

# **CODATA**

## **Thermodynamic Tables**

---

**SELECTIONS FOR SOME COMPOUNDS  
OF CALCIUM AND RELATED MIXTURES:  
A PROTOTYPE SET OF TABLES**

**D. Garvin  
V. B. Parker  
H. J. White, Jr.**

# **CODATA THERMODYNAMIC TABLES**

## **Selections for Some Compounds of Calcium and Related Mixtures: A Prototype Set of Tables**

*Edited by*

**D. Garvin**

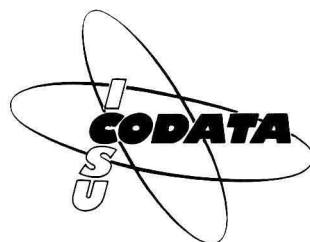
**V. B. Parker**

**H. J. White, Jr.**

National Bureau of Standards

Gaithersburg, Maryland, USA

Report of the CODATA Task Group  
on Chemical Thermodynamic Tables.



● **HEMISPHERE PUBLISHING CORPORATION**  
A subsidiary of Harper & Row, Publishers, Inc.  
Washington    New York    London

**DISTRIBUTION OUTSIDE NORTH AMERICA**

**SPRINGER-VERLAG**

Berlin    Heidelberg    New York    London    Paris    Tokyo

## **CODATA THERMODYNAMIC TABLES**

Copyright © 1987 by CODATA. All Rights reserved. Printed in the United States of America. Except as permitted under the United States Copyright Act of 1976, no part of this publication may be reproduced or distributed in any form or by any means, or stored in a data base or retrieval system, without the prior written permission of the publisher.

1 2 3 4 5 6 7 8 9 0 B R B R 8 9 8 7

### **Library of Congress Cataloging-in-Publication Data**

CODATA thermodynamic tables.

"Report of the CODATA Task Group on Chemical Thermodynamic Tables."

Bibliography: p.

1. Thermodynamics—Tables. I. Garvin, David,  
II. Parker, Vivian B. III. White, H. J., Jr.

IV. CODATA Task Group on Chemical Thermodynamic Tables.

QD504.C63 1987 541.3'69'0212 87-135

ISBN 0-89116-730-7 Hemisphere Publishing Corp.

### **Distribution outside North America:**

ISBN 3-540-17788-4 Springer-Verlag Berlin

**CODATA  
THERMODYNAMIC  
TABLES**

# LIST OF TABLES

## THERMODYNAMIC FUNCTIONS at 0.1 MPa Compounds of magnesium, calcium and potassium

Table 6.1.1.	Mg(cr & l)	44
Table 6.1.2.	Mg(cr)	47
Table 6.1.3.	Mg(l)	48
Table 6.1.4.	Mg(g)	49
Table 6.1.5.	MgO(cr & l)	51
Table 6.1.6.	MgF <sub>2</sub> (cr & l)	53
Table 6.1.7.	MgF <sub>2</sub> (cr)	55
Table 6.1.8.	MgF <sub>2</sub> (l)	57
Table 6.1.9.	Ca(cr(α, β) & l)	59
Table 6.1.10.	Ca(cr, α)	62
Table 6.1.11.	Ca(cr, β)	63
Table 6.1.12.	Ca(l)	64
Table 6.1.13.	Ca(g)	65
Table 6.1.14.	Ca <sup>+</sup> (g)	68
Table 6.1.15.	Ca <sub>2</sub> (g)	70
Table 6.1.16.	CaO(cr & l)	72
Table 6.1.17.	CaO(g)	75
Table 6.1.18.	CaH(g)	77
Table 6.1.19.	CaH <sub>2</sub> (cr & l)	79
Table 6.1.20.	CaOH(g)	81
Table 6.1.21.	CaOH <sup>+</sup> (g)	83
Table 6.1.22.	Ca(OH) <sub>2</sub> (cr & l)	85
Table 6.1.23.	Ca(OH) <sub>2</sub> (g)	87
Table 6.1.24.	CaF <sub>2</sub> (cr & l)	89
Table 6.1.25.	CaCl(g)	91
Table 6.1.26.	CaCl <sub>2</sub> (cr & l)	93
Table 6.1.27.	CaCl <sub>2</sub> (cr)	96
Table 6.1.28.	CaCl <sub>2</sub> (l)	97
Table 6.1.29.	CaCl <sub>2</sub> (g)	98
Table 6.1.30.	CaCO <sub>3</sub> (cr & l)	100
Table 6.1.31.	CaMg <sub>2</sub> (cr & l)	102
Table 6.1.32.	CaMg <sub>2</sub> (cr)	105
Table 6.1.33.	CaMg <sub>2</sub> (l)	106
Table 6.1.34.	KCl(cr & l)	107
Table 6.1.35.	KCl(cr)	109
Table 6.1.36.	KCl(l)	110
Table 6.1.37.	KCl(g)	111

