nitrate decomposition (see below).

5.4.16.2 $\text{Pb}(\text{NO}_3)_2$

The thermal decomposition of this salt has been studied by a number of researchers.^{57–59} There is general agreement that decomposition occurs without oxidation of a $\text{Pb}(\text{II})$ ion to a higher valent state, but it is not clear whether a nitrite may be an intermediate in the decomposition. In the course of the decomposition several oxynitrates are formed, but there is no general agreement as to the composition of these salts. The most careful study seems to have been carried out by Neumann and Sonntag^{58,61} who measured the total pressure involved in three reversible equilibria and analyzed the solid phases. The equilibria (renotated from the original papers) and the temperature ranges over which they were measured are



The overlapping of the temperature ranges is accounted for by the fact that the continuous removal of product gas will result in the disappearance of a lower oxide and the formation of a higher one, with the resulting establishment of a new equilibrium.

Nothing seems to be known of the structures of the oxynitrates, so the writing of the formulas is somewhat arbitrary, e.g., $\text{Pb}(\text{NO}_3)_2 \cdot 2 \text{PbO} = 3\text{PbO} \cdot \text{N}_2\text{O}_5$.

Neumann and Sonntag calculated equilibrium constants for the above three reactions by calculating the partial pressures of NO_2 and O_2 , using the equilibrium constants of Bodenstein⁶⁰ for the equilibrium reaction $\text{NO}_2 = \text{NO} + 1/2 \text{O}_2$. Since these differ slightly from current data, they were used to reanalyze the three reactions. It was noted that a plot of $\ln K$ of reaction I vs. $1/T$ could only very approximately be described as linear, but rather consisted of three linear portions. A plot of $\ln K$ vs. $1/T$ for reaction III could also more accurately be described as consisting of two linear portions. For reaction II the plot was linear over the entire temperature range. ΔH° values calculated for the various portions are

| Reaction | T(K) | ΔH (kJ) |
|----------|---------|-----------------|
| I | 539–583 | 694 |
| | 583–603 | 629 |
| | 613–632 | 758 |
| II | 625–719 | 337 |
| III | 688–763 | 390 |
| | 763–809 | 324 |

There seems to be no simple way to choose among the enthalpies for the various slopes, although the high-temperature plot of I does not join smoothly to the lower two and may represent experimental error. The low-temperature plot of I shows more scatter than the plot at the higher temperature.

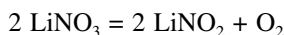
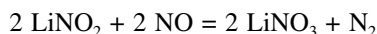
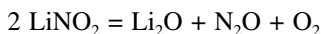
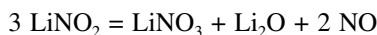
Thermodynamic data for $\text{Pb}(\text{NO}_3)_2$ are given in Table 5.36, and for its decomposition in Tables 5.37 and 5.38, but there are no data for the oxynitrates.

In addition to the decompositions discussed above, an autocatalytic decomposition resulting in the formation of Pb(IV) has also been reported,⁶² but no details are available.

5.4.17 LITHIUM

5.4.17.1 LiNO_2

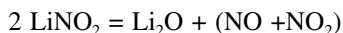
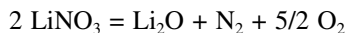
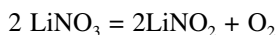
The thermal decomposition of LiNO_2 results in the formation of LiNO_3 , N_2 , O_2 , and oxides of nitrogen.⁶³ In order to disentangle the various reactions giving rise to these products, Lee and Johnson⁶⁴ studied the decomposition by sweeping out product gases from a thin, quiescent layer of molten nitrite, and using only the results from the first few percent of decomposition. The exit gases were analyzed by starting with fresh batches each time. From the results, the following first-order reaction steps are proposed:



Decomposition begins at 433 K. Up to 623 K no NO_2 is detected, but it was produced at 723 K.

5.4.17.2 LiNO_3

The isothermal decomposition of LiNO_3 proceeds according to the following three reactions:



The first reaction begins at 853 to 893 K, with the others beginning only at 893 K.^{65,66}

Densities of the two salts are given in [Tables 5.39](#) and [5.40](#) transitions in [Table 5.41](#), and thermodynamic data in [Tables 5.42](#) and [5.44](#).

5.4.18 MAGNESIUM

$\text{Mg}(\text{NO}_3)_2$ is stable to nearly 600 K. Its decomposition was studied from 575 to 725 K.⁷² Initially, NO_2 is liberated and the decomposition reactions are inferred from the NO_2 liberated. The curves follow first-order topochemical kinetics. Thermodynamic data are given in [Tables 5.45](#) to [5.47](#).

5.4.19 MANGANESE

Reports about the decomposition of $\text{Mn}(\text{NO}_3)_2$ differ somewhat. According to the older work of Guntz and Martin,⁷³ decomposition begins near 160°C and produces the dioxide



More careful analysis of the remaining solid phase⁷⁴ shows that it is $\text{MnO}_{1.655}$ and that both NO_2 and O_2 are evolved. Under dry N_2 the decomposition rate reaches a maximum near 230°C. A very elaborate study by a Dutch group⁷⁵ concludes that decomposition proceeds in a single step to MnO_2 , but since their starting material was an aqueous solution, and water vapor frequently affects the course of these reactions, their kinetic analysis is probably not relevant.

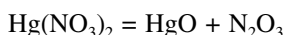
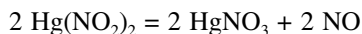
The salt is characterized as covalent by Addison and Gatehouse,⁷⁶ but Dehnicke and Strähle⁷⁷ find that it, like $\text{Co}(\text{NO}_3)_2$, possesses considerable ionic character.

Thermodynamic data are given in [Tables 5.48](#) and [5.49](#).

5.4.20 MERCURY

5.4.20.1 $\text{Hg}(\text{NO}_2)_2$

The salt appears to have been prepared for the first time by Ray⁷⁸ and in the pure state by Oza, Jha, and Ezekiel.⁷⁹ It is a yellow powder which begins to decompose at 50°C and readily decomposes at 90°C. HgO and $\text{Hg}(\text{NO}_3)_2$ appear as products and so the reactions probably are



5.4.20.2 HgNO_3

The salt has been prepared only relatively recently in the anhydrous state.⁸⁰ It decomposes to a yellow solid with the evolution of brown fumes when heated above 100°C. It appears to be covalent.

5.4.20.3 $\text{Hg}(\text{NO}_3)_2$

The anhydrous salt has been prepared,⁸¹ but aside from infrared studies which indicate that the compound is covalent,^{81,82} little has been done to determine its properties.

Decomposition of the salt is appreciable at 160°C and appears to lead to a basic nitrate, $\text{HgO} \cdot \text{Hg}(\text{NO}_3)_2$. At 300°C this compound is stable and the final product is HgO . In the presence of NO some nitrite and NO_2 are formed.⁷⁹

Thermodynamic data at 298 K are listed in [Table 5.50](#).

5.4.21 NICKEL

5.4.21.1 $\text{Ni}(\text{NO}_2)_2$

The salt is stable up to 260°C in an argon atmosphere and decomposes at 220°C in a vacuum. It is slightly volatile.⁸³

5.4.21.2 $\text{Ni}(\text{NO}_3)_2$

The salt decomposes on heating, the initial decomposition, near 260°C, resulting in formation of the nitrite.⁸⁴ Thermodynamic data are given in [Tables 5.51](#) and [5.52](#).

5.4.22 PALLADIUM

5.4.22.1 $\text{Pd}(\text{NO}_2)_2$

A compound of approximately this composition was reported.⁸⁵

5.4.22.2 $\text{Pd}(\text{NO}_3)_2$

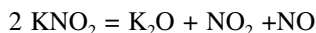
The anhydrous salt has been prepared.⁸⁶ The infrared spectrum indicates it is covalent and sufficiently stable in the vapor to permit sublimation in a vacuum.

No entropy data are available; enthalpies at 298 K are listed in [Table 5.53](#).

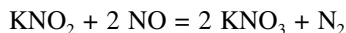
5.4.23 POTASSIUM

5.4.23.1 KNO_2

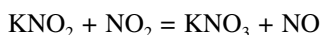
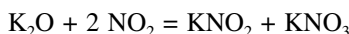
No solid-phase transitions have been reported. The salt begins to decompose noticeably at 410°C. The first step in the decomposition sequence is probably^{87,88}



Between 410 and 460°C the NO produced reacts with KNO_2 :



The NO_2 produced in the first reaction reacts further:



Which reactions are favored depend largely on the atmospheric composition. For example, in an inert atmosphere which removes the gaseous products the first reaction will predominate. Otherwise, since KNO_3 is stable in this temperature range and N_2 is unreactive, the net result of the above reactions is the production of KNO_3 and N_2 . In an oxygen atmosphere, particularly in the temperature range 550 to 600°C, the reaction $\text{KNO}_2 + 1/2 \text{O}_2 = \text{KNO}_3$ goes to completion. In the range

650 to 750°C, KNO₃ becomes increasingly unstable and the reaction attains equilibrium. Above 800°C the reaction $2 \text{KNO}_2 = \text{K}_2\text{O} + \text{N}_2 + 3/2 \text{O}_2$ goes to completion.^{87–89} These results are consistent with endothermic peaks observed by differential scanning calorimetry.⁹⁰

5.4.23.2 KNO₃

The phase transitions are fairly complicated and have been discussed by several authors.^{91–93} In addition to the stable low-temperature orthorhombic form II which transforms at 401 K to the rhombohedral I, there exists a metastable form III which can be obtained by cooling I to 396 K; III then transforms to II on further cooling to 386 K.

KNO₃ melts without decomposition to a liquid which is stable in air to at least 803 K.⁹⁴ When heated in air, it begins to decompose near 923 K.⁹⁵ Between 823 and 1023 K the quasi-equilibrium $\text{KNO}_3 = \text{KNO}_2 + 1/2 \text{O}_2$ is set up.^{89,95,96} The activation energy for the forward reaction is 274 kJ. If the O₂ is removed, KNO₂ decomposes, various oxides of nitrogen are produced, and the reaction is more complicated (see discussion under KNO₂). As pointed out above, the two salts tend to interconvert over a limited temperature range. Above the melting points this leads to a solution containing both salts. For some specified oxygen partial pressure, e.g., air, the solution composition is then a unique function of temperature if equilibrium is established. In the range 823 to 1023 K the equilibrium has been studied by several authors.^{89,95,96} All these results have been summarized by Kramer, Munir, and Volponi⁹⁰ and are consistent with their DSC results.

Densities are listed in [Tables 5.54](#) and [5.55](#), transitions in [Table 5.56](#) and thermodynamic data in [Tables 5.57](#) to [5.61](#).

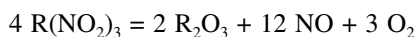
5.4.24 RADIUM

Ra(NO₃)₂ has a cubic lattice, isomorphous with Ba(NO₃)₂. Its density is calculated to be 4.11 gcm⁻³.⁹⁷ Thermodynamic properties are listed in [Table 5.62](#).

5.4.25 RARE EARTHS

5.4.25.1 Nitrites

Several anhydrous nitrites have been prepared and their decomposition studied by TGA.⁹⁸ They all decompose at lower temperatures than the corresponding nitrates. With the exception of Pr(NO₂)₃ whose decomposition product is Pr₆O₁₁, the nitrites decompose according to



Below are listed the initial decomposition and minimum oxide formation temperatures as given by Freeman.⁸⁹

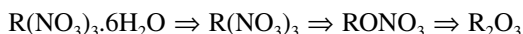
| Salt | Initial Decomposition °C | Minimum Oxide Formation °C |
|-----------------------------------|--------------------------------|----------------------------------|
| La(NO ₂) ₃ | 240 | 580 |
| Pr(NO ₂) ₃ | 220 | 450 |
| Nd(NO ₂) ₃ | 200 | 510 |
| Sm(NO ₂) ₃ | 200 | 500 |
| Dy(NO ₂) ₃ | 110 | 500 |
| Yb(NO ₂) ₃ | 90 | 350 |

These authors also measured the decomposition kinetics of Nd, Dy, and Tb nitrites. The reactions were first order with very low (4 to 15 kJ) activation energies which they attributed to metal-oxygen interaction.

5.4.25.2 Nitrates

There has been considerable discussion as to (a) whether the anhydrous nitrates are stable intermediates in the thermal decomposition of the corresponding hydrates and (b) whether some of the anhydrous nitrates are ionic or covalent.

A study of the infrared spectra by Walker and Ferraro⁹⁹ seems to have established rather firmly that the anhydrous nitrates are covalent. Unfortunately, there appear to have been no TGA or other thermal decomposition studies of rare-earth nitrates originally prepared in the anhydrous state. Both Wendlandt^{100,101} and Patil, Gosavi, and Rao⁹⁸ studied the thermal decomposition of the hydrated salts. They agree that oxynitrates of composition RONO_3 are formed as intermediates in nearly all cases, but differ as to whether the anhydrous nitrates are also intermediates. Wendlandt¹⁰¹ found that the lighter rare earths, La, Pr, Nd, gave the anhydrous salt as a stable intermediate:



whereas the heavier rare earths decomposed directly to the oxynitrate. However, Patil, Gosavi, and Rao⁹⁸ claimed that most rare earths on careful decomposition do give the anhydrous nitrate as an intermediate, but only in the limited temperatures given below:

| Salt | Stability Range of Anhydrous Nitrate (°C) | Stability Range of RONO_3 (°C) |
|----------------------------|---|--|
| $\text{La}(\text{NO}_3)_3$ | 240–420 | 525–575 |
| $\text{Nd}(\text{NO}_3)_3$ | 280–350 | 460–500 |
| $\text{Dy}(\text{NO}_3)_3$ | 260–280 | 420–440 |
| $\text{Yb}(\text{NO}_3)_3$ | 260–270 | 340–400 |
| $\text{Lu}(\text{NO}_3)_3$ | 220–230 | 370–390 |

$\text{Pr}(\text{NO}_3)_3$ is exceptional in that the final oxide is Pr_6O_{11} . The hydrated cerium salt shows no stable intermediates, but goes to CeO_2 . The above uncertainties could probably be cleared up by TGA studies of anhydrous nitrates. The above data indicate that these should be stable to about 300°C.

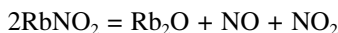
The kinetics of the nitrate decompositions of Nd, Dy, and Yb were found to be first order with activation energies ranging from 23 to 46 kJ higher than those of the corresponding nitrites.⁹⁸

5.4.26 RUBIDIUM

5.4.26.1 RbNO_2

The salt appears to be quite stable up to 450°C and decomposes with increasing rapidity above that temperature.¹⁰² Bagaratian et al.³⁸ give the sublimation enthalpy of the monomer as 162 kJ and 209 kJ for the dimer.

Decomposition reactions appear to be similar to those of the other alkali metal nitrites, i.e., the course of the decomposition depends on the gas phase. If the gas is continually removed, the reaction proceeds directly to the oxide:



In the presence of the nitrogen oxides the salt may be oxidized to the nitrate, particularly in the temperature range where the nitrate is stable.

5.4.26.2 RbNO_3

The salt is stable up to 600°C and begins to lose weight above that temperature.¹⁰³ The phase transitions and high temperature heat capacity have been studied by Mustajoki,¹⁰⁴ but the lack of

a reliable entropy value for the salt and high-temperature data for the oxide prevent the calculation of decomposition equilibria. Although no experimental studies of the decomposition seem to have been reported, it is expected to resemble that of the other alkali metal nitrates. Like them, the salt can be vacuum distilled above 350°C.¹⁰⁵

A mass-spectrometric study³⁸ gives 183 kJ for the sublimation enthalpy of the monomer and 198 kJ for the dimer. The dimerization enthalpy is –167 kJ.

Densities of the salts are given in [Tables 5.63](#) and [5.64](#), transitions in [Table 5.65](#), and thermodynamic data in [Tables 5.66](#) to [5.68](#).

5.4.27 SCANDIUM

Mellor¹⁰⁸ summarizes earlier work which claims preparation of $\text{Sc}(\text{NO}_3)_3$ by heating the 4-hydrate at 100°C in a vacuum. The melting point is said to lie in the range 125 to 150°C.

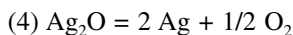
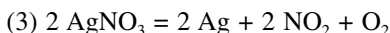
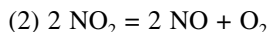
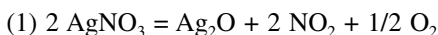
5.4.28 SILVER

5.4.28.1 AgNO_2

The thermal decomposition of this salt has not been studied in detail, but experiments¹⁰⁹ indicate that it decomposes at 120°C to give metallic silver and NO_2 with first-order kinetics and an activation energy of about 25 kJ.

5.4.28.2 AgNO_3

The decomposition equilibria are complicated by the thermal instability of Ag_2O . This means that instead of the usual two equilibria the system can be considered in terms of four reactions only three of which are independent:



Equilibrium constants for (1), (3), and (4) have been listed. Ag_2O is quite unstable above 400 K and hence reactions (1) and (4) are not in equilibrium for reasonable pressures of O_2 . Below 500 K, $P(\text{O}_2)$ is fixed by reaction (4). $P(\text{NO}_2)$ and $P(\text{NO})$ can then be calculated from K_1 , K_3 , and K_4 . Qualitatively, decomposition is negligible in the solid state, but becomes appreciable at 30 to 40°C above the melting point.¹¹⁰

Densities are listed in [Table 5.69](#), transitions in [Table 5.70](#), and thermodynamic data in [Tables 5.71](#) to [5.73](#).

5.4.29 SODIUM

5.4.29.1 NaNO_2

NaNO_2 is unstable above 330°C.¹¹¹ The first step in the decomposition is probably $2 \text{NaNO}_2 = \text{Na}_2\text{O} + \text{NO}_2 + \text{NO}$ (N_2O_5 is too unstable at and above this temperature to be significant). Between 330 and 380°C the reaction sequence seems to be as follows:



The NO produced in (1) reacts with NaNO_2



The NO_2 produced in (1) reacts further¹¹²

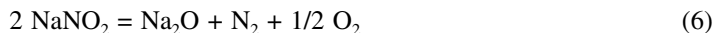


Of these, at least reaction (4) is reversible.¹¹³ Since NaNO_3 is stable in this temperature range and N_2 is unreactive, the net result of reactions (1) to (4) is the production of NaNO_3 and N_2 . If the gas phase is continually removed, only (1) will occur.

At higher temperatures, 600 to 750°C, NaNO_2 reacts with O_2 to establish the equilibrium with NaNO_3 :



If the decomposition is carried out in an inert atmosphere the first decomposition product is N_2 , accompanied by increasing concentrations of O_2 in the later stages of the reaction.¹¹⁴ The stoichiometry of this reaction can be written as¹¹⁵



Freeman¹¹⁴ attributes the evolution of N_2 to the formation of a superoxide which later decomposes to Na_2O and O_2 . This view is supported by Bond and Jacobs¹¹⁵ who report that this reaction also proceeds in air. For reaction (5) the Arrhenius activation energy is given by Freeman¹¹⁴ as 187 kJ and by Bond and Jacobs¹¹⁵ as 169 kJ. For reaction (6) it is 179 kJ.¹¹⁵ Both reactions are fitted by a contracting sphere model which was originally derived for solids.

Equations of this type generally describe sigmoid α vs. t curves. In view of the complexity of these reactions, calculation of these equilibria, except for reaction (5), would probably not be useful.

5.4.29.2 NaNO_3

NaNO_3 melts without decomposition to a liquid which is stable in air to at least 500°C¹¹⁶ and begins to decompose slowly at 600°C.¹¹⁴ Between 600 and 750°C a pseudoequilibrium is established between air and a liquid containing NaNO_3 and NaNO_2 whose composition is temperature dependent. As an example of the stability of NaNO_3 in the solid state some calculations of its decomposition to Na_2O and NaNO_2 have been made. In the liquid state nitrate and nitrite are completely miscible; the solution is virtually ideal; and the liquid composition depends on $p(\text{O}_2)$.

Densities are given in [Tables 5.74](#) and [5.75](#), transitions in [Table 5.76](#), and thermodynamic data in [Tables 5.77](#) to [5.82](#).

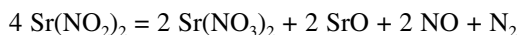
5.4.30 STRONTIUM

5.4.30.1 $\text{Sr}(\text{NO}_2)_2$

The melting point of this salt is in doubt since the reported values^{117,118} vary by 37°C. The solid phases have not been characterized.

The thermal decomposition has been studied by several authors.^{117–119} It is similar to those of the barium and calcium salts. A measurable decomposition pressure has been reported at 537 K,

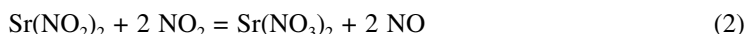
but most studies have been carried out at higher temperatures. At 675 to 775 K, where $\text{Sr}(\text{NO}_3)_2$ is stable, the overall reaction is given as¹¹⁸



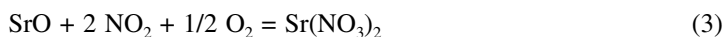
From a careful analysis of the condensed- and vapor-phase components in the range 813 to 973 K, Oza and Patel¹¹⁹ deduce the following reaction sequence:



A part of the NO_2 reacts with the remaining nitrite



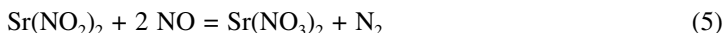
In a closed system this reaction may be reversible. The rest of the NO_2 reacts with the oxide, if oxygen is present



The oxygen may be produced by the dissociation of NO_2



Up to 873 K, reaction (3) produces nitrate while above 915 K, $\text{Sr}(\text{NO}_3)_2$ decomposes. N_2 is produced by



Reaction (5) probably occurs only at the higher temperatures since it was not reported below 642 K.¹¹⁷

There are no high-temperature thermodynamic data which would permit the calculation of equilibria for any of the above reactions.

5.4.30.2 $\text{Sr}(\text{NO}_3)_2$

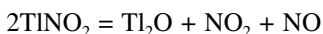
The melting point of this salt is uncertain. The value listed is that selected by Lumsden,¹²⁰ but Gordon and Campbell¹²¹ report 891 K, and Addison and Coldrey¹²² give 878 K. Similarly, reports on the stability of the salt above its melting point vary from slight “bubbling at 888 K” to 945 K.¹²³ Crystalline transitions appear to be absent.¹²³

Transitions are listed in [Table 5.83](#), and thermodynamic data in [Tables 5.84](#) to [5.86](#).

5.4.31 THALLIUM

5.4.31.1 TlNO_2

Very little is known about this salt. Phase transitions have been reported, but no details are given by the authors.¹²⁴ The salt has been reported to decompose above its melting point (182°C) according to Protsenko and Brykova¹⁵



5.4.31.2 TINO₃

The heat of fusion of TINO₃ has also been determined by Kleppa and McCarthy¹²⁵ who obtained 9.47 kJ, but their melting point was 5°C lower than the commonly accepted one.

The vaporization of TINO₃ was studied by Cubiciotti¹²⁶ in the range 539 to 612 K. He found that, in addition to NO as the decomposition product, TINO₃ also vaporized as the salt. In the range 490 to 612 K the vapor pressure is given by $\log P(\text{atm}) = -7486/T - \log T + 21.77$ and the enthalpy of vaporization by $\Delta H (\text{Jmol}^{-1}) = 143,344 - 41.84 T$, and the entropy of vaporization by $\Delta S (\text{Jdeg}^{-1}\text{mol}^{-1}) = 370.9 - 96 \log T$.

Densities are given in [Table 5.87](#), transitions in [Table 5.88](#), and thermodynamic data in [Tables 5.89](#) to [5.91](#).

5.4.32 THORIUM

Th(NO₃)₄ decomposes without the formation of basic salts according to Misciatelli¹⁴⁴



Thermodynamic functions are given in [Tables 5.92](#) and [5.93](#).

5.4.33 TIN

Sn(NO₃)₄ melts at 364 K and begins to decompose at 371 K. No intermediate oxide nitrate appears to form, and the final product is SnO₂.¹²⁷ There appears to be no information on the decomposition of Sn(NO₃)₂, but thermodynamic calculations indicate that it is unstable above 500 K.

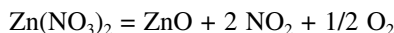
Thermodynamic data of Sn(NO₃)₂ are given in [Tables 5.94](#) and [5.95](#).

5.4.34 TITANIUM

Ti(NO₃)₄ is a covalent salt, stable at least to its melting point at 331 K.¹²⁸ It decomposes to TiO₂ with the evolution of O₂ and NO₂.¹²⁹

5.4.35 ZINC

Zn(NO₃)₂ is stable up to 373 K, and decomposes only slightly even at 513 K. Above this temperature, decomposition becomes increasingly rapid, consistent with the equation¹³⁰



Thermodynamic data are only available at 298 K. These are listed in [Table 5.96](#).

5.4.36 ZIRCONIUM

Anhydrous Zr(NO₃)₄ has been prepared. It can be purified by sublimation. The compound is covalent and very hygroscopic.¹³¹

TABLE 5.1
Thermodynamic Data of O₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | 0.000 | 205.15 | -61.17 | Barin 1993 |
| 400.00 | 3.06 | 213.96 | -82.53 | Barin 1993 |
| 500.00 | 6.21 | 220.98 | -104.28 | Barin 1993 |
| 600.00 | 9.44 | 226.87 | -126.68 | Barin 1993 |
| 700.00 | 12.74 | 231.95 | -149.63 | Barin 1993 |
| 800.00 | 16.09 | 236.42 | -173.05 | Barin 1993 |
| 900.00 | 19.48 | 240.42 | -196.90 | Barin 1993 |
| 1000.00 | 22.92 | 244.04 | -221.12 | Barin 1993 |
| 1100.00 | 26.39 | 247.35 | -245.70 | Barin 1993 |
| 1200.00 | 29.91 | 250.41 | -270.59 | Barin 1993 |

TABLE 5.2
Thermodynamic Data of N₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | 0.00 | 191.61 | -57.13 | JANAF 1985 |
| 400.00 | 2.97 | 200.19 | -77.10 | JANAF 1985 |
| 500.00 | 5.91 | 206.74 | -97.46 | JANAF 1985 |
| 600.00 | 8.89 | 212.13 | -118.41 | JANAF 1985 |
| 700.00 | 11.94 | 216.87 | -139.82 | JANAF 1985 |
| 800.00 | 15.05 | 221.02 | -161.77 | JANAF 1985 |
| 900.00 | 18.22 | 224.76 | -184.06 | JANAF 1985 |
| 1000.00 | 21.46 | 228.17 | -206.71 | JANAF 1985 |
| 1100.00 | 24.76 | 231.31 | -229.69 | JANAF 1985 |
| 1200.00 | 28.11 | 234.23 | -252.97 | JANAF 1985 |

TABLE 5.3
Thermodynamic Data of NO

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | 90.29 | 210.76 | 27.45 | Knacke et al. 1991 |
| 400.00 | 93.34 | 219.57 | 5.52 | Knacke et al. 1991 |
| 500.00 | 96.41 | 226.40 | -16.79 | Knacke et al. 1991 |
| 600.00 | 99.53 | 232.11 | -39.72 | Knacke et al. 1991 |
| 700.00 | 102.73 | 237.02 | -63.19 | Knacke et al. 1991 |
| 800.00 | 105.97 | 241.35 | -87.11 | Knacke et al. 1991 |
| 900.00 | 109.26 | 245.23 | -111.44 | Knacke et al. 1991 |
| 1000.00 | 112.61 | 248.75 | -136.14 | Knacke et al. 1991 |
| 1100.00 | 116.00 | 251.98 | -161.18 | Knacke et al. 1991 |
| 1200.00 | 119.43 | 254.97 | -186.53 | Knacke et al. 1991 |

TABLE 5.4
Thermodynamic Data of NO₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | 33.10 | 240.02 | -38.47 | Knacke et al. 1991 |
| 400.00 | 37.06 | 251.44 | -63.51 | Knacke et al. 1991 |
| 500.00 | 41.30 | 260.88 | -89.14 | Knacke et al. 1991 |
| 600.00 | 45.78 | 269.04 | -115.65 | Knacke et al. 1991 |
| 700.00 | 50.46 | 276.25 | -142.92 | Knacke et al. 1991 |
| 800.00 | 55.30 | 282.71 | -170.87 | Knacke et al. 1991 |
| 900.00 | 60.29 | 288.59 | -199.44 | Knacke et al. 1991 |
| 1000.00 | 65.41 | 293.99 | -228.57 | Knacke et al. 1991 |
| 1100.00 | 70.65 | 298.97 | -258.22 | Knacke et al. 1991 |
| 1200.00 | 75.97 | 303.81 | -288.36 | Knacke et al. 1991 |

TABLE 5.5
Thermodynamic Data of N₂O

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | 82.05 | 219.98 | 16.46 | Knacke et al. 1991 |
| 400.00 | 86.15 | 231.79 | -6.57 | Knacke et al. 1991 |
| 500.00 | 90.54 | 241.57 | -30.25 | Knacke et al. 1991 |
| 600.00 | 95.28 | 250.20 | -54.84 | Knacke et al. 1991 |
| 700.00 | 100.30 | 257.94 | -80.36 | Knacke et al. 1991 |
| 800.00 | 105.52 | 264.90 | -100.40 | Knacke et al. 1991 |
| 900.00 | 110.87 | 273.21 | -135.22 | Knacke et al. 1991 |
| 1000.00 | 116.34 | 276.97 | -160.63 | Knacke et al. 1991 |
| 1100.00 | 121.90 | 282.27 | -188.59 | Knacke et al. 1991 |
| 1200.00 | 127.54 | 287.17 | -217.07 | Knacke et al. 1991 |

TABLE 5.6
Thermodynamic Data of N₂O₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | 82.84 | 309.34 | -9.39 | Knacke et al. 1991 |
| 400.00 | 89.84 | 329.51 | -41.96 | Knacke et al. 1991 |
| 500.00 | 97.36 | 346.25 | -75.77 | Knacke et al. 1991 |
| 600.00 | 105.47 | 361.03 | -111.14 | Knacke et al. 1991 |
| 700.00 | 114.06 | 374.25 | -147.92 | Knacke et al. 1991 |
| 800.00 | 122.97 | 386.14 | -185.95 | Knacke et al. 1991 |
| 900.00 | 133.00 | 396.70 | -225.11 | Knacke et al. 1991 |
| 1000.00 | 141.42 | 406.72 | -265.30 | Knacke et al. 1991 |
| 1100.00 | 150.88 | 415.73 | -306.43 | Knacke et al. 1991 |
| 1200.00 | 160.45 | 424.06 | -348.42 | Knacke et al. 1991 |

