NATIONAL BUREAU OF STANDARDS REPORT

10 907

ELECTROLYTE DATA CENTER

Thermochemistry Section
Physical Chemistry Division
for
Office of Standard Reference Data
National Bureau of Standards
Washington, D.C.

NBS

U.S. DEPARTMENT OF COMMERCE
NATIONAL BUREAU OF STANDARDS

NATIONAL BUREAU OF STANDARDS

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[1] Headquarters and Laboratories at Gaithersburg, Maryland, unless otherwise noted; mailing address Washington, D.C. 20234.

[2] Part of the Center for Radiation Research.

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NATIONAL BUREAU OF STANDARDS REPORT

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ELECTROLYTE DATA CENTER

Scope and Outline of Activities

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Table of Contents

Page

Preface

Preface

The Electrolyte Data Center was organized in-house at the National Bureau of Standards in order to meet the needs of the Technological and Scientific Community for reliable and carefully evaluated data primarily in the field of aqueous electrolytes. An informal steering committee consisting of Dr. Howard J. White, Dr. David Garvin and Dr. George T. Armstrong made most of the preliminary arrangements.

In order to provide initial guidance to the Data Center in the most fruitful and useful activities to be carried out, priorities to be assigned, and other technical basis of activities, a Panel of the National Academy of Sciences/National Academy of Engineering/National Research Council was formed under the auspicies of Dr. Hendrick van Olphen of the Numerical Data Advisory Board. This Panel consists of Dr. Harold S. Friedman, Chairman; Dr. S. Bruckenstein; Dr. John T. Edsall, Dr. Alphonse Fortziati, Dr. George J. Janz Dr. W. T. Lindsay; Dr. Ricardo Pytkowicz, and Dr. Robert E. Wood.

The Panel had its first meeting 27 October, 1971, in Washington, D.C. at which a presentation was made of NBS activities related to the Electrolyte Data Center and individual members of the Panel made presentations. The meeting was summarized in a report dated 22 December 1971.

The present report, by the staff of the Electrolyte Data Center, is at the same time a response to the December, 1971, report of the Panel and a summary of Data Center activities up to the present time.

George T. Armstrong, Chief
Thermochemistry Section

Electrolyte Data Center

I. Purpose. The purpose of the Data Center is to provide on a continuing basis information services, evaluations, and critical reviews of the thermodynamic data on aqueous electrolytes.

II. Scope of Coverage. The data center will emphasize the study of equilibrium thermodynamic properties of aqueous electrolyte systems, and will cover the whole range of temperatures, pressures, and concentrations for which data are available. A list of physical properties falling within the scope of the data center's primary concern is attached (appendix 1.). The data center will take cognizance of certain related physical properties and also of transport properties, but will not presume to provide complete coverage of them. Solutions of single electrolytes in water will be given primary emphasis. Mixed electrolyte solutions are being studied by scientists at a rapidly increasing rate. These solutions will be included in the activities of this data center. Aqueous solutions of non-electrolytes and non-aqueous systems, including fused salts, will not presently be covered by the data center.

III. Significance and Justification.

A multitude of technological uses for electrolyte solution data exist. Very important applications exist in the chemical process industries and in the various electrochemical industries. Even a very brief survey must also include areas such as environmental protection, water resources management, physiological and biomedical research, clinical practice and sanitation.

Industrial applications are widespread, and the fields of foods and food processing, agriculture, textiles, refrigeration, and construction must be included into the list of fields in which applications are found.

As a simple illustration of a particular property, the osmotic coefficient, in physiology, the following example can be cited. The intercellular and extracellular fluids exist in a state of osmotic equilibrium. This equilibrium is complex but does include not only the colloidal osmotic pressure due to plasma proteins but also the electrolyte osmotic pressure.

One of the most important characteristics of the internal cell environment, which is critical to the normal life and activity of the cell, is its total electrolytic osmotic pressure, and of all the parameters of the extracellular fluid, this is the one that is most strictly regulated. It may also be noted that the main constituent in the extracellular water is sodium chloride.

The main protective mechanism of zinc rich paints is electrochemical. The fact that zinc metal is electropositive to iron and in a simple aqueous galvanic cell will form the anode and react to dissolve preferentially to the iron is of great importance for protecting steel parts in a marine environment, for example, a ship hull. Data on galvanic potentials are necessary for studies of corrosion problems. Other examples of this type of sacrifical protection are widespread in industry.

In many basic scientific methods for investigating thermodynamic properties of aqueous solutions, for example, isopiestic measurement, a few solutions, such as NaCl, serve as the reference standards. The available data on such reference standards is critical to scientific research in many areas. Other data often serve as the basis for developing theories concerning the properties and behavior of electrolyte solutions, which may result in important practical applications. Reference data would also provide a means of testing theories and models of electrolyte solutions.

In addition to the technological users of electrolyte data, research scientists require sets of consistent and accurate data. Theoretical studies of electrolyte solutions can be tested only by use of such data. Chemists studying reactions in solution need data on the properties of the species present in the solutions.

The need for electrolyte data within this enormous framework indicates the usefulness of an Electrolyte Data Center to the scientific and industrial complex.

IV Organizational Affiliation.

The Electrolyte Data Center is sponsored and initially funded by the Office of Standard Reference Data (OSRD) (Dr. David R. Lide, Chief) as part of the National Standard Reference Data System (NSRDS). In the OSRD it is under the supervision of Dr. H. J. White, Jr., as part of the program of Thermodynamics and Transport Data.