Table 6.1.38.	$K_2Cl_2(g)$	113
Table 6.1.39.	$KCaCl_3(cr \& l)$	115
Table 6.1.40.	$KCaCl_3(cr)$	118
Table 6.1.41.	$KCaCl_3(l)$	119

### Auxiliary Substances

Table 6.1.42.	$e^-(g)$	120
Table 6.1.43.	$O(g)$	122
Table 6.1.44.	$O_2(g)$	124
Table 6.1.45.	$H(g)$	126
Table 6.1.46.	$H_2(g)$	128
Table 6.1.47.	$OH(g)$	130
Table 6.1.48.	$H_2O(cr \& l)$	132
Table 6.1.49.	$H_2O(g)$	135
Table 6.1.50.	$F_2(g)$	137
Table 6.1.51.	$Cl_2(g)$	139
Table 6.1.52.	$ClO(g)$	141
Table 6.1.53.	$ClO_2(g)$	143
Table 6.1.54.	$S(g)$	145
Table 6.1.55.	$SO(g)$	147
Table 6.1.56.	$SO_2(g)$	149
Table 6.1.57.	$N_2(g)$	151
Table 6.1.58.	$C(graphite)$	153
Table 6.1.59.	$CO(g)$	155
Table 6.1.60.	$CO_2(g)$	157
Table 6.1.61.	$Al(g)$	159
Table 6.1.62.	$AlCl(g)$	161
Table 6.1.63.	$MoO_2(g)$	163
Table 6.1.64.	$MoO_3(g)$	165
Table 6.1.65.	$WO_2(cr)$	167

### Tables in the Text

Table 6.1.66.	Molecular Parameters of $CaO$ , $CaH$ , $CaCl$ , $KCl$ , and $Ca_2$	169
Table 6.1.67.	Molecular Constants for Gaseous $CaOH$ , $CaOH^+$ , $Ca(OH)_2$ , $CaCl_2$ and $K_2Cl_2$	171
Table 6.1.68.	Analytical Expressions for the "Gibbs Energy Function"	172
Table 6.2.1.	Selected Values for $\Delta_f H^0$ , $\Delta_f G^0$ , $S^0$ and $C_p^0$ at 298.15 K and $\Delta_f H^0$ at 0 K, at 0.1 MPa	180
Table 6.3.1.	Thermodynamic Properties of Mixing at $T/K = 1000$ for $x_1Ca(l) + x_2Mg(l) = Ca_{x_1}Mg_{x_2}(l)$	196
Table 6.4.1.	Thermodynamic Properties of Mixing at $T/K = 1100$ for $x_1CaCl_2(l) + x_2KCl(l) = (CaCl_2)_{x_1}(KCl)_{x_2}(l)$	204