TABLE 5.7
Thermodynamic Data of N₂O₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | 9.08 | 304.37 | -81.67 | Knacke et al. 1991 |
| 400.00 | 17.48 | 328.53 | -113.93 | Knacke et al. 1991 |
| 500.00 | 26.72 | 349.12 | -147.84 | Knacke et al. 1991 |
| 600.00 | 36.84 | 367.55 | -183.69 | Knacke et al. 1991 |
| 700.00 | 47.65 | 384.20 | -221.29 | Knacke et al. 1991 |
| 800.00 | 58.92 | 399.24 | -260.47 | Knacke et al. 1991 |
| 900.00 | 70.50 | 412.88 | -301.09 | Knacke et al. 1991 |
| 1000.00 | 82.36 | 425.37 | -345.01 | Knacke et al. 1991 |
| 1100.00 | 94.41 | 436.86 | -386.13 | Knacke et al. 1991 |
| 1200.00 | 106.61 | 447.47 | -430.35 | Knacke et al. 1991 |

TABLE 5.8
Thermodynamic Data of N₂O₅

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | 11.30 | 346.55 | -92.03 | Barin 1989 |
| 400.00 | 22.09 | 377.94 | -128.93 | Barin 1989 |
| 500.00 | 34.03 | 404.16 | -168.05 | Barin 1989 |
| 600.00 | 46.70 | 427.24 | -209.64 | Barin 1989 |
| 700.00 | 59.84 | 447.47 | -253.40 | Barin 1989 |
| 800.00 | 73.30 | 465.45 | -299.06 | Barin 1989 |
| 900.00 | 87.01 | 481.60 | -346.43 | Barin 1989 |
| 1000.00 | 100.92 | 496.25 | -395.33 | Barin 1989 |
| 1100.00 | 115.00 | 509.67 | -445.64 | Barin 1989 |
| 1200.00 | 129.22 | 522.04 | -497.23 | Barin 1989 |

TABLE 5.9
Density of Ba(NO₃)₂

| Phase | T(K) | d | Reference |
|-------|------|-------|-----------|
| c | 298 | 3.232 | 132 |
| l | 550 | 3.254 | 133 |
| | 560 | 3.247 | 133 |
| | 570 | 3.240 | 133 |
| | 580 | 3.233 | 133 |
| | 590 | 3.226 | 133 |
| | 600 | 3.219 | 133 |
| | 610 | 3.212 | 133 |
| | 620 | 3.205 | 133 |

TABLE 5.10
Thermodynamic Data of Ba(NO₃)₂

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|---------|------------------------------|---|------------------------------|-------------------|
| 298.15 | -992.07 | 213.80 | -1055.81 | Barin et al. 1977 |
| 400.00 | -975.39 | 261.77 | -1080.09 | Barin et al. 1977 |
| 500.00 | -956.93 | 302.87 | -1108.37 | Barin et al. 1977 |
| 600.00 | -936.70 | 339.71 | -1140.53 | Barin et al. 1977 |
| 700.00 | -914.82 | 373.41 | -1176.20 | Barin et al. 1977 |
| 800.00 | -891.34 | 404.73 | -1215.13 | Barin et al. 1977 |
| 900.00 | -866.31 | 434.20 | -1257.09 | Barin et al. 1977 |
| 1000.00 | -839.73 | 462.19 | -1301.92 | Barin et al. 1977 |

TABLE 5.11
Ba(NO₃)₂ = BaO + 2 NO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|--------|-------------------------|---------|--------------|
| 298.15 | 504.71 | 439.10 | 373.797 | 3.213E - 066 |
| 400.00 | 502.47 | 432.70 | 329.388 | 9.610E - 044 |
| 500.00 | 499.16 | 425.37 | 286.478 | 1.173E - 030 |
| 600.00 | 494.77 | 417.38 | 244.336 | 5.332E - 022 |
| 700.00 | 489.26 | 408.93 | 203.017 | 7.070E - 016 |
| 800.00 | 482.64 | 400.092 | 162.563 | 2.426E - 011 |
| 900.00 | 474.09 | 390.95 | 123.009 | 7.247E - 008 |
| 1000.00 | 465.91 | 381.53 | 84.383 | 3.908E - 005 |

TABLE 5.12
Decomposition Pressures of Ba(NO₃)₂

| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|---------|-------------------------|--------------------------|--------------------|--------------------|
| 298.15 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 400.00 | 3.83E - 015 | <10 ⁻¹⁵ | 5.03E - 015 | 8.94E - 015 |
| 500.00 | 1.46E - 010 | 3.05E - 013 | 1.94E - 010 | 3.40E - 010 |
| 600.00 | 1.64E - 007 | 1.11E - 009 | 2.18E - 007 | 3.84E - 007 |
| 700.00 | 2.40E - 005 | 3.67E - 007 | 3.18E - 005 | 5.61E - 005 |
| 800.00 | 9.75E - 004 | 2.69E - 005 | 1.29E - 003 | 2.29E - 003 |
| 900.00 | 2.2E - 002 | 1.1E - 003 | 2.8E - 002 | 5.1E - 002 |
| 1000.00 | 0.15 | 9.1E - 003 | 0.20 | 0.36 |

TABLE 5.13
Thermodynamic Data of Be(NO₃)₂ at 298.15K

| | ΔHf° kJmol ⁻¹ | S° Jmol ⁻¹ | Reference |
|-----------------------------------|--------------------------|-----------------------|-----------|
| Be(NO ₃) ₂ | -602 ± 8 | 184 | 133 |
| BeO | -606.09 | 14.14 | 133 |

TABLE 5.14
Transitions of Cd(NO₃)₂

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------|------|-------------------|----------------------|-----------|
| c → l | 633 | 18.3 | 28.8 | 125 |

TABLE 5.15
Thermodynamic Data of Cd(NO₃)₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -456.96 | 207.95 | -518.95 | Knacke et al. 1991 |
| 400.00 | -438.63 | 260.82 | -542.96 | Knacke et al. 1991 |
| 500.00 | -415.40 | 312.73 | -571.77 | Knacke et al. 1991 |
| 600.00 | -394.06 | 351.63 | -605.04 | Knacke et al. 1991 |
| 700.00 | -372.73 | 384.53 | -641.89 | Knacke et al. 1991 |
| 800.00 | -351.39 | 413.02 | -681.80 | Knacke et al. 1991 |
| 900.00 | -330.05 | 438.15 | -724.39 | Knacke et al. 1991 |
| 1000.00 | -308.71 | 460.63 | -769.34 | Knacke et al. 1991 |

TABLE 5.16
Cd(NO₃)₂ = CdO + 2 NO₂(g) + 1/2 O₂

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 264.16 | 429.48 | 136.106 | 1.422E - 024 |
| 400.00 | 259.92 | 417.16 | 93.053 | 7.040E - 013 |
| 500.00 | 251.50 | 398.27 | 52.366 | 3.380E - 006 |
| 600.00 | 245.65 | 387.59 | 13.098 | 7.238E - 002 |
| 700.00 | 240.34 | 379.39 | -25.233 | 7.649E + 001 |
| 800.00 | 235.38 | 372.90 | -62.836 | 1.268E + 004 |

TABLE 5.17
Decomposition Pressures of Cd(NO₃)₂

| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|--------|-------------------------|--------------------------|-------------|-------------|
| 298.15 | 1.09E - 010 | 3.69E - 010 | 2.27E - 10 | 7.05E - 010 |
| 400.00 | 5.60E - 006 | 1.72E - 005 | 1.72E - 006 | 2.45E - 005 |
| 500.00 | 2.85E - 003 | 7.96E - 003 | 1.15E - 003 | 1.20E - 002 |
| 600.00 | 0.167 | 0.421 | 8.21E - 002 | 0.670 |
| 700.00 | 2.92 | 6.69 | 1.66 | 11.27 |

TABLE 5.18
Transitions of $\text{Ca}(\text{NO}_3)_2$

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|---|------|-------------------|----------------------|-----------|
| $\text{Ca}(\text{NO}_3)_2 \text{ s} \rightarrow \text{s}$ | 539 | | | 15 |
| $\text{s} \rightarrow \text{s}$ | 633 | | | 15 |
| $\text{s} \rightarrow \text{l}$ | 665 | | | 39 |
| $\text{Ca}(\text{NO}_3)_2 \text{ s} \rightarrow \text{l}$ | 834 | 23.4 | 28.1 | 120 |

TABLE 5.19
Thermodynamic Data of $\text{Ca}(\text{NO}_3)_2$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -938.39 | 193.30 | -966.03 | Knacke et al. 1991 |
| 400.00 | -921.88 | 240.78 | -1018.19 | Knacke et al. 1991 |
| 500.00 | -903.52 | 281.66 | -1044.35 | Knacke et al. 1991 |
| 600.00 | -883.34 | 318.41 | -1074.38 | Knacke et al. 1991 |
| 700.00 | -861.45 | 352.11 | -1107.93 | Knacke et al. 1991 |
| 800.00 | -837.92 | 383.51 | -1144.73 | Knacke et al. 1991 |
| 900.00 | -812.78 | 413.10 | -1184.57 | Knacke et al. 1991 |
| 1000.00 | -786.05 | 441.25 | -1227.30 | Knacke et al. 1991 |

TABLE 5.20
 $\text{Ca}(\text{NO}_3)_2 = \text{CaO} + 2 \text{NO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 369.49 | 427.39 | 242.068 | 3.866E - 043 |
| 400.00 | 367.07 | 420.26 | 198.881 | 1.063E - 026 |
| 500.00 | 363.57 | 412.71 | 157.216 | .753E - 017 |
| 600.00 | 358.94 | 404.30 | 116.361 | 7.397 - 011 |
| 700.00 | 353.15 | 395.40 | 76.372 | 1.998E - 006 |
| 800.00 | 346.16 | 386.08 | 37.295 | 3.670E - 003 |
| 900.00 | 337.95 | 376.43 | -0.833 | 1.118E + 000 |
| 1000.00 | 328.50 | 366.48 | -37.981 | 9.640E + 001 |

TABLE 5.21
Decomposition Pressures of $\text{Ca}(\text{NO}_3)_2$

| T K | P (O_2) bar | P (NO_2) bar | P (NO) bar | P (Tot) bar |
|--------|------------------------|-------------------------|--------------------|--------------------|
| 298.15 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 400.00 | 3.04E - 010 | 2.68E - 011 | 3.96E - 010 | 7.27E - 010 |
| 500.00 | 1.14E - 006 | 2.02E - 007 | 1.45E - 006 | 2.80E - 006 |
| 600.00 | 2.73E - 004 | 7.08E - 005 | 3.41E - 004 | 6.85E - 004 |
| 700.00 | 1.33E - 002 | 4.40E - 003 | 1.62E - 002 | 3.39E - 002 |
| 800.00 | 0.235 | 9.16E - 002 | 0.283 | 0.609 |

TABLE 5.22
Density of CsNO₂

| Phase | T(K) | d (gcm ⁻³) | Reference |
|--------|------|------------------------|-----------|
| Liquid | 681 | 2.844 | 106 |
| | 691 | 2.835 | 106 |
| | 701 | 2.826 | 106 |
| | 711 | 2.815 | 106 |
| | 721 | 2.805 | 106 |
| | 732 | 2.793 | 106 |
| | 742 | 2.783 | 106 |
| | 752 | 2.772 | 106 |

TABLE 5.23
Density of CsNO₃

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| c | 293 | 3.643 | 107 |
| l | 690 | 2.8160 | 69 |
| | 700 | 2.8044 | 69 |
| | 710 | 2.7927 | 69 |
| | 720 | 2.7810 | 69 |
| | 730 | 2.7694 | 69 |
| | 740 | 2.7577 | 69 |
| | 750 | 2.7461 | 69 |
| | 760 | 2.734 | 69 |

TABLE 5.24
Transitions of CsNO₂ and CsNO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|-------------------------------------|------|-----------|--------------|-----------|
| CsNO ₂ s → l | 679 | | | 134 |
| CsNO ₃ hexagonal → cubic | 425 | 3.7 | 8.7 | 134 |
| cubic → l | 679 | 14.1 | 20.8 | 134 |
| s → g | 298 | 28.2 | | 38 |

TABLE 5.25
Thermodynamic Data of CsNO₂

| T K | ΔH ^o kJ mol ⁻¹ | S ^o J mol ⁻¹ deg ⁻¹ | ΔG ^o kJ mol ⁻¹ | Reference |
|---------|---|---|---|--------------------|
| 298.15 | -369.45 | 181.17 | -423.46 | Knacke et al. 1991 |
| 400.00 | -360.10 | 208.13 | -443.35 | Knacke et al. 1991 |
| 500.00 | -350.93 | 228.61 | -465.23 | Knacke et al. 1991 |
| 600.00 | -341.75 | 245.33 | -488.95 | Knacke et al. 1991 |
| 700.00 | -332.58 | 259.48 | -514.21 | Knacke et al. 1991 |
| 800.00 | -323.40 | 271.73 | -540.78 | Knacke et al. 1991 |
| 900.00 | -314.22 | 282.54 | -568.51 | Knacke et al. 1991 |
| 1000.00 | -305.05 | 292.21 | -597.25 | Knacke et al. 1991 |

TABLE 5.26
Thermodynamic Data of CsNO₃

| T K | ΔH° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -505.85 | 153.72 | -551.68 | Knacke et al. 1991 |
| 400.00 | -495.53 | 183.41 | -568.89 | Knacke et al. 1991 |
| 500.00 | -479.59 | 219.32 | -589.25 | Knacke et al. 1991 |
| 600.00 | -466.96 | 242.35 | -612.37 | Knacke et al. 1991 |
| 700.00 | -440.11 | 282.72 | -638.02 | Knacke et al. 1991 |
| 800.00 | -426.52 | 300.88 | -667.22 | Knacke et al. 1991 |
| 900.00 | -412.92 | 316.90 | -698.12 | Knacke et al. 1991 |
| 1000.00 | -399.32 | 331.22 | -730.54 | Knacke et al. 1991 |

TABLE 5.27
2 CsNO₃ = Cs₂O + 2 NO₂(g) + 1/2 O₂

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 731.91 | 422.03 | 606.076 | 6.443E - 107 |
| 400.00 | 728.65 | 412.70 | 563.567 | 2.510E - 075 |
| 500.00 | 714.94 | 381.37 | 524.250 | 1.688E - 055 |
| 600.00 | 708.68 | 369.95 | 486.714 | 4.209E - 043 |
| 700.00 | 674.77 | 319.68 | 450.994 | 2.206E - 034 |
| 800.00 | 668.05 | 310.69 | 419.493 | 4.052E - 028 |
| 900.00 | 661.97 | 303.53 | 388.80 | 2.710E - 023 |
| 1000.00 | 656.50 | 297.76 | 358.74 | 1.818E - 019 |

TABLE 5.28
CsNO₃ = CsNO₂ + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 136.40 | 130.02 | 97.632 | 7.830E - 018 |
| 400.00 | 136.95 | 131.70 | 84.275 | 9.862E - 012 |
| 500.00 | 131.77 | 119.78 | 71.880 | 3.091E - 008 |
| 600.00 | 129.93 | 116.42 | 60.076 | 5.882E - 006 |
| 700.00 | 113.91 | 92.73 | 48.993 | 2.207E - 004 |
| 800.00 | 111.16 | 89.06 | 39.908 | 2.478E - 003 |
| 900.00 | 108.43 | 85.85 | 31.165 | 1.553E - 002 |
| 1000.00 | 105.73 | 83.00 | 22.725 | 6.499E - 002 |

TABLE 5.29
Decomposition Pressures of CsNO₃

| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|---------|-------------------------|--------------------------|--------------------|--------------------|
| 298.15 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 400.00 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 500.00 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 600.00 | 1.56E – 013 | <10 ⁻¹⁵ | 2.08E – 013 | 3.62E – 013 |
| 700.00 | 1.26E – 010 | 4.45E – 015 | 1.68E – 010 | 2.94E – 010 |
| 800.00 | 1.59E – 008 | 1.79E – 010 | 2.12E – 008 | 3.73E – 008 |
| 900.00 | 6.65E – 007 | 1.82E – 010 | 8.86E – 007 | 1.55E – 006 |
| 1000.00 | 1.29E – 005 | 7.13E – 009 | 1.71E – 005 | 3.01E – 005 |

TABLE 5.30
Thermodynamic Data of Co(NO₃)₂

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|--------|------------------------------|---|------------------------------|--------------------|
| 298.15 | –421.55 | 176.98 | –474.31 | Knacke et al. 1991 |
| 400.00 | –405.15 | 224.24 | –494.84 | Knacke et al. 1991 |
| 500.00 | –388.20 | 262.01 | –519.21 | Knacke et al. 1991 |
| 600.00 | –370.42 | 294.41 | –547.07 | Knacke et al. 1991 |
| 700.00 | –351.80 | 323.10 | –577.97 | Knacke et al. 1991 |

TABLE 5.31
Co(NO₃)₂ = Co + 2 NO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|--------|-------------------------|--------|--------------|
| 298.15 | 249.79 | 458.60 | 113.06 | 1.550E – 20 |
| 400.00 | 248.39 | 454.55 | 66.57 | 2.024E – 009 |
| 500.00 | 246.86 | 451.15 | 21.29 | 5.971E – 003 |
| 600.00 | 245.03 | 447.81 | –23.66 | 1.148E + 002 |
| 700.00 | 242.81 | 444.41 | –68.27 | 1.245E + 010 |

TABLE 5.32
Transitions of CuNO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol*K) | Reference |
|--------------|---------|-----------|--------------|-----------|
| c → l | 528 | | | 48 |
| c → g | 453–493 | 65.3 | 87.0 | 48 |

TABLE 5.33
Thermodynamic Data of Cu(NO₃)₂ (298.15 K)

| | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-----------------------------------|--|--|-----------|
| Cu(NO ₃) ₂ | -302.9 | 193.3 | 71, 133 |
| Cu ₂ O | -168.6 | 93.14 | 133 |
| CuO | -157.3 | 42.64 | 133 |

TABLE 5.34
Thermodynamic Data of Ga(NO₃)₂ (298.15 K)

| | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-----------------------------------|--|--|-----------|
| Ga(NO ₃) ₂ | -619 ± 17 | | 51 |
| GaO(g) | 279 | 231 | 133 |
| Ga ₂ O ₃ | -1089 | 84.98 | 133 |

TABLE 5.35
Thermodynamic Data of In(NO₃)₃

| | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-----------------------------------|--|--|-----------|
| In(NO ₃) ₃ | -632 | | 51 |
| In ₂ O ₃ | 925.79 | 104 | 133 |

TABLE 5.36
Thermodynamic Data of Pb(NO₃)₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|--------------------|
| 298.15 | -456.85 | 224.68 | -523.84 | Knacke et al. 1991 |
| 400.00 | -440.14 | 272.72 | -549.23 | Knacke et al. 1991 |
| 500.00 | -421.66 | 313.88 | -578.60 | Knacke et al. 1991 |
| 600.00 | -401.41 | 350.75 | -611.86 | Knacke et al. 1991 |
| 700.00 | -379.51 | 384.48 | -648.64 | Knacke et al. 1991 |
| 800.00 | -356.01 | 415.84 | -688.68 | Knacke et al. 1991 |

TABLE 5.37
Pb(NO₃)₂ = PbO + 2 NO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 304.97 | 426.63 | 177.774 | 7.115E - 032 |
| 400.00 | 302.55 | 419.71 | 134.663 | 2.590E - 018 |
| 500.00 | 299.06 | 411.98 | 93.073 | 1.888E - 010 |
| 600.00 | 294.52 | 403.72 | 52.285 | 2.804E - 005 |
| 700.00 | 288.90 | 395.09 | 12.342 | 1.199E - 001 |
| 800.00 | 282.28 | 386.16 | -26.723 | 5.559E + 001 |

TABLE 5.38
Decomposition Pressures of $\text{Pb}(\text{NO}_3)_2$

| T K | P (O_2) bar | P (NO_2) bar | P (NO) bar | P (Tot) bar |
|---------|------------------------|-------------------------|-----------------------|-------------|
| 298.15 | 3.63E – 013 | 3.44E – 013 | 3.68E – 013 | 1.08E – 012 |
| 400.00 | 8.24E – 008 | 9.50E – 008 | 7.82E – 008 | 2.56E – 007 |
| 500.00 | 1.08E – 004 | 1.35E – 004 | 9.95E – 005 | 3.42E – 004 |
| 600.00 | 1.24E – 002 | 1.58E – 003 | 1.13E – 002 | 2.53E – 003 |
| 700.00 | 0.120 | 0.353 | 0.449 | 0.922 |
| 800.00 | 55.6 | 4.17 | 5.22 | 64.99 |
| 900.00 | 27.3 | 33.4 | 25.3 | 86.0 |
| 1000.00 | 118. | 140.8 | 111.4 | 370.2 |

TABLE 5.39
Density of LiNO_2

| Phase | T(K) | d (gcm^{-3}) | Reference |
|-------|------|-------------------------|-----------|
| I | 493 | 1.638 | 67 |
| | 498 | 1.636 | 67 |
| | 503 | 1.632 | 67 |
| | 512 | 1.629 | 67 |
| | 518 | 1.626 | 67 |
| | 532 | 1.620 | 67 |
| | 543 | 1.615 | 67 |

TABLE 5.40
Density of LiNO_3

| Phase | T(K) | d (gcm^{-3}) | Reference |
|-------|------|-------------------------|-----------|
| c | 293 | 2.366 | 68 |
| I | 550 | 1.768 | 68 |
| | 560 | 1.762 | 68 |
| | 570 | 1.757 | 68 |
| | 580 | 1.751 | 68 |
| | 590 | 1.746 | 68 |
| | 600 | 1.740 | 68 |
| | 610 | 1.735 | 68 |
| | 620 | 1.729 | 68 |
| | 630 | 1.724 | 68 |
| | 640 | 1.719 | 68 |
| | 650 | 1.713 | 68 |
| | 660 | 1.708 | 68 |
| | 670 | 1.702 | 68 |
| | 680 | 1.697 | 68 |
| | 690 | 1.691 | 68 |

TABLE 5.41
Transitions of LiNO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|-------------------------|------|-------------------|----------------------|-----------|
| LiNO ₂ c → l | 493 | | | 69 |
| LiNO ₃ c → l | 526 | 26.7 | 50.8 | 70 |

TABLE 5.42
Thermodynamic Data of LiNO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|---|--|--------------------|
| 298.15 | -483.13 | 90.00 | -509.96 | Knacke et al. 1991 |
| 400.00 | -473.59 | 117.46 | -520.58 | Knacke et al. 1991 |
| 500.00 | -463.33 | 140.31 | -533.49 | Knacke et al. 1991 |
| 600.00 | -426.35 | 209.76 | -552.20 | Knacke et al. 1991 |
| 700.00 | -415.22 | 226.92 | -574.06 | Knacke et al. 1991 |
| 800.00 | -404.09 | 241.78 | -597.51 | Knacke et al. 1991 |
| 900.00 | -392.96 | 254.89 | -622.36 | Knacke et al. 1991 |
| 1000.00 | -381.83 | 266.61 | -548.44 | Knacke et al. 1991 |

TABLE 5.43
2 LiNO₃ = Li₂O + 2 NO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | $\Delta\Delta S^\circ$ J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|---|---------------------|--------------|
| 298.15 | 433.72 | 440.50 | 302.385 | 1.045E - 053 |
| 400.00 | 430.21 | 430.35 | 258.069 | 1.918E - 034 |
| 500.00 | 426.54 | 422.19 | 215.447 | 3.094E - 023 |
| 600.00 | 370.45 | 315.87 | 180.926 | 1.769E - 016 |
| 700.00 | 366.86 | 310.32 | 149.633 | 6.812E - 012 |
| 800.00 | 363.92 | 306.39 | 118.809 | 1.745E - 008 |
| 900.00 | 361.56 | 303.60 | 88.318 | 7.477E - 006 |
| 1000.00 | 359.70 | 301.64 | 58.062 | 9.266E - 004 |

TABLE 5.44
Decomposition Pressures of LiNO₃

| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|---------|-------------------------|--------------------------|--------------------|--------------------|
| 298.15 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 400.00 | 1.69E - 012 | 1.23E - 014 | 2.25E - 012 | 3.95E - 012 |
| 500.00 | 1.95E - 008 | 4.70E - 010 | 2.59E - 008 | 4.59E - 008 |
| 600.00 | 6.35E - 006 | 2.65E - 007 | 8.38E - 006 | 1.54E - 005 |
| 700.00 | 3.38E - 004 | 1.92E - 005 | 4.44E - 004 | 8.01E - 004 |
| 800.00 | 6.56E - 003 | 4.65E - 004 | 8.59E - 003 | 1.56E - 002 |
| 900.00 | 6.47E - 002 | 5.42E - 003 | 8.45E - 002 | 0.155 |
| 1000.00 | 0.401 | 3.83E - 002 | 0.521 | 0.960 |

TABLE 5.45
Thermodynamic Data of $\text{Mg}(\text{NO}_3)_2$

| T K | ΔH° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG° kJ mol ⁻¹ | Reference |
|--------|--|---|--|------------|
| 298.15 | -790.65 | 164.00 | -839.55 | Barin 1989 |
| 400.00 | -774.87 | 209.35 | -858.61 | Barin 1989 |
| 500.00 | -756.62 | 243.95 | -881.59 | Barin 1989 |
| 600.00 | -735.52 | 288.34 | -908.52 | Barin 1989 |
| 700.00 | -711.51 | 325.39 | -939.22 | Barin 1989 |
| 800.00 | -684.56 | 361.23 | -973.55 | Barin 1989 |

TABLE 5.46
 $\text{Mg}(\text{NO}_3)_2 = \text{MgO} + 2 \text{NO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------------|--|---------------------------|--------------|
| 298.15 | 255.60 | 445.54 | 122.762 | 3.096E - 022 |
| 400.00 | 253.39 | 439.25 | 77.692 | 7.140E - 011 |
| 500.00 | 249.63 | 430.93 | 34.162 | 2.696E - 004 |
| 600.00 | 243.77 | 420.31 | -8.418 | 5.406E + 000 |
| 700.00 | 235.58 | 407.73 | -49.835 | 5.237E + 003 |
| 800.00 | 224.92 | 393.54 | -89.911 | 7.431E + 005 |

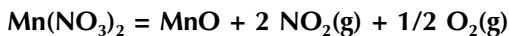
TABLE 5.47
Decomposition Pressures of $\text{Mg}(\text{NO}_3)_2$

| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|---------|-------------------------|--------------------------|-------------|-------------|
| 298.15 | 8.65E - 010 | 3.25E - 009 | 7.10E - 011 | 3.25E - 005 |
| 400.00 | 3.17E - 005 | 1.13E - 004 | 4.73E - 006 | 1.49E - 004 |
| 500.00 | 2.70E - 004 | 1.42E - 002 | 4.76E - 002 | 6.21E - 002 |
| 600.00 | 0.784 | 2.47 | 0.222 | 3.48 |
| 700.00 | 12.95 | 38.27 | 4.51 | 55.73 |
| 800.00 | 99.1 | 273.2 | 41.1 | 413.4 |
| 900.00 | 452.6 | 1160 | 216.3 | 1830 |
| 1000.00 | 1440 | 3410 | 776.3 | 5626 |

TABLE 5.48
Thermodynamic Data of $\text{Mn}(\text{NO}_3)_2$

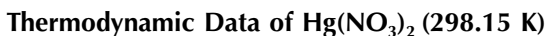
| T K | ΔH° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG° kJ mol ⁻¹ | Reference |
|--------|--|---|--|-----------|
| 298.15 | -576.30 | 168.62 | -626.57 | CRC 1994 |
| 400.00 | -576.30 | 168.62 | -643.75 | CRC 1994 |
| 500.00 | -576.30 | 168.62 | -660.61 | CRC 1994 |
| 600.00 | -576.30 | 168.62 | -677.47 | CRC 1994 |
| 700.00 | -576.30 | 168.62 | -694.33 | CRC 1994 |

TABLE 5.49



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 257.27 | 473.71 | 116.03 | 4.673E – 021 |
| 400.00 | 271.45 | 514.52 | 65.64 | 2.679E – 009 |
| 500.00 | 286.32 | 547.67 | 12.48 | 4.966E – 002 |
| 600.00 | 301.87 | 576.00 | –43.737 | 6.427E + 003 |
| 700.00 | 317.96 | 600.80 | –102.60 | 4.539E + 007 |

TABLE 5.50



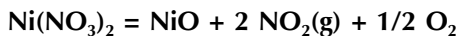
| | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-----------------------------------|--|--|-----------|
| Hg(NO ₃) ₂ | –285 + 17 | 230 + 8 | 25 |
| HgO(red) | –90.83 | 70.29 | 133 |

TABLE 5.51



| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|-----------------------|
| 298.15 | –415.00 | 192.05 | –472.26 | Fabricius et al. 1994 |
| 400.00 | –415.00 | 192.05 | –491.82 | Fabricius et al. 1994 |
| 500.00 | –415.00 | 192.05 | –511.02 | Fabricius et al. 1994 |
| 600.00 | –415.00 | 192.05 | –530.23 | Fabricius et al. 1994 |
| 700.00 | –415.00 | 192.00 | –549.43 | Fabricius et al. 1994 |

TABLE 5.52



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 241.49 | 428.56 | 113.71 | 1.192E – 020 |
| 400.00 | 255.87 | 469.92 | 67.90 | 1.358E – 009 |
| 500.00 | 271.62 | 505.00 | 19.12 | 1.005E – 002 |
| 600.00 | 288.10 | 535.08 | –32.95 | 7.388E + 002 |
| 700.00 | 304.40 | 560.20 | –87.74 | 3.530E + 006 |

TABLE 5.53



| | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-----------------------------------|--|--|-----------|
| Pd(NO ₃) ₂ | –238 ± 17 | — | 25 |
| PdO | –85.4 | — | 133 |

TABLE 5.54
Density of KNO₂

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| I | 710 | 1.797 | 69 |
| | 720 | 1.692 | 69 |
| | 730 | 1.685 | 69 |
| | 740 | 1.679 | 69 |
| | 750 | 1.672 | 69 |

TABLE 5.55
Density of KNO₃

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| I | 700 | 1.805 | 69 |
| | 710 | 1.797 | 69 |
| | 720 | 1.790 | 69 |
| | 730 | 1.783 | 69 |
| | 740 | 1.776 | 69 |
| | 750 | 1.768 | 69 |
| | 760 | 1.761 | 69 |
| | 770 | 1.754 | 69 |
| | 780 | 1.746 | 69 |
| | 790 | 1.739 | 69 |
| | 800 | 1.732 | 69 |
| | 810 | 1.725 | 69 |
| | 820 | 1.717 | 69 |
| | 830 | 1.710 | 69 |
| | 840 | 1.703 | 69 |
| | 850 | 1.695 | 69 |
| | 860 | 1.688 | 69 |
| | 870 | 1.681 | 69 |

TABLE 5.56
Transitions of KNO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|---|------|-------------------|----------------------|-----------|
| KNO ₂ , c → I | 713 | | | 135 |
| KNO ₃ III, rhombohedral → II, orthorhombic | 386 | 2.34 | 6.1 | 91 |
| II → I | 401 | 5.42 | 13.3 | 91 |
| I → liquid | 607 | 9.62 | 15.8 | 70 |