It is organizationally part of the Thermochemistry Section (Dr. George T. Armstrong, Chief). The Thermochemistry Section is one of five sections of the Physical Chemistry Division (Dr. M. D. Scheer, Chief). The other sections are: Surface Chemistry (Dr. Ralph Kline, Chief), Photochemistry (Dr. Pierre Ausloos, Chief), Radiation Chemistry (Dr. Dolphius E. Mulligan, Chief), and Elementary Processes (Dr. Henry M. Rosenstock, Chief). There are also in the Physical Chemistry Division a Thermodynamics Group (Dr. C. W. Beckett, leader), a Quantum Chemistry Group (Dr. Morris Krauss, leader), and a Data Programs Group (Dr. David Garvin, leader).

In the Physical Chemistry Division Dr. David Garvin, as coordinator of Data Programs, has general oversight of data centers in Kinetics, Elementary Processes, and Chemical Thermodynamics, as well as the Electrolyte Data Center. The Chemical Thermodynamic Data Center (Mr. Donald D. Wagman, manager) is also in the Thermochemistry Section, and interacts closely with the Electrolyte Data Center, but the two Centers are physically and organizationally separate.

The Physical Chemistry Division is in the Institute for Materials Research of the National Bureau of Standards (Dr. John D. Hoffman, Chief).

V. Resources.

A. Personnel

The manager of the data center is Dr. Ralph L. Nuttall; the principal other scientist is Dr. Bert R. Staples.

The initial funding of the data center permits operation at a rate somewhat less than one man year per year. In the sixteen months of operation to date, approximately one man year has been funded. Of this time, Dr. Nuttall accounted for about 0.4 man year and Dr. Staples has accounted for the remaining 0.6 man year for the tasks of the Data Center. Dr. George T. Armstrong, Chief of the Thermochemistry Section, provided administrative time as needed. Additional time, not reimbursed from project funds, was contributed by several scientists associated with other programs. These included Dr. Robert N. Goldberg, experimental thermochemistry; Mr. D. D. Wagman, Dr. W. H. Evans, and Dr. V. B. Parker of the Chemical Thermodynamic Data Center; Dr. David Garvin, Coordinator of Data Programs for the Physical Chemistry Division; Dr. H. J. White, Office of Standard Reference Data; Dr. W. J. Hamer NBS Electricity Division, now retired, and Dr. Y. C. Wu, Institute of Applied Technology. Clerical assistance was provided for a few months by Miss Cathy Worthington, a student trainee. Miss Debra Miro of the Thermochemistry Section has handled the bulk of the clerical operations for the Data Center since its inception.

B. Space and equipment

The Data Center occupies Room A-164, Chemistry Building, a modified laboratory-type module with about 23 m^2 (3.2 m X 7.2 m) floor space. It is equipped with six filing cabinets, about 40 book shelves ($\sim$2.8 m^3),

and appropriate other office furniture.

Equipment assigned to the Data Center includes: Control Data Corporation tape typewriter (Typetronic 2816) with tape reader and tape punch; Friden electromechanical desk calculator; Wang 450 Scientific Calculator (electronic) with card program attachment (on order); and a microcard reader. Also available in adjoining rooms for use by the Data Center are Teletype typewriters with tape punch and computer interface; IBM card keypunches, Hewlett-Packard 7200A Graphic plotter; 3M microfilm 400 Reader-Printer; and an Olivetti Copia III quick copier.

General NBS equipment useful for the Electrolyte Data Center includes the Univac 1108 computer, and special data and manuscript processing facilities of the Office of Standard Reference Data.

C. Library and literature files

The ultimate library resource of the Electrolyte Data Center is the NBS main library, which has one of the most complete scientific collections in the nation. By interlibrary loan essentially all the library resources of the nation are available for special needs.

Additional resources are provided by the library of the Office of Standard Reference Data, which has a special collection of evaluated scientific reference data, and the library and files of the Chemical Thermodynamic Data Center. The applicability of the latter to the needs of the Electrolyte Data Center is discussed below in more detail.

In addition to the above, the Data Center has a special collection of journals, books, and working files, emphasizing properties of electrolytes. These are described below and in Appendix 2.

(1) Journals

The Data Center has the following journals in its files and currently being received by subscription:

J. Phys. Chem.

J. Chem. Phys.

J. Chem. Soc. Faraday

J. Solution Chem.

J. Am. Chem. Soc.

Other journals received in the adjoining Chemical Thermodynamic Data Center include:

Chemical Abstracts

J. Thermodynamics and Thermochemistry

J. Chem. Eng. Data

J. Research NBS

(2) Secondary Source Literature

The Data Center has on hand about 45 monographs and reference works on thermodynamic and transport properties of aqueous and non-aqueous electrolyte solutions. About ten additional books are on order. A list of the books and other secondary source literature is given in Appendix 2. Some other relevant monographs and reference works are found in the Chemical Thermodynamic Data Center and are available to the Electrolyte Data Center.

(3) Reports, reprints, and special files.

The technical files of the Electricity Division electrolyte data project have been acquired. These consist of technical reports (listed in Appendix 2), manuscripts in preparation, reprints, bibliographical files, computer programs, partially evaluated data files.

Limited files of bibliographical material and some miscellaneous reports on special topics discussed later in this report have also been obtained.

(4) Chemical Thermodynamic Data Center files.

The principal data files for use of the Data Center are those of the Chemical Thermodynamic Data Center. The relationship of these files to the work of the Electrolyte Data Center is discussed in Section VI. These files comprise, perhaps, the largest indexed files related to chemical thermodynamic properties existing in the world.

The files of the Chemical Thermodynamic Data Center may be outlined briefly as follows.

(a) Substance-property index card file (more than 100,000 items). These files are classified by substance, including organic and inorganic substances. Recent accessions (about three years) are completely stored on magnetic tape so that storage, retrieval, and sorting manipulations are possible. Each substance is indexed in ten categories of thermodynamic properties. Each card gives bibliographical information about the single source of the data described on it.