Table 6.4.2.	Summary of Experimental Thermodynamic Investigations on the $\text{CaCl}_2\text{-KCl}$ System	209
Table 6.5.1.	Thermodynamic Functions of $\text{CaCl}_2(\text{aq std. state})$	213
Table 6.5.2.	Activity Coefficients of Aqueous Calcium Chloride	215
Table 6.5.3.	Osmotic Coefficients of Aqueous Calcium Chloride	217
Table 6.5.4.	Excess Enthalpy of Aqueous Calcium Chloride	119
Table 6.5.5.	Excess Heat Capacity and Standard Partial Molar Heat Capacity of Aqueous Calcium Chloride	221
Table 6.5.6.	Values for the Parameters in the Correlating Equations for use at 298.15 K	223
Table 6.5.7.	Debye-Hückel Parameters Consistent with Tables 6.5.2–6.5.5	223
Table 6.5.8.	Solubility and Freezing Point Data	226
Table 6.5.9.	Sources of Data for Calculation of $C_p^{\text{ex}}$	236
Table 6.5.10.	Sources of Data for Calculation of $H^{\text{ex}}$ at 298.15 K	237
Table 7.1.1.	Values Calculated for Thermochemical Properties of Selected Compound of Calcium	241
Table 7.1.2.	Catalog of Thermochemical Measurements: Calcium Compounds	251
Table 7.1.3.	Catalog of Measurements of the Thermochemical Properties of $\text{CaF}_2$	301
Table 7.2.1.	Catalog of Measurements for the $\text{Ca-Mg}$ Alloy System	306
Table 7.3.1.	Catalog of Heat Capacity Measurements for the $\text{CaCl}_2\text{-H}_2\text{O}$ System	313
Table 7.3.2.	Catalog of Enthalpy Measurements for the $\text{CaCl}_2\text{-H}_2\text{O}$ System	323

## LIST OF FIGURES

1.2.1	Flow Diagram for a System for the Preparation of Critically Evaluated Chemical Thermodynamic Data	3
6.2.1	Thermochemical Network	186
6.3.1	Phase Diagram Ca-Mg	195
6.4.1	Phase Diagram $\text{CaCl}_2\text{-KCl}$	203
6.5.1	Phase Diagram $\text{CaCl}_2\text{-H}_2\text{O}$	211
6.5.2	Activity Coefficients of $\text{CaCl}_2\text{-H}_2\text{O}$ Solutions, 298.15–373.15 K	224
6.5.3	Osmotic Coefficients of $\text{CaCl}_2\text{-H}_2\text{O}$ Solutions, 298.15–373.15 K	224
6.5.4	Excess Enthalpy of $\text{CaCl}_2\text{-H}_2\text{O}$ Solution, 298.15–373.15 K	225
6.5.5	Excess Heat Capacity of $\text{CaCl}_2\text{-H}_2\text{O}$ Solutions, 298.15–373.15 K	225



## FOREWORD

CODATA\* is particularly concerned with improvement of the quality and accessibility of data that span the interests of several scientific disciplines. Thermodynamics, with its broad importance in chemistry, physics, geology, and several branches of engineering, is clearly such a field. Thus CODATA has had an active interest in thermodynamic data since its inception.

The CODATA Task Group on Chemical Thermodynamic Tables has been charged with developing a comprehensive series of internationally accepted, thermodynamically consistent tables. This volume presents the first set of tables from the task group and is the prototype of what is intended to become a comprehensive series.

CODATA attaches great importance to this task and would welcome readers' comments on the format and content of these prototype tables.

*David R. Lide*  
*President, CODATA*

\* Committee on Data for Science and Technology of the International Council of Scientific Unions (ICSU)

## PREFACE

Recommended values are presented for chemical thermodynamic properties of selected compounds of calcium and their mixtures. These have been prepared in accord with a previously developed plan and as a test of it. All values in the present table are mutually consistent and are consistent with the CODATA Key Values for Thermodynamics. The values are recommended for general use. This work has been an activity of the CODATA Task Group on Chemical Thermodynamic Tables.

This volume of chemical thermodynamic data is intended as the first of many to be prepared as a cooperative, ongoing international project by experts who are geographically separated, but in computer-to-computer communications, and share both data and calculational resources.

The evaluated data are for common compounds of calcium (element, oxide, hydroxide, peroxide, fluoride, chloride, sulfate, nitrate and carbonate, their hydrates and their ions in aqueous solution) and for three systems: Ca-Mg, CaCl<sub>2</sub>-KCl and CaCl<sub>2</sub>-H<sub>2</sub>O.