TABLE 5.57
Thermodynamic Data of KNO₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -359.18 | 152.09 | -415.16 | Knacke et al. 1991 |
| 400.00 | -359.18 | 182.82 | -432.30 | Knacke et al. 1991 |
| 500.00 | -348.62 | 206.35 | -451.80 | Knacke et al. 1991 |
| 600.00 | -337.46 | 226.68 | -473.47 | Knacke et al. 1991 |
| 700.00 | -325.49 | 245.12 | -497.07 | Knacke et al. 1991 |
| 800.00 | -312.59 | 262.33 | -522.45 | Knacke et al. 1991 |
| 900.00 | -298.71 | 278.67 | -549.51 | Knacke et al. 1991 |
| 1000.00 | -283.81 | 294.36 | -578.17 | Knacke et al. 1991 |

TABLE 5.58
Thermodynamic Data of KNO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -496.63 | 133.05 | -534.30 | Knacke et al. 1991 |
| 400.00 | -484.19 | 163.07 | -549.42 | Knacke et al. 1991 |
| 500.00 | -467.05 | 202.64 | -568.38 | Knacke et al. 1991 |
| 600.00 | -455.00 | 224.62 | -589.77 | Knacke et al. 1991 |
| 700.00 | -433.06 | 259.44 | -614.67 | Knacke et al. 1991 |
| 800.00 | -420.73 | 275.91 | -641.46 | Knacke et al. 1991 |
| 900.00 | -408.39 | 290.45 | -669.79 | Knacke et al. 1991 |
| 1000.00 | -396.05 | 303.45 | -699.49 | Knacke et al. 1991 |

TABLE 5.59
2 KNO₃ = K₂O + 2 NO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 693.95 | 418.52 | 569.167 | 1.888E - 100 |
| 400.00 | 690.38 | 408.31 | 527.061 | 1.469E - 069 |
| 500.00 | 674.22 | 369.54 | 489.449 | 7.301E - 052 |
| 600.00 | 669.04 | 360.07 | 452.994 | 3.632E - 040 |
| 700.00 | 644.73 | 320.58 | 420.319 | 4.294E - 032 |
| 800.00 | 640.19 | 314.52 | 388.576 | 4.231E - 026 |
| 900.00 | 636.17 | 309.77 | 357.371 | 1.807E - 021 |
| 1000.00 | 632.61 | 306.02 | 326.589 | 8.696E - 018 |

TABLE 5.60
 $\text{KNO}_3 = \text{KNO}_2 + 1/2 \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 124.81 | 121.61 | 88.551 | 3.055E – 016 |
| 400.00 | 126.55 | 126.73 | 75.855 | 1.240E – 010 |
| 500.00 | 121.53 | 114.19 | 64.437 | 1.853E – 007 |
| 600.00 | 122.26 | 115.59 | 52.962 | 2.448E – 005 |
| 700.00 | 113.94 | 101.66 | 42.784 | 6.415E – 004 |
| 800.00 | 116.18 | 104.63 | 32.477 | 7.573E – 003 |
| 900.00 | 119.42 | 108.44 | 21.830 | 5.407E – 002 |
| 1000.00 | 123.70 | 112.94 | 10.766 | 2.739E – 001 |

TABLE 5.61
 Decomposition Pressures of KNO_3

| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|---------|-------------------------|--------------------------|--------------------|--------------------|
| 298.15 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 400.00 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 500.00 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 600.00 | 1.08E – 012 | <10 ⁻¹⁵ | 1.43E – 012 | 2.51E – 012 |
| 700.00 | 5.67E – 010 | 4.24E – 014 | 7.56E – 010 | 1.33E – 009 |
| 800.00 | 6.01E – 008 | 1.31E – 011 | 8.02E – 008 | 1.40E – 007 |
| 900.00 | 2.21E – 006 | 1.10E – 009 | 2.94E – 006 | 5.16E – 006 |
| 1000.00 | 3.88E – 005 | 3.74E – 008 | 5.17E – 005 | 9.05E – 005 |

TABLE 5.62
 Thermodynamic Data of $\text{Ra}(\text{NO}_3)_2$

| | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|----------------------------|--|--|-----------|
| $\text{Ra}(\text{NO}_3)_2$ | –992 | 222 | 133 |
| RaO | –523 | — | 133 |

TABLE 5.63
 Density of RbNO_2

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| 1 | 696 | 2.347 | 106 |
| | 706 | 2.339 | 106 |
| | 715 | 2.333 | 106 |
| | 726 | 2.322 | 106 |
| | 734 | 2.316 | 106 |
| | 745 | 2.306 | 106 |
| | 755 | 2.299 | 106 |
| | 759 | 2.295 | 106 |

TABLE 5.64
Density of RbNO₃

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| c | 293 | 3.112 | 23 |
| I | 590 | 2.476 | 69 |
| | 600 | 2.466 | 69 |
| | 610 | 2.456 | 69 |
| | 620 | 2.446 | 69 |
| | 630 | 2.437 | 69 |
| | 640 | 2.427 | 69 |
| | 650 | 2.417 | 69 |
| | 660 | 2.407 | 69 |
| | 670 | 2.398 | 69 |
| | 680 | 2.388 | 69 |

TABLE 5.65
Transitions of RbNO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--------------------------|------|-------------------|----------------------|-----------|
| rhombic(IV) → cubic(III) | 433 | 3.90 | 9.00 | 104 |
| III → trigonal(II) | 488 | 3.21 | 6.58 | 104 |
| II → I | 554 | 0.96 | 1.74 | 104 |
| I → I | 583 | 4.64 | 7.96 | 104 |

TABLE 5.66
Thermodynamic Data of RbNO₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------|
| 298.15 | -367.00 | 162.00 | -415.30 | Gurvich 1990 |
| 400.00 | -358.30 | 187.08 | -433.13 | Gurvich 1990 |
| 500.00 | -349.48 | 206.75 | -452.86 | Gurvich 1990 |
| 600.00 | -340.38 | 223.33 | -474.38 | Gurvich 1990 |
| 700.00 | -318.86 | 255.25 | -497.54 | Gurvich 1990 |
| 800.00 | -308.46 | 269.14 | -523.77 | Gurvich 1990 |
| 900.00 | -298.06 | 281.39 | -551.31 | Gurvich 1990 |
| 1000.00 | -287.66 | 292.35 | -580.01 | Gurvich 1990 |

TABLE 5.67
Thermodynamic Data of RbNO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------|
| 298.15 | -494.70 | 144.90 | -537.90 | Gurvich 1990 |
| 400.00 | -484.03 | 175.60 | -554.26 | Gurvich 1990 |
| 500.00 | -467.79 | 211.96 | -573.77 | Gurvich 1990 |
| 600.00 | -447.78 | 244.40 | -594.42 | Gurvich 1990 |
| 700.00 | -433.18 | 266.91 | -620.02 | Gurvich 1990 |
| 800.00 | -418.58 | 286.40 | -647.71 | Gurvich 1990 |
| 900.00 | -403.98 | 303.60 | -677.22 | Gurvich 1990 |
| 1000.00 | -389.38 | 318.98 | -708.37 | Gurvich 1990 |

TABLE 5.68
2 RbNO₃ = Rb₂O + 2 NO₂(g) + 1/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 716.59 | 418.33 | 591.86 | 1.992E - 104 |
| 400.00 | 712.43 | 406.43 | 549.86 | 1.550E - 071 |
| 500.00 | 697.91 | 373.74 | 511.04 | 4.049E - 054 |
| 600.00 | 677.56 | 344.68 | 470.75 | 1.034E - 041 |
| 700.00 | 672.13 | 336.67 | 436.46 | 2.683E - 033 |
| 800.00 | 684.17 | 351.69 | 402.81 | 4.976E - 027 |
| 900.00 | 675.85 | 341.90 | 368.14 | 4.282E - 022 |
| 1000.00 | 667.82 | 333.43 | 334.39 | 3.403E - 018 |

TABLE 5.69
Density of AgNO₃

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| 1 | 490 | 3.954 | 69 |
| | 500 | 3.954 | 69 |
| | 510 | 3.934 | 69 |
| | 520 | 3.924 | 69 |
| | 530 | 3.913 | 69 |
| | 540 | 3.903 | 69 |
| | 550 | 3.893 | 69 |
| | 560 | 3.888 | 69 |
| | 570 | 3.873 | 69 |
| | 580 | 3.862 | 69 |
| | 590 | 3.852 | 69 |
| | 600 | 3.842 | 69 |

TABLE 5.70
Transitions of AgNO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--|------|-------------------|----------------------|-----------|
| c, α (orthorhombic) \rightarrow C, β (rhombohedral) | 433 | 2.4 | 5.5 | 136 |
| c, $\beta \rightarrow 1$ | 483 | 12.49 | 25.9 | 137 |

TABLE 5.71
Thermodynamic Data of AgNO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|------------|
| 298.15 | -124.39 | 140.63 | -166.32 | Barin 1993 |
| 400.00 | -113.93 | 170.66 | -182.20 | Barin 1993 |
| 500.00 | -87.57 | 227.73 | -201.43 | Barin 1993 |
| 600.00 | -74.77 | 251.07 | -225.41 | Barin 1993 |
| 700.00 | -61.96 | 270.80 | -251.53 | Barin 1993 |
| 800.00 | -49.16 | 287.90 | -287.90 | Barin 1993 |

TABLE 5.72
 $2 \text{ AgNO}_3 = \text{Ag}_2\text{O} + 2 \text{ NO}_2(\text{g}) + 1/2 \text{ O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 283.92 | 422.66 | 157.906 | 2.154E - 028 |
| 400.00 | 279.51 | 410.10 | 115.472 | 8.310E - 016 |
| 500.00 | 244.30 | 335.01 | 76.798 | 9.470E - 009 |
| 600.00 | 237.21 | 322.06 | 43.978 | 1.483E - 004 |
| 700.00 | 231.00 | 312.47 | 12.275 | 1.213E - 001 |
| 800.00 | 225.59 | 305.23 | -18.594 | 1.637E + 001 |

TABLE 5.73
 $2 \text{ AgNO}_3 = 2 \text{ Ag} + 2 \text{ NO}_2(\text{g}) + \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 314.97 | 489.29 | 169.090 | 2.364E - 030 |
| 400.00 | 310.27 | 475.91 | 119.902 | 2.193E - 016 |
| 500.00 | 274.38 | 399.32 | 74.718 | 1.562E - 008 |
| 600.00 | 266.29 | 384.56 | 35.556 | 8.023E - 004 |
| 700.00 | 258.78 | 372.97 | -2.299 | 1.484E + 000 |
| 800.00 | 251.80 | 363.64 | -39.114 | 3.582E + 002 |

TABLE 5.74
Density of NaNO₂

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| c | 293 | 2.266 | 115 |
| l | 570 | 1.801 | 69 |
| | 580 | 1.793 | 69 |
| | 590 | 1.786 | 69 |
| | 600 | 1.778 | 69 |
| | 610 | 1.771 | 69 |
| | 620 | 1.763 | 69 |
| | 630 | 1.756 | 69 |
| | 640 | 1.749 | 69 |
| | 650 | 1.741 | 69 |
| | 660 | 1.734 | 69 |
| | 670 | 1.726 | 69 |
| | 680 | 1.719 | 69 |
| | 690 | 1.711 | 69 |
| | 700 | 1.704 | 69 |
| | 710 | 1.696 | 69 |
| | 720 | 1.686 | 69 |

TABLE 5.75
Density of NaNO₃

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| l | 570 | 1.898 | 69 |
| | 580 | 1.891 | 69 |
| | 590 | 1.884 | 69 |
| | 600 | 1.877 | 69 |
| | 610 | 1.870 | 69 |
| | 620 | 1.862 | 69 |
| | 630 | 1.855 | 69 |
| | 640 | 1.848 | 69 |
| | 650 | 1.841 | 69 |
| | 660 | 1.834 | 69 |
| | 670 | 1.827 | 69 |
| | 680 | 1.820 | 69 |

TABLE 5.76
Transitions of NaNO₃

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol ^o K) | Reference |
|--|------|-------------------|-----------------------------------|-----------|
| NaNO ₂ , c \rightarrow l | 554 | 10.4 | 18.8 | 138 |
| NaNO ₃ , c,II \rightarrow c,I | 548 | 3.95 | 7.21 | 139 |
| c,I \rightarrow l | 579 | 15.5 | 26.8 | 70, 120 |

TABLE 5.77
Thermodynamic Data of NaNO₂

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -358.99 | 121.34 | -395.16 | Barin 1993 |
| 400.00 | -350.94 | 144.42 | -408.70 | Barin 1993 |
| 500.00 | -341.05 | 166.39 | -424.25 | Barin 1993 |
| 600.00 | -314.39 | 214.55 | -443.12 | Barin 1993 |
| 700.00 | -302.26 | 233.26 | -465.53 | Barin 1993 |
| 800.00 | -290.12 | 249.46 | -489.69 | Barin 1993 |
| 900.00 | -277.99 | 263.75 | -515.36 | Barin 1993 |
| 1000.00 | -265.85 | 276.53 | -542.39 | Barin 1993 |

TABLE 5.78
Thermodynamic Data of NaNO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -467.98 | 116.32 | -502.66 | Barin 1989 |
| 400.00 | -457.33 | 146.87 | -516.08 | Barin 1989 |
| 500.00 | -444.60 | 175.19 | -532.20 | Barin 1989 |
| 600.00 | -414.96 | 227.92 | -551.71 | Barin 1989 |
| 700.00 | -399.40 | 251.90 | -575.74 | Barin 1989 |
| 800.00 | -383.84 | 272.68 | -601.99 | Barin 1989 |
| 900.00 | -368.28 | 291.01 | -630.19 | Barin 1989 |
| 1000.00 | -352.72 | 307.40 | -660.13 | Barin 1989 |

TABLE 5.79
2 NaNO₂ = Na₂O + N₂(g) + 3/2 O₂(g)

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 299.99 | 331.70 | 201.096 | 5.833E - 036 |
| 400.00 | 298.89 | 328.72 | 167.398 | 1.375E - 022 |
| 500.00 | 294.68 | 319.47 | 134.945 | 7.965E - 015 |
| 600.00 | 257.51 | 252.60 | 105.952 | 5.961E - 010 |
| 700.00 | 249.92 | 240.89 | 81.298 | 8.570E - 007 |
| 800.00 | 242.76 | 231.32 | 57.703 | 1.706E - 004 |
| 900.00 | 235.98 | 223.34 | 34.981 | 9.324E - 003 |
| 1000.00 | 229.54 | 216.54 | 12.996 | 2.095E - 001 |

TABLE 5.80
 $\text{NaNO}_3 = \text{NaNO}_2 + 1/2 \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 108.99 | 107.60 | 76.914 | 3.341E – 014 |
| 400.00 | 107.92 | 104.53 | 66.114 | 2.321E – 009 |
| 500.00 | 106.65 | 101.68 | 55.804 | 1.478E – 006 |
| 600.00 | 105.29 | 100.07 | 45.253 | 1.148E – 004 |
| 700.00 | 103.52 | 97.33 | 35.387 | 2.286E – 003 |
| 800.00 | 101.76 | 94.99 | 25.774 | 2.075E – 002 |
| 900.00 | 100.04 | 92.95 | 16.380 | 1.120E – 001 |
| 1000.00 | 98.33 | 91.15 | 7.176 | 4.218E – 001 |

TABLE 5.81
 $2 \text{NaNO}_3 = \text{Na}_2\text{O} + 2 \text{NO}_2(\text{g}) + 1/2 \text{O}_2(\text{g})$

| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 584.17 | 425.02 | 457.447 | 7.087E – 081 |
| 400.00 | 579.77 | 412.55 | 414.752 | 6.829E – 055 |
| 500.00 | 572.25 | 395.90 | 374.298 | 7.837E – 040 |
| 600.00 | 531.89 | 324.81 | 336.994 | 4.613E – 030 |
| 700.00 | 520.46 | 307.27 | 305.367 | 1.627E – 023 |
| 800.00 | 509.68 | 292.87 | 275.383 | 1.042E – 018 |
| 900.00 | 499.45 | 280.82 | 246.716 | 4.784E – 015 |
| 1000.00 | 489.72 | 270.56 | 219.16 | 3.559E – 012 |

TABLE 5.82
Decomposition Pressures of NaNO_3

| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|---------|-------------------------|--------------------------|--------------------|--------------------|
| 298.15 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 400.00 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 500.00 | 3.53E – 013 | <10 ⁻¹⁵ | 4.70E – 013 | 8.23E – 013 |
| 600.00 | 8.30E – 010 | 4.00E – 013 | 1.11E – 009 | 1.94E – 009 |
| 700.00 | 1.60E – 007 | 2.02E – 010 | 2.14E – 007 | 3.74E – 007 |
| 800.00 | 7.78E – 006 | 1.93E – 008 | 1.04E – 005 | 1.82E – 005 |
| 900.00 | 1.51E – 004 | 6.24E – 007 | 2.01E – 004 | 3.52E – 004 |
| 1000.00 | 1.56E – 003 | 9.50E – 006 | 2.07E – 003 | 3.63E – 003 |

TABLE 5.83
Transitions of $\text{Sr}(\text{NO}_3)_2$

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|---|------|-------------------|----------------------|-----------|
| $\text{Sr}(\text{NO}_3)_2 \gamma \rightarrow \beta$ | 547 | | | 15 |
| $\beta \rightarrow \alpha$ | 558 | | | 15 |
| $\alpha \rightarrow \text{l}$ | 676 | | | 13, 14 |
| $\text{Sr}(\text{NO}_3)_2\text{c} \rightarrow \text{l}$ | 918 | 44.6 | 48.6 | 140 |

TABLE 5.84
Thermodynamic Data of Sr(NO₃)₂

| T K | ΔH ^o kJ mol ⁻¹ | S ^o J mol ⁻¹ deg ⁻¹ | ΔG ^o kJ mol ⁻¹ | Reference |
|---------|---|---|---|--------------|
| 298.15 | -988.72 | 194.56 | -1046.56 | Ruzinov 1975 |
| 400.00 | -972.40 | 241.65 | -1069.06 | Ruzinov 1975 |
| 500.00 | -956.38 | 277.41 | -1095.08 | Ruzinov 1975 |
| 600.00 | -940.35 | 306.62 | -1124.32 | Ruzinov 1975 |
| 700.00 | -924.33 | 331.32 | -1156.25 | Ruzinov 1975 |
| 800.00 | -908.30 | 352.72 | -1190.48 | Ruzinov 1975 |
| 900.00 | -892.28 | 371.60 | -1226.71 | Ruzinov 1975 |
| 1000.00 | -876.25 | 388.48 | -1264.73 | Ruzinov 1975 |

TABLE 5.85
Sr(NO₃)₂ = SrO + 2 NO₂(g) + 1/2 O₂(g)

| T K | ΔH ^o kJ | ΔS ^o J deg ⁻¹ | ΔG ^o kJ | K |
|---------|--------------------|-------------------------------------|--------------------|--------------|
| 298.15 | 462.88 | 443.58 | 330.622 | 1.179E - 058 |
| 400.00 | 460.82 | 437.55 | 285.796 | 4.740E - 038 |
| 500.00 | 459.79 | 435.24 | 242.176 | 4.988E - 026 |
| 600.00 | 459.47 | 434.63 | 198.693 | 5.021E - 018 |
| 700.00 | 459.72 | 435.00 | 155.217 | 2.610E - 012 |
| 800.00 | 460.44 | 435.96 | 111.673 | 5.104E - 008 |
| 900.00 | 461.58 | 437.29 | 68.013 | 1.128E - 004 |
| 1000.00 | 463.08 | 438.87 | 24.207 | 5.438E - 002 |

TABLE 5.86
Decomposition Pressures of Sr(NO₃)₂

| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|---------|-------------------------|--------------------------|--------------------|--------------------|
| 298.15 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ |
| 400.00 | 1.56E - 013 | <10 ⁻¹⁵ | 2.08E - 011 | 3.64E - 013 |
| 500.00 | 3.10E - 009 | 2.99E - 011 | 4.13E - 009 | 7.24E - 009 |
| 600.00 | 2.29E - 006 | 5.76E - 008 | 3.03E - 006 | 5.33E - 006 |
| 700.00 | 2.57E - 004 | 1.28E - 005 | 3.38E - 004 | 6.08E - 004 |
| 800.00 | 8.92E - 003 | 7.35E - 004 | 1.16E - 002 | 2.12E - 002 |
| 900.00 | 0.141 | 1.73E - 002 | 0.183 | 0.344 |
| 1000.00 | 1.30 | 0.219 | 1.66 | 3.18 |

TABLE 5.87
Density of TiNO_2

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-------|------|------------------------|-----------|
| l | 480 | 4.905 | 69 |
| | 490 | 4.885 | 69 |
| | 500 | 4.867 | 69 |
| | 510 | 4.849 | 69 |
| | 520 | 4.830 | 69 |
| | 530 | 4.811 | 69 |
| | 540 | 4.792 | 69 |
| | 550 | 4.773 | 69 |
| | 560 | 4.755 | 69 |

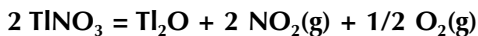
TABLE 5.88
Transitions of TiNO_2

| 0.00 | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--|-------|-------------------|----------------------|-----------|
| $\text{TiNO}_{2s} \rightarrow s$ | 442 | | | 15 |
| $s \rightarrow l$ | 459 | | | 15 |
| TiNO_3 orthorhombic \rightarrow | 334.2 | 1.0 | 3.0 | 135 |
| hexagonal \rightarrow cubic | 416 | 3.8 | 9.1 | 141 |
| cubic \rightarrow liquid | 483 | 8.83 | 18.3 | 143 |

TABLE 5.89
Thermodynamic Data of TiNO_3

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------|
| 298.15 | -243.93 | 164.43 | -292.95 | Ruzinov 1975 |
| 400.00 | -232.07 | 198.54 | -311.49 | Ruzinov 1975 |
| 500.00 | -205.23 | 257.53 | -334.00 | Ruzinov 1975 |
| 600.00 | -192.21 | 281.28 | -360.97 | Ruzinov 1975 |
| 700.00 | -179.18 | 301.75 | -390.13 | Ruzinov 1975 |
| 800.00 | -166.15 | 318.75 | -421.15 | Ruzinov 1975 |
| 900.00 | -153.13 | 334.10 | -453.81 | Ruzinov 1975 |
| 1000.00 | -140.10 | 347.82 | -487.92 | Ruzinov 1975 |

TABLE 5.90



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|---------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 385.01 | 398.94 | 266.068 | 2.411E – 047 |
| 400.00 | 378.96 | 381.61 | 226.320 | 2.774E – 030 |
| 500.00 | 343.68 | 304.63 | 191.362 | 1.016E – 020 |
| 600.00 | 336.78 | 292.04 | 161.558 | 8.589E – 015 |
| 700.00 | 330.54 | 282.40 | 132.857 | 1.217E – 010 |
| 800.00 | 324.88 | 274.83 | 105.010 | 1.390E – 007 |
| 900.00 | 351.10 | 305.55 | 76.107 | 3.824E – 005 |
| 1000.00 | 348.77 | 303.09 | 45.680 | 4.109E – 003 |

TABLE 5.91

Decomposition Pressures of TiNO_3

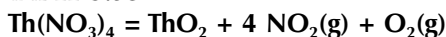
| T K | P (O ₂) bar | P (NO ₂) bar | P (NO) bar | P (Tot) bar |
|---------|-------------------------|--------------------------|--------------------|--------------------|
| 298.15 | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹⁵ | <10 ⁻¹³ |
| 400.00 | 2.59E – 011 | 7.38E – 013 | 3.43E – 011 | 6.09E – 011 |
| 500.00 | 1.03E – 007 | 5.64E – 009 | 1.35E – 007 | 2.39E – 007 |
| 600.00 | 1.93E – 005 | 1.40E – 006 | 2.53E – 006 | 6.40E – 005 |
| 700.00 | 7.74E – 004 | 6.62E – 005 | 1.01E – 003 | 1.78E – 003 |
| 800.00 | 1.19E – 002 | 1.13E – 003 | 1.55E – 002 | 2.85E – 002 |
| 900.00 | 0.103 | 1.09E – 002 | 0.134 | 0.247 |
| 1000.00 | 0.615 | 7.24E – 002 | 0.796 | 1.481 |

TABLE 5.92

Thermodynamic Data of $\text{Th}(\text{NO}_3)_4$

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|--------|--|--|--|----------------------|
| 298.15 | –1446.00 | 335.00 | –1543.88 | Phillips et al. 1988 |
| 400.00 | –1446.00 | 335.00 | –1580.00 | Phillips et al. 1988 |
| 500.00 | –1446.00 | 335.00 | –1613.50 | Phillips et al. 1988 |
| 600.00 | –1446.00 | 335.00 | –1647.00 | Phillips et al. 1988 |
| 700.00 | –1446.00 | 335.00 | –1680.50 | Phillips et al. 1988 |

TABLE 5.93



| T K | ΔH° kJ | ΔS° J deg ⁻¹ | ΔG° kJ | K |
|--------|---------------------|--------------------------------------|---------------------|--------------|
| 298.15 | 351.97 | 895.45 | 84.99 | 1.286E – 015 |
| 400.00 | 377.54 | 969.06 | –10.084 | 2.075E + 001 |
| 500.00 | 404.58 | 1029.33 | –110.087 | 3.174E + 011 |

TABLE 5.94
Thermodynamic Data of $\text{Sn}(\text{NO}_3)_2$

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|--------|---|---|---|--------------------------|
| 298.15 | -456.10 | 208.80 | -518.35 | Kubaschewski et al. 1993 |
| 400.00 | -434.79 | 270.28 | -542.90 | Kubaschewski et al. 1993 |
| 500.00 | -413.87 | 316.96 | -572.35 | Kubaschewski et al. 1993 |
| 600.00 | -392.95 | 355.10 | -606.01 | Kubaschewski et al. 1993 |
| 700.00 | -372.03 | 387.35 | -643.18 | Kubaschewski et al. 1993 |

TABLE 5.95
Thermodynamic Data of SnO

| T K | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔGf° kJ mol ⁻¹ | Reference |
|--------|---|---|---|------------|
| 298.15 | -285.77 | 56.48 | -302.61 | Barin 1993 |
| 400.00 | -280.72 | 71.04 | -309.13 | Barin 1993 |
| 500.00 | -275.50 | 82.67 | -316.84 | Barin 1993 |
| 600.00 | -270.11 | 92.50 | -325.61 | Barin 1993 |
| 700.00 | -264.58 | 101.02 | -335.20 | Barin 1993 |

TABLE 5.96
Thermodynamic Data of $\text{Zn}(\text{NO}_3)_2$ (298.15 K)

| | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|----------------------------|---|---|-----------|
| $\text{Zn}(\text{NO}_3)_2$ | -483.7 | 193.7 | 49, 133 |
| ZnO | -348.2 | 43.64 | 133 |

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6 Oxysalts of the Halogens

6.1 GENERAL

All of the halogens except fluorine, which is more electronegative than oxygen, form oxyanions in which the valence of the halogen varies, e.g., chlorite, chlorate, perchlorate.

The chemistry of specific classes of salts, e.g., chlorates, is discussed in the introduction to the particular halogen. Further information is available in textbooks on inorganic chemistry.

A book by Solymosi¹ deals with the chemistry of solid oxyhalogens in great detail. This book covers the literature through 1974, and includes kinetic studies. The author's previous monograph² was published the same year as part of a larger work on salts with oxyanions. A search of the literature through 1996 has shown a noticeable decrease in publications in this field since about 1985. Material from all of the above works has been included in this and succeeding chapters.

In contrast to other classes of salts with oxyanions, high-temperature thermodynamic data are largely lacking; e.g., HSC only lists data for four. These have been listed as well as ΔH_f° and S° from Wagman et al.³ In this chapter thermodynamic data for the three halogen gases have been listed (Tables 6.1 to 6.3)

6.2 PHASE TRANSITIONS

Since many oxyhalogen salts decompose in the solid state, melting points are available for relatively few compounds. In some cases the decomposition is slow enough that the melting point of a nearly pure salt can be measured. Values have been listed whenever possible, even if they are not very precise.

6.3 DENSITY

Except for LiClO_4 , which is stable for some distance above its melting point, no molten salt densities seem to have been measured. Most ambient-temperature measurements are of fairly low accuracy. The most reasonable values have been listed for convenience. These are obtained either experimentally (usually pycnometrically, by displacement of a liquid such as CCl_4) or calculated from X-ray data. Solids frequently exhibit voids and/or occlude solvent so that reported values may scatter considerably. X-ray values are those for a perfect lattice and thus are only approximate guides to densities of "real" crystals. Whenever recent data are not available, the evaluation from *International Critical Tables*⁴ has been accepted.

6.4 CHEMISTRY OF THE HALOGEN-OXYSALTS

Apparently the halogen-oxysalts are predominantly ionic, i.e., the anion constitutes a definite charged entity with covalent bonds between the halogen and oxygen atoms, but only electrostatic interactions between cations and anions. This is in contrast to the nitrates where some are ionic and some covalent. Because the outer electronic structure of the halogens is so similar, it is not surprising that the structures of corresponding ions are also similar, e.g. ClO_3^- , BrO_3^- , and IO_3^- are pyramidal. Table 6.4 is a listing of halogen oxyanions given by Wells.⁵

One of the most striking differences between the halogens is the large number of anhydrous iodine compounds, compared to those of chlorine and bromine. However, this difference may only be due to lack of interest exhibited by chemists in preparing these compounds. For example, although chlorites have been known for a long time, anhydrous bromites and iodites have been synthesized only relatively recently. Similarly, perbromates were said to be too unstable to exist, but several of them have now been synthesized, and the BrO_4^- ion seems about as stable as ClO_4^- and IO_4^- . This topic has been discussed in detail by Cox and Moore.⁶ In nearly all respects the parallelism is complete: hypohalites (XO^-) are not known as pure anhydrous salts; the halites ClO_2^- , BrO_2^- , and IO_2^- are known, although relatively few bromites and iodites have been prepared; the halates ClO_3^- , BrO_3^- , and IO_3^- exist; the (meta) perhalates ClO_4^- , BrO_4^- , and IO_4^- are known. In each of these groups the structures are quite similar. Only the tendency of iodine in its +7 oxidation state to polymerize leads to a variety of iodates, a phenomenon apparently quite absent from chlorine and bromine.

In general, the stabilities of the anions for each oxidation state increase in the order $\text{Cl} < \text{Br} < \text{I}$. How great this difference is may depend on the property used to measure it. For example, both perchlorates and metaperiodates may be heated to several hundred degrees before decomposing, but this similarity is probably due to the kinetics of the decomposition, since perchlorates are thermodynamically unstable even at ambient temperature.

Since the chemistry of the individual classes of oxyhalogens, i.e., chlorine, bromine, and iodine, are independent of each other, they have been placed in separate chapters, each with their own references.