(b) Reprint file (microfilm). Complete articles are stored on microfilm, and filed with complete bibliographical information in alphabetical order of first author's surname.

(c) The Bulletin of Thermodynamics and Thermochemistry is prepared by the Chemical Thermodynamic Data Center and the information contained is on magnetic tape with machine-search capabilities available.

VI Mode of Operation of the Data Center.

The Electrolyte Data Center has the following functions:

(1) Acquisition and organization of information on the properties of electrolyte solutions (coordinated with the work of other data centers).

(2) Provision of information services on electrolytes directly to the public and the scientific community.

(3) Preparation and dissemination of lists, bibliographies, surveys, and critical reviews relating to the field of electrolyte solutions.

These are discussed briefly below.

(1) The acquisition of information from the primary source literature (mainly technical journals) consists first of a search in which relevant articles are identified and obtained. This is then followed by an abstracting process in which the relevant information and data are abstracted from the article and stored in a retrievable mode. This information may then be organized by substance, by property by source, and in other ways for ready retrieval. To do a complete search such as this is a very large task.

The Data Center is not conceived as a completely self-sufficient operation, but will depend upon other data compilation activities for at least part of its technical files. In this instance, the work of the center will be coordinated with that of the Chemical Thermodynamic Data Center.

In the Chemical Thermodynamic Data Center a very thorough search of the current chemical literature is made on a continuing basis.

This search includes scanning the contents of about forty-five important journals in which is found a large fraction of the significant work in thermochemistry and thermodynamics. It also includes scanning page by page most sections of the Chemical Abstracts. Following this search, the articles and abstracts are examined closely for thermodynamic information, and those which contain such information are accessed for the files of the Chemical Thermodynamic Data Center. This accession includes preparation of a bibliographical reference and preparation of a microfilm copy of the article for the files.

In the Electrolyte Data Center this search will not be duplicated. The subject and substance coverage of the search initially performed by the Chemical Thermodynamic Data Center included most of the subjects required for the Electrolyte Data Center. By a minor expansion of the search complete coverage of the topics listed for emphasis in Appendix 1 is being obtained. Subjects for which prior coverage was inadequate, but which are now being covered as completely as other topics are: density, expansibility, compressibility, phase diagrams (aqueous), solubility, salting coefficients, and changes of freezing and boiling points. Transport properties, surface tension, dielectric constant, and other properties not emphasized in Appendix 1 are not included among the subjects for which articles are accessed.

As a result of this, the files of the Chemical Thermodynamic Data Center will, for current and future primary source literature be nearly complete with respect to all properties emphasized in Appendix 1. References to prior work will be notably deficient in the

newly covered topics mentioned above. These deficiencies will be dealt with as required in particular applications of the work of the Center.

A second phase of the accession of information for the Chemical Thermodynamic Data Center files is the abstraction of data from the articles in the files. This provides the principal information for the subject-property files. This is a process for which the work can be divided so that articles containing data relevant to the Electrolyte Data Center can be abstracted in the Electrolyte Data Center supplementing the work of the Chemical Thermodynamic Data Center. The information thus obtained will be merged with the Chemical Thermodynamic Data Center files. Copies of the abstracted information may also be kept in the Electrolyte Data Center

(2) Close contact will be maintained by correspondence and personal contacts with selected scientists in the field, and with organizations having special interest in the field of electrolytes and solution processes.

This type of contact is important (1) to maintain awareness in the Data Center of work in progress elsewhere, (2) to determine the impact of scientific data for electrolytes on technological programs, (3) to establish and maintain liaison between the Data Center and potential users.

(3) The principal productive activity of the Data Center is to prepare material for distribution. The material may be prepared in response to requests for information or may be prepared in response to anticipated needs. Three categories of output material may be identified and are given below.

(1) Lists and Bibliographies

(2) Surveys (no evaluation of data)

(3) Critical Reviews (critical evaluation of data)

Examples and priorities are given in Section VII.

VII Needs and Proposed Priorities.

Three categories of outputs identified in Section VI are discussed here with respect to particular examples. Examples are listed in each category in order of their priorities assigned on the basis of need, cost, difficulty of completion, and availability of personnel.

1. Lists and Bibliographies
    - (a) List of laboratories active in the field
    - (b) List of data centers active in the field
    - (c) List of scientists active in the field
    - (d) Bibliography of reference works in electrolyte thermodynamics
    - (e) Bibliographies of primary source literature in special areas of electrolytes
    - (f) Annual bibliography of work done and cumulative bibliography
2. Surveys (no evaluation of data)
    - (a) Subject-property index of previously compiled data (reference literature) on electrolytes
    - (b) Subject-property index of annual work done and cumulative index
    - (c) Uncritical compilations of data in selected areas
    - (d) Surveys of schemes for estimating particular properties
3. Critical Reviews (critical evaluation of data)
    - (a) Thermodynamic properties of aqueous uni-polyvalent electrolytes and poly-polyvalent electrolytes
        - (1) Osmotic coefficients and activity coefficients at 25°C
        - (2) Thermal properties
    - (b) Single-substance monographs with broad coverage of selected substances (NaCl), (CO_2, HCO_3^-, $CO_3^=$)

(c) Thermodynamic properties of biological electrolytes

(d) Monograph on selected properties of about 100 key electrolytes

(e) Critical evaluation of material in the Sillén-Martel compendia

Of the lists and bibliographies a single compilation combining items (a), (b), and (c) can be prepared in a relatively short time. It is given a high priority because of its ease of preparation, its brevity, and its general utility to scientists and technologists interested in electrolyte properties. A bibliography of reference works (d) in electrolyte thermodynamics is also easy to prepare but has less general utility. Bibliographies of primary source literature (e), in special areas and annual and cumulative bibliographies are good awareness information; however they tend to be outweighed in importance by subject-property indexes.