Forty one tables of thermal functions (heat capacity, entropy, enthalpy, and Gibbs energy functions) are given for those compounds of magnesium, calcium and potassium for which the properties have been evaluated in this work. Twenty four tables of thermal functions are given for auxiliary substances. Each table spans the temperature range 0 to 4000 K, to the extent that data are available. Formation properties at 298.15 K (enthalpy and Gibbs energy of formation) are given for 68 compounds of calcium, magnesium and potassium plus the relevant values for 54 auxiliary substances. For each of the three systems the data given are mixing properties (enthalpies and Gibbs energies), partial molar or excess properties (activities, enthalpies, heat capacities) and phase transformation data. All selections of data are accompanied by uncertainties, and are documented. Detailed lists of the measurements used in the evaluations are given for the thermochemical, alloy, and aqueous solution sections.

The technical formalities needed for the project are described in an introduction (contents of tables, tabulation intervals, units, definitions of properties). Plans for the future are discussed.

## TASK GROUP ON CHEMICAL THERMODYNAMIC TABLES

### CHAIRMAN:

Dr. H. J. White, Jr.  
Office of Standard Reference Data  
National Bureau of Standards  
Gaithersburg, MD 20899, USA

### MEMBERS

DR. I. ANSARA  
Laboratoire de Thermodynamique et Physico-Chimie Metallurgiques  
(L.T.P.C.M.—E.N.S.E.E.G.)  
Domaine Universitaire, B.P. 75  
38402 St. Martin d'Heres Cedex, France

DR. D. GARVIN  
Chemical Thermodynamics Division  
National Bureau of Standards  
Gaithersburg, MD 20899, USA

DR. L. V. GURVICH  
USSR Thermocenter  
Institute for High Temperatures  
Izorskaya Street 13/17  
Moscow, USSR 127412

DR. M. H. RAND  
Atomic Energy Research Establishment  
Harwell, Didcot  
Oxon, UK OX11 0RA

PROFESSOR E. U. FRANCK  
Institute of Physical Chemistry  
University of Karlsruhe  
Karlsruhe D-7500, FRG  
(1977–1979)

### SUBCOMMITTEE ON KEY VALUES

MR. D. D. WAGMAN  
7104 Wilson Lane  
Bethesda, MD 20817, USA

DR. V. A. MEDVEDEV  
USSR Thermocenter  
Institute for High Temperatures  
Izorskaya Street 13/17  
Moscow, USSR 127412

**CONSULTANTS**

DR. J. B. PEDLEY  
School of Chemistry and Molecular Sciences  
University of Sussex  
Brighton, Sussex, UK BN1 9QJ

DR. M. W. CHASE\*  
The Dow Chemical Company  
1707 Building  
Midland, MI 48674, USA

**CORRESPONDING  
MEMBERS**

PROFESSOR C. B. ALCOCK  
Department of Metallurgy and Materials Science  
University of Toronto  
Toronto, Ontario, Canada M5S 1A4

DR. JOHN L. HAAS, JR.  
U.S. Geological Survey  
National Center  
Reston, VA 22092, USA

DR. V. B. PARKER  
Chemical Thermodynamics Division  
National Bureau of Standards  
Gaithersburg, MD 20899, USA

PROFESSOR E. F. WESTRUM, JR.  
Department of Chemistry  
University of Michigan  
Ann Arbor, MI 48109, USA

Dr. V. S. YUNGMAN  
USSR Thermocenter  
Institute for High Temperatures  
Izorskaya Street 13/17  
Moscow, USSR 127412

\* Present address:

Chemical Thermodynamics Division  
National Bureau of Standards  
Gaithersburg, MD USA 20899

# CONTENTS

List of Tables	ix
List of Figures	xiii
Foreword	xv
Preface	xvii
Task Group on Chemical Thermodynamic Tables	xix

## 1. INTRODUCTION 1

1.1	The CODATA Task Group on Chemical Thermodynamic Tables	1
1.2	The Preparation of Thermodynamic Tables	2
1.3	The Prototype Tables	2