TABLE 6.1
Thermodynamic Data of $\text{Cl}_2(\text{g})$

| T K | ΔH° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | 0.00 | 223.08 | -66.51 | JANAF 1985 |
| 400.00 | 3.53 | 233.26 | -89.77 | JANAF 1985 |
| 500.00 | 7.11 | 241.24 | -113.51 | JANAF 1985 |
| 600.00 | 10.74 | 247.86 | -137.97 | JANAF 1985 |
| 700.00 | 14.41 | 235.52 | -163.05 | JANAF 1985 |
| 800.00 | 18.11 | 258.46 | -188.65 | JANAF 1985 |
| 900.00 | 21.83 | 262.84 | -214.72 | JANAF 1985 |
| 1000.00 | 25.56 | 266.77 | -241.21 | JANAF 1985 |
| 1100.00 | 29.31 | 270.34 | -268.07 | JANAF 1985 |
| 1200.00 | 33.07 | 273.61 | -295.27 | JANAF 1985 |

TABLE 6.2
Thermodynamic Data of $\text{Br}_2(\text{g})$

| T K | ΔH° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG° kJ mol ⁻¹ | Reference |
|---------|--|--|--|-------------------|
| 298.15 | 30.91 | 245.39 | -42.25 | Barin et al. 1977 |
| 400.00 | 34.62 | 256.10 | -67.81 | Barin et al. 1977 |
| 500.00 | 38.31 | 264.33 | -93.85 | Barin et al. 1977 |
| 600.00 | 42.03 | 271.11 | -120.64 | Barin et al. 1977 |
| 700.00 | 45.77 | 276.87 | -148.04 | Barin et al. 1977 |
| 800.00 | 49.52 | 281.87 | -175.98 | Barin et al. 1977 |
| 900.00 | 53.27 | 286.30 | -204.40 | Barin et al. 1977 |
| 1000.00 | 57.04 | 290.27 | -233.23 | Barin et al. 1977 |
| 1100.00 | 60.81 | 293.86 | -262.44 | Barin et al. 1977 |
| 1200.00 | 64.59 | 297.16 | -291.99 | Barin et al. 1977 |

TABLE 6.3
Thermodynamic Data of I₂(g)

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | 62.42 | 260.69 | -15.30 | Barin 1993 |
| 400.00 | 66.20 | 271.58 | -42.43 | Barin 1993 |
| 500.00 | 69.93 | 279.91 | -70.02 | Barin 1993 |
| 600.00 | 73.68 | 286.75 | -98.37 | Barin 1993 |
| 700.00 | 77.45 | 292.55 | -127.34 | Barin 1993 |
| 800.00 | 81.22 | 297.59 | -156.85 | Barin 1993 |
| 900.00 | 85.00 | 302.04 | -186.84 | Barin 1993 |
| 1000.00 | 88.79 | 306.03 | -217.25 | Barin 1993 |
| 1100.00 | 92.58 | 309.65 | -248.03 | Barin 1993 |
| 1200.00 | 96.38 | 312.96 | -279.17 | Barin 1993 |

TABLE 6.4
Bonding of the Halogen Oxyanions

| Number of σ -Electron Pairs | Type of Hybrid | Number of Lone Pairs | Bond Arrangement | Examples |
|---------------------------------------|--------------------------------|-------------------------|-----------------------|---|
| 4 | sp ³ | 0 | Tetrahedral | ClO ₄ , IO ₄ |
| | | 1 | Trigonal bi-pyramidal | ClO ₃ , BrO ₃ , IO ₃ |
| 5 | sp ³ d _z | 0 | Trigonal bi-pyramidal | IO ₅ (?) |
| 6 | sp ³ d _y | 0 | Octrahedral | IO ₆ |

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7 Oxysalts of Chlorine

7.1 GENERAL

There are only three oxyanions that form anhydrous salts: chlorites (ClO_2^-), chlorates (ClO_3^-), and perchlorates (ClO_4^-). Their stability increases with the increasing oxidation state of the halogen. There is no clear evidence for the existence of stoichiometric, anhydrous hypochlorites (ClO^-). Even for the few reported salts (NaClO , $\text{Ca}(\text{ClO})_2$) one finds reports of “smell of chlorine,” indicating continuous decomposition at ambient temperature.

The known and doubtful salts are shown in [Figures 7.1 to 7.3](#). Although more elements form perchlorates than chlorites and chlorates, the chlorates seem underrepresented. Any metal that forms a chlorite should also form a chlorate. One would also expect the lanthanides to form all three classes of salts.

The quantitative high-temperature chemistry of chlorine oxysalts is rather underdeveloped. There are very few thermodynamic data for these compounds above 298 K. Even when they exist, they must be applied cautiously, since there may be kinetic rather than thermodynamic factors that determine decomposition behavior. Although the thermal decomposition of a few compounds has been studied very carefully (e.g., the KClO_4 literature extends back for more than a hundred years because of the compound's use in explosives), the bulk of the available information is qualitative or semiquantitative. In recent years this has changed somewhat with increasing use of automated techniques such as DTA and TGA. Many of the reactions are complex, with mechanisms frequently controversial and not completely worked out. Decomposition products may depend on experimental conditions; e.g., salts are frequently prepared by dehydration of their hydrates, and residual water may affect the course of the decomposition.

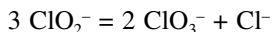
As pointed out above, perchlorates are thermodynamically unstable even at ambient temperature so that calculations are not useful in predicting the actual behavior of the salt. Thermodynamic properties of only a few salts have been listed by HSC above 298 K, and these are reproduced in this work, but no calculations have been done for reactions. Thermodynamic data at 298.15 K are given¹ under each element.

7.2 CLASSES OF OXYCHLORINE SALTS

7.2.1 CHLORITES

The best-studied chlorite, AgClO_2 , is probably not typical of chlorites generally, since the short Ag–Cl distance is suggestive of AgClO_2 molecules. The O–Cl–O angle in the ClO_2^- ion is 110° , with a Cl–O interatomic distance of 1.5 Å.

When heated, most chlorites disproportionate according to



although under very rapid heating only O_2 and chlorides may form explosively, probably because the chlorate then decomposes simultaneously.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides Ce Pr Nd Pm Sm Eu Gd **Tb** Dy Ho **Er** Tm Yb Lu
Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 7.1 The known chlorites.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

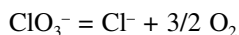
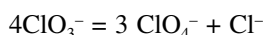
Lanthanides Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 7.2 The known chlorates.

7.2.2 CHLORATES

The chlorate ion is a rather flat pyramid with Cl at the apex and the O–Cl–O bond angle of 110°. The Cl–O distance is near 1.46 Å. A picture of the ion, constructed by Weigel et al.² from known data, is shown in [Figure 7.4](#).

Most chlorates undergo two decomposition reactions which usually occur simultaneously:



The subsequent fate of the perchlorate depends on the temperature. At relatively low temperatures it is stable and thus remains. At temperatures high enough for it to decompose, the final products are chloride and oxygen. When the metal exists in more than one oxidation state, the oxide may form. The chlorates of the rare earths, scandium, and yttrium form oxychlorides.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides **Ce** **Pr** Nd Pm **Sm** Eu **Gd** Tb Dy **Ho** Er Tm **Yb** **Lu**
Actinides **Th** Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 7.3 The known perchlorates.

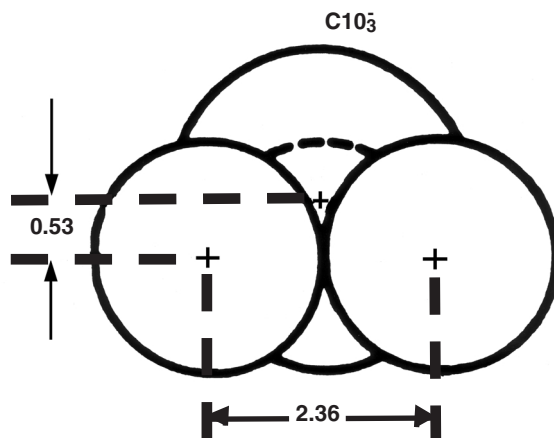


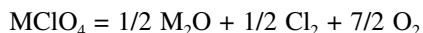
FIGURE 7.4 Structure of the chlorate ion. (From Weigel, D., Imelik, B., and Prettre, M., *Bull. Soc. Chim. France*, 1427, 1962. With permission.)

7.2.3 PERCHLORATES

The perchlorate ion (ClO_4^-) is tetrahedral, with a Cl-O distance near 1.4\AA (Figure 7.5).² The perchlorates decompose by one of two reactions: salts of the more electropositive metals go to the chloride



the others, e.g., Cd, Zn, go to the oxide:



Only $\text{Mg}(\text{ClO}_4)_2$ simultaneously decomposes by both reactions.

Markowitz^{2a} has discussed perchlorate decomposition in terms of the thermodynamics of the above two reactions. Since ΔS° for both reactions is highly positive (because gaseous products are

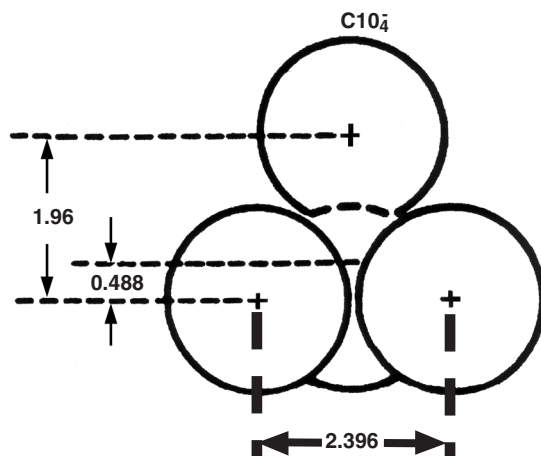


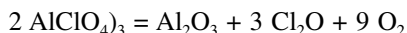
FIGURE 7.5 Structure of the perchlorate ion. (From Weigel, D., Imelik, B., and Prettre, M., *Bull. Soc. Chim. France*, 1427, 1962. With permission.)

formed) the determining factor is ΔH° . Since ΔH° is not very temperature dependent, values at 298 K can be used to predict the reaction. In effect, when the difference per equivalent in ΔH_f° (chloride-oxide) is negative, the product will be the chloride. Most perchlorates form either the chloride or the oxide. $\text{Mg}(\text{ClO}_4)_2$ and some transition metal perchlorates form both because the enthalpy difference is not very large. However, for both kinds of reaction ΔH is negative, so it is only a question of which reaction is more spontaneous.

7.3 INDIVIDUAL SALTS

7.3.1 ALUMINUM

The anhydrous salt, $\text{Al}(\text{ClO}_4)_3$, decomposes according to the stoichiometry



Between 240 and 290°C decomposition kinetics fit the Erofeev equation, according to which the fraction decomposed is given by

$$\alpha = 1 - \exp(-kt^n)$$

where the value of n depends on the shape of the nuclei. From the temperature dependence of k , an Arrhenius activation energy of 82.8 kJ was calculated.⁴

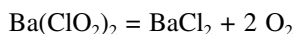
7.3.2 BARIUM

7.3.2.1 $\text{Ba}(\text{ClO}_2)_2$

The salt is rather unstable, but its precise mode of decomposition depends on the rate at which it is heated.^{5,6} If it is heated slowly or at a constant temperature in the range 130 to 180°C, it disproportionates according to

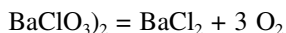


In this temperature range, $\text{Ba}(\text{ClO}_3)_2$ is stable. If the salt is heated so rapidly that the reaction has not been completed, $\text{Ba}(\text{ClO}_2)_2$ decomposes explosively at 200°C according to



7.3.2.2 $\text{Ba}(\text{ClO}_3)_2$

Two studies of the decomposition disagree somewhat.^{7,8} There is agreement that both the perchlorate and the chloride are formed:



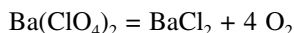
Both agree that the decomposition does not become appreciable until about 380°C. (The disproportionation does not lead to a weight loss and can only be detected by analysis.) At 396°C the salt melts and decomposition then becomes rapid since it occurs in the liquid. At this temperature the second reaction predominates, whereas slow decomposition is the major one below 396°C.⁸ $\text{Ba}(\text{ClO}_2)_2$ may be an intermediate in the decomposition, but it is too unstable to detect.

7.3.2.3 $\text{Ba}(\text{ClO}_4)_2$

The salt exhibits two solid-state transitions: a rhombic-cubic one at 557 K, and a cubic to γ one at 633 K.⁹

The density of the salt is 3.681 gcm⁻³ at 298 K.¹⁰

Above 435°C the salt decomposes according to the overall reaction¹¹⁻¹³



However, the decomposition mechanism appears to be quite complex and has been the subject of several studies. Acheson and Jacobs¹¹ found that α = fraction decomposed vs. time plots showed a distinct break at $\alpha = 0.52$, corresponding to the formation of $\text{Ba}(\text{ClO}_2)_2$. This discontinuity can be prevented by pumping off the oxygen. Addition of BaCl_2 to the perchlorate before decomposition (a) removes the induction period and (b) reduces the value of α at which the discontinuity occurs. Solymosi and Braun¹² proposed that the rapid reaction occurs in the melt, the slower rate being caused by the freezing of the reaction mixture, whereas Acheson and Jacobs¹¹ proposed that (a) the perchlorate decomposes by successive removal of oxygen atoms, and (b) $\text{Ba}(\text{ClO}_2)_2$ undergoes disproportionation as it is formed. The discrepancies between the two studies were then resolved by a newer study.¹⁴ The main features are that O atoms are successively removed from the perchlorate ion; in an isothermal experiment these stages overlap; the complete removal of perchlorate is not achieved by $\alpha = 0.52$, nor is there any accumulation of chlorate. The authors also emphasize the differences between experiments carried out isothermally and under rising temperature regimes, such as DTA and TGA. For a more complete explanation the original literature should be consulted.

The detailed kinetics of the decomposition mechanism have also been reexamined by Bohidar and Mohanty¹⁵ who also studied the effect of radiation. The decomposition proceeds through four stages: initial rapid gas evolution, induction, a short acceleratory stage, and a long decay stage. The kinetics follow the Prout-Tompkins equation, according to which individual product nuclei catalyze neighboring molecules, which is clearly more feasible in the molten state. The activation energy corresponds to the Cl–O bond energy.

Thermodynamic data at 298.15 K are given in [Table 7.1](#).

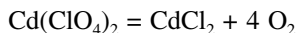
7.3.3 CADMIUM

7.3.3.1 $\text{Cd}(\text{ClO}_3)_2$

The anhydrous salt has been prepared,¹⁶ but its high-temperature properties have not yet been determined.

7.3.3.2 $\text{Cd}(\text{ClO}_4)_2$

Decomposition of the anhydrous salt has been determined in the range 377 to 403°C.¹⁷ At the lower end of the range the decomposition is quite slow, approximately 10% of the material decomposing in two hours. In contrast, Hering and Leray¹⁸ report decomposition in the range 150 to 200°C. This would be expected in the presence of traces of water. Most of the decomposition goes according to



and about 3% to the oxide:



There are no thermodynamic data for $\text{Cd}(\text{ClO}_3)_2$ at 298.15 K. An older NBS compilation gives $-227.7 \text{ kJmol}^{-1}$,¹⁹ but this has been dropped from the newer publication.¹

7.3.4 CALCIUM

7.3.4.1 $\text{Ca}(\text{ClO})_2$

Although several authors have described various materials containing this compound,²⁰ these have usually been commercial bleaching powders containing various amounts of CaCl_2 , $\text{Ca}(\text{ClO}_3)_2$, CaCO_3 , and H_2O . The most nearly pure anhydrous salt seems to have been prepared by Urano.²¹ The compound is quite stable at 45°C, losing weight only slightly (<5%) over several hundred hours. Above 150°C it decomposes violently with the evolution of O_2 , leaving CaCl_2 .

7.3.4.2 $\text{Ca}(\text{ClO}_2)_2$

This salt is a white, crystalline powder, probably pseudocubic in structure.²² A nearly (93%) pure preparation has been decomposed at 180 to 200°C. At this temperature the salt decomposes according to²³



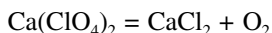
The compound has been reported to explode due to mechanical shock.

7.3.4.3 $\text{Ca}(\text{ClO}_3)_2$

The high-temperature properties of this salt appear not to have been studied since about 1900. According to the older literature,²⁰ the salt is very hygroscopic.

7.3.4.4 $\text{Ca}(\text{ClO}_4)_2$

The thermal decomposition of this salt has been studied by several researchers.^{24,25} The anhydrous salt exhibits polymorphic transitions at 615 and 679 K. It begins to decompose at 666 K, mostly by the reaction



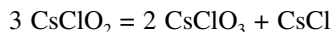
At 681 K a liquid phase forms, probably containing perchlorate and chloride.

The densities of $\text{Ca}(\text{ClO}_2)_2$ and $\text{Ca}(\text{ClO}_4)_2$ are shown in [Table 7.2](#), thermodynamic data in [Table 7.3](#).

7.3.5 CESIUM

7.3.5.1 CsClO₂

In the temperature range 190 to 210°C the salt disproportionates according to Levi and Cippolone²⁹



In this temperature range the chlorate is stable.

7.3.5.2 CsClO₃

The salt is stable to the melting point and at least a little beyond it.³⁰ As expected from the large cationic size, CsClO₃ is the most stable of the chlorates. Like the other alkali metal chlorates, the salt decomposes by the parallel paths



Since the perchlorate is stable near the melting point of the chlorate, both CsCl and CsClO₄ accumulate. No detailed study of the relative rates of the two reactions seems to have been carried out, but indications are that the rate of reaction (b) is about three times as fast as that of (a) at 400°C.³⁰ At higher temperatures CsClO₄ also decomposes.

7.3.5.3 CsClO₄

The temperature of the orthorhombic-cubic transition is somewhat dependent on the heating rate. Cabane and Benard³¹ think the transition occurs reversibly at 489 K. The melting point is estimated because the salt begins to decompose in the solid state. As is usual for the perchlorates, overall decomposition leads to the chloride and O₂, with CsClO₃ as an unstable intermediate:



Decomposition kinetics has been studied by Cabane and Benard³¹ in the range 385 to 467°C and by Solymosi³² between 528 and 558°C, both using weight loss measurements. In addition, Cordes and Smith³³ studied the first 3% of the solid decomposition mass spectrometrically between 330 and 500°C. This study has the advantage of avoiding melting, which occurs as the melting point is lowered by the accumulation of reaction products. CsClO₄, in contrast to the other alkali metal perchlorates, is quite volatile, approximately 50% of the sample subliming above 500°C in 1 to 2 hours.³³ The solid residue contains approximately ten times as much CsClO₃ as CsCl. Cabane and Benard³¹ found an Arrhenius activation energy of 117 kJ, approximately equal to the activation energy for diffusion, and argued that the rate-determining step involved the diffusion of the perchlorate ion. Cordes and Smith³³ obtained 187 ± 8.8 kJ over the same temperature range. Their mechanism, which is virtually the same for all the alkali metal perchlorates is discussed under KClO₄. At the higher temperature,

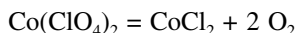
Solymosi found the activation energy to be near 233 kJ, so there may be a change of mechanism as the temperature increases.

Densities of CsClO_4 are given in Table 7.4, phase transitions of CsClO_3 and CsClO_4 in Table 7.5, thermodynamic data at 298 K in Table 7.6, and high-temperature thermodynamic data of CsClO_4 in Table 7.7.

7.3.6 COBALT

The preparation of the pure anhydrous salt, $\text{Co}(\text{ClO}_4)_2$, has been reported.³⁴ Its density is 3.2 gcm^{-3} , and it is stable in a vacuum to 90°C .

The decomposition kinetics have been studied³⁵ between 150 and 185°C . The major reaction is



with a lesser contribution from



7.3.7 COPPER

7.3.7.1 $\text{Cu}(\text{ClO}_2)_2$

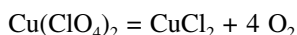
The nearly pure anhydrous salt, but with a slightly low chlorine content, has been prepared.²⁹ It is very unstable, transforming into a green powder even in a closed vessel and exploding on being heated.

7.3.7.2 CuClO_4

The preparation of this salt was first described by Gomberg,³⁶ but no further work seems to have been reported since then.

7.3.7.3 $\text{Cu}(\text{ClO}_4)_2$

Studies of this salt are in serious disagreement. Hathaway³⁷ reported the preparation of the anhydrous salt by fractional vacuum sublimation of $\text{Cu}(\text{ClO}_4)_{2-x}(\text{NO}_3)_x$. An approximate melting point of 230 to 240°C was found. On the other hand, Vilcu and Georgescu³⁵ report the melting point of the (supposedly) anhydrous salt begins near 75°C , simultaneously with decomposition, which they studied in the range 80 to 110°C . It involves the simultaneous reactions



The ratio of the two reactions is determined by the gas-phase composition through the equilibrium

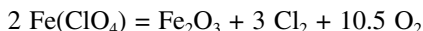


Particularly above 110°C the oxide is favored. It is possible that some water was present (the starting material was a hydrate) and the salt melted in its hydration water, but not enough information is given in the paper to know whether this the case. In contrast, Hathaway³⁷ reports that $\text{Cu}(\text{ClO}_4)_2$ decomposes at 130°C to a basic perchlorate.

7.3.8 IRON

7.3.8.1 Fe(ClO₄)

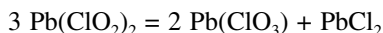
The thermal decomposition of a “dried” (at 110°C) hydrate in the range 90 to 135°C proceeds entirely to the oxide³⁵



7.3.9 LEAD

7.3.9.1 Pb(ClO₂)₂

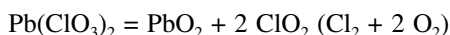
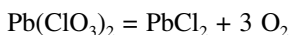
The salt is pseudotetragonal.³⁸ It disproportionates in the range 70 to 95°C according to the reaction



If the compound is heated rapidly, this conversion is apparently not complete and the chlorite decomposes explosively between 100 and 125°C.³⁹ A complete analysis was not carried out, but apparently both O₂ and Cl₂ evolve.

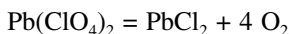
7.3.9.2 Pb(ClO₃)₂

Decomposition is complex.⁴⁰ Decomposition rates were measured between 194° and 216°C in terms of the gas evolved. Four stages could be distinguished: (1) initial rapid decomposition, (2) slow reaction, (3) extremely rapid decomposition in which approximately two thirds of the material react, (4) a short, slow decay period. The major part of the residue is PbO₂, with some PbCl₂. No perchlorate is formed. The reactions, therefore, probably are



7.3.9.3 Pb(ClO₄)₂

The salt is very hygroscopic, but can be prepared by vacuum treatment of its pyridine adduct.⁴¹ At the melting point, decomposition is slow, but becomes more rapid above 300°C. Decomposition goes to both the chloride and to the oxide:⁴²



The first of these reactions is the major one.⁴³ Kinetics were studied in the range 320 to 355°C.⁴³ The melting point is estimated as 546 K.⁴¹ Densities of Pb(ClO₃)₂ and Pb(ClO₄)₂ are listed in [Table 7.8](#), ΔHf° values of Pb(ClO₄)₂ and PbCl₂ in [Table 7.9](#). Entropies are not known.

7.3.10 LITHIUM

7.3.10.1 LiClO

Preparation of the anhydrous salt has been described in numerous patents, e.g., Robson and Soule⁴⁴ and Soule,⁴⁵ because of its importance as a bleaching agent, but not even the range of its thermal stability seems to be known.

7.3.10.2 LiClO₂

When heated in the range 200 to 210°C, the salt disproportionates rather violently:⁴⁶

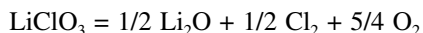


7.3.10.3 LiClO₃

The phase transitions of this salt are in some doubt. Based on the measurements of Bruehl, three crystalline forms (two transitions) have been listed in a critical compilation.⁴⁷ A careful reexamination by DTA³⁰ has yielded only a single solid-state transition. The high-temperature form was found to supercool easily, by as much as 50°C, which may account for the earlier results. Liquid LiClO₃ is stable over a longer temperature range than other chlorates. Up to 300°C⁴⁸ no weight loss was detected. At 330°C⁴⁸ the salt decomposes slowly. The major reactions are



Both of these reactions, occurring in the ratio Rate 1/ Rate 2 = 5.3, are catalyzed by LiCl. At the temperature of the experiment, LiClO₃ decomposes quite slowly. Approximately 4% disappears through oxide formation:



At 370°C decomposition becomes quite rapid. At this and higher temperatures decomposition of LiClO₄ is appreciable, so that the kinetics become quite complicated.

7.3.10.4 LiClO₄

The decomposition of this salt has been the subject of several studies^{49,50} that agree on the major features. In contrast to the other alkali metal perchlorates, LiClO₄ is stable in the solid state and in the liquid up to approximately 390°C. The overall reaction is



Very small amounts of LiClO₃ form as an intermediate, but this salt is very unstable at temperatures at which LiClO₄ decomposes. Very small quantities of Cl₂ and Li₂O have also been detected. Markowitz and Boryta⁵¹ studied by TGA the decomposition kinetics of both pure LiClO₄ and LiClO₄-LiCl mixtures below 420°C, the highest temperature at which the reaction mixture was not heated appreciably by the heat released in the exothermic reaction. The α vs. time curve of pure LiClO₄ exhibits an induction period and is sigmoidal, indicating that it is autocatalytic. For that range of the decomposition corresponding to the attainment of a saturated solution of LiCl in LiClO₄, the kinetics fit the Prout-Tompkins equation originally derived for branching reaction nuclei in solids. When the decomposition is studied for LiClO₄ initially saturated with LiCl, the autocatalytic behavior is absent and kinetics are first order. Evidently, LiCl functions as a catalyst. Solymosi⁵⁰ studied the kinetics of pure LiClO₄ decomposition by measuring gas evolution between 411 and 430°C and reached similar conclusions. For the autocatalytic phase both studies obtained 222 kJ for the activation energy, consistent with LiClO₄ = LiClO₃ + O, i.e., with the breaking of a Cl-O bond as the rate-determining step. For first-order kinetics, however, there is no agreement. Solymosi finds 172 kJ and Markowitz gives 259 kJ. There is no obvious reason for this discrepancy.

Densities of LiClO_3 and LiClO_4 are listed in Table 7.10, phase transitions in Table 7.11, and high-temperature thermodynamic data of LiClO_4 in Table 7.12.

7.3.11 MAGNESIUM

7.3.11.1 $\text{Mg}(\text{ClO}_2)_2$

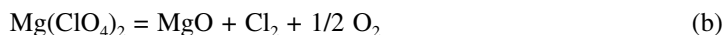
Preparation of this salt has been reported,⁵⁶ but no evidence was presented that it is completely anhydrous.

7.3.11.2 $\text{Mg}(\text{ClO}_3)_2$

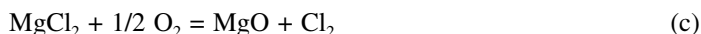
Although the infrared spectrum of this salt has been described,⁵⁷ there exists no evidence that the anhydrous salt has been prepared.

7.3.11.3 $\text{Mg}(\text{ClO}_4)_2$

Decomposition of this salt has been studied by several investigators^{11,43,58–60} who obtained different results, indicating that the reaction is complex. The two major reactions that have been proposed are

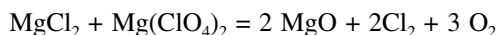


As pointed out by Markowitz,¹¹³ ΔG° of MgCl_2 and MgO are comparable (they are equal at 427°C) so that they may interconvert through the equilibrium



This equilibrium is achievable in practice and thus product distribution will be determined by the gas composition at the reaction interface and the rate of equilibration of reaction (c). These predictions are borne out by a number of experimental studies. For example, Chudinova⁶¹ found reaction (a) to be dominant at the lower end of the temperature range 360 to 420°C, and (b) at the higher end in a system in which the condensed phase remained in contact with the gas. Very similar results were obtained by Solymosi⁴³ in the same temperature range. In contrast, Acheson and Jacobs¹¹ found MgO to be the predominant product when the salt was heated under vacuum in the range 390 to 440°C. This suggests that reaction (b) occurs directly since reaction (c) could not occur in a vacuum. Above 600°C the product distribution appeared to depend only on the internal gaseous environment and to be independent of the gaseous atmosphere above the solid phase.

A more recent, very careful experimental reexamination of this problem was carried out by Lemesheva and Krivtsov.⁶² In this work, both the gas and solid phase were examined under isothermal conditions in the range 360 to 440°C, and also under increasing temperature. They found the first stage to be reaction (a). The MgCl_2 formed then reacts with the perchlorate:

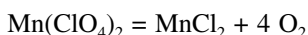


Thus the overall reaction will depend on experimental conditions, e.g., whether gas is continuously removed.

The density of $\text{Mg}(\text{ClO}_4)_2$ has been reported as 2.21 gcm⁻³.^{62a} Thermodynamic data of $\text{Mg}(\text{ClO}_4)_2$ and MgCl_2 are given in Table 7.13.

7.3.12 MANGANESE

The decomposition of a $\text{Mn}(\text{ClO}_4)_2$ sample of unknown water content (vacuum dried at 150°C) was studied in the range 125 to 155°C .⁶³ The main reaction is



with a smaller fraction decomposing to the oxide:



7.3.13 MERCURY

7.3.13.1 $\text{Hg}_2(\text{ClO}_2)_2$

The salt is so unstable that its existence must be regarded as marginal. Several attempts to prepare it^{64,65} resulted in the preparation of somewhat basic, yellow crystals which turned red in air and decomposed explosively on slight heating.

7.3.13.2 $\text{Hg}(\text{ClO}_2)_2$

The salt has been prepared.^{38,66} It consists of red crystals whose composition indicates some contamination by HgO . It is fairly unstable, tending to decompose even at ambient temperatures.

7.3.13.3 $\text{Hg}(\text{ClO}_3)_2$

A salt of approximately this composition was prepared and studied by several investigators in the 19th century. This work has been summarized by Gmelin. However, it is questionable whether the pure salt has ever been prepared. No work seems to have been done since 1910.

7.3.13.4 $\text{Hg}_2(\text{ClO}_4)_2$

A salt of this composition was obtained by dehydration of the 6-hydrate.⁶⁷ It melts at 210°C , with the evolution of chlorine oxides.

7.3.14 NICKEL

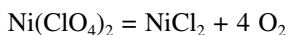
7.3.14.1 $\text{Ni}(\text{ClO}_3)_2$

There is no detailed description of the anhydrous salt, although spectral measurements of a vacuum-dried salt were reported by Rocchiccioli.⁶⁸

7.3.14.2 $\text{Ni}(\text{ClO}_4)_2$

Attempts to prepare the salt by vacuum dehydration of the 2-hydrate were unsuccessful.⁶⁹ A light-green, not quite pure anhydrous salt was prepared by the incomplete reaction of HClO_4 with $\text{Ni}(\text{CF}_3\text{COO})_2$ in trifluoroacetic acid.⁷⁰ Borgne and Weigel⁷¹ reported the preparation of the anhydrous salt by the slow, stepwise dehydration of the hexahydrate. Final heating was carried out at 180°C . Its structure was determined by X-ray diffraction, and a density of 2.985 g cm^{-3} calculated. This result conflicts with a more recently reported preparation⁷² in which the density (probably determined pycnometrically) is given as 3.4 g cm^{-3} . The salt was said to be stable up to 130°C in a vacuum.