The proposed surveys of electrolyte thermodynamic data are based on our own conviction that there is no better way to become thoroughly aware of the work being done in the field than to prepare such surveys; and that the information thus gained would be of greater value if disseminated than if retained in our own files. In particular, a survey of previously compiled work found in the reference or secondary source literature provides a guide to the kind and currency of information already published. It thus provides important information needed in assigning priorities for extensive critical reviews. Thus its greatest value will probably be in the operation of the Electrolyte Data Center. It will indicate what types of data, and on what substances these data are available in the well-known and some of the lesser known

secondary sources and monographs on electrolytes.

An annual and cumulative index classified by subject and property with associated bibliography essentially consists of a fraction of the work already appearing in the annual Bulletin of Thermochemistry and Thermodynamics, augmented with respect to certain properties. A separate listing of the electrolyte information would probably be more intensively read in a narrower circle of readers. However, the priority is somewhat reduced by the existence of the Bulletin as an alternate source of the same information.

Under critical reviews (3) priorities are difficult to assign. First priority is given to completing osmotic coefficients and activity coefficients of the electrolytes in addition to uni-univalent charge types. This work was begun by Wu and Hamer. The completion requires up-dating available data from 1967 where Wu and Hamer stopped compilation. However, the extensive work already done should not be lost and its existence reduces the effort needed to complete the publication of this monograph.

A single-substance monograph on NaCl (b) was proposed by Dr. W. T. Lindsay, based on the ubiquity of NaCl in the physical and biological sciences and in industrial processes. The suggestion was favorably viewed by the study group. This monograph, containing critically evaluated data, will be a comprehensive review of the system $NaCl-H_2O$. The reviews will cover all available thermodynamic properties and related information over all ranges of pressure, temperature, and concentration. An outline of such a monograph is given in Appendix 3.

Thermodynamic properties of biological electrolytes (c) are very important now and a review would be particularly useful for an international subcommission associated with the IUB-IUPAB-IUPAC. The principal difficulty is lack of a suitable staff person. When a person to do this work is available, it assumes a high priority.

A monograph on selected properties of some carefully selected key electrolytes (d) would be very useful. These compounds can serve as reference standards and as models for the properties of other substances where no experimental data are available.

VIII Activities of the Data Center.

This section covers the principal activities carried on in and in behalf of the Data Center since its inception.

1. Organization and physical establishment of the Data Center

   The center was brought into being by a steering committee (White, Garvin, Armstrong), staffed (see Section III), provided with space and some physical facilities (see Section IV), and arrangements were made for an advisory panel of the Numerical Data Advisory Board (NAS-NAE-NRC).

2. Establishment of program and priorities

   (a) The ad-hoc panel on thermodynamic properties of aqueous electrolyte solutions (H. L. Friedman, Chairman) met 27 October 1971, at the National Academy of Sciences, with Data Center staff and other interested scientists in attendance. The report of this panel, submitted 22 December 1971, was carefully analyzed and strongly influenced the present document, which is in part a response to the report.

   (b) An in-house study group met weekly or bi-weekly during a period of several months to help establish guidelines for the activities of the Data Center. The composition of this study group varied somewhat, but included: Dr. G. T. Armstrong, Dr. R. L. Nuttall, Dr. B. R. Staples, of the Data Center staff, Dr. R. N. Goldberg of the Thermochemistry Section; Mr. D. D. Wagman, Dr. W. H. Evans

and Dr. V. B. Parker of the Chemical Thermodynamic Data Center; Dr. W. J. Hamer of the Electricity Division; Dr. H. J. White, OSRD; and Dr. D. Garvin, Physical Chemistry Division office.

The study group was convened to carry out technical discussions that would allow definition of the scope and extent of electrolyte data evaluation and procedures for the operation of the Data Center. The study group considered and discussed in detail the following subjects:

(1) The extent and types of existing compilations and current literature on electrolyte properties.

(2) Extent of coverage of appropriate properties by the Chemical Thermodynamic Data Center, and modes of interaction between the two Centers.

(3) Relationships between technical treatments of electrolyte data by Hamer and Wu and by the Chemical Thermodynamic Data Center.

(4) A compendium of subject-property information in the secondary source literature (existing reference works).

(5) Selected monograph subjects (see Section VII for topics and priorities.

As a result of these discussions the scope of the Data Center was limited to aqueous solutions and to thermodynamic properties. It does not appear feasible to include non-aqueous solutions or transport properties in the data center operations at this time. It was also agreed that the Electrolyte Data Center should take advantage of the existing files and abstracting procedures already in operation in the

Chemical Thermodynamic Data Center. Duplication of effort is to be avoided.

Discussions were held with Mr. Wagman to review the operations of this data center and to establish a system for obtaining abstracts of articles dealing with electrolyte solutions.

3. Completed work

(a) The monograph on activity and osmotic coefficients for uni-univalent electrolytes at 25°C by W. J. Hamer and Y. C. Wu was reviewed in detail and the tables and constants were verified using the computer programs developed by Hamer and Wu. Corrections and some modifications were recommended. This monograph is now in press in the Journal of Physical and Chemical Reference Data (Issue No. 4.).

(b) A substantial amount of the data that had been acquired from Hamer on computer cards has been placed on magnetic tape to allow more efficient use of storage space in the Data Center. Two tapes will be used; one to be retained on file by the NBS Computer Services Division and one to be stored in the Data Center. The computer cards will be stored in inactive storage space at the NBS records storage area. At least once a year the magnetic tape will be recopied onto a new tape to preserve the quality of the tapes over long storage periods.