## 2. CONVENTIONS, STRUCTURES AND CONTENTS OF THE TABLES 6

2.1	General	6
2.2	Nomenclature and Symbols	6
2.3	Units and Scales	6
2.4	Fundamental Constants and Related Values	7
2.5	Molar Masses	8
2.6	State of Aggregation	8
2.7	Standard and Reference States, Reference Temperatures	8
2.7.1	Pure Substances and Mixtures of Constant Composition	9
2.7.2	Systems of Variable Composition (Mixtures)	9
2.7.2.1	Mixtures with all Components Treated Alike	10
2.7.2.2	Mixtures in which One Component Predominates	11
2.7.3	Reference Temperatures	13
2.7.4	Reference States	13
2.8	Reliability	14
2.8.1	Limitations on the Expression of Reference Data	14
2.8.2	Conventions Used in Reporting Recommended Values	16
2.9	Thermal Function	17
2.10	Thermochemical Properties at 298.15 K	20
2.11	Systems of Variable Composition	21
2.11.1	General	21
2.11.2	The System Ca-Mg	22
2.11.3	The System $\text{CaCl}_2\text{-KCl}$	23
2.11.4	The System $\text{CaCl}_2\text{-H}_2\text{O}$	23
2.12	Reaction Catalogs	24
2.12.1	Thermochemical Catalog and Data Networks	24
2.12.2	Other Catalogs	25

2.13	Bibliography	26
2.14	Credits and Acknowledgements	26
<b>3.</b>	<b>THE FUTURE</b>	<b>28</b>
3.1	The Current Status and Immediate Plans	28
3.2	Cooperative Activities	28
3.3	Quality Control and Continuity	29
3.4	Updating and Expanding the Tables	29
3.5	Summary	30
<b>4.</b>	<b>REFERENCES IN CHAPTERS 1 TO 3</b>	<b>31</b>
<b>5.</b>	<b>GLOSSARY OF SYMBOLS</b>	<b>33</b>
5.1	Symbols	33
5.2	Definitions Used for Properties of Mixtures	38
5.2.1	For Mixtures in which One Substance Predominates	38
5.2.2	Generally Applicable Definitions	39
<b>6.</b>	<b>TABLES OF CHEMICAL THERMODYNAMIC DATA</b>	<b>40</b>
6.1	Thermodynamic Properties of Individual Substances	40
6.1.1	Properties as a Function of Temperature	41
6.1.2	Discussion	41
6.1.3	Equations for the Functions	42
	<i>Tables: Compounds of Magnesium, Calcium, and Potassium</i>	
	<i>Auxiliary Substances</i>	44
6.2	Thermochemical Properties at 0 and 298.15 K	178
6.2.1	Table of Values of Formation Properties	179
6.2.2	Discussion	179
6.2.2.1	General	179
6.2.2.2	Conventions for Formation Properties	185
6.2.2.3	Uncertainties for Substances and Processes	185
6.2.2.4	Major Aspects of the Evaluation	188
6.2.2.5	Remarks on Individual Substances	189
6.2.3	Network Diagram	193
	<i>Tables: Compounds of Magnesium, Calcium and Potassium</i>	
6.3	The Alloy System Ca-Mg	194
6.3.1	Introduction	195
	<i>Phase Diagram</i>	195
	<i>Table of Mixing Properties</i>	196
6.3.2	Gibbs Energies of Mixing, Liquid and hcp Phases	197
6.3.3	Thermochemistry of $\text{CaMg}_2(\text{hcp})$	197
6.3.4	Gibbs Energies of Transformation of the Components	198
6.3.5	Discussion	199

6.4	The Fused Salt System $\text{CaCl}_2\text{-KCl}$	202
6.4.1	Introduction	203
	<i>Phase Diagram</i>	203
	<i>Table of Mixing Properties</i>	204
6.4.2	Gibbs Energies of Mixing, Liquid Phase	205
6.4.3	Thermochemistry of $\text{KCaCl}_3(\text{cr})$	205
6.4.4	Gibbs Energies of Transformation of the Components	206
6.4.5	Discussion	207
6.5	System $\text{CaCl}_2\text{-H}_2\text{O}$	210
6.5.1	Introduction	211
	<i>Phase Diagram</i>	211
	<i>Tables of Excess Properties</i>	213
6.5.2	Correlating Equations	228
6.5.3	Discussion	230
7.	CATALOGS OF MEASUREMENTS USED IN THE EVALUATIONS	238
7.1	Thermochemical Reaction Catalog	239
7.1.1	Values for Properties of Substances	239
	<i>Table: Thermochemical Properties of Substances and Index to the Measurements</i>	241
7.1.2	The Catalog of Reactions	249
7.1.3	Interpreting the Catalog	250
	<i>Table: Catalog of Measurements</i>	251
7.2	Ca-Mg Reaction Catalog	305
7.3	$\text{CaCl}_2\text{-H}_2\text{O}$ Reaction Catalogs	312
8.	BIBLIOGRAPHY	328

