

Inorganic energetics

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Inorganic energetics

AN INTRODUCTION

W.E.DASENT

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FOREWORD

The first edition of this book appeared in the Penguin Library of Physical Sciences; it provided one of the most useful sources of inorganic thermochemical data, coupled with a ready introduction to the application of thermodynamics to inorganic systems. As such the book has been extensively used in the inorganic chemistry courses in the University of Cambridge over the past decade and has proved to be particularly useful. The large amount of data in the book allows a student to calculate for himself the energetics of a multitude of inorganic systems and amply encourages a student to study the complementary work by the same author, *Non-existent Compounds*. The assumption that is made in the present text is that the student will have an understanding of thermodynamics although the use of basic thermodynamic equations is well illustrated.

Thermodynamics may be considered to be the 'science of the possible' and the importance of thermodynamics and kinetics in governing stability within inorganic systems is ably explored. The text allows the student to familiarise himself with the various energy terms that make for the potential for a reaction to occur using both the ionic and covalent models. The kinetic limitations of many reactions which are emphasised and of prime importance in the teaching of organic chemistry then become a feature of a broader chemistry, for instance, the kinetic rather than thermodynamic 'stability' of the oxides of nitrogen.

Analysis of these various steps in the total energy profile accentuates the complexity and the fine balance between these terms and emphasises the difficulty in dealing with what appear to be 'simple' concepts in chemistry such as solubility or stability of complex ions. This allows for a better understanding of the application of the theory of bonding within inorganic systems, and certainly augments the more classical and theoretical approaches to inorganic chemistry. The author has been at some pains to emphasise the application to real inorganic systems. I have found that this approach certainly provides a stimulus to the teaching of the subject and the text provides a short and effective complement to any course of inorganic chemistry.

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Perhaps one of the main problems that is implicit in the text is the need for more extensive thermochemical measurements on a wide range of inorganic systems.

It certainly was with enthusiasm and the recognition of a real teaching need that I encouraged the author to update the text. I believe that the present work will enhance, and I hope enthuse, a large number of courses in inorganic chemistry.

J. LEWIS, FRS

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Preface to the second edition

This book provides an elementary discussion of the energetic aspects of inorganic substances: the thermodynamic principles which underlie their formation in chemical reactions, their stabilities, and their binding energies.

It is assumed that the reader has taken, or is taking concurrently, a course in elementary thermodynamics, and the book is in no way a substitute for such a course. Its purpose is rather to amplify those aspects of thermodynamics which are of particular interest to the student of inorganic chemistry, and to provide a wider selection of inorganic examples than is usually encountered in more general texts.

The method of approach which has been adopted is based on general procedures for dividing inorganic reactions into sets of sequential sub-reactions. Standard tabulated quantities (principally ΔG_f^\ominus , ΔH_f^\ominus , and S_{298}^\ominus , together with some subsidiary data covering the energy changes which occur when electrons are removed from, or added to, atoms and radicals, and when atoms or ions combine) are then used to identify the thermodynamic factors which influence the course of the reactions. Many of the everyday facts of inorganic chemistry – such as the solubilities of salts in water – are likely to remain incomprehensible without this sort of analysis, many examples of which are given in the text.

In this second edition, the chapter headings and basic content of the first edition have been preserved, but much of the material has been rewritten and the numerical data revised. An effort has been made to keep the volume brief and self-contained, but at the same time reasonably balanced and comprehensive in its coverage. To achieve these objectives it has been necessary to be selective in the topics chosen for detailed discussion, more particularly in the chapter dealing with reactions in solution. It is hoped nevertheless that the general method of approach and extensive tabulations of data will encourage students to make their own thermodynamic analyses of reactions which are not specifically discussed.

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W. E. Dasent

Victoria University of Wellington

New Zealand

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Units and Conversion Factors; Constants; Data Sources

Units and conversion factors

The units used throughout this book are those of the SI system (Système International d'Unités). The basic SI units are those in (a) below. Some familiar derived SI units are those in (b):

	Physical quantity	Name of unit	Symbol	Definition
(a)	length	metre	m	
	mass	kilogram	kg	
	time	second	s	
	electric current	ampere	A	
	thermodynamic temperature	kelvin	K	
	luminous intensity	candela	cd	
	amount of substance	mole	mol	
(b)	energy	joule	J	$\text{kg m}^{-2} \text{s}^{-2}$
	pressure	pascal	Pa	$\text{kg m}^{-1} \text{s}^{-2}$
	frequency	hertz	Hz	s^{-1}
	electric charge	coulomb	C	A s
	electric potential difference	volt	V	$\text{kg m}^2 \text{s}^{-3} \text{A}^{-1}$
	electric capacitance	farad	F	$\text{A}^2 \text{s}^4 \text{kg}^{-1} \text{m}^{-2}$

The electron volt (eV), which is not an SI unit, is widely encountered in spectroscopic literature. In several tables energy quantities have been shown in both eV and kJ mol^{-1} .

The standard pressure to which the superscript \ominus refers in symbols such as ΔH^\ominus is 1 atmosphere, which = 101 325 Pa.

Interatomic distances are recorded in picometres (pm). Note that 1 pm = 10^{-12} m; 1 angstrom = 10^{-10} m = 100 pm.

Some further conversion factors are as follows:

$$1 \text{ eV} \equiv 96.49 \text{ kJ mol}^{-1}$$

$$1 \text{ cm}^{-1} \text{ (electromagnetic radiation)} \equiv 0.011 96 \text{ kJ mol}^{-1}$$

$$1 \text{ joule} = 4.184 \text{ calorie.}$$

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Constants

Avogadro constant	N_A	$6.022 \times 10^{23} \text{ mol}^{-1}$
Faraday constant	F	$96\,485 \text{ C mol}^{-1}$
charge of proton	e	$1.602 \times 10^{-19} \text{ C}$
Planck constant	h	$6.626 \times 10^{-34} \text{ J s}$
permittivity of a vacuum	ϵ_0	$8.854 \times 10^{-12} \text{ F m}^{-1}$
gas constant	R	$8.314 \text{ J K}^{-1} \text{ mol}^{-1}$
Boltzmann constant	k	$1.381 \times 10^{-23} \text{ J K}^{-1}$
Also,		
	π	3.142
	$\ln x$	$2.303 \log x$
base of natural logarithms	e	2.718

Data sources

Standard Gibbs free energies of formation, standard enthalpies of formation, and standard entropies have for the most part been taken from the NBS and JANAF compilations listed below. References to other sources have been given in the text where it has seemed important to do so, but the documentation is not exhaustive.

NBS Tables:

Selected Values of Chemical Thermodynamic Properties, U.S.

National Bureau of Standards Circular 500, Washington, D.C. (1952) and its revisions, *Technical Note 270-3* (1968), Tables for the first 34 elements in the standard order of arrangement; *Technical Note 270-4* (1969), elements 35-53; *Technical Note 270-5* (1971), elements 54-61; *Technical Note 270-6* (1971), elements 92-97; *Technical Note 270-7* (1973), elements 62-76.

JANAF Tables:

JANAF Thermochemical Tables, 2nd edition, NSRDS-NBS 37, U.S. Government Printing Office, Washington, D.C. (1971), and its supplements, 1974 Supplement, *Journal of Physical and Chemical Reference Data*, **3**, 311-480; 1975 Supplement, *Journal of Physical and Chemical Reference Data*, **4**, 1-75; and 1978 Supplement, **7**, 793-940.