(c) The machine programs developed by Hamer and Wu to correlate activity coefficients and osmotic coefficients are

generally applicable to electrolytes of various valence types. They provide theoretical fits in the Debye-Hackel region and empirical polynomial fits in the more concentrated solutions. They are complete and are considered to be of sufficiently general interest for the Data Center to make them available as NBS Reports or Technical Notes.

4. Technical Work in Progress

(a) A compendium of information available in data compilations and secondary source literature (reference works) on properties of aqueous electrolytes has been started and is in preparation.

(b) A study was made of the extent of technical literature to be covered by the Electrolyte Data Center. This study in intended to provide guidance as to the amount of personnel effort needed to cope with organization of the data and files and to review and evaluate the data. The study is summarized in Appendix 4.

(c) A partial bibliography of data sources, both primary and secondary sources, for numerous properties of NaCl has been prepared. This was initiated in preparation for a monograph on aqueous sodium chloride. The monograph was outlined (see appendix 3).

(d) A compilation of most of the primary reference sources for osmotic and activity coefficient data at 25°C has been completed for 1:2, 2:1, 1:3 and 3:1 electrolytes up to about 1968. The critical evaluation of the data was initiated by Hamer and Wu.

(e) A list of workers in the field of electrolytes was begun.

(f) Initial steps have been taken to establish communications and cooperative relationships with other data centers in the field. The symposium in honor of H. S. Frank (Pittsburgh June, 1972) was attended. Letters to persons active in electrolyte solution research are being prepared, not only to allow the Center to keep abreast of recent developments but also to maintain a helpful liaison with regard to their opinions of the usefulness of various projects that the Electrolyte Data Center may undertake. Letters to other data centers outside of NBS will not only inform them of our operations but will also provide interaction through requests for information and services and sharing of some reference data.

IX Summary.

This document has presented the scope and activities of the Electrolyte Data Center. These are limited by funds and personnel available. Dependence on the Chemical Thermodynamic Data Center for literature searching has been pointed out. In section VII are given some possible activities, with some estimates of priorities, of the data center. In section VIII the present activities are discussed. Activity will be transferred to other tasks as present ones are completed.

The data center will try to respond to all needs expressed by the scientific community within the scope of its activities.

Appendix 1.

Properties

I. Scope of properties

A. Treatment of properties in the following modes will be of interest.

- 1.a. Experimental treatments
  - b. Theoretical treatments
- 2.a. Molar quantities
  - b. Specific quantities
- 3.a. Partial quantities
  - b. Apparent quantities
- 4. T,P,X variables

B. The functions that describe these properties are also readily classified into four types.

1. Energy functions of aqueous solutions
   - a. Internal energy (U) $(\partial U/\partial T)V$ $(\partial U/\partial V)T$
   - b. Enthalpy (H) $(\partial H/\partial T)P$ $(\partial H/\partial P)T$
   - c. parameters associated with phase changes (ΔH_{fus} and ΔH_{vap}; also freezing point lowering and boiling point elevation).
2. Ordering functions of aqueous solutions
   - a. Entropy (S)
3. Equilibrium functions
   - a. Helmholtz energy (A)
   - b. Gibbs Energy (G)
   - c. E.M.F. and chemical potentials (E, μ)

d. Equilibrium constants and related T and P.

K_a, K_b, K_i, K_{instab}, K_{sp}, K_A(assoc), P_{vap}, solubility, phase diagram and associated activity coefficients (osmotic coefficient; mean activity coefficients)

4. PVT relationships

a. density of aqueous solutions and associated molar volumes

b. expansibility

c. compressibility

C. The remaining related physical properties which are not to be emphasized at this time, fall into two categories:

1. Transport properties

a. conductivity-electrical

b. conductivity-thermal

c. diffusion

Including related constants such as:

(a) diffusion coefficient

(b) transference number

(c) ionic mobility

(d) viscosity

2. Related physical properties

a. dielectric constant

b. light absorption coefficients

c. polarization

d. surface tension

e. ionic radius

f. decomposition potential

g. velocity of sound in solutions

h. electro-kinetic properties (e.g. voltammetry--polarography, etc.)

II. Classes of substances and systems

Systems in both aqueous media and mixed solvents that include water as one component

a. Strong electrolytes

b. Weak electrolytes

c. Mixed electrolytes

d. Zero-charge types of solutes

III. Ranges of Properties

A. Temperature -- From -30 to +400°C is needed with special interest in the range from 0 to 40°C, and in particular 25°C.

B. Pressure -- From 0-1000 atmospheres is needed (10,000 atm. as an upper limit), with special interest at 1 atmosphere.

C. Concentration -- From infinitely dilute solutions ($X = 0$) to saturation, with special emphasis on standard states.

Appendix 2.

List of Publications Contained in the Electrolyte Data Center

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9040	I	(Terms) 1966
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9876	X	Electrolytic Conductivity of Aqueous Solutions of the Alkali Metal Hydroxides, 1968
9908	XI	Osmotic Mean Activity Coefficients of Aqueous Solutions of HCl, HBr, HI, and the Chlorides, Bromides and Iodides of the Alkali Metals at 25°C, 1968, (Wu and Hamer)
9979	XII	Electrolytic Conductivity of Aqueous Solutions of the Sodium Halides, 1969
10052	XIV	Osmotic Coefficients and Mean Activity Coefficients of a Series of Uni-Bivalent and Bi-Univalent Electrolytes in Aqueous Solutions at 25°C, 1969
10076	XV	Electrolytic Conductivity of Aqueous Solutions of the Potassium Halides, 1969
10088	XVI	Osmotic Coefficients and Mean Activity Coefficients of a Number of Uni-Trivalent and Tri-Univalent Electrolytes in Aqueous Solution at 25°C.

Appendix 3.