The decomposition of a salt of unknown water content was studied by Vilcu and Georgescu⁶³ between 130 and 170°C . They found the major reaction to be



with a minor simultaneous reaction forming the oxide



7.3.15 POTASSIUM

7.3.15.1 KClO_2

The salt is quite hygroscopic. When sealed into glass tubes and heated at 180 to 200°C, 98% of it disproportionates, as do all the other alkali metal chlorites, according to Levi and Garrini⁷³

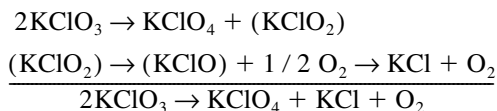


7.3.15.2 KClO_3

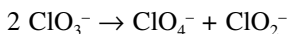
Although the molten salt is stable for some distance above its melting point,⁷⁴ no density data for the liquid are available. A mass-spectrometric study⁷⁵ shows no KClO_3 molecules in the vapor. The thermal decomposition of the salt has been studied by many investigators, frequently as part of the decomposition of KClO_4 in which it occurs as an intermediate (see below). The earlier literature has been summarized by Rudloff and Freeman⁷⁶ who studied the kinetics in detail. Below 500°C, where KClO_4 is stable, the decomposition products are KCl , O_2 , and KClO_4 , consistent with the frequently cited overall stoichiometry⁷⁴ in terms of two reactions:



Clearly, reaction (b) cannot correspond to a simple mechanism. However, Rudloff and Freeman⁷⁶ found that below 500°C KClO_3 loses only one third of the weight expected from reaction (a), and equivalent amounts of KClO_4 and KCl are formed. In this range the kinetics are second order. On this basis they propose the reaction sequence



KClO_2 is unstable above 200°C and cannot be detected.⁷⁴ It can therefore only be present as an unstable intermediate. The rate-determining step is thus an oxygen atom transfer between two chlorate ions:



The frequently observed deceleration of the reaction by KCl is attributed to dilution. Above 500°C the decomposition becomes more complicated because KClO_4 then also decomposes and KClO_3 appears as an intermediate reaction product. Moreover, KCl now catalyzes the reaction. Explanations for this phenomenon, e.g., in terms of polarization centers, are quite speculative.

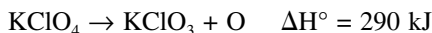
7.3.15.3 KClO₄

Because of its use in pyrotechnics and propellants, thermal decomposition of this salt has been studied for a long time. Simchen⁷⁷ has given references back to 1816. High-temperature thermodynamic functions are listed in the JANAF tables. We have given those listed by HSC.

The course of the decomposition is complicated by simultaneously occurring phase changes resulting from a lowering of the melting point by the accumulating reaction products, KCl and KClO₃, and a subsequent freezing of the melt as the material becomes predominantly KCl. For this reason it is also impossible to determine a precise melting point, although it appears to be near 580°C.⁷⁸

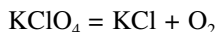
Tracer experiments have established that O₂ and Cl⁻ are formed^{79,80} irreversibly, but that ClO₃⁻ is transformed to ClO₄⁻. Harvey et al.^{81,82} established that in the range 556 to 580°C the decomposition of KClO₄ is first order. As reaction products accumulate, the solid melts and the rate increases 50-fold.

The kinetics of the liquid-state reaction are also first order. For both the solid and liquid the activation enthalpies and entropies are the same, $\Delta S = 8 \text{ J deg}^{-1}$, indicating that the rate-determining step is the breaking of a Cl–O bond, with the formation of atomic oxygen



The activated complex does not differ much from the ClO₄⁻ ion. These kinetic results have been confirmed by Solymosi.³²

Reactions subsequent to the rate-determining step are presumably those described under KClO₃ above. Since KCl and O₂ are formed irreversibly, the final result is consistent with the stoichiometry of the overall reaction



Two studies at lower temperatures have obtained much lower activation energies. Cabane and Benard⁸³ measured both decomposition rates and ClO₄⁻ diffusion between 375 and 480°C. Since for both of these processes the activation energy was the same for several alkali metal perchlorates, 126 kJ for KClO₄, they argued that the rate-determining step must be the same, i.e., diffusion of ClO₄⁻.

A much more detailed experimental and theoretical study of the decomposition kinetics over approximately the same temperature range was carried out by Cordes and Smith,⁸⁴ using only the first 3% of the solid-state decomposition in their analysis. For KClO₄, an extrapolation of their data on an Arrhenius plot fits smoothly into the high-temperature data of Harvey et al.,^{81,82} i.e., at lower temperatures the plot is linear but exhibits a curvature corresponding to a higher apparent activation energy at higher temperatures. For KClO₄ the low temperature data are represented by

$$k = A \exp(-E/RT)$$

where $A = 10^7 \text{ s}^{-1}$ and $E = 210 \text{ kJ}$. They argue from this, that at least at low temperatures, the rate-determining step cannot be $\text{ClO}_4^- \rightarrow \text{ClO}_3^- + \text{O}$. Instead, they carried out a detailed analysis in terms of Cordes' theory⁸⁵ of pre-exponential factors and a molecular model in which internal motions are specified, which leads to a pre-exponential factor in good agreement with experiment. In this model the activated complex is assumed to consist of two neighboring, freely rotating ClO₄⁻ ions joined by a peroxide linkage (ClO₃)–O–(ClO₃⁻). The rate-determining step then consists in the formation of O₂ and two ClO₃⁻ ions.

To account for the higher activation energies at higher temperatures, it is necessary to postulate either increased freedom of motion of the ClO_3^- ion in the lattice, or a change in the mechanism proposed by Harvey et al.^{81,82} A similar rise in the activation energy is observed for NaClO_4 .

Since 1968 no further work has been reported on this problem.

Densities of KClO_3 and KClO_4 are listed in Table 7.14, phase transitions in Table 7.15, and high-temperature thermodynamic data in Tables 7.16 and 7.17 for KClO_3 and KClO_4 , respectively.

7.3.16 RARE EARTHS

7.3.16.1 Chlorites

Nearly anhydrous $\text{Tb}(\text{ClO}_2)_3$ and $\text{Er}(\text{ClO}_2)_3$ have been prepared, but none of their properties have been reported. Chlorites of several other rare earths (La, Ce, Pr, Nd, Sm) have been prepared as hydrates.⁸⁶

7.3.16.2 Chlorates

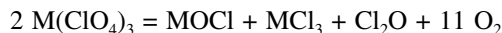
Only hydrates of the chlorates of the general formula $\text{Ln}(\text{ClO}_3)_3 \cdot 5 \text{H}_2\text{O}$ of the following rare earths have been prepared: La, Nd, Gd, Dy, Er, Th, Y, Lu.⁸⁷

When these salts are heated, or when they are just kept under vacuum for a long time at ambient temperature, they decompose with the evolution of O_2 and Cl_2 . The kinetics of the decomposition have been reported,⁸⁸ but in view of the simultaneous evolution of H_2O , Cl_2 , and O_2 , the interpretation of the data probably cannot result in an unambiguous mechanism.

7.3.16.3 Perchlorates

The preparation of the anhydrous salts (by vacuum-drying in the presence of P_2O_5 with the temperature gradually rising to 155°C) has been reported.⁸⁹ Whether or not the anhydrous salts can be prepared in this way may depend on experimental conditions, such as the heating rate. For example, Bel'kova and Aleksenko⁹⁰ and Bel'kova, Aleksenko, and Serebrennikov⁹¹ reported brief plateaus in the TGA curves of the hydrated perchlorates of La, Ce, Pr, and Sn at weights corresponding to the anhydrous salts, whereas Steinberg and Shidlovsky⁹² reported finding only inflections for these salts and $\text{Nd}(\text{ClO}_4)_3$. Except for Nd, these findings are consistent since the latter authors used a faster heating rate.

Bel'kova, Aleksenko, and Serebrennikov⁹³ reported an isothermal decomposition study of several rare-earth perchlorates in which weight loss was measured under flowing nitrogen. The stoichiometry of all the salts could be represented by



Between 240 and 370°C the kinetics followed the Erofeev equation in which the fraction decomposed is represented by

$$\alpha = 1 - \exp(-kt^n)$$

The value of n is determined by the properties of the nucleus. The Arrhenius activation energy was determined from the temperature dependence of the rate constant k . The results are shown in Table 7.18. In any case there is still a question as to whether the kinetics were studied for truly anhydrous salts.

7.3.17 RUBIDIUM

7.3.17.1 RbClO₂

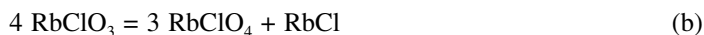
When heated in a closed container at 200 to 210°C the salt disproportionates according to Levi and Garrini⁷³



Similar results have been obtained by Solymosi and Bansagi.⁹⁴

7.3.17.2 RbClO₃

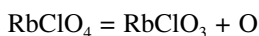
Knowledge of high-temperature properties is largely based on a study by Markowitz, Boryta, and Stewart.⁷⁴ In contrast to the perchlorate (see below) the salt is quite stable for 20 to 30°C above its melting point (342°C). Decomposition becomes rapid at 480°C. The salt disappears by two paths:



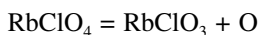
Reaction (b) is the major one by a factor of eight. Only near 600°C does the reaction proceed further with decomposition of the perchlorate. Chlorites and hypochlorites seem to be absent as intermediates.

7.3.17.3 RbClO₄

The salt decomposes during fusion⁶⁰ and therefore the melting point can only be determined approximately. The decomposition is exothermic and yields only RbCl and O₂ as the final products. The high-temperature kinetic data can be fitted by various rate equations, all of which yield an Arrhenius activation energy near 293 K,⁹⁵ consistent with the loss of one oxygen as the rate-determining step:



Since RbClO₃ is quite unstable in the decomposition range of the perchlorate, decomposition proceeds to the chloride. In addition to the decomposition reactions



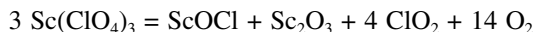
the salts also undergo fusion or solution in the reaction melt, so the physical state of the system depends on both the temperature and the extent of decomposition.

At lower temperatures (330 to 480°C) a much lower activation energy, 192 kJ, was observed for the initial 3% of the solid-state decomposition.⁸⁴ This, and the observed pre-exponential factor, were interpreted in terms of the abstraction of O₂ from two neighboring ClO₄ ions, (ClO₃=O=O=(ClO₃)). The theory is discussed in more detail under KClO₄.

Densities of RbClO₃ and RbClO₄ are listed in Table 7.19, transitions in Table 7.20, and thermodynamic data at 298.15 K in Table 7.21.

7.3.18 SCANDIUM

The thermal decomposition of the anhydrous salt, $\text{Sc}(\text{ClO}_4)_2$, proceeds according to



in the range 240 to 370°C the kinetics follow the Erofeev equation (see under Rare Earths) with an Arrhenius activation energy of 87.4 kJ.⁹¹

7.3.19 SILVER

7.3.19.1 AgClO_2

The anhydrous salt exists as shiny, yellow platelets, orthorhombic in structure.^{96,97} The compound is rather unstable and disproportionates, beginning at 83°C:



The reaction is first order with an activation energy of 109 kJ.

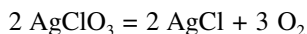
Above 100°C the thermal decomposition of the salt becomes increasingly important. The precise nature of the decomposition is not quite clear, but the major gaseous product is ClO_2 , and the solid residue contains both silver and silver oxide. Above 145°C the reaction becomes explosive. A detailed kinetic analysis of the disproportionation reaction and decomposition has been published.⁹⁸

The density is 4.30 gcm⁻³.⁹⁹

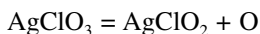
7.3.19.2 AgClO_3

The salt undergoes a crystalline transition from tetragonal to cubic at 412 K; ΔH for the transition is 2.49 kJ mol⁻¹. The temperature dependence of the lattice parameters and thermal expansion coefficient has been carefully studied.¹⁰⁰

The decomposition has been measured in the range 316 to 339°C,¹⁰¹ i.e., of the liquid salt. However, the accumulation of reaction products increases the melting point, so the mass solidifies in this temperature range after about 80% of it has decomposed. The gaseous product is mainly O_2 , with 2 to 3% Cl_2 . The reaction is therefore



The activation energy is 239 kJ, consistent with the rupture of a Cl–O bond as the rate-determining step:



Approximately 10% of the chlorate disproportionates:



These reactions were also found by Udupa,¹⁰² except that he found decomposition begins at a much lower temperature.

7.3.19.3 AgClO₄

There are some contradictions in the literature concerning the high-temperature behavior of this salt. Several authors agree that AgClO₄ undergoes a transition from rhombic to cubic in the range 155 to 159°C,^{9,59,103} but there is some confusion regarding the melting point and thermal decomposition. For example, Gordon and Campbell⁵⁹ report a slight decomposition in the solid state at 277°C, with violent bubbling of the melt at 473°C. However, Carnelly and O'Shea¹⁰⁵ report a melting point of 476°C. Markowitz has suggested that in Gordon and Campbell's experiment, the AgCl, which is formed as decomposition product, lowers the melting point. This suggestion was confirmed experimentally by Solymosi¹⁰¹ who reports a melting point of 476°C. This author also studied the decomposition kinetics between 415 and 445°C. The only reaction is



The absence of AgClO₃ is not surprising, since this salt decomposes at a much lower temperature. The reaction is probably autocatalytic.

Densities of the silver salts are listed in [Table 7.22](#), transitions in [Table 7.23](#), and thermodynamic data at 298.15 K in [Table 7.24](#). Thermodynamic data for AgClO₃ are listed in [Table 7.25](#).

7.3.20 SODIUM

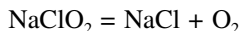
7.3.20.1 NaClO₂

Thermal decomposition has been studied by several researchers who agree on the main features of the reaction.^{6,22,106,107}

In an open container, reaction begins as low as 140°C and is certainly rapid above 160°C. The major reaction is disproportionation:



The fraction of NaClO₂ which disappears by this path as compared with the direct decomposition



varies from 75 to 99%, depending on the experimental details. The lower value was reported for rapid heating.¹⁰⁷ All others report 97 to 99%. The kinetics are first order, with an Arrhenius activation energy of 227 kJ, which is less than the Cl–O bond energy.

7.3.20.2 NaClO₃

A very thorough crystallographic study has been reported by Abrahams and Bernstein.¹⁰⁴

The thermal expansion coefficient of the solid was measured by Sharma,¹⁰⁸ using an interferometric method, and by Deshpande and Mudholker,¹⁰⁹ using X-ray diffraction data. At ambient temperature both sets of data agree within 5%, but near 500 K, Sharma's values are much higher. Deshpande and Mudholker suggested that the macroscopic expansion coefficient is made up of a sum of terms:

$$\alpha(\text{macr.}) = \alpha(\text{lattice}) + \alpha(\text{Schottky}) - \alpha(\text{readjustment})$$

so that $\alpha(\text{macr.})$ may differ, depending on the relative contributions of the defects and the readjustment of the small single crystals packed together in a mosaic structure with a small amount of

misorientation. Sharma's data are within 3% of those given by Kelley,¹¹⁰ so the interferometric measurements may reflect the behavior to be expected from "real" NaClO₃, whereas the X-ray results refer to an ideal lattice.

NaClO₃ is stable to well above its melting point. Three thermal decomposition studies of liquid NaClO₃ have been published^{40,74,111} that agree in their main features. Decomposition starts near 400°C. No Cl₂ and ClO₂ are formed. The major reaction is



However, NaClO₄ is also found to be a product. The amount of this formed product probably depends on reaction conditions. The overall stoichiometry can be written as



but this is not a likely mechanism. Osada et al.¹¹¹ suggested that the atomic oxygen formed as the initial product in reaction (a) oxidizes unreacted NaClO₃:



A proper stoichiometric combination of (a) and (c), and allowing for $\text{O} + \text{O} = \text{O}_2$, yields reaction (b). Perchlorate formation becomes increasingly important with increasing temperature, from a few percent at the lower end to perhaps equal amounts with NaCl near 450°C. NaClO₄ is stable to near 530°C. The activation energy of 285 kJ⁴⁰ is consistent with the breaking of a Cl–O bond as the rate- determining step of reaction (a).

The relation between events occurring on the surface and the bulk substructure close to the melting point has been studied in single crystals.¹¹² As the melting point is approached, dislocations in both regions increase.

7.3.20.3 NaClO₄

In contrast to NaClO₃, the perchlorate begins to decompose well below the melting point. Hence the melting point can only be determined approximately. However, since the temperature at which this decomposition becomes appreciable is higher than the stability region of the chlorate, very little NaClO₃ is found in the decomposition of NaClO₄, even though the initial reaction is probably



The initial stages of the solid-state decomposition have been studied by Cordes and Smith⁸⁴ between 330 and 440°C. An Arrhenius plot was linear to 390°C. Above this temperature, the slope of the plot increased. This result, as well as the low preexponential factor, was accounted for by a detailed molecular model (discussed under KClO₄) in which O₂ is abstracted from two neighboring perchlorate ions:



The increase in activation energy with rising temperature is accounted for by increased rotational freedom of the chlorate ion.

In contrast, Cabane and Benard³¹ observed an activation energy of only 117 kJ between 390 and 428°C, equal to that for diffusion of ClO₃ through the lattice. They argued that this implies that ion diffusion is the rate- determining step.

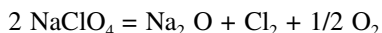
In the liquid state (495 to 515°C) the reaction is catalyzed by NaCl, but the activation energy is near 250 kJ which is more consistent with the breaking of a Cl–O bond as the rate-determining step:



NaClO₃ decomposes to NaCl as rapidly as it is formed. The overall decomposition therefore is



although a small part of the perchlorate disappears by the reaction¹¹³



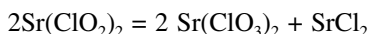
Above 525°C decomposition becomes quite rapid.

Transitions of NaClO₃ and NaClO₄ are shown in [Table 7.26](#), and high-temperature thermodynamic data of NaClO₃ and NaClO₄ in [Tables 7.27](#) and [7.28](#).

7.3.21 STRONTIUM

7.3.21.1 Sr(ClO₂)₂

The preparation of the salt has been described.^{114,115} Heating in the range 180 to 200°C leads to virtually complete disproportionation according to Levi and Garrini¹¹⁶



7.3.21.2 Sr(ClO₃)₂

The salt is of orthorhombic-bipyramidal structure.¹¹⁷ It can be heated to at least 120°C without decomposing.¹¹⁸

7.3.21.3 Sr(ClO₄)₂

Only a brief decomposition has been carried out.¹¹⁹ Oxygen evolution begins near 415°C. During the decomposition the salt appears to melt at 450°C, but it is then no longer pure. The product is almost entirely SrCl₂.

Densities of the strontium salts are listed in [Table 7.29](#) and thermodynamic data in [Table 7.30](#).

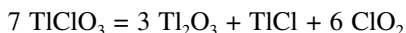
7.3.22 THALLIUM

7.3.22.1 TlClO₂

Little is known about this salt. It explodes from mechanical shock and thermally decomposes above 70°C.¹²⁰

7.3.22.2 TlClO₃

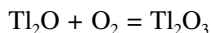
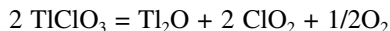
Decomposition becomes noticeable near 150°C. The kinetics have been studied from this temperature up to 170°C.⁸ The overall reaction can be represented by



but the mechanism is obviously more complex. Possible reactions by which Tl₂O₃ and TlCl might be produced are



Tl_2O may also be formed and oxidized to Tl_2O_3 :



7.3.22.3 TlClO_4

The phase transitions are well established, but little work has been done on the decomposition. DTA measurements¹²¹ indicate that it occurs near 400°C. Both TlCl and Tl_2O_3 are formed.

Densities of the thallium salts are listed in [Table 7.31](#) and transitions in [Table 7.32](#).

7.3.23 THORIUM

7.3.23.1 $\text{Th}(\text{ClO}_4)_4$

The evidence for the existence of the anhydrous salt is not conclusive. Some crystals were reported to have formed in the reaction between thoria and perchloric acid,¹²² but no analysis was carried out. The salt would certainly be very hygroscopic. Attempts to dehydrate the hydrate $\text{Th}(\text{ClO}_4)_4 \cdot 4 \text{H}_2\text{O}$ resulted in the formation of the anhydrous oxysalt $\text{ThO}(\text{ClO}_4)_2$.¹²³

7.3.24 TIN

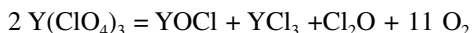
7.3.24.1 Perchlorates

Neither the stannous nor the stannic salts seem to have been prepared in the pure anhydrous state, although there are indications that they could be. Thus Gomberg¹²⁴ reported the preparation of several anhydrous perchlorates, including stannous and stannic perchlorates, by reacting the metal with an ethereal solution of chlorine tetroxide, but the products were not characterized. Schmidt¹²⁵ reported an acetonitrile adduct $\text{Sn}(\text{ClO}_4)_2 \cdot 2 \text{CH}_3\text{CN}$, but did not attempt to remove the acetonitrile.

7.3.25 YTTRIUM

7.3.25.1 $\text{Y}(\text{ClO}_4)_3$

Thermal decomposition of the anhydrous salt follows the overall stoichiometry



In the range 240 to 370°C the kinetics follow the Erofeev equation (see Rare Earths) with an Arrhenius activation energy of 116.3 kJ.⁶

7.3.26 ZINC

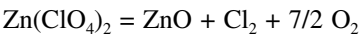
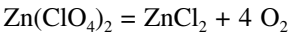
7.3.26.1 $\text{Zn}(\text{ClO}_3)_2$

The preparation of several divalent chlorides, including $\text{Zn}(\text{ClO}_3)_2$, was reported by Amiel,¹²⁶ but the salts were not characterized or analyzed. It is therefore doubtful that the anhydrous salt has been prepared,

7.3.26.2 Zn(ClO₄)₂

The anhydrous salt has been prepared in a two-stage process whereby the water of hydration is first replaced with dioxane which can then be removed under vacuum without decomposing the salt.¹²⁷ The salt is quite stable up to 130°C. Chudinova has reported the decomposition to occur above 190°C.¹²⁷ The kinetics were studied by Solymosi⁴³ in the range 280 to 310°C.

The salt decomposes by two parallel reactions:



which take place to nearly the same extent. Both reactions appear to be first order.

Rosolovskii and Krivtsov¹²⁸ have used their measurements of the enthalpy of solution of Zn(ClO₄)₂ in 0.9M HClO₄ to calculate ΔHf° for this salt. Recalculating their values with newer data gives −247.86 ± 2.18 kJ mol^{−1}.

TABLE 7.1
Thermodynamic Data (298.15 K)

| Compound | ΔHf° kJ mol ^{−1} | S° J mol ^{−1} deg ^{−1} | Reference |
|------------------------------------|------------------------------|---|-----------|
| Ba(ClO ₂) ₂ | −680.3 | 197 | 1 |
| Ba(ClO ₃) ₂ | −771.5 | — | 1 |
| Ba(ClO ₄) ₂ | −800.0 | — | 1 |
| BaCl ₂ | −858.6 | 123.68 | 1 |

TABLE 7.2
Densities of Ca-Cl salts

| Phase | T(K) | d (gcm ^{−3}) | Reference |
|------------------------------------|------|------------------------|-----------|
| Ca(ClO ₂) ₂ | 298 | 2.71 | 26 |
| | 293 | 2.65 | 27 |
| Ca(ClO ₄) ₂ | 298 | 2.651 | 28 |

TABLE 7.3
Thermodynamic Data (298.15 K)

| Compound | ΔHf° kJ mol ^{−1} | S° J mol ^{−1} deg ^{−1} | Reference |
|------------------------------------|------------------------------|---|-----------|
| Ca(ClO ₂) ₂ | −678.2 | — | 1 |
| Ca(ClO ₄) ₂ | −736.79 | — | 1 |
| CaCl ₂ | −795.8 | 104.6 | 1 |

TABLE 7.4
Densities of Cs-Cl Salts

| Phase | T(K) | d (gcm ⁻³) | Reference |
|-----------------------------------|---------|------------------------|-----------|
| CsClO ₃ | Ambient | 3.626 | 26 |
| CsClO ₄ (orthorhombic) | 289 | 3.327 | 27, 28 |
| CsClO ₄ (cubic) | >498 | 3.01 | 29 |

TABLE 7.5
Transitions of Cs-Cl Salts

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol ^o K) | Reference |
|---|----------|-------------------|-----------------------------------|-----------|
| CsClO ₃ , $\alpha \rightarrow \beta$ | 578 | — | — | 26 |
| $\beta \rightarrow$ liquid | 615 | — | — | 26 |
| CsClO ₄ (orthorhombic) \rightarrow cubic | 498 | 8.4 | — | 30 |
| $\beta \rightarrow$ liquid | 850(est) | — | — | 30 |

TABLE 7.6
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|--------------------|--|--|-----------|
| CsClO ₃ | -411.7 | 151.6 | 1 |
| CsClO ₄ | -443.09 | 175.06 | 1 |
| CsCl | -443.04 | 101.17 | 1 |

Note: High temp. data for CsClO₄ (Table 7.7) differ at 298 K.

TABLE 7.7
Thermodynamic Data of CsClO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -437.23 | 175.27 | -489.48 | Knacke et al. 1991 |
| 400.00 | -424.89 | 210.66 | -509.16 | Knacke et al. 1991 |
| 500.00 | -410.17 | 243.42 | -531.88 | Knacke et al. 1991 |
| 600.00 | -385.04 | 290.54 | -559.36 | Knacke et al. 1991 |
| 700.00 | -367.42 | 317.69 | -589.81 | Knacke et al. 1991 |
| 800.00 | -349.81 | 341.21 | -622.78 | Knacke et al. 1991 |
| 900.00 | -332.19 | 361.96 | -657.96 | Knacke et al. 1991 |
| 1000.00 | -314.58 | 380.52 | -695.10 | Knacke et al. 1991 |

TABLE 7.8
Density of Pb-Cl Salts

| Phase | T(K) | d (gcm ⁻³) | Reference |
|------------------------------------|---------|------------------------|-----------|
| Pb(ClO ₃) ₂ | 393 | 3.89 | 41 |
| Pb(ClO ₄) ₂ | Ambient | 3.86 | 42 |

TABLE 7.9
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|------------------------------------|--|--|-----------|
| Pb(ClO ₄) ₂ | -218.4 | — | 43 |
| PbCl ₂ | -326.31 | — | 1 |

TABLE 7.10
Densities of Li-Cl Salts

| Phase | T(K) | d (gcm ⁻³) | Reference |
|--------------------|---------|------------------------|-----------|
| LiClO ₃ | Ambient | 2.631 | 52 |
| | 410 | 2.0832 | 53 |
| | 421 | 2.0756 | 53 |
| | 430 | 2.0681 | 53 |
| | 440 | 2.0605 | 53 |
| | 450 | 2.0529 | 53 |
| | 530 | 2.013 | 53 |
| LiClO ₄ | 540 | 2.007 | 53 |
| | 550 | 2.000 | 53 |
| | 560 | 1.994 | 53 |
| | 570 | 1.988 | 53 |
| | 580 | 1.982 | 53 |
| | 590 | 1.976 | 53 |
| | 600 | 1.970 | 53 |
| | 610 | 1.964 | 53 |
| | 620 | 1.958 | 53 |
| | 630 | 1.951 | 53 |
| | 640 | 1.945 | 53 |
| | 650 | 1.939 | 53 |

TABLE 7.11
Transitions of Li-Cl Salts

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|----------------------------------|------|-------------------|----------------------|-----------|
| LiClO ₃ , c,II → c, I | 384 | — | — | 52 |
| c,I → liquid | 402 | — | — | 52 |
| LiClO ₄ , c → liquid | 520 | 20.9 | 40 | 54, 55 |

TABLE 7.12
Thermodynamic Data of LiClO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | -380.74 | 125.52 | -418.17 | Barin 1989 |
| 400.00 | -368.69 | 160.12 | -432.74 | Barin 1989 |
| 500.00 | -354.95 | 190.72 | -450.31 | Barin 1989 |
| 600.00 | -309.71 | 277.32 | -476.10 | Barin 1989 |
| 700.00 | -293.60 | 302.16 | -505.11 | Barin 1989 |
| 800.00 | -277.49 | 323.67 | -536.42 | Barin 1989 |
| 900.00 | -261.38 | 342.64 | -569.76 | Barin 1989 |
| 1000.00 | -245.28 | 359.61 | -604.89 | Barin 1989 |

TABLE 7.13
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|------------------------------------|--|--|-----------|
| Mg(ClO ₄) ₂ | -568.90 | — | 1 |
| MgCl ₂ | -641.32 | 89.62 | 1 |

TABLE 7.14
Density of K-Cl Salts

| Phase | T(K) | d(gcm ⁻³) | Reference |
|-------------------|------|-----------------------|-----------|
| KClO ₃ | 293 | 2.338 | 130 |
| KClO ₄ | 284 | 2.524 | 131 |
| | 291 | 2.527 | 104 |
| | 298 | 2.530 | 132 |
| | 613 | 2.181 | 103 |

TABLE 7.15
Transitions of K-Cl Salts

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--|------------|-------------------|----------------------|-----------|
| KClO ₃ , c → liquid | 357 | — | — | 129 |
| KClO ₄ c, rhombic → c,cubic | 572.7 | 13.8 | 24.0 | 19 |
| c, cubic → liquid | 853 (est.) | — | — | 81 |

TABLE 7.16
Thermodynamic Data of KClO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -389.11 | 143.09 | -431.76 | Knacke et al. 1991 |
| 400.00 | -378.17 | 174.57 | -448.00 | Knacke et al. 1991 |
| 500.00 | -366.36 | 200.89 | -466.80 | Knacke et al. 1991 |
| 600.00 | -356.72 | 223.91 | -488.07 | Knacke et al. 1991 |
| 700.00 | -340.35 | 244.51 | -511.51 | Knacke et al. 1991 |
| 800.00 | -326.29 | 263.28 | -536.91 | Knacke et al. 1991 |
| 900.00 | -311.57 | 280.60 | -564.11 | Knacke et al. 1991 |
| 1000.00 | -296.21 | 296.79 | -592.99 | Knacke et al. 1991 |

TABLE 7.17
Thermodynamic Data of KClO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -430.12 | 151.04 | -475.15 | Knacke et al. 1991 |
| 400.00 | -417.18 | 188.17 | -492.45 | Knacke et al. 1991 |
| 500.00 | -402.50 | 220.87 | -512.94 | Knacke et al. 1991 |
| 600.00 | -372.77 | 273.98 | -537.16 | Knacke et al. 1991 |
| 700.00 | -355.79 | 300.13 | -565.88 | Knacke et al. 1991 |
| 800.00 | -337.95 | 323.94 | -597.10 | Knacke et al. 1991 |
| 900.00 | -319.32 | 345.87 | -630.61 | Knacke et al. 1991 |
| 1000.00 | -299.96 | 366.27 | -666.23 | Knacke et al. 1991 |