## Chapter 1

# INTRODUCTION

### 1.1 The CODATA Task Group on Chemical Thermodynamic Tables

The predecessor of this Task Group was the Task Group on Internationalization and Systematization of Thermodynamic Tables (ISTT). It was established at the 5th International CODATA Conference in Boulder, Colorado, in 1976, and reconstituted and given its present name in 1982. Most of the work reported on here was carried out during the period 1976-1985. The ISTT Task group was provided with the following terms of reference.

- a. To reach international agreement on functions, conventions, standard states, intervals of tabulation, etc., for thermodynamic tables.
- b. To develop a suitable system for international cooperation in compilation of papers, extraction of data, and storage of information and data, so that the same base of primary measurements will become available to all.
- c. To develop suitable techniques for evaluation of data and the formation of tables such that the efforts of independent evaluators will lead to thermodynamically consistent tables, and new data and substances can be added in a consistent fashion to existing tables.
- d. To promote international cooperation in the production of thermodynamic tables so that the needs of users can be met in a timely, efficient manner.
- e. To provide a forum for discussion of the problems of preparing tables of critically evaluated chemical thermodynamic data and to develop an informative literature on the subject.

It is apparent that the principal thrust of the terms of reference is the development of a system of international cooperation leading to the preparation of thermodynamically consistent tables in a timely and efficient manner. In carrying out its responsibilities the Task Group focussed on chemical thermodynamics, that is the thermodynamics of chemical reactions and the thermodynamics of the change of state of a substance without chemical reaction.

The Task Group has accomplished four things:

- a. It carried out an extensive systematic analysis of the preparation of large sets of tables of thermodynamic properties.



- b. Using this analysis, it defined the structure of an international system and developed a plan for the preparation of tables as a joint international cooperative effort.
- c. It specified the contents of several tables and data banks intended for general use.
- d. It prepared a prototype set of tables using the plan and specifications mentioned above.

The purpose of this paper is to present this prototype set of Tables.

### 1.2 The Preparation of Thermodynamic Tables

The Task Group has already published the results of its analysis and planning under the title "Systematic Approach to the Preparation of Chemical Thermodynamic Tables" [82WHI]. This material will not be repeated in detail here. It does, however, underlie the tables and influences their structure and content.

Figure 1.2.1 is taken from the publication mentioned. It is a flow diagram through the proposed system. Raw data from the scientific literature enter at the top and comprehensive sets of evaluated data are produced at the bottom. The solid arrows indicate flow through the system as well as the intellectual input required in moving from one step to another. The small circles represent the intellectual synthesis of materials from several files. The bold broken arrows complete the major feedback loops. The rectangular boxes represent recognizable data files that are important states of the system. The tables and bibliography presented here give examples of files 1, 4A, 5A, 6, 7, 8, 9A, 9B and 10. Readers interested in the detailed explanation of Figure 1 are encouraged to read [82WHI].

### 1.3 The Prototype Tables

The tables focus on calcium, the element, and its compounds with hydrogen, oxygen and chlorine, as well as magnesium and potassium chloride. Additional compounds of calcium and other substances are also present. These are needed to solve the primary network of thermochemical reactions required to introduce thermodynamic consistency. The thermodynamic values chosen are consistent with the June 1984 draft of the final report on the CODATA Recommended Key Values for Thermodynamics [84COD], in which some values have been revised from the earlier publication [78COX] and take into account recent measurements. To the best of the Task Group's knowledge they provide as reliable a set of values as exists for the substances concerned.