Sodium Chloride Monograph Prospectus

Note: The prospectus on aqueous sodium chloride is a preliminary arrangement of possible data which may be included in such a monograph. The tables and values given are used only as illustrative examples of possible forms that the data presentation may take. It is not intended as a complete outline.

Aqueous Sodium Chloride

1. Introduction

A. Purpose of the monograph

Over the years a copious amount of data of both valuable as well as less valuable results, has been compiled on the properties of the system: Sodium chloride-Water. Various investigators have reported careful studies on limited regions of temperature, pressure, and concentration. At times, evaluations of such data for various selected properties covering segments of the available data have appeared. Yet, to our knowledge, no comprehensive treatment and critical evaluation of all the available thermodynamic data has been published.

It, therefore, appears timely that an exhaustive collection of data and its critical evaluation be made to represent accurately the behavior of the sodium chloride-water system within the wide ranges of temperature, pressure, and concentration in which data are available.

This evaluation will not only update previous treatments of data but also will bring together a comprehensive collection of data in one critical review.

B. Summary of secondary data sources

A list of general sources of data compilations:

1. Bulletins of Thermodynamics and Thermochemistry
2. Chapman and Newman, A Compilation of Selected Thermodynamic and Transport Properties of Binary Electrolytes in Aqueous Solution, (1968)
3. Circular 500 Series
4. Harned and Owen, The Physical Chemistry of Electrolyte Solutions, (1958)
5. International Critical Tables
6. JANAF Tables
7. Kaufmann, D. W., Sodium Chloride (1960)
8. Lewis and Randall, Thermodynamics, (1961)
9. Office of Saline Water Reports
10. Parker, Thermal Properties of Aqueous Uni-univalent Electrolytes
11. Robinson and Stokes, Electrolyte Solutions, (1965)
12. Wu and Hamer, (Osmotic and Activity Coefficients...at 25°C), (1968)

2. Thermodynamic properties

a. Standard state of hypothetical 1m aqueous solution

at T = 298.15 kelvins (25°C) (Ref. 1)