TABLE 7.18
**Activation Energies for the
Decomposition of Rare Earth
Perchlorates**

| Salt | E_a (kJ) |
|------------------------------------|------------|
| La(ClO ₄) ₃ | 142.7 |
| Sm(ClO ₄) ₃ | 120.5 |
| Gd(ClO ₄) ₃ | 119.2 |
| Ho(ClO ₄) ₃ | 108.8 |
| Yb(ClO ₄) ₃ | 105.9 |
| Lu(ClO ₄) ₃ | 105.0 |

TABLE 7.19
Densities of Rb-Cl Salts

| Phase | T(K) | d(gcm ⁻³) | Reference |
|--------------------|---------|-----------------------|-----------|
| RbClO ₃ | Ambient | 3.184 | 60 |
| RbClO ₄ | Ambient | 3.04 | 50 |

TABLE 7.20
Transitions of Rb-Cl Salts

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--|------|-------------------|----------------------|-----------|
| RbClO ₃ , $\alpha \rightarrow \beta$ | 596 | — | — | 48 |
| RbClO ₄ , rhombohedral \rightarrow cubic | 557 | 12.6 | — | 60 |
| cubic \rightarrow liquid | 597 | — | — | 60 |

TABLE 7.21
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|--------------------|--|--|-----------|
| RbClO ₃ | -402.9 | 151.9 | 1 |
| RbClO ₄ | -437.23 | 161.1 | 1 |
| RbCl | -435.35 | 95.90 | 1 |

TABLE 7.22
Density of Ag-Cl Salts

| Phase | T(K) | d(gcm ⁻³) | Reference |
|--------------------|---------|-----------------------|-----------|
| AgClO ₂ | 493 | 4.67 | 97 |
| AgClO ₃ | 493–496 | 4.43–4.46 | |
| AgClO ₄ | 433 | 3.96 (cubic,calc.) | 133 |

TABLE 7.23
Transitions of Ag-Cl Salts

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--|------|-------------------|----------------------|-----------|
| AgClO ₃ , c \rightarrow l | 504 | — | — | 19 |
| AgClO ₄ , rhombic \rightarrow cubic | 412 | — | — | 59 |
| cubic \rightarrow l | 759 | — | — | 105 |

TABLE 7.24
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|--------------------|--|--|-----------|
| AgClO ₂ | 8.79 | 134.56 | 1 |
| AgClO ₃ | -30.29 | 142. | 1 |
| AgClO ₄ | -31.13 | 38.8 (est.) | 1 |
| AgCl | -127.068 | 96.2 | 1 |

TABLE 7.25
Thermodynamic Data of AgClO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|------------|
| 298.15 | 30.29 | 141.84 | 72.58 | Barin 1989 |
| 400.00 | 19.43 | 173.10 | 88.67 | Barin 1989 |
| 500.00 | 7.50 | 199.65 | 107.33 | Barin 1989 |
| 600.00 | 5.68 | 223.66 | 128.51 | Barin 1989 |
| 700.00 | 20.15 | 245.93 | 152.00 | Barin 1989 |
| 800.00 | 35.89 | 266.93 | 177.66 | Barin 1989 |
| 900.00 | 52.91 | 286.97 | 205.36 | Barin 1989 |
| 1000.00 | 71.22 | 306.25 | 235.02 | Barin 1989 |

TABLE 7.26
Transitions of Na-Cl Salts

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|---|------|-------------------|----------------------|-----------|
| NaClO ₃ , c → l | 528 | 22.6 | 42.7 | 19 |
| NaClO ₄ , c, rhombic → cubic | 582 | 2.5 | — | 60 |
| c → l | 741 | — | — | 19 |

TABLE 7.27
Thermodynamic Data of NaClO₃

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|--|--------------------|
| 298.15 | -357.73 | 126.36 | -395.41 | Knacke et al. 1991 |
| 400.00 | -346.66 | 158.19 | -409.94 | Knacke et al. 1991 |
| 500.00 | -334.22 | 185.88 | -427.16 | Knacke et al. 1991 |
| 600.00 | -298.29 | 252.99 | -450.09 | Knacke et al. 1991 |
| 700.00 | -284.99 | 273.50 | -476.44 | Knacke et al. 1991 |
| 800.00 | -271.68 | 291.27 | -504.70 | Knacke et al. 1991 |
| 900.00 | -258.38 | 306.94 | -534.62 | Knacke et al. 1991 |
| 1000.00 | -245.07 | 320.96 | -566.03 | Knacke et al. 1991 |
| 1100.00 | -231.77 | 333.64 | -598.77 | Knacke et al. 1991 |
| 1200.00 | -281.46 | 345.22 | -632.72 | Knacke et al. 1991 |

TABLE 7.28
Thermodynamic Data of NaClO₄

| T K | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | ΔG_f° kJ mol ⁻¹ | Reference |
|---------|--|--|---|------------|
| 298.15 | -382.75 | 142.26 | -425.17 | Barin 1989 |
| 400.00 | -370.01 | 178.84 | -441.55 | Barin 1989 |
| 500.00 | -355.65 | 210.82 | -461.06 | Barin 1989 |
| 600.00 | -326.14 | 263.18 | -484.05 | Barin 1989 |
| 700.00 | -309.69 | 288.52 | -511.65 | Barin 1989 |
| 800.00 | -292.47 | 311.50 | -541.67 | Barin 1989 |
| 900.00 | -274.56 | 332.58 | -573.89 | Barin 1989 |
| 1000.00 | -256.00 | 352.13 | -608.14 | Barin 1989 |
| 1100.00 | -236.83 | 370.41 | -644.27 | Barin 1989 |
| 1200.00 | -217.05 | 387.61 | -682.18 | Barin 1989 |

TABLE 7.29
Density of Sr-Cl Salts

| Phase | T(K) | d (gcm ⁻³) | Reference |
|------------------------------------|---------|------------------------|-----------|
| Sr(ClO ₂) ₂ | Ambient | 3.23 | 27 |
| Sr(ClO ₃) ₂ | Ambient | 3.152 | 90 |
| Sr(ClO ₄) ₂ | 298 | 3.00 | 28, 119 |

TABLE 7.30
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|------------------------------------|--|--|-----------|
| Sr(ClO ₄) ₂ | -762.79 | — | 1 |
| SrCl ₂ | -828.9 | 114.85 | 1 |

TABLE 7.31
Density of Tl-Cl Salts

| Phase | T(K) | d | Reference |
|--------------------|---------|-----------------|-----------|
| TlClO ₃ | Ambient | 4.58 | 134 |
| TlClO ₄ | Ambient | 4.959 (rhombic) | 135 |
| | 553 | 4.58 (cubic) | 103 |

TABLE 7.32
Transitions of Tl-Cl Salts

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol ^o K) | Reference |
|-------------------------------|------|-------------------|-----------------------------------|-----------|
| TlClO ₄ c, rhombic | 539 | — | — | 136,137 |
| cubic → 1 | 778 | — | — | 136 |

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8 Oxysalts of Bromine

8.1 GENERAL

Less is known about the anhydrous bromine-containing oxysalts than about the corresponding compounds of chlorine and iodine. This is true both with respect to the total number of such salts, as well as the information available on each salt. Since 1974, when the last review of these compounds was published,¹ the situation has changed only slightly, with the number of known bromites increasing from 2 to 3, bromates from 15 to 17, and perbromates from 3 to 8. There are still no thermodynamic data above 298 K. Consequently, this chapter is fairly brief, includes no high-temperature equilibrium calculations, and updates qualitative and semi-quantitative information using material published since 1972.

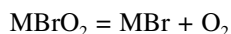
There are only three oxyanions which form anhydrous salts: bromites (BrO_2^-), bromates (BrO_3^-), and perbromates (BrO_4^-). There is no evidence for the existence of stoichiometric, anhydrous hypobromites (BrO^-), nor is there any literature concerning a search for them.

The known and doubtful oxybromine salts are shown in [Figures 8.1 to 8.3](#).

8.2 CLASSES OF OXYBROMINE SALTS

8.2.1 BROMITES

So far, only the bromites of barium, lithium, and strontium have been prepared,² by heating the corresponding bromate and bromide together. The method should be applicable to other bromites as well. So far, very little is known of these salts, except that heating produces the bromide

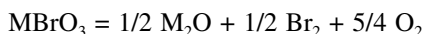


Other methods that have also been used for the preparation of bromites are (a) disproportionation of hypobromites³⁻⁵ and (b) radiolysis of bromates,^{6,7} and decomposition of bromates.^{8,9} The former depends on the use of a hydrate as the starting material and is thus outside the scope of this work; similarly for (b). The cited references will allow the interested reader access to the literature.

8.2.2 BROMATES

These constitute the largest group of bromine oxysalts. The BrO_3^- ion is a flattened pyramid similar to ClO_3^- and IO_3^- . A model derived by Weigel et al.¹⁰ from literature data is shown in [Figure 8.4](#). The quadrupole spectra of bromates¹¹ show that the electronic structure of bromine is affected by the metal cation of the salt. The cation is nearer to one of the oxygen atoms than to bromine, e.g., in NaBrO_3 , $\text{Na}-\text{Br}$ 4.1 Å, $\text{Na}-\text{O}$ 2.38 Å. The $\text{Br}-\text{O}$ distance of 1.78 Å is consistent with a virtually pure single-bond character.

As pointed out by Bancroft and Gesser,^{4,12} bromates may decompose by two competing reactions:



| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
 Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 8.1 The known bromites.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
 Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 8.2 The known bromates.

If thermodynamics were the sole determinant as to which reaction occurs, the argument developed by Markowitz¹³ for predicting the decomposition products of the perchlorates could be used, i.e., if $[\Delta G_f^\circ(\text{MBr}) - \Delta G_f^\circ] > 0$, the oxide should form. Bancroft and Gesser⁴ applied this method to the results of their TGA experiments on several bromates. Their results are shown in Table 8.1.

The rule works reasonably well, particularly when the Gibbs energy difference is large, the most notable exception being $\text{Cd}(\text{BrO}_3)_2$. However, it cannot be expected to be exact in predicting the composition of product mixtures since this is frequently affected by kinetic factors which are particularly difficult to analyze for reactions involving solids. In this connection it is of interest to examine the activation energies for the decomposition reactions in Table 8.1. Bancroft and Gesser⁴ applied a method developed by Horowitz and Metzger¹⁴ which requires that the rate constant obeys an Arrhenius equation. If the reaction is first order, the resulting expression is

$$\ln \left[\ln \frac{W_o - W_f}{W - W_f} \right] = \frac{E^\ddagger \Theta}{RT_s^2}$$

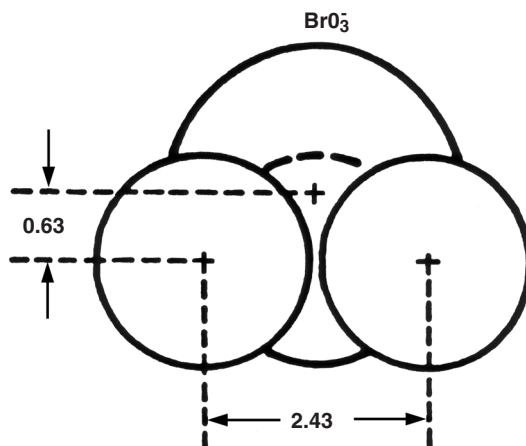


FIGURE 8.3 Structure of the bromate ion. (From Weigel, D., Imelik, B., and Prettre, M., *Bull. Soc. Chim. France*, 1427, 1962. With permission.)

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
 Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 8.4 The known perbromates.

where W_o and W_f are the initial and final weights, respectively; T_s is the temperature at which $[(W - W_f) - (W_o - W_f)] = 1/e$ and $\eta = T - T_s$. Most of the bromates obeyed this equation over at least the first half of the decomposition.

For RbBrO_3 and CsBrO_3 the higher value was obtained with a higher heating rate. In addition, differences in constitutional factors, such as particle size, and defects in the crystal structure, may affect the activation energy in some unknown way.¹⁵ Large anomalies are quite apparent for LiBrO_3 and $\text{Ca}(\text{BrO}_3)_2$, but it is not known whether this is because the reaction is not first order, or for some other reason. It is also noticeable that E^\ddagger values vary considerably even when salts which decompose only to the bromide are considered. This is true even within the same group in the periodic table, such as alkali metal and alkali earth bromates, where great differences in the mechanism and/or bond energies within the BrO^- would not be expected. Clearly, Table 8.1 is only an argument for further kinetic studies, particularly isothermal ones. For convenience, information on decomposition of bromates, collected by Solymosi,¹⁶ has been given in Table 8.2. From this it appears that the stabilities of the alkali metal bromates decrease in the order $\text{Li} > \text{Na} > \text{K} > \text{Cs} > \text{Rb}$.

The kinetics consist of rapid nucleation, followed by a contracting sphere model.¹⁷

Trivalent bromates generally exist only as hydrates, although some of them, La, Pr, Nd, Sm, Er, are reported to have been dehydrated to the anhydrous compound without decomposition.¹⁸

8.2.3 PERBROMATES

In contrast to the well-known +7 oxidation state of chlorine and iodine exhibited by the perchlorates and periodates, attempts to prepare perbromates were, until rather recently, unsuccessful. References to the earlier work are given by Bancroft and Gesser.⁴

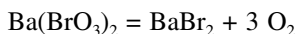
The synthesis of HBrO_4 and rubidium and potassium salts was accomplished, using oxidation of bromate by XeF_2 or (preferably) molecular fluorine in aqueous solution.¹⁹ Spectral studies²⁰ show that the perbromate ion is tetrahedral in both the solid-state and aqueous solutions. The thermodynamic properties and thermal decomposition of individual salts are discussed under each element. A more general article on various properties of the perbromates was published by Herrell and Gayer.²¹

8.3 INDIVIDUAL BROMINE — OXYSALTS

8.3.1 BARIUM

8.3.1.1 $\text{Ba}(\text{BrO}_2)_2$

The salt has been prepared²² by the thermal decomposition of $\text{Ba}(\text{BrO}_3)_2$ at 280°C under an O_2 atmosphere. Decomposition probably proceeds according to

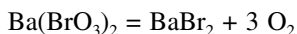


BaBr_2 is separated by extraction with anhydrous ethanol. Above 795°C the bromite decomposes rapidly.

8.3.1.2 $\text{Ba}(\text{BrO}_3)_2$

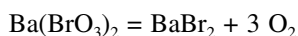
Two crystalline forms of $\text{Ba}(\text{BrO}_3)_2$ have been reported.²³ The low-temperature form was produced by rapid heating of the monohydrate, whereas isothermal heating of the hydrate between 105 and 120°C produced the high-temperature form. The transformation I \rightarrow II was detected by DTA at 160°C.

Several groups have studied the thermal decomposition of the salt.^{23,24} They agree that the final product is BaBr_2 , i.e., the overall reaction is



but both $\text{Ba}(\text{BrO}_2)_2$ (see above) and $\text{Ba}(\text{BrO}_4)_2$ have been suggested as intermediates, the latter on the basis of a great increase in the rate after one third of the oxygen had disappeared. However, no such increase was noted by Bancroft and Gesser.⁴ Dupuis and Rocchiccioli²⁵ observed differences in the spectra of $\text{Ba}(\text{BrO}_3)_2$ heated below and above 159°C. They argued against the formation of bromite at the higher temperature and hypothesized the existence of two crystalline forms of the bromite. It seems, however, that the work of Tanguy et al.²² provides firmer evidence for the formation of bromite as an intermediate. The kinetics of the overall decomposition were measured by Lumme and Lumme^{22a} using TGA. They found decomposition occurring in the range 290 to 380°C in air, and 265 to 315°C in vacuum. The Arrhenius activation energy of 209 kJ calculated from their data agrees well with the 218 kJ given by Bancroft and Gesser.¹²

The decomposition kinetics were also studied by Mohanty and co-workers,^{26–28} who were interested in elucidating the effect of radiation and doping. The effect of both is to introduce defects into the crystal structure. In the range 219 to 315°C the decomposition of normal Ba(BrO₃)₂ can be divided into five regions: (1) initial gas evolution, up to $\alpha = 0.06$; (2) a short induction period; (3) a slow linear reaction followed by a sigmoidal zone consisting of (4) acceleratory and (5) decay stages. The decomposition begins entirely in the solid state:



and the initial stage (1) is likely due to physical desorption and removal of occluded gases. The induction period is attributed to the formation of a small number of nuclei at lattice imperfections. The linear stage is attributable to surface decomposition caused by these nuclei. These nuclei slowly penetrate the interior of the crystal. The following sigmoidal stage has been attributed to the formation of new nuclei and the formation of cracks at $\alpha = 0.2$, with the reaction proceeding down these cracks. Irradiation produces various kinds of defects which affect different stages of the decomposition differently.

8.3.1.3 Ba(BrO₄)₂

The decomposition of this salt was studied by Russian researchers²⁹ who prepared it by the reaction of HBrO₄ with BaO. The salt may not have been entirely anhydrous. Studies by DTA and TGA showed that decomposition to the bromate occurred at 462 K, which then decomposed further at 548 K.

Thermodynamic data of Ba(BrO₃)₂ and BaBr₂ are given in [Table 8.3](#).

8.3.2 CADMIUM

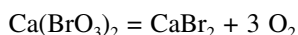
8.3.2.1 Cd(BrO₃)₂

The salt can be prepared by step-wise dehydration of the dihydrate. The salt is then stable up to 250°C, above which it decomposes, largely to the oxide.¹²

8.3.3 CALCIUM

8.3.3.1 Ca(BrO₃)₂

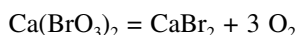
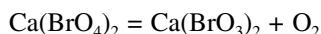
Not much work has been done on this salt. It decomposes in the solid state according to



in the range 260 to 340°C.¹² In vacuum the decomposition begins at 220°C. The kinetics follows the same mechanism³⁰ as was described for Ba(BrO₃)₂.

8.3.3.2 Ca(BrO₄)₂

The salt decomposes according to the following scheme:



The first decomposition occurs at 464 K, the second at 532 K.

Thermodynamic data are shown in [Table 8.4](#).

8.3.4 CESIUM

8.3.4.1 CsBrO₃

A specific gravity at 16°C of 4.109 was reported.³³ Thermal decomposition proceeds to the bromide:



The kinetics at 673 K were reported³² to follow Prout-Tompkins kinetics, passing through an initial period of gas evolution, short acceleratory regime, and long decay.

8.3.4.2 CsBrO₄

The decomposition proceeds according to



in the range 473 to 592 K.²⁹

Thermodynamic data are shown in [Table 8.5](#).

8.3.5 COPPER

8.3.5.1 Cu(BrO₃)₂

The anhydrous salt has not yet been definitely prepared. The hydrate decomposes at 180 K, with the loss of oxygen and possibly bromine, and the formation of Cu₂O and a basic bromate or oxybromate.³⁴

8.3.6 LEAD

8.3.6.1 Pb(BrO₃)₂

Very little work has been done on this salt since two people were killed³⁵ while grinding the material which had been prepared from KBrO₃ and lead acetate, although it was later established that the compound thus formed is diacetatoplumbo bromate.³⁶ Pb(BrO₃)₂·H₂O is reported to decompose near 100°C into PbO₂, PbBr₂, and Br₂.

The only thermodynamic value is $\Delta G_f^\circ = -16.30 \text{ kJ}$ at 298.15 K.⁵⁶

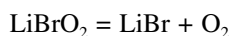
8.3.7 LITHIUM

8.3.7.1 LiBrO₂

Preparation of this salt was carried out by heating LiBrO₃ and LiBr between 190 and 220°C:

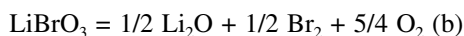


The salt is very hygroscopic. Near 225°C it decomposes while melting:



8.3.7.2 LiBrO₃

The salt decomposes by two competing reactions:^{2,12}



95% of the decomposition proceeds by reaction (a). Curiously, the oxide is formed predominantly in the initial stages; it then stops and the major part of the decomposition goes to LiBr. The products of (b) do not react further so that LiBr cannot be formed by the reaction $1/2 \text{ Li}_2\text{O} + 1/2 \text{ Br}_2 = \text{LiBr} + 1/4 \text{ O}_2$. The decomposition temperature is in doubt. Bancroft and Gesser¹² report it to occur as low as 214°C, whereas Simmons and Waldeck³⁷ report the melting point to lie between 248° and 260°C. The former results were obtained at very low pressures and this may account for the difference.

8.3.7.3 LiBrO₄

Decomposition follows the sequence



The decomposition temperature of LiBrO₄, 573 K, coincides with its melting.

Densities are given in [Table 8.6](#), thermodynamic data in [Table 8.7](#).

8.3.8 MAGNESIUM

8.3.8.1 Mg(BrO₃)₂

No thermodynamic data are available. The only thermal decomposition study is that of Bancroft and Gesser¹² who found that decomposition, beginning near 250°C, goes almost entirely to the oxide:



8.3.8.2 Mg(BrO₄)₂

Decomposition to Mg(BrO₃)₂ occurs at 472 K²⁹ and, in contrast to the barium salt, proceeds largely to the oxide.

8.3.9 MERCURY

8.3.9.1 HgBrO₃

The preparation of this salt is mentioned by Mellor³⁸ and Gmelin.³⁹ Its thermal decomposition apparently leads to the formation of metallic mercury, but the decomposition does not seem to have been studied in detail.

8.3.9.2 $\text{Hg}(\text{BrO}_3)_2$

The anhydrous salt decomposes slightly when heated to near 125°C and then deflagrates near 155°C, with HgBr_2 as the major product.⁴⁰

8.3.10 NICKEL

8.3.10.1 $\text{Ni}(\text{BrO}_3)_2$

The salt begins to decompose near 160°C, the product being largely NiO , with some NiBr_2 formed as a secondary product.¹²

8.3.11 POTASSIUM

8.3.11.1 KBrO_3

There appears to be no reliable melting point for this salt since its decomposition begins in the solid state. Japanese workers⁴¹ report an endothermic DTA peak at 698 K which they identify with the melting point. However, decomposition has been reported as low as 615 K;⁴² somewhat higher decomposition temperatures were reported by Duval⁴³ and Bancroft and Gesser,¹² but this obviously depends on the sensitivity with which weight loss can be measured.

Jach⁴² studied decomposition kinetics from 615 K up. The overall decomposition is entirely



Jach found somewhat different kinetics over the ranges 615 to 640 K and 652 to 685 K, with a transition region between the two ranges. Over both the reaction appeared to be first order, but the Arrhenius activation energies in the low and high regions were 260 and 221 kJ, respectively. Over the higher range melting evidently occurred, with the formation of a eutectic at the interface between KBr and KBrO_4 and bulk melting near the top of the range. Over both ranges the reaction begins with rapid nucleation of the entire surface, followed by a contracting reaction zone. However, the first-order kinetics do not fit this mechanism, and Jach suggested that extensive cracking of crystals, which is observed during decomposition, is responsible for this. The chemical mechanism of the decomposition has not yet been studied.

8.3.11.2 KBrO_4

The salt decomposes in two stages:²⁹



The decomposition begins at 275°C, a temperature at which KBrO_3 is still stable.

The density of KBrO_3 is 3.27 gcm⁻³ at 290 K.³³

Thermodynamic data at 298.15 K are given in [Table 8.8](#).

8.3.12 RARE EARTHS

8.3.12.1 Bromates

The anhydrous bromates of Y, La, Pr, Nd, Sm, Gd, Dy, Ho, Er, Yb, and Lu have been prepared by treating the oxides with HBrO_3 .^{44,45} The salts decompose near 170°C to the oxybromides:⁴⁵



and finally to the oxides. Rate constants and activation energies for the decomposition have been reported.⁴⁶

8.3.13 RUBIDIUM

8.3.13.1 RbBrO_3

A specific gravity value at 16°C of 3.680 has been reported.⁴⁷

The salt decomposes entirely to the bromide:



beginning at 360°C.²⁹ This value is clearly inconsistent with the melting point of 430°C reported by Buell and McCroskey⁴⁸ for a carefully purified sample. The very low pressures in Bancroft and Gesser's apparatus would favor the decomposition.

8.3.13.2 RbBrO_4

The salt decomposes in the solid state near 285°C to RbBrO_3 .²⁹

An ambient temperature density of 3.68 gcm⁻³ has been reported.³³

Thermodynamic data are listed in [Table 8.9](#).

8.3.14 SILVER

8.3.14.1 AgBrO_3

The salt decomposes to the bromide:



Decomposition starts near 200°C and is complete near 300°C.^{12a} In the presence of dust, decomposition is explosive.⁴⁹

A density value of 5.206 gcm⁻³ at 293 K has been reported.⁴⁷ Thermodynamic data are given in [Table 8.10](#).

8.3.15 SODIUM

8.3.15.1 NaBrO_3

The linear thermal expansion coefficient has been measured by Sharma⁵⁰ between 36.5 and 285.1°C, and by Ganesan⁵¹ between -149 and +171.5°C. Although both authors agree well in their results for NaClO_3 , they disagree considerably for NaBrO_3 . Near 50°C both sets of data agree fairly well, but Sharma obtained a much smaller temperature coefficient for α . There is no obvious reason for the difference.

NaBrO_3 decomposes entirely to the bromide:



At low pressures decomposition begins near 320°C.¹² The kinetics were studied by Jach⁴² in the range 323 to 430°C. Surface nucleation by NaBr is very rapid, after which a contracting envelope mechanism is followed. An Arrhenius plot exhibits a marked discontinuity at 330°C. Above this

temperature the plot is linear, below it the rate drops abruptly to rates much lower than expected from the extrapolation of the high-temperature plot. In the high-temperature region, Jach postulates a liquid eutectic at the NaBrO_3 - NaBr interface. The effect of particle size and dislocation is discussed, but no detailed mechanism is presented.

A density value of 3.339 gcm^{-3} at 290 K has been reported.³³

8.3.15.2 NaBrO_4

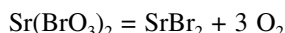
The salt was prepared from NaOH and HBrO_4 . Its decomposition occurred at $266 \pm 10^\circ\text{C}$.²⁹

Thermodynamic data are given in [Table 8.11](#).

8.3.16 STRONTIUM

8.3.16.1 $\text{Sr}(\text{BrO}_3)_2$

Very little information is available for this salt. According to the older literature⁵² decomposition begins near 240°C and results mainly in the formation of SrBr_2 , as well as some SrO . The more recent results of Bancroft and Gesser¹² show that the decomposition is entirely to the bromide:



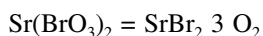
beginning near 265°C . Similar results were also obtained earlier by Hackspill and Winterer.³

8.3.16.2 $\text{Sr}(\text{BrO}_4)_2$

The decomposition of this salt has been studied by TGA and DTA,⁵³ beginning with a hydrate. At 473 K the salt decomposes to the bromate:



which then decomposes at 532 K:



8.3.17 THALLIUM

8.3.17.1 TlBrO_3

Decomposition kinetics have been studied in considerable detail.^{54,55} Decomposition becomes appreciable near 125°C and results largely in the formation of black thallic oxide:



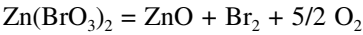
A small amount of TlBr also seems to be formed.

Kinetically, the reaction appears to occur in three stages: (a) an initial phase of up to 3 to 4% decomposition which fits a first-order rate equation, the activation energy for this stage is 150 kJ; (b) an acceleratory stage fitted by the Prout-Tompkins equation, the activation energy for this stage, terminating near 35% decomposition, is 209 kJ; (c) the decay stage is well fitted by the contracting sphere model with an activation energy of 150 kJ. A tentative mechanism proposed to account for these observations identifies the initial phase with rapid decomposition at the subgrain boundaries, followed by progression of the reaction into the subgrains.

No thermodynamic data are available.

8.3.18 ZINC

The thermal decomposition of $\text{Zn}(\text{BrO}_3)_2$ was studied by Bancroft and Gesser.¹² Decomposition begins near 150°C and proceeds nearly entirely to the oxide:



No thermodynamic data are available.

TABLE 8.1
Gibbs Energy Differences $[\Delta\text{Gf}^\circ (\text{Br}^-) - \Delta\text{Gf}^\circ (\text{O}^{2-})]_{\text{equ.}}$ (kJ)

| Salt | T(K) | | | |
|------------------------------------|-------------------|-------|-------|----------------|
| | % Br ⁻ | 300 | 1000 | E [#] |
| LiBrO ₃ | 90 | -57.7 | -47.3 | 1159 |
| NaBrO ₃ | 100 | -151 | -137 | 352 |
| KBrO ₃ | 100 | -217 | -196 | 494 |
| RbBrO ₃ | 100 | -233 | | 205-226 |
| CsBrO ₃ | 100 | | | 100-138 |
| Mg(BrO ₃) ₂ | 5 | +70.7 | +94.6 | 84 |
| Ca(BrO ₃) ₂ | 100 | -50.2 | -21 | 1205 |
| Sr(BrO ₃) ₂ | 100 | -143 | -110 | 278 |
| Ba(BrO ₃) ₂ | 100 | -205 | -162 | 218 |
| Zn(BrO ₃) ₂ | 1 | +12 | +21 | 193 |
| Cd(BrO ₃) ₂ | 2 | -70.7 | -36 | 159 |
| AgBrO ₃ | 100 | -80.3 | | 188 |
| Ni(BrO ₃) ₂ | 7 | +3 | +35 | 193 |

TABLE 8.2
Characteristic Data on the Thermal Stability of Bromates^{4,16,46}

| Salt | Temperature Range of Decomposition (°C) |
|------------------------------------|---|
| LiBrO ₃ | 236-256 |
| NaBrO ₃ | 298-368 |
| KBrO ₃ | 366-395 |
| RbBrO ₃ | 328-416 |
| CsBrO ₃ | 265-388 |
| Mg(BrO ₃) ₂ | 245-329 |
| Ca(BrO ₃) ₂ | 245-270 |
| Sr(BrO ₃) ₂ | 248-275 |
| Ba(BrO ₃) ₂ | 267-328 |
| Ni(BrO ₃) ₂ | 168-221 |
| Zn(BrO ₃) ₂ | 160-205 |
| Cd(BrO ₃) ₂ | 240-310 |
| La(BrO ₃) ₃ | 210-231 |
| Pr(BrO ₃) ₃ | 197-235 |
| Sm(BrO ₃) ₃ | 214-242 |
| Dy(BrO ₃) ₃ | 210-232 |
| Ho(BrO ₃) ₃ | 205-232 |
| Er(BrO ₃) ₃ | 214-235 |
| Yb(BrO ₃) ₃ | 212-231 |
| Lu(BrO ₃) ₂ | 225-252 |

TABLE 8.3
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|------------------------------------|--|--|-----------|
| Ba(BrO ₃) ₂ | -718.18 | 247. | 56 |
| BaBr ₂ | -757.3 | 146. | 56 |

TABLE 8.4
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|------------------------------------|--|--|-----------|
| Ca(BrO ₃) ₂ | -685.8 | — | 56 |
| CaBr ₂ | -682.8 | 130 | 56 |

TABLE 8.5
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|--------------------|--|--|-----------|
| CsBrO ₃ | -375.81 | 163.6 | 56 |
| CsBr | -405.8 | 113.05 | 56 |

TABLE 8.6
Density of LiBrO₃

| Phase | T(K) | d | Reference |
|--------------------|---------|--------------|-----------|
| LiBrO ₃ | Ambient | 3.62 (pyk) | 57 |
| | Ambient | 3.76 (X-ray) | |

TABLE 8.7
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|--------------------|--|--|-----------|
| LiBrO ₃ | -346.98 | — | 56 |
| LiBr | -351.213 | 74.27 | 56 |
| Li ₂ O | -597.94 | 37.57 | 56 |

TABLE 8.8
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-------------------|--|--|-----------|
| KBrO ₄ | -287.86 | 170.08 | 56 |
| KBrO ₃ | -360.24 | 149.16 | 56 |
| KBr | -397.798 | 95.90 | 56 |

TABLE 8.9
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|--------------------|--|--|-----------|
| RbBrO ₃ | -367.27 | 161.1 | 56 |
| RbBr | -394.6 | 109.96 | 56 |

TABLE 8.10
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|--------------------|--|--|-----------|
| AgBrO ₃ | -10.5 | 151.9 | 56 |
| AgBr | -100.37 | 107.1 | 56 |

TABLE 8.11
Thermodynamic Data (298.15 K)

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|--------------------|--|--|-----------|
| NaBrO ₃ | -334.09 | 128.9 | 56 |
| NaBr | -361.0 | 86.82 | 56 |

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9 Oxysalts of Iodine

9.1 GENERAL

The chief difference between the oxyanions of iodine and those of chlorine and bromine is the large number of periodates (see below). Otherwise, differences between the respective anions are largely accounted for by the larger size of iodine and its more metallic character.

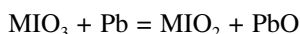
Although thermodynamic data at 298.15 K, e.g., Wagman et al.¹ are available, very little above this temperature is in the standard compilations. In earlier work [2] equilibrium constants for decomposition reactions involving alkali metal and alkaline earth salts were calculated from a variety of sources. In the absence of newer data these were retained in this chapter.

The known oxysalts of iodine are shown in [Figures 9.1 to 9.5](#).

9.2 CLASSES OF OXYIODINE SALTS

9.2.1 IODITES

Until recently no anhydrous iodites were known. In 1965 Harmelin and Duval³ reported a general method for the preparation of iodites: the solid-state reduction of iodates by metallic lead. Since the reaction occurs without loss of weight, it was postulated to occur according to



The iodites of Na, K, Ca, Ba, and Pb were prepared in this way at 420 to 425°C and the existence of IO_2^- determined from its infrared spectrum. However, the pure compounds were not isolated and no further synthetic work seems to have been done since 1965. Since no further information is available, these compounds are not described under the respective elements.

9.2.2 IODATES

The iodates all contain the pyramidal IO_3^- ion in which the iodine atom is bonded covalently to the three oxygens. (See [Figure 9.2](#).) As shown in [Figure 9.1](#), all the alkali metals (except Fr) and alkaline earths (except Be) form anhydrous iodates. Beryllium salts are frequently difficult to obtain in the anhydrous state because of the high charge density of Be^{+2} . Dasent and Waddington⁴ studied the infrared spectra of several iodates. They distinguish between ionic iodates in which the crystals contain discrete, pyramidal IO_3 groups, e.g., NaIO_3 , and iodate compounds ($-\text{O}-\text{IO}_2$) in which the metal is bound covalently to oxygen. Examples of the latter type are $\text{Pb}(\text{IO}_3)_2$, and both mercuric and mercurous iodate.

In general, iodates are thermally rather stable. Many of them can be heated to several hundred °C without appreciable decomposition. When they do decompose, it is frequently in the solid state or on melting. Thus there are virtually no properties of liquid iodates known. The decomposition reactions fall into three groups:

| | | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne | |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar | |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | | |

Lanthanides **Ce** Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinides **Th** Pa U Np **Pu** Am Cm Bk Cf Es Fm Md No Lw

FIGURE 9.1 The known iodates.

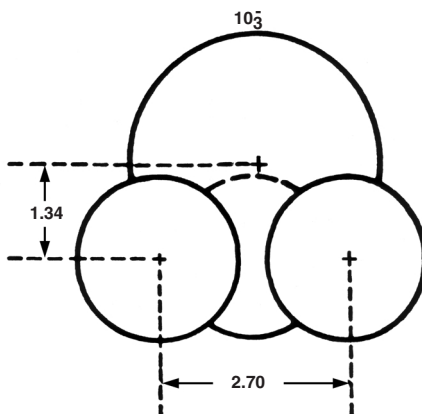


FIGURE 9.2 Structure of the IO_3 ion. (From Weigel, D., Imelik, B., and Prettre, M., *Bull. Soc. Chim. France*, 1427, 1962, With permission.)

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 9.3 The known orthoperiodates.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides **Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu**
Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 9.4 The known mesoperiodates.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

Lanthanides Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

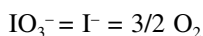
FIGURE 9.5 The known pyroperiodates.

| | | | | | | | | | | | | | | | | | | |
|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----|
| | | | | | | | | | | | | | | | | | H | He |
| Li | Be | | | | | | | | | | | | B | C | N | O | F | Ne |
| Na | Mg | | | | | | | | | | | | Al | Si | P | S | Cl | Ar |
| K | Ca | Sc | Ti | V | Cr | Mn | Fe | Co | Ni | Cu | Zn | Ga | Ge | As | Se | Br | Kr | |
| Rb | Sr | Y | Zr | Nb | Mo | Tc | Ru | Rh | Pd | Ag | Cd | In | Sn | Sb | Te | I | Xe | |
| Cs | Ba | La | Hf | Ta | W | Re | Os | Ir | Pt | Au | Hg | Tl | Pb | Bi | Po | At | Rn | |
| Fr | Ra | Ac | | | | | | | | | | | | | | | | |

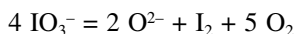
Lanthanides Ce Pr Nd Pm Sm Eu Gd Tb Dy Ho Er Tm Yb Lu
Actinides Th Pa U Np Pu Am Cm Bk Cf Es Fm Md No Lw

FIGURE 9.6 The known metaperiodates.

- a. Iodates of the alkali metals (except Li), Ag, Co, and probably both Hg(I) and Hg(II) decompose according to

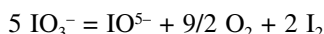


- b. Iodates of Cu, Cd, Zn, Ni, and probably Mg, Ti(I), and Pb go to the oxide



In addition, iodates of Na and K appear to go partly by this route.

- c. Iodates of Li, Ca, Ba, Sr, and the rare earths form the orthoperiodate



Reactions of type (a) for Na, K, Rb, and Cs can attain equilibrium, and those constants were calculated. Calculations are in good agreement with experimentally determined values. No calculations could be carried out for type (b) reactions. Only for $\text{Mg}(\text{IO}_3)_2$ have enthalpy increments above 298 K been measured, but in this case $S^\circ(298 \text{ K})$ is not known. There are no experimental studies. For reactions of type (c) only the calculation for Ca could be done since no $S^\circ(298 \text{ K})$ values for the periodates of Li, Ba, and Sr are available.

9.2.3 PERIODATES

The number of iodine-containing acids and salts in which the formal valence of iodine is +7 is far greater than that for the corresponding chlorine and bromine compounds. This behavior is generally consistent with the increasing metallic character of the heavier elements in a particular group.

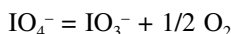
Although various authors do not agree in all details on the number of periodic acids and periodates that exist, or their nomenclature, we list for the convenience of the reader the acids and salts which are generally recognized (see [Table 9.1](#)).

Structural information on the solid periodates is rather scarce. The IO_4^- ion is known to be tetrahedral^{5,6} and IO_5^{5-} is octahedral.^{6,7} The I–O bonding in these ions has been described [6], but the cation-anion distance has not been studied. Of the other periodates, only the structure of $\text{K}_4\text{I}_2\text{O}_9$ has been studied. The oxygen-bridged structure of the ion is described under potassium.

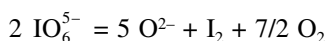
In [Figures 9.3 to 9.6](#) the known anhydrous periodates have been listed. It is likely that the figures merely reflect work that has been done, rather than a limitation on the periodates that *could* exist. There are undoubtedly many more periodates that could be synthesized.

The various periodates decompose according to several different schemes, generally in the solid state; only the metaperiodates seem to have a melting point.

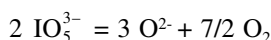
- a. The metaperiodates of Na, K, Rb, and Mg decompose to the iodate:



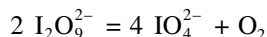
- b. The orthoperiodates of Li, Na, Ca, Sr, and Ba go to the oxide:



- c. Decomposition of the mesoperiodates has not been studied except for the rare earths and Y:



d. Of the pyroperiodates, only cadmium salt has been studied:



In this reaction a salt of hexavalent iodine is formed. Very little work on salts containing the IO_4^- ion has been reported yet. Decomposition of diorthosalts has not yet been studied.

9.3 INDIVIDUAL SALTS

9.3.1 ALUMINUM

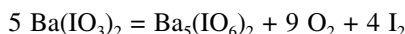
9.3.1.1 $\text{Al}(\text{IO}_3)_3$

Anhydrous $\text{Al}(\text{IO}_3)_3$ can be prepared by the dehydration of its octahydrate. It then decomposes to the oxide in two stages in the range 460 to 560°C.⁸ No further information was provided by the authors.

9.3.2 BARIUM

9.3.2.1 $\text{Ba}(\text{IO}_3)_2$

The salt is stable to near 580°C.⁹⁻¹¹ Above this temperature it undergoes the Rammelsberg reaction:

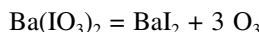


The *gef* for the iodate was calculated from the 298.15 K values in Wagman et al.,¹ and the enthalpy increments determined calorimetrically by David et al.¹² Unfortunately, equilibrium constants for the above reaction cannot be calculated, because no $S^\circ_{298.15}$ is available for barium paraperiodate.

The density at 293 K is 5.23 gcm⁻³.¹³

9.3.2.2 $\text{Ba}(\text{IO}_4)_2$

This salt decomposes to the iodate and O_2 in the range 150 to 250°C.^{14,15} The iodate then decomposes further at 400 to 500°C:



9.3.2.3 $\text{Ba}_5(\text{IO}_6)_2$

This salt is stable to near 950°C.^{9,11,16} Above this temperature it decomposes according to



This reaction is reversible.¹⁶ The temperature at which decomposition occurs depends therefore on the gas phase; for example, under vacuum, decomposition becomes noticeable at as low as 500°C. The lack of S° values for this salt prevents any equilibrium calculations for the above reaction, as well as the *gef* calculation for the paraperiodate. The enthalpy and entropy increments are based on the calorimetric enthalpy increments of David, Mathurin, and Thevenot.¹²

Thermodynamic data for these salts are given in [Tables 9.2](#) and [9.3](#).

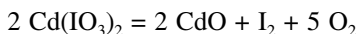
9.3.3 BISMUTH

Although the existence of $\text{Bi}(\text{IO}_3)_3$ has been reported,^{17,18} the pure anhydrous salt has probably not yet been prepared.

9.3.4 CADMIUM

9.3.4.1 $\text{Cd}(\text{IO}_3)_2$

The salt is stable to $\approx 560^\circ\text{C}$. Above this temperature it decomposes according to Varhely and Kekedy¹¹



A ΔG° value of 377.1 kJ has been reported.¹

9.3.4.2 $\text{Cd}_3(\text{IO}_5)_2$

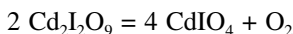
Varhely and Kekedy¹¹ report that this salt forms by the dehydration of its monohydrate near 210°C . It is then stable to near 525°C . Above this temperature it decomposes to the oxide.

9.3.4.3 $\text{Cd}_5(\text{IO}_6)_2$

Preparation of this compound has been reported,¹⁷ but its properties have not yet been reported.

9.3.4.4 $\text{Cd}_2\text{I}_2\text{O}_9$

The anhydrous compound has been prepared and its decomposition studied.¹⁷ At temperatures as low as 110°C decomposition leads to the formation of hexavalent cadmium iodate



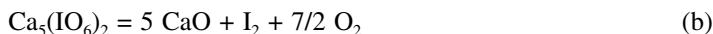
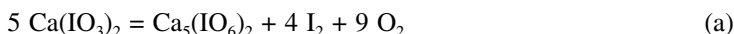
At a higher temperature the latter decomposes to the oxide.

The density of $\text{Cd}(\text{IO}_3)_2$ is 6.48 gcm^{-3} .¹³

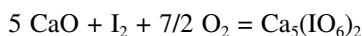
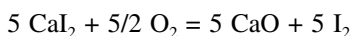
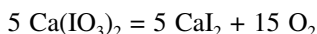
9.3.5 CALCIUM

9.3.5.1 $\text{Ca}(\text{IO}_3)_2$, $\text{Ca}_5(\text{IO}_6)_2$

It is generally agreed^{20,21} that the decomposition of $\text{Ca}(\text{IO}_3)_2$ occurs in two successive steps:



Since both reactions produce gaseous products, the stability range would be expected to vary with the gas-phase pressure and composition. Reaction (a) appears to begin near 550°C and to be complete near 770°C .²¹ However, the reaction appears to be reversible and according to Bousquet and Remy²⁰ is the sum of the reactions



Thus, in vacuum, heating of $\text{Ca}(\text{IO}_3)_2$ would produce CaI_2 . In air, the first reaction is not displaced appreciably to the right below 510°C .²² For this reason the calculation of the equilibrium constant for reaction (a) is somewhat misleading since it suggests appreciable decomposition of $\text{Ca}(\text{IO}_3)_2$

in air above 325°C. However, the equilibrium can probably not be established unless some CaI_2 is formed. Similarly, $\text{Ca}_5(\text{IO}_6)_2$ seems to be stable to a somewhat higher temperature, probably at least 725°C, than indicated by the calculation for reaction (b), but the reasons for this are not clear.

9.3.5.2 CaI_2O_9

This salt has been reported¹¹ as an intermediate in the dehydration of its 9-hydrate and to be stable to near 550°C. Above this temperature it decomposes, first to the hexavalent IO_4 ion and subsequently to the orthoperiodate.¹⁴ The overall reaction is



Thermodynamic data at 298.15 K are given in Table 9.4, and thermodynamic data for the decomposition of $\text{Ca}(\text{IO}_3)_2$ and $\text{Ca}_5(\text{IO}_3)_2$ are in Tables 9.5 and 9.6, respectively.

9.3.6 CESIUM

9.3.6.1 CsIO_3

The ambient temperature density of CsIO_3 is uncertain. Pycnometrically determined values listed by Bousquet and David²³ vary from 4.83 to 4.94 gcm^{-3} , compared to 4.99 calculated from X-ray data. This suggests that crystals with varying void content were used.

Decomposition occurs on melting with oxygen evolution:^{24,25}



In order to calculate the equilibrium constant for this reaction, $S^\circ(298.15 \text{ K})$ of CsIO_3 was estimated and enthalpy and entropy increments were calculated from the calorimetric data. The corresponding increments for CsI were obtained from the estimated C_p values of Kelley.²⁶ The resulting equilibrium constants indicate decomposition well below the melting point, but the rate in the solid state may be too slow to be detectable. Bousquet and Remy²⁷ calculated the equilibrium pressure of O_2 using thermodynamic values which differ little from those used here. They also measured oxygen pressures by both static and dynamic methods between 533 and 740 K and obtained good agreement with their own calculation. Their values of $\log K$ are approximately 0.5 more negative than those listed here over the entire temperature range. Most of this difference is accounted for by the different S° values selected by Bousquet and Remy.²⁷

CsIO_3 and CsI form a eutectic at 781 K. Above this temperature decomposition leads to the formation of a liquid phase, but the oxygen pressure will remain independent of composition as long as a solid phase is present.

9.3.6.2 CsIO_4

The salt exists in three crystalline modifications.²⁸ Forms II and III are probably tetragonal and orthorhombic, respectively. The structure of I is less certain. The transformation $\text{I} \rightarrow \text{II}$ exhibits a large hysteresis. The transformation listed was obtained with rising temperature. On decreasing the temperature, it occurs about 30°C lower. The density of what is probably II is 4.25 gcm^{-3} .²⁹ Decomposition is reported³⁰ to go to the iodate near 500°C:



but no quantitative data on the reaction are available.

Thermodynamic data at 298.15 K are given in Table 9.7, and data for the decomposition of CsIO_3 are in Table 9.8.

9.3.7 CHROMIUM

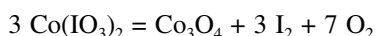
9.3.7.1 $\text{Cr}(\text{IO}_3)_3$

The preparation of the anhydrous salt has been reported,³¹ but no information about its properties was given except that it decomposes with the formation of a volatile compound near 420°C.

9.3.8 COBALT

9.3.8.1 $\text{Co}(\text{IO}_3)_2$

The blue-violet salt appears to be stable to at least 220°C³² but decomposes in the range 415 to 425° to give Co_3O_4 according to the reaction^{10,11}



A density value of 5.138 gcm⁻³ has been given by Duval.³²

9.3.9 COPPER

9.3.9.1 $\text{Cu}(\text{IO}_3)_2$

The salt exists in three crystalline modifications with different densities:³³

| | |
|---|-------|
| α light yellow green, monoclinic | 5.275 |
| β light green, triclinic | 4.91 |
| γ dark yellow, monoclinic | 5.328 |

At 450°C it decomposes to the oxide:^{10,34}



An activation energy of 325 kJ has been reported for this reaction in air from TGA data.³⁴

No thermodynamic data have been listed in Wagman et al.,¹ but older values are given in [Table 9.9](#).

9.3.10 INDIUM

9.3.10.1 $\text{In}(\text{IO}_3)_3$

The anhydrous white salt was first prepared by Mathers and Schluederberg³⁵ and the existence of the compound confirmed.³⁶ On heating, the crystals turn brown and evolve iodine vapor.³⁵ Decomposition at much higher temperature, 530 to 600°C, has been reported.⁸

9.3.10.2 InIO_5

Preparation of the yellowish crystalline compound was reported,³⁶ but none of its properties were examined.

9.3.11 IRON

9.3.11.1 $\text{Fe}(\text{IO}_3)_3$

Preparation of the anhydrous salt was reported by Endredy³⁷ with a decomposition temperature in air of 130°C. More recent studies^{31,33,38} found $\text{Fe}(\text{IO}_3)_3$ to be much more stable. It began to decompose slowly only at 370°C, and rapidly at 470°C.

9.3.11.2 $\text{Fe}_5(\text{IO}_6)_2$

Reported by Kimmins³⁹ to be a brick-red crystalline salt, the iron content was slightly below the theoretical value.

9.3.11.3 $\text{Fe}(\text{IO}_4)_3$

Preparation was reported by both Kimmins³⁹ and Endredy.³⁷ The dry salt can be heated in air up to 125°C. Above this temperature it turns first brown and then black, while I_2 is evolved. The residue is Fe_2O_3 .

9.3.11.4 $\text{Fe}_5(\text{IO}_6)_3$

Preparation of the salt was reported,⁴⁰ but its properties were not studied.

9.3.12 LEAD

9.3.12.1 $\text{Pb}(\text{IO}_3)_2$

The salt is stable up to 400°C. Above this temperature it decomposes with the evolution of I_2 and O_2 .⁴¹ A density of 6.50 g cm^{-3} for $\text{Pb}(\text{IO}_3)_2$ at ambient temperature has been reported.⁴⁵

9.3.12.2 $\text{Pb}(\text{IO}_3)_4$

The anhydrous salt was prepared by dehydration of its dihydrate between 100 and 120°C,⁴² but no further work seems to have been reported.

9.3.12.3 $\text{Pb}(\text{IO}_4)_2$

The preparation of this salt in a slightly impure state was described by Kimmins.³⁹

9.3.12.4 $\text{Pb}_3(\text{IO}_5)_2$

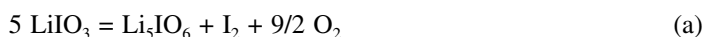
The preparation of this salt was described by Willard and Thompson.⁴³ Decomposition begins in the range 430 to 450°C. Nasanen and Uggla⁴⁴ report an intermediate $8 \text{ PbO} \cdot \text{PbI}_2$, whereas Varhelyi and Kekedy show only a plateau on their TGA curve corresponding to PbO .

Thermodynamic data for $\text{Pb}(\text{IO}_3)_2$ at 298.15 K are shown in [Table 9.10](#).

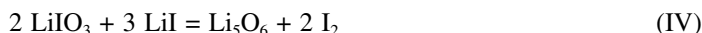
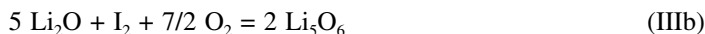
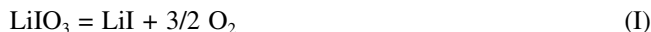
9.3.13 LITHIUM

9.3.13.1 LiIO_3

The salt exists in two crystalline modifications.^{18,46,47} Vaporization of an aqueous solution below 60°C yields hexagonal crystals, above 90°C it yields the tetragonal form; the area between it yields both. At 260°C the hexagonal transforms to the tetragonal with a volume change of $3.2 \text{ cm}^3 \text{ mol}^{-1}$. The latter decomposes on melting. The decomposition has been studied by Bousquet and David.⁴⁸ The overall process is the formation of the paraperiodate:



analogous to the reactions of the alkaline earth iodates. The reaction proceeds a little faster in an O_2 than N_2 atmosphere. The authors, on the basis of numerous subsidiary experiments, propose the following mechanism to account for the overall reaction (a).



with I and IV constituting the major steps.

Enthalpy increments of LiIO_3 and Li_5IO_6 have been measured⁴⁹ up to 623 and 867 K, respectively. The experimental values were used to generate enthalpy and entropy increments for the two salts. Since entropy data are lacking, it was not possible to calculate equilibrium constants for the decomposition reactions.

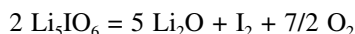
A density 4.502 g cm^{-3} at 305 K was reported for this salt.⁴⁸

9.3.13.2 Li_2IO_4

This unusual compound, in which the valence of iodine is +6, between iodate (+5) and periodate (+7), results from the thermal decomposition of $\text{Li}_2\text{H}_3\text{IO}_6$.⁵⁰ Detailed X-ray, infrared, and magnetic susceptibility measurements were used to establish the chemical individuality of the salt which is stable to about 450°C.

9.3.13.3 Li_5IO_6

The salt sublimates at 730°C. At 850°C it decomposes by the reaction^{47,51}



Phase transitions of LiIO_3 are shown in [Table 9.11](#), thermodynamic data at 298.15 K in [Table 9.12](#), and high-temperature enthalpy and entropy increments for LiIO_3 and Li_5IO_6 in [Table 9.13](#).

9.3.14 MAGNESIUM

9.3.14.1 $\text{Mg}(\text{IO}_3)_2$

Very little information about this salt is available. According to Unezawa et al.,⁵² the anhydrous salt, prepared by dehydrating the 4-hydrate is stable up to 575°C. Above this temperature it decomposes to the oxide. No thermodynamic data, not even at 298.15 K, are listed in the standard compilations. Enthalpy increments were measured calorimetrically by Sanyai and Nag.¹⁴

9.3.14.2 $\text{Mg}(\text{IO}_4)_2$

This salt has been reported as an intermediate in the decomposition of its 8-hydrate,⁵⁴ stable up to near 525°C. Above this temperature decomposition to $\text{Mg}(\text{IO}_3)_2$ occurs.

9.3.14.3 $\text{Mg}_2\text{I}_2\text{O}_9$

This salt is probably not stable in the anhydrous state. Varhely and Kekedy¹¹ report the dehydration of a 12-hydrate, but their TGA curve is not horizontal and MgO is formed gradually. A more careful examination by Dratovsky and Koslerova⁵⁴ indicates the starting material to be

the 13- hydrate. Heating leads to the successive formation of the 2.5-hydrate, $\text{MgIO}_4 \cdot 1/2\text{H}_2\text{O}$, and MgO .

Enthalpy and entropy increments for $\text{Mg}(\text{IO}_3)_2$ are given in [Table 9.14](#).

9.3.15 MANGANESE

9.3.15.1 $\text{Mn}(\text{IO}_3)_2$

Minovici and Kollo⁵⁵ reported that the salt is stable up to 200°C, but according to Duval⁵⁶ it increases up to 2% in weight on being heated to 340°C due to uptake of oxygen. Apparently the iodate is partially transformed to the periodate on heating. Decomposition of both salts is complete at 875°C, the only solid phase remaining is Mn_3O_4 . However, other oxides (MnO , MnO_2) have also been reported as products in the range 555 to 835°C.¹¹ The oxide formed is expected to depend on the partial pressure of oxygen in the system.

9.3.15.2 $\text{Mn}_3(\text{IO}_5)_2$

Preparation of this compound has been reported.⁵⁷ The pink crystals decomposed above 12°C. Since the product was stated to be manganese hydroxide, it is questionable whether the salt was really anhydrous.

The density of $\text{Mn}(\text{IO}_3)_2$ is 4.934 gcm⁻³.⁵⁸ Wagman et al.¹ lists $\Delta\text{H}_f^\circ = -669 \text{ kJ mol}^{-1}$, $S^\circ = 264 \text{ J deg}^{-1}\text{mol}^{-1}$. Data for the oxides can be found in Chapter 2.

9.3.16 MERCURY

Several iodates and periodates of both Hg(I) and Hg(II) have been known for a long time. The older literature is summarized by Gmelin⁵⁹ and Mellor.⁶⁰ However, for more than 60 years very little work has been done on these compounds. No thermodynamic data are listed by Wagman et al.¹ A brief summary relating to thermal decomposition is given below.

9.3.16.1 $\text{Hg}_2(\text{IO}_3)_2$

The salt is stable to near 175°C. Above 500 K, decomposition results in the formation of HgI_2 , which sublimes.⁵⁹

9.3.16.2 $\text{Hg}(\text{IO}_3)_2$

Heating results in the formation of HgI_2 and O_2 .⁵⁹

9.3.16.3 $\text{Hg}_2(\text{IO}_4)_2$

The salt is stable to near 100°C. Decomposition begins near 130°C and is complete at 200°C.⁵⁹

9.3.16.4 $\text{Hg}_5(\text{IO}_6)_2$

The salt can be heated to at least 100°C without weight loss.⁶¹ There is disagreement concerning stability above this temperature. Duval⁵⁶ finds continuous weight loss above 200°C, whereas Varhely and Kekedy,¹¹ also using TGA, find no weight loss up to 500°C. The decomposition reactions have not been studied in detail, but Hg_2I_2 , HgI_2 , HgO , and Hg have been reported as products.⁵⁹

9.3.16.5 $\text{Hg}_4\text{I}_2\text{O}_9$

Preparation of this salt has been reported.^{62,63} Its mode of decomposition is not known, but it is probably similar to that of the other mercury periodates.

9.3.17 NICKEL

9.3.17.1 Ni(IO₃)₂

This salt may exist in two modifications: green and yellow. The latter appears to be the form reported by Meusser.⁶⁴ Martinez-Cros and Le Boucher⁶⁵ report distinctly different densities for the two forms. Pechkovskii and Sofronova⁶⁶ find from DTA and TGA that the salt is stable up to 487°C and decomposes above this temperature by the reaction



9.3.17.2 Ni₃(IO₅)₂

The preparation of a greenish-yellow amorphous salt of this composition was described by Kimmins.³⁹

9.3.17.3 Ni₂I₂O₄

The black crystalline salt is stable to at least 100°C.³⁹

The density of the two modifications of Ni(IO₃)₂ is given in [Table 9.15](#), and thermodynamic data in [Table 9.16](#).

9.3.18 PLUTONIUM

9.3.18.1 Pu(IO₃)₄

The preparation of submicrogram quantities of the yellow salt were reported more than 50 years ago,⁶⁷ but its properties were not studied.

9.3.19 POTASSIUM

9.3.19.1 KIO₃

A melting point of 833 K has been reported.^{68,69}

The decomposition of the salt has been studied experimentally by both a dynamic and a static method⁷⁰ between 655 and 736 K. Over this temperature range the reaction:



required 50 to 600 days to reach equilibrium. Using the *gef* values for K in Stull and Prophet⁷¹ and *C_p* for KIO₃ determined by Ahlberg and Latimer,⁷² equilibrium constants for the reaction were calculated ([Table 9.19](#)). Calculated values were about 0.3 more negative in log K than experimental values, with the same Δ*H*°.

The KIO₃-KI system exhibits a eutectic at 730 K.⁷³ Above this temperature a liquid phase is present. If the system is one component, however, *p*(O₂) will be a unique function of temperature. This will be true as long as there is a solid phase present (see Chapter 1).

It is interesting to note that Duval⁷⁴ found no weight loss when KIO₃ was heated *rapidly* to 500°C, the temperature at which the equilibrium pressure exceeds 1 atm. As is also evident from the long equilibration times, the decomposition is very sluggish. There is also some indication that there is also a secondary decomposition to the oxide:



9.3.19.1.1 Periodates

Several anhydrous periodates are known. Their description is complicated by the fact that some authors describe these salts in terms of the formula $n\text{K}_2\text{O} \cdot m \text{I}_2\text{O}_7$, although (1) I_2O_7 probably does not exist as a discrete compound, and (2) the I_2O_7 group apparently does not exist in the crystal structure of periodates. The main reason for the system seems to be that I_2O_7 can be regarded as the (hypothetical) anhydride of HI_2O_4 (HIO_4), and hydrates of the salts can then be represented on the ternary $\text{I}_2\text{O}_7\text{-K}_2\text{O-H}_2\text{O}$ diagram (see Bianco et al.⁷⁵).

9.3.19.2 KIO_4

The formula of this salt is frequently given as $\text{K}_2\text{I}_2\text{O}_8$, although the existence of tetrahedral IO_4 groups in the solid is well established.⁷⁶ The salt is stable to at least 260 to 290°C^{74,75} and perhaps 330°C.⁷⁶ The decomposition reaction is



No thermodynamic values have been measured. Decomposition kinetics have been studied in some detail,^{77–80} with some of the studies being concerned with the effect of additives and irradiation on the course of decomposition. Various equations were used to represent different stages of the reaction. The activation energy is 209 kJ, consistent with the breaking of an I–O bond and the formation of atomic oxygen as the rate-determining step.

9.3.19.3 $\text{K}_4\text{I}_2\text{O}_9$ (2 $\text{K}_2\text{O} \cdot \text{I}_2\text{O}_7$)

The anhydrous salt is stable to 445°C.⁷⁵ Its crystal structure has been determined.⁸⁰ The $\text{I}_2\text{O}_9^{4-}$ ion is a distinct entity that can be represented as shown in Figure 9.7, but its decomposition reaction is not known, although, like all potassium periodates, the final product is KI.

9.3.19.4 K_3IO_5 (3 $\text{K}_2\text{O} \cdot \text{I}_2\text{O}_7$)

The salt was prepared by dehydration of its hydrates.⁷⁵ It is stable to 440°C, but its decomposition reaction has not been studied, nor are its properties known.

9.3.19.5 K_5IO_6 (5 $\text{K}_2\text{O} \cdot \text{I}_2\text{O}_7$)

The orthoperiodate is stable up to 570°C,⁷⁵ but no further information is available.