1. Heat of formation

$\Delta H_f^\circ = -97.302$

2. Free Energy of formation

$\Delta G_f^\circ = -93.939$

3. Equilibrium constant of formation

$\log_{10} K_f = 68.8560$

4. Entropy in solution

$S^\circ_{298.15} = 27.6 \text{ cal deg}^{-1}\text{mol}^{-1}$

$[Na^+ + Cl^- = 14.4 + 13.17 = 27.57]$

b. Heat Capacity

V. Parker (2) has evaluated heat capacity as a function of temperature and this is illustrated in Table 1.

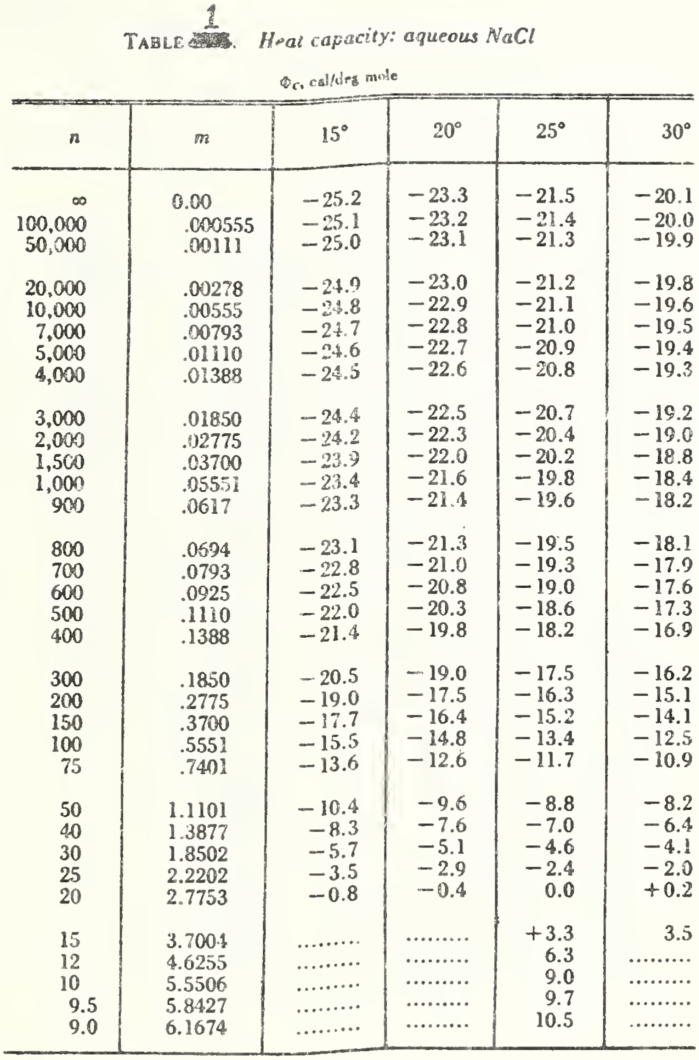

TABLE 1. *Heat capacity: aqueous NaCl*

Φ_C, cal/deg mole

n	*m*	15°	20°	25°	30°
∞	0.00	−25.2	−23.3	−21.5	−20.1
100,000	.000555	−25.1	−23.2	−21.4	−20.0
50,000	.00111	−25.0	−23.1	−21.3	−19.9
20,000	.00278	−24.9	−23.0	−21.2	−19.8
10,000	.00555	−24.8	−22.9	−21.1	−19.6
7,000	.00793	−24.7	−22.8	−21.0	−19.5
5,000	.01110	−24.6	−22.7	−20.9	−19.4
4,000	.01388	−24.5	−22.6	−20.8	−19.3
3,000	.01850	−24.4	−22.5	−20.7	−19.2
2,000	.02775	−24.2	−22.3	−20.4	−19.0
1,500	.03700	−23.9	−22.0	−20.2	−18.8
1,000	.05551	−23.4	−21.6	−19.8	−18.4
900	.0617	−23.3	−21.4	−19.6	−18.2
800	.0694	−23.1	−21.3	−19.5	−18.1
700	.0793	−22.8	−21.0	−19.3	−17.9
600	.0925	−22.5	−20.8	−19.0	−17.6
500	.1110	−22.0	−20.3	−18.6	−17.3
400	.1388	−21.4	−19.8	−18.2	−16.9
300	.1850	−20.5	−19.0	−17.5	−16.2
200	.2775	−19.0	−17.5	−16.3	−15.1
150	.3700	−17.7	−16.4	−15.2	−14.1
100	.5551	−15.5	−14.8	−13.4	−12.5
75	.7401	−13.6	−12.6	−11.7	−10.9
50	1.1101	−10.4	−9.6	−8.8	−8.2
40	1.3877	−8.3	−7.6	−7.0	−6.4
30	1.8502	−5.7	−5.1	−4.6	−4.1
25	2.2202	−3.5	−2.9	−2.4	−2.0
20	2.7753	−0.8	−0.4	0.0	+0.2
15	3.7004	....	....	+3.3	3.5
12	4.6255	....	....	6.3	....
10	5.5506	....	....	9.0	....
9.5	5.8427	....	....	9.7	....
9.0	6.1674	....	....	10.5	....

c. Relative Apparent Molal Enthalpy has been similarly evaluated (Ref. 2) and is presented in Table 2.

TABLE 2 *Thermal properties of aqueous NaCl at 25 °C*

n	m	$d\Phi_L/dm^{1/2}$	Φ_L	$\bar{L}_2$
			cal/mole	cal/mole
∞	0.00	472	0	0
100,000	.000555	436	11	16
50,000	.00111	423	14	21
20,000	.00278	395	22	32
10,000	.00555	365	31	45
7,000	.00793	344	37	52
5,000	.01110	322	42	59
4,000	.01388	304	46	64
3,000	.01850	282	51	70
2,000	.02775	245	59	79
1,000	.05551	167	73	93
900	.0617	155	75	94
800	.0694	139	78	96
700	.0793	120	80	97
600	.0925	99	83	98
500	.1110	71	85	97
400	.1388	+35	87	94
300	.1850	−14	88	85
200	.2775	−87	83	+60
100	.5551	−220	49	−33
75	.7401	−275	+20	−98
50	1.1101	−344	−41	−222
40	1.3877	−373	−85	−304
30	1.8502	−394	−156	−424
25	2.2202	−394	−207	−501
20	2.7753	−376	−274	−587
15	3.7004	−321	−367	−676
12	4.6255	−242	−430	−690
10	5.5506	−135	−469	−628
9.5	5.8427	−93	−476	−588

d. Heat of neutralization has been determined in various laboratories and Table 3 (Ref. 2) shows the results of each.

3

TABLE [redacted]. ΔH_N° at 25 °C

Investigator	System	n, moles H_2O/mole solute			Original temp of meas	No. of meas	$-\Delta H_N$,(T)	$-\Delta H_N$, (25 °C)	$-\Delta H_N^\circ$, (25 °C)
		Acid	Base	Salt					
					°C		*cal/mole*	*cal/mole*	*cal/mole*
Richards and Rowe [224]	NaCl	100	100	201	16.80	5	14,059 ± 15	13,687	13,364
					15.67	4	14,114 ± 8	13,689	13,366
Gillespie, Lambert and Gibson [356]	NaCl	540	540	1081	20	1	13,773	13,516	13,349
		283	283	567	20	1	13,793	13,545	13,333
		550	550	1101	24.99	1	13,571	13,571	13,407
		284	284	569	32.27	1	13,199	13,525	13,315
		282.5	282.5	566	32.27	1	13,261	13,588	13,376
		260	260	521	32.30	1	13,271	13,596	13,377
Bender and Biermann [213]	NaCl	18.42	18.42	37.84	25	2	14,249 ± 12	14,249	13,332
		17.14	17.14	35.30	25	4	14,314 ± 10	14,314	13,331
Pitzer [206]	NaCl	46.5	1065.5	1112	25	3	13,828 ± 12	13,828	13,366

e. <u>Heat of solution</u> (at infinite dilution) values determined by 26 investigators are compiled in Table 4.

TABLE 4 ΔH°_∞ of NaCl in H_2O at 25 °C (Ref. 2)