Densities are shown in Table 9.17, thermodynamic data at 298.15 K in Table 9.18, and data for the thermal decomposition $\text{KIO}_3 = \text{KI} + 3/2 \text{O}_2$ in Table 9.19.

9.3.20 RADIUM

9.3.20.1 $\text{Ra}(\text{IO}_3)_2$

The salt has been reported,⁸¹ but no high-temperature properties have been measured.

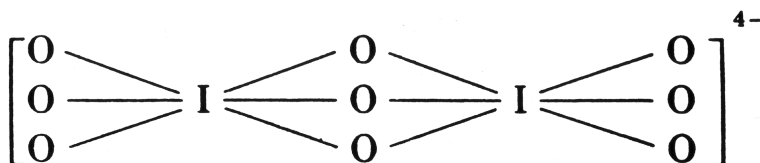


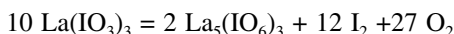
FIGURE 9.7 The structure of the $[\text{I}_2\text{O}_9]^{4-}$ ion.

9.3.21 RARE EARTHS

9.3.21.1 Iodates

During the early 1970s researchers at Bell Laboratories studied these salts, both hydrated and anhydrous, because of their interest in the electrical, magnetic, and structural properties of the compounds. Syntheses were also studied and the results were compared with previously published results.^{82,83} Densities of all the anhydrous rare-earth iodates, derived from crystallographic data,^{83a} are listed in Table 9.20. Extensive crystallographic data of these salts are also provided, as is a comparison with previous work cited in our earlier publication.²

Further work has been reported since 1980. Roy, Ghosh, and Nag⁸⁴ have studied phase transitions for the iodates of La, Pr, and Nd. These are listed in Table 9.21. Note that S° for these compounds is not known. The thermal decomposition of hydrated $\text{La}(\text{IO}_3)_3$ has also been studied.⁸⁵ The final H_2O is driven off at 250°C , and the iodate then decomposes to the periodate at 560°C :

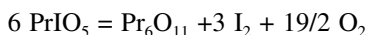
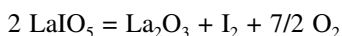


This decomposition has also been reported for other lanthanide iodates^{86,87} at temperatures between 400 and 500°C .

The periodate then decomposes to the oxide at 715 to 720°C .

9.3.21.2 Periodates

The orthoperiodates, $\text{M}_5(\text{IO}_6)_3$, that are formed by the thermal decomposition of iodates (see above) are stable to near 1000°C , but their decomposition has not been studied in detail. They decompose to the oxides. The mesoperiodates of La and Pr have been reported.⁸⁸ LaIO_5 is stable to near 420°C , PrIO_5 to 400°C . Decomposition goes to the oxides:



Thermodynamic data are listed in Table 9.22.

9.3.22 RUBIDIUM

9.3.22.1 RbIO_3

The salt decomposes according to



Bousquet and Remy²⁷ determined the melting point, ΔH_m and ΔS_m from the phase diagram of the RbIO_3 - RbI system. The eutectic is at 777 K . Consequently, any decomposition above this temperature will result in the formation of a liquid phase, but the O_2 pressure will remain a unique function of temperature, as long as a solid phase is present and the system is one component.

Enthalpy increments of RbIO_3 were measured calorimetrically by Bousquet, Perachon, and Remy⁸⁹ up to 707 K . The resultant data were fitted to a power series in T which was then used to generate enthalpy and entropy increments at equal temperature intervals. Since only the lack of an S° (298.15 K) value for RbIO_3 prevented the calculation of gef values, it was estimated by comparison with other alkali metal halates. The estimate agrees with similar ones made by Bousquet and Remy.⁷⁰ C_p values of RbI estimated by Kelley²⁶ were used to generate enthalpy and entropy

increments. In this way equilibrium constants for the decomposition reaction were calculated that are probably good to within an order of magnitude. These calculations indicate that decomposition in air becomes appreciable between 600 and 700 K, well below the melting point.

Bousquet and Remy⁹⁰ have carried out a similar calculation with values that differ only slightly from those used in this work. They also measured the equilibrium pressure of O₂ by both static and dynamic methods between 597 and 740 K. Under static conditions, 25 to 200 days (at various temperatures) were required to reach a steady pressure. Agreement between both sets of calculations and experimental values is quite good.

The melting point is 863 K. ΔH and ΔS for the phase change are 8.8 kJ mol⁻¹ and 10.2 J deg⁻¹mol⁻¹, respectively.

9.3.22.2 RbIO₄

Older references are given by Gmelin.⁵⁹ No recent work has been reported. By analogy with CsIO₄ the decomposition probably proceeds according to



Densities are in Table 9.23; thermodynamic data for the decomposition reaction are in Table 9.24.

9.3.23 SILVER

9.3.23.1 AgIO₃

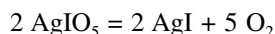
Little work has been done on the thermal decomposition of this salt. It is apparently stable to near 405°C. Above this temperature decomposition yields AgI.⁹¹⁻⁹³

9.3.23.2 AgIO₄

The salt decomposes near 200°C, and explosively at a lower temperature in a vacuum. The products are AgIO₃ and AgI.⁹⁴

9.3.23.3 AgIO₅

The thermal decomposition of this salt has been studied by several researchers. The products reported seem to vary with the temperature. The lowest temperature is reported by Curti and Coggiola,⁹⁵ who find formation of AgIO₃ near 175°C. However, both Varhely and Kekedy¹⁸ and Pacesova, Rathanova, and Rosicky⁹⁴ find the salt to be stable to near 425 to 445°C. Since AgIO₃ is unstable at this temperature, decomposition proceeds directly to the iodide:



9.3.23.4 Ag₃IO₆

This salt has been reported to be stable at least to 60°C.⁹⁴ Both it and Ag₃IO₅ are black and give the same X-ray pattern.⁹⁵ However, the existence of the salt seems to be beyond question, particularly since the reaction



in the presence of base has been studied.⁹⁵

9.3.23.5 Ag₄I₂O₉

There is some question as to whether the pure anhydrous salt has been prepared. The 3-hydrate has been synthesized, but attempts to remove H₂O by a variety of procedures always leads to the loss of some O₂ along with the water.⁹⁵⁻⁹⁷

Densities of AgIO₃ and AgIO₅ are listed in Table 9.25, thermodynamic data at 298.15 K in Table 9.26.

9.3.24 SODIUM

9.3.24.1 NaIO₂

This salt has been prepared by treating NaIO₃ with Pb in a nitrogen atmosphere at 420 to 425°C.⁹⁸ Some optical properties are reported.

9.3.24.2 NaIO₃

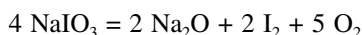
The salt decomposes according to



Equilibrium pressures were measured by Bousquet and Remy⁹⁹ by two different methods between 593 and 900 K, but the results exhibit considerable scatter. The same authors also calculated equilibrium pressures from thermodynamic data⁹⁰ up to 593 K. We have calculated equilibrium values up to 700 K, since C_p values for NaIO₃ are only available up to this temperature.⁹⁰ For NaI we have accepted the evaluation of Stull and Prophet,⁷¹ although the value of ΔHf° (298.15 K) differs somewhat from the newer value¹ of −481.788 kJ.

Since NaIO₃ decomposes only slowly, the melting point obtained by a short extrapolation of the NaIO₃-NaI phase diagram is probably accurate to within 1°C.

If the compound is heated fairly rapidly, as in DTA measurements,¹⁰⁰ the salt can be melted without appreciable decomposition, perhaps to near 460°C. There is some evidence that, at least under nonequilibrium conditions, about 28% of the NaIO₃ decomposes to the oxide:



9.3.24.3 Na₂IO₄

This salt, in which iodine is in a +6 oxidation state, results from heating Na₂H₃IO₆ at 120 to 180°C.¹⁰¹ Using X-ray diffraction, magnetic susceptibility, and infrared absorption, the chemical individuality of the salt was established; i.e., it is not a mixture of NaIO₃ and Na₃IO₅. The compound is stable up to 370°C, but its decomposition products were not identified.

9.3.24.4 NaIO₄

The thermal expansion of the salt is quite different along the a and c axes. Between 25 and 120°C the expansion coefficients are represented by¹⁰²

$$\alpha_a = 36.57 \times 10^{-6} + 3.89 \times 10^{-8}t + 14.19 \times 10^{-11}t^2$$

$$\alpha_c = 49.49 \times 10^{-6} + 18.42 \times 10^{-8}t - 9.22 \times 10^{-11}t^2$$

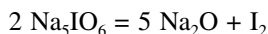
Heating of NaIO₄ at 290 to 300°C leads to the formation of NaIO₃:^{103,104}



No high-temperature thermodynamic data for the periodate are available.

9.3.24.5 Na₅IO₆

As with the alkaline earths, this is the stablest of the periodates. It decomposes above 700°C according to Zintl and Morawietz:¹⁰⁵

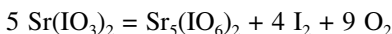


Densities of NaIO₃ and NaIO₄ are given in Table 9.27, transitions in Table 9.28, thermodynamic data at 298.15 K in Table 9.29, and thermodynamics of the decomposition of NaIO₃ in Table 9.30.

9.3.25 STRONTIUM

9.3.25.1 Sr(IO₃)₂

The salt is stable to at least 550°C. Above 600°C it forms the periodate:^{11,106}



gef values for the iodate were calculated from *m*, Δ*H*[°], and *S*[°] values in Wagman et al.¹ and the enthalpy increments determined by David et al.¹⁰⁷ However, a lack of *S*[°] (298.15 K) for the paraperiodate prevents the calculation of the equilibrium constant for the above reaction.

9.3.25.2 Sr₅(IO₆)₂

The salt is stable to near 930°C. At about 1000°C it decomposes to the oxide at an appreciable rate:⁵²



Enthalpy and entropy increments are based on the calorimetric measurements of David et al.¹⁰⁷ The lack of *S*[°] prevents further calculation.

9.3.25.3 SrI₂O₉

The dimesoperiodate may only exist as a hydrate, since heating it results in the formation of SrIO₄ at 230°C:¹⁴



On further heating this decomposes to SrI₂O₇.

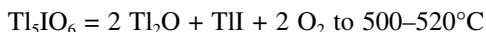
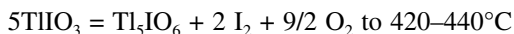
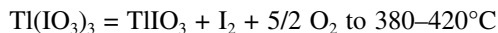
The density of Sr(IO₃)₂ is 5.045 gcm⁻³ at 288 K.¹³

Thermodynamic data for Sr(IO₃)₂ and Sr(IO₆)₂ at 298.15 K are given in Table 9.31, high-temperature thermodynamic data in Table 9.32.

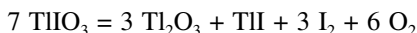
9.3.26 THALLIUM

9.3.26.1 Tl(IO₃)₃

Two studies agree that the salt decomposes with the simultaneous evolution of I₂ and O₂.^{8,108}



In addition to these reactions, Udupa¹⁰⁹ proposed a decomposition of the iodate at 480 to 600°C:



9.3.26.2 Ti_5IO_6

The preparation and X-ray spectrum of this salt have been reported.¹⁰⁹

Thermodynamic data are given in Table 9.33.

9.3.27 THORIUM

9.3.27.1 $\text{Th}(\text{IO}_3)_4$

This salt probably exists as an anhydrous compound up to near 300°C. However, since it is very hygroscopic, it has not yet been prepared in the anhydrous state at ambient temperature, but only by the thermal dehydration of a hydrate.¹¹⁰

9.3.28 TITANIUM

9.3.28.1 $\text{Ti}(\text{IO}_3)_4$

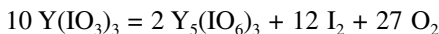
Preparation of the anhydrous salt by the dehydration of a dihydrate at 100°C has been reported.¹¹¹

The density at 305 K (determined pycnometrically) is 4.080 gcm⁻³.¹³

9.3.29 YTTRIUM

9.3.29.1 $\text{Y}(\text{IO}_3)_3$

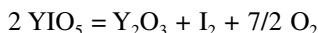
The anhydrous salt can be prepared by the dehydration of its 4-hydrate below 100°C. It then decomposes, beginning near 470°C, according to the overall reaction.¹¹²



The periodate decomposes to the oxide near 1000°C, but this reaction has not been studied in detail.

9.3.29.2 YIO_5

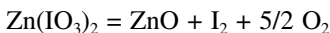
The anhydrous salt can be prepared by the thermal decomposition of $\text{YH}_2\text{IO}_5 \cdot 3\text{H}_2\text{O}$.¹¹³ It is stable up to 250°C and then decomposes to the oxide:



9.3.30 ZINC

9.3.30.1 $\text{Zn}(\text{IO}_3)_2$

The salt is stable up to about 520°C. Above this temperature it decomposes according to Varhely and Kekedy.¹¹⁴



9.3.30.2 $\text{Zn}(\text{IO}_3)_2$

Preparation of the anhydrous compound has been reported,^{115,116} but its properties have not yet been studied.

The density of $\text{Zn}(\text{IO}_3)_2$ is 5.064 g cm^{-3} at 298 K.¹¹⁷ No enthalpies and entropies are available, but Wagman et al.¹ gives ΔG° at 298.15 K = $-433.70 \text{ kJ mol}^{-1}$.

9.3.31 ZIRCONIUM

9.3.31.1 $\text{Zr}(\text{IO}_3)_4$

The crystal structure of the anhydrous salt has been determined.¹¹⁸ The density of the tetragonal prisms is 5.00 g cm^{-3} at ambient temperature.

TABLE 9.1
Classification of the Periodates

| Periodic Acids | | | |
|---|--|---|------------|
| As Hydrates of I_2O_7 | Acid | As Hydrates of HIO_4 | Prefix |
| $\text{I}_2\text{O}_7 \cdot \text{H}_2\text{O}$ | HIO_4 | HIO_4 | meta- |
| $\text{I}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ | $\text{H}_4\text{I}_2\text{O}_9$ | $2\text{HIO}_4 \cdot \text{H}_2\text{O}$ | di-, meso- |
| $3\text{I}_2\text{O}_7 \cdot 7\text{H}_2\text{O}$ | $\text{H}_7\text{I}_3\text{O}_{14}$ | — | tri- |
| $\text{I}_2\text{O}_7 \cdot 4\text{H}_2\text{O}$ | $\text{H}_8\text{I}_2\text{O}_{11}$ | $2\text{HIO}_4 \cdot 3\text{H}_2\text{O}$ | diortho- |
| $\text{I}_2\text{O}_7 \cdot 5\text{H}_2\text{O}$ | H_5IO_6 | $\text{HIO}_4 \cdot 2\text{H}_2\text{O}$ | ortho- |
| Periodates | | | |
| Salts ^a | As $\text{M}_2\text{O} \cdot \text{I}_2\text{O}_7$ | Prefix | |
| $\text{MIO}_4(\text{M}_2\text{I}_2\text{O}_8)$ | $\text{M}_2\text{O} \cdot \text{I}_2\text{O}_7$ | meta- | |
| $\text{M}_4\text{I}_2\text{O}_9$ | $2\text{M}_2\text{O} \cdot \text{I}_2\text{O}_7$ | dimeso-, pyro- | |
| M_3IO_5 | $3\text{M}_2\text{O} \cdot \text{I}_2\text{O}_7$ | meso- | |
| M_2HIO_5 | | | |
| $\text{M}_6\text{I}_2\text{O}_{11}$ | $4\text{M}_2\text{O} \cdot \text{I}_2\text{O}_7$ | diortho- | |
| $\text{M}_3\text{H}_2\text{IO}_6$ | | | |
| $\text{M}_2\text{H}_3\text{O}_6$ | | | |

^a Formulas written for a monovalent cation.

TABLE 9.2
Thermodynamic Data (298.15 K) of Ba-I Salts

| Compound | ΔHf° kJ mol^{-1} | S° $\text{J mol}^{-1} \text{ deg}^{-1}$ | Reference |
|------------------------------|--|---|-----------|
| $\text{Ba}(\text{IO}_3)_2$ | -1027.2 | 249.4 | 1 |
| $\text{Ba}_5(\text{IO}_6)_2$ | -3952 | — | 1 |

TABLE 9.3
High-Temperature Thermodynamic Data²

| T(K) | Ba(IO ₃) ₂ gef J deg ⁻¹ | BaO gef J deg ⁻¹ | Ba ₅ (IO ₆) ₂ | |
|--------|--|--------------------------------|---|---|
| | | | H _T – H ₂₉₈ J | S _T – S ₂₉₈ J deg ⁻¹ |
| 298.15 | –294.4 | –70.3 | 0 | 0 |
| 400 | –256.7 | –72.1 | 42873 | 123.38 |
| 500 | –271.8 | –75.8 | 90523 | 229.56 |
| 600 | –289.4 | –79.9 | 140746 | 321.11 |
| 700 | | –85.2 | 190615 | 398.05 |
| 800 | | –88.4 | 237212 | 460.37 |

TABLE 9.4
Thermodynamic Data (298.15 K) of Ca-I Salts

| Compound | ΔHf° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|---|------------------------------|---|-----------|
| Ca(IO ₃) ₂ | –1002.5 | 230. | 1 |
| Ca ₅ (IO ₆) ₂ | –3828 | 453.6 | 1, 2 |

TABLE 9.5
5 Ca(IO₃)₂ = Ca₅(IO₆)₂ + 4 I₂(g) + 9 O₂(g)

| T K | Δ _{gef} J deg ⁻¹ | G°/T | K | p _{tot} (atm) |
|--------|---|--------|-------------|------------------------|
| 298.15 | –2190 | 2619 | 1.56E – 137 | 6.99E – 11 |
| 400.00 | –2187 | 1398 | 9.40E – 74 | 4.48E – 6 |
| 500.00 | –2180 | 687.6 | 1.21E – 36 | 3.19E – 3 |
| 600.00 | –2173 | 216.7 | 4.79E – 12 | 2.50E – 1 |
| 700.00 | –2167 | –118.7 | 1.59E + 6 | 5.56 |

TABLE 9.6
Ca₅(IO₆)₂ = 5 CaO + I₂(g) + 7/2 O₂(g)

| T K | Δ _{gef} J deg ⁻¹ | G°/T | K | p _{tot} (atm) |
|---------|---|--------|------------|------------------------|
| 298.15 | –723.2 | 1466.7 | 2.45E – 77 | 1.61E – 17 |
| 400.00 | –721.7 | 910.6 | 2.73E – 48 | 4.58E – 11 |
| 500.00 | –716.9 | 588.9 | 1.74E – 31 | 2.48E – 7 |
| 600.00 | –711.2 | 376.9 | 2.05E – 20 | 7.16E – 5 |
| 700.00 | –706.4 | 226.3 | 1.52E – 12 | 4.01E – 3 |
| 800.00 | –702.1 | 114.1 | 1.10E – 6 | 8.05E – 2 |
| 900.00 | –696.9 | 28.6 | 3.22E – 2 | 0.79 |
| 1000.00 | –692.8 | –39.8 | 120.5 | 4.92 |

TABLE 9.7
Thermodynamic Data (298.15 K) of Cs-I Salts

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-------------------|--|--|-----------|
| CsIO ₃ | -525.95 | 167 | 2 |
| CsIO ₄ | — | 130 | 2 |
| CsI | -345.82 | 123.05 | 1 |

TABLE 9.8
CsIO₃ = CsI + 3/2 O₂(g)

| T K | Δ_{gef} J deg ⁻¹ | G°/T | K | p_{tot} (atm) |
|--------|---------------------------------------|-------------|------------|-----------------|
| 298.15 | -270.55 | 325.78 | 9.62E - 18 | 4.52E - 12 |
| 400.00 | -271.80 | 172.69 | 9.53E - 10 | 9.68E - 7 |
| 500.00 | -276.04 | 81.57 | 5.49E - 5 | 1.44E - 3 |
| 600.00 | -276.60 | 19.73 | 9.32E - 2 | 2.05E - 1 |
| 700.00 | -279.25 | -25.26 | 20.8 | 7.57 |

TABLE 9.9
Thermodynamic Data (298.15K) of Cu(IO₃)₂

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-----------------------------------|--|--|-----------|
| Cu(IO ₃) ₂ | -389.5 | 218 | 122 |

TABLE 9.10
Thermodynamic Data (298.15 K) of Pb(IO₃)₂

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-----------------------------------|--|--|-----------|
| Pb(IO ₃) ₂ | -495.4 | 313.0 | 1 |

TABLE 9.11
Transitions of Li-I Salts

| Phase Change | T(K) | ΔH kJ/mol | ΔS J/(mol·K) | Reference |
|--|------|-------------------|----------------------|-----------|
| LiIO ₃ , hexagonal → tetragonal | 533 | 2.2 | 4.2 | 46 |
| LiIO ₃ , tetragonal → liquid | 723 | — | — | 23 |

TABLE 9.12
Thermodynamic Data (298.15 K) of Li-I Salts

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|---------------------------------|--|--|-----------|
| LiIO ₃ | -503.38 | — | 1 |
| Li ₅ IO ₆ | -2044 | — | 123 |

TABLE 9.13
Enthalpy and Entropy Increments of LiIO₃ and Li₅IO₆

| T(K) | LiIO ₃ | | Li ₅ IO ₆ | |
|------|--|---|--|---|
| | $H_T - H_{298.15}$ kJ mol ⁻¹ | $S_T - S_{298.15}$ J deg ⁻¹ mol ⁻¹ | $H_T - H_{298.15}$ kJ mol ⁻¹ | $S_T - S_{298.15}$ J deg ⁻¹ mol ⁻¹ |
| 400 | 10.98 | 31.54 | 25.76 | 74.08 |
| 500 | 22.94 | 58.18 | 51.02 | 130.43 |
| 600 | 36.09 | 82.11 | 76.27 | 176.48 |
| 700 | | | 105.71 | 215.41 |
| 800 | | | 126.78 | 249.13 |

TABLE 9.14
**Enthalpy and Entropy Increments of
Mg(IO₃)₂ [2]**

| T(K) | $H_T - H_{298.15}$ kJ mol ⁻¹ | $S_T - S_{298.15}$ J deg ⁻¹ mol ⁻¹ |
|------|--|---|
| 400 | 21.84 | 63.19 |
| 500 | 53.96 | 110.98 |
| 600 | 64.67 | 150.03 |
| 700 | 86.08 | 183.05 |
| 800 | 107.50 | 211.65 |

TABLE 9.15
Density of Ni(IO₃)₂

| Phase | T(K) | d | Reference |
|--|------|------|-----------|
| Ni(IO ₃) ₂ (yellow) | 298 | 5.02 | 65 |
| Ni(IO ₃) ₂ (green) | 298 | 4.61 | 65 |

TABLE 9.16
Thermodynamic Data (298.15 K) of Ni(IO₃)₂

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-----------------------------------|--|--|-----------|
| Ni(IO ₃) ₂ | -489.1 | 213.1 | 1 |

TABLE 9.17
Densities of K-I Salts

| Phase | T(K) | d | Reference |
|--|---------|-------|-----------|
| KIO ₃ | 305 | 3.93 | 111 |
| KIO ₄ | 288 | 3.618 | 119 |
| K ₄ I ₂ O ₉ | Ambient | 3.7 | 124 |

TABLE 9.18
Thermodynamic Data (298.15 K) of K-I Salts

| Compound | ΔH_f° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|------------------|--|--|-----------|
| KIO ₃ | -501.37 | 151.46 | 1 |
| KIO ₄ | -467.23 | 176. | 1 |
| KI | -327.9 | 106.38 | 1 |

TABLE 9.19
KIO₃ = KI + 3/2 O₂(g)

| T K | Δ_{gef} J deg ⁻¹ | G°/T J deg ⁻¹ | K | p _{tot} (atm) |
|--------|---------------------------------------|-----------------------------|------------|------------------------|
| 298.15 | -262.48 | 348.39 | 6.33E - 19 | 7.37E - 13 |
| 400.00 | -262.19 | 193.13 | 8.16E - 11 | 1.84E - 11 |
| 500.00 | -261.54 | 102.73 | 4.31E - 6 | 2.65E - 6 |
| 600.00 | -260.81 | 42.74 | 5.86E - 3 | 5.86E - 3 |
| 700.00 | -260.14 | 0.043 | 0.995 | 1.00 |
| 800.00 | -259.63 | -31.97 | 4.67 | 46.7 |

TABLE 9.20
Densities of the Rare-Earth Iodates
(calculated, Abrahams et al.^{83a})

| Rare Earth | d(gcm ⁻³) |
|------------|-----------------------|
| Ce | 5.35 |
| Pr | 5.39 |
| Nd | 5.44 |
| Sm | 5.58 |
| Eu | 5.65 |
| Gd | 5.68 |
| Tb | 5.75 |
| Dy | 5.86 |
| Ho | 5.92 |
| Er | 5.95 |
| Tm | 6.03 |
| Yb | 6.03 |
| Lu | 6.12 |
| Y | 5.26 |

TABLE 9.21
Enthalpy Changes for Phase Transitions of
Rare-Earth Iodates⁸⁴

| Compound | Transition (°C) | ΔH (kJ mol ⁻¹) |
|-----------------------------------|-------------------|------------------------------------|
| La(IO ₃) ₃ | 352 (endothermic) | 20.75 |
| | 355 (endothermic) | 20.75 |
| | 380 (exothermic) | 4.39 |
| | 484 (endothermic) | 10.25 |
| Pr(IO ₃) ₃ | 356 (exothermic) | 2.09 |
| | 371 (exothermic) | 19.46 |
| | 412 (exothermic) | 14.02 |
| Nd(IO ₃) ₃ | 350 (exothermic) | 1.46 |
| | 372 (exothermic) | 12.97 |
| | 418 (exothermic) | 10.08 |

TABLE 9.22
 ΔH_f° (298.15K) of Rare-Earth
Iodates¹

| Rare Earth | ΔH_f° (kJ mol ⁻¹) |
|------------|--|
| Lu | -1339 |
| Yb | -1347 |
| Tm | -1372 |
| Er | -1381 |
| Ho | -1381 |
| Dy | -1377 |
| Tb | -1364 |
| Gd | -1368 |
| Eu | -1290.3 |
| Sm | -1381 |
| Nd | -1389 |
| Pr | -1396.6 |
| Ce | -1389 |
| La | -1397 |

TABLE 9.23
Density of Rb-I Salts

| Phase | T(K) | d (g cm ⁻³) | Reference |
|-------------------|------|-------------------------|-----------|
| RbIO ₃ | 305 | 4.471 | 119 |
| RbIO ₄ | 289 | 3.918 | 111 |

TABLE 9.24
 $\text{RbIO}_3 = \text{RbI} + 3/2 \text{O}_2$

| T K | Δ_{gef} J deg ⁻¹ | G°/T J deg ⁻¹ | K | p(O ₂) atm |
|--------|--|-----------------------------|------------|------------------------|
| 298.15 | -264.88 | 346.20 | 8.25E - 19 | 8.80E - 13 |
| 400.00 | -264.46 | 191.02 | 1.05E - 10 | 2.23E - 11 |
| 500.00 | -263.65 | 100.73 | 5.47E - 6 | 3.10E - 7 |
| 600.00 | -262.71 | 40.94 | 2.73E - 3 | 3.75E - 4 |
| 700.00 | -261.89 | -1.62 | 1.21 | 1.14 |

TABLE 9.25
Density of Ag-I Salts

| Phase | T(K) | d (g cm ⁻³) | Reference |
|---------------------------------|---------|-------------------------|-----------|
| AgIO ₃ | 293 | 5.525 | 13 |
| Ag ₅ IO ₆ | Ambient | 1.884 | 98a |

TABLE 9.26
Thermodynamic Data (298.15 K)

| Compound | Δ_{Hf}° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-------------------|--|---|-----------|
| AgIO ₃ | -171.1 | 149.4 | 1 |
| AgI | -61.84 | 115.5 | 1 |

TABLE 9.27
Density of Na-I salts

| Phase | T(K) | d (g cm ⁻³) | Reference |
|-------------------|------|-------------------------|-----------|
| NaIO ₃ | 293 | 4.277 | 13 |
| NaIO ₄ | 289 | 3.865 | 127 |

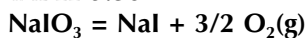
TABLE 9.28
Transition of NaIO₃

| Phase Change | T(K) | Δ_{H} kJ/mol | Δ_{S} J/(mol·K) | Reference |
|----------------------------|------|----------------------------|-------------------------------|-----------|
| NaIO ₃ , c→liq. | 695 | 35.1 | 50.9 | 128 |

TABLE 9.29
Thermodynamic Data (298.15 K) of Na-I Salts

| Compound | Δ_{Hf}° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-------------------|--|---|-----------|
| NaIO ₃ | -481.788 | 135.1 | 1 |
| NaIO ₄ | -429.28 | 163 | 1 |
| NaI | -287.78 | 98.53 | 1 |

TABLE 9.30



| T K | Δ_{gef} J deg ⁻¹ | $\Delta G^\circ/T$ J deg ⁻¹ | K | p(O ₂) atm |
|--------|--|---|------------|------------------------|
| 298.15 | -270.91 | 409.47 | 4.09E - 22 | 5.51E - 15 |
| 400.00 | -283.42 | 223.71 | 2.06E - 12 | 1.63E - 8 |
| 500.00 | -148.58 | 115.45 | 9.32E - 7 | 9.43E - 5 |
| 600.00 | -293.72 | 44.37 | 4.81E - 3 | 2.83E - 2 |
| 700.00 | -194.55 | -4.76 | 1.77 | 1.46 |

TABLE 9.31

Thermodynamic Data (298.15 K) of Sr-I Salts

| Compound | Δ_{Hf}° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|---|--|--|-----------|
| Sr(IO ₃) ₂ | -1019.2 | 234 | 1 |
| Sr ₅ (IO ₆) ₂ | -3975 | — | 129 |

TABLE 9.32

High-Temperature Thermodynamic Data of Strontium Compounds²

| T K | Sr(IO ₃) ₂ <i>gef</i> J deg ⁻¹ | SrO <i>gef</i> J deg ⁻¹ | Sr ₅ (IO ₆) ₂ | |
|--------|---|---------------------------------------|---|--|
| | | | H _T - H _{298.15} kJ | S _T - S _{298.15} J deg ⁻¹ |
| 298.15 | -243.3 | -54.3 | 0 | 0 |
| 400 | -242.0 | -56.2 | 42.39 | 121.60 |
| 500 | -257.2 | -59.7 | 89.89 | 227.32 |
| 600 | -275.2 | -63.7 | 140.48 | 319.42 |
| 700 | -294.0 | -67.9 | 191.44 | 397.92 |
| 800 | | -71.9 | 240.06 | 462.82 |

TABLE 9.30

Thermodynamic Data (298.15 K) of Tl-I Salts

| Compound | Δ_{Hf}° kJ mol ⁻¹ | S° J mol ⁻¹ deg ⁻¹ | Reference |
|-------------------|--|--|-----------|
| TlIO ₃ | -267.4 | 176.6 | 1 |
| TlI | -123.8 | 127.6 | 1 |

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