Investigator	Year reported	Temp of meas	No. of meas	Conc. range moles NaCl/1000g H_2O	ΔH°_∞
		°C			*cal/mole*
1. Winkelmann [94]	1873	16–30	20	5.50 to 0.53	914 ±30
2. Ostwald [443]	1882	16–17	4	0.19	970
3. Thomsen [30]	1883	16.8	2	.56	897 ±20
4. Pickering [384]	1887	15–25	35	.28	935 ±20
5. Colson [535]	1915	21	1	.42	894
6. Randall and Bisson [143]	1920	25	7	.54 to 0.13	929 ±5
7. Wüst and Lange [21]	1925	25	14	5.62 to 0.52	[a] 931 ±10
8. Lange and Dürr [389]	1926	25	10	0.56	841
9. Lipsett, Johnson, and Maass [323]	1927	25	20	5.50 to 0.07	923 ±5
[536]	1927	20	15	5.92 to 0.04	922 ±8
10. Cohen and Kooy [391]	1928	25	4	0.56	915 ±5
		20	5	.56	921 ±8
11. Askew, Bullock, Smith, Tinkler, Gatty, and Wolfenden [499]	1934	20	9	.03	904 ±30
12. Becker and Roth [228]	1935	19.7	5	.09 to 0.04	918 ±10
13. Lange and Martin [397]	1937	25	1	.25	934
14. Slansky [399]	1940	25	?	?	[a] 915 ±10
15. Tichelaar [401]	1946	25	5	0.02?	950 ±30
16. Voskresenskaya and Ponomareva [400]	1946	25	?	.37	970
17. Fineman and Wallace [404]	1948	25	?	?	[a] 925 ±5
18. Samoĭlov [407, 408]	1951	25	1	0.19	932
19. Kapustinskii and Drakin [411]	1952	25	1	.0008	932 ±30
20. Seki and Suzuki [537]	1953	18	?	.14	913 ±20
21. Benson and Benson [324]	1955	25	16	1.3 to 0.05	928 ±3
22. Benson, Goddard, and Hoeve [538]	1956	25	3	0.50	927 ±3
23. Attree, Cushing, Ladd, and Pieroni [539]	1958	25	?	.01	927 ±10
24. Lister and Myers [540]	1958	25	?	.18	914 ±10
25. Samoĭlov and Buslaeva [444]	1960	15, 35	2	.14	874 ±100
26. Criss and Cobble [541]	1961	25	17	.02 to 0.001	914 ±10

[a] Authors' extrapolation.

f. Solubility

1. At 1 atmosphere and temperatures from -10 to 107.0°C (boiling point) are presented in Table 5 (International Critical Tables Ref. 3).

5

TABLE [redacted]. DENSITY OF SATURATED SOLUTIONS

Temp. (°C)	Per Cent NaCl by Weight in Soln SOLUBILITY	d_4^t
−10		1.2000
0	26.34	1.2093
+10	26.35	1.2044
20	26.43	1.1999
25	26.48	1.1978
30	26.56	1.1957
40	26.71	1.1914
50	26.89	1.1872
60	27.09	1.1830
70	27.30	1.1787
80	27.53	1.1745
90	27.80	1.1703
100	28.12	1.1660
107.0*	28.39	1.1631

* Boiling point.

2. At high temperatures

Tables 6a and 6b show results for solubility at high temperatures. (Berkley (4), Tilden and Shenstone (5), Froehlich, et al (6), Schoeder, et al (7), Brenrath, et al (8), and Lill and Lindsay (9)

Table 6a. Solubility, Activity Coefficients, and Salt Activity for Saturated NaCl Solutions (Ref. 9)

Temperature (°C)	Solubility, m_s (moles NaCl/kg H_2O)	Activity coefficient γ_s	ln γ_s	ln ($\gamma_s m_s$) (footnote a)
75	6.460	0.996	−0.0038	1.8613
100	6.680	0.935	−0.0676	1.8316
125	6.935	0.835	−0.1808	1.7558
150	7.198	0.721	−0.3270	1.6468
175	7.573	0.610	−0.4942	1.5305
200	7.973	0.501	−0.6914	1.3847
225	8.435	0.398	−0.9222	1.2101
250	8.989	0.303	−1.1951	1.0009
275	9.649	0.218	−1.5247	0.7421
300	10.413	0.144	−1.9375	0.4056

[a] Salt activity = $\gamma_s m_s$.

TABLE 6b. SOLUBILITY IN AQUEOUS SOLUTION AT HIGH TEMPERATURES (Ref. 18)

Temp. (°C)	Per Cent by Weight in Solution
100	28.12
107*	28.39
150	29.7
200	31.6
250	34.1
300	37.3
350	41.8
400	46.4
450	50.8

* Boiling point at atmospheric pressure.

3. Effect of pressure on solubility was investigated by Adams and Hall (10), who used resistance measurements, and is shown in Table 7.

Table 7. Effect of Pressure on Solubility at 25°C

Pressure (atm)	Grams NaCl per 100 g Soln	Grams NaCl per 100 g H_2O	Mole Per Cent of NaCl
0	26.42	35.91	9.97
250	26.59	36.22	10.05
500	26.74	36.50	10.12
750	26.88	36.76	10.18
1000	27.01	36.99	10.24
1250	27.11	37.18	10.29
1500	27.20	37.37	10.33

g. <u>Activity coefficients</u> have been evaluated by Wu and Hamer at 25°C (11) from an equation of the form:

$$\log \gamma_{\pm} = \frac{- Z_{+}Z_{-} A_{m} I^{\frac{1}{2}}}{1 + B^{*}_{m} I^{\frac{1}{2}}} + \beta I + CI^{2} + DI^{3}$$

The results are shown in Table 8.

Table 8. Osmotic and mean activity coefficients of NaCl

m	ϕ	γ	m	ϕ	γ
0.001	0.988	0.965	1.0	0.936	0.657
.002	.994	.952	1.2	.944	.655
.005	.976	.928	1.4	.953	.656
.01	.968	.903	1.6	.962	.658
.02	.959	.872	1.8	.973	.662
.05	.944	.822	2.0	.984	.668
.1	.933	.779	2.5	1.013	.688
.2	.924	.734	3.0	1.045	.714
.3	.921	.709	3.5	1.080	.746
.4	.920	.693	4.0	1.116	.783
.5	.921	.681	4.5	1.153	.826
.6	.923	.673	5.0	1.192	.874
.7	.926	.667	5.5	1.231	.928
.8	.929	.662	6.0	1.270	.986
.9	.932	.659			

$B^{*} = 1.4495$

$\beta = 2.0442 \times 10^{-2}$

$C = 5.7927 \times 10^{-3}$

$D = -2.8860 \times 10^{-4}$

$\sigma(\phi) = 0.00064$

$\sigma(\gamma) = 0.00049$

$VAR(\phi) = 4.12 \times 10^{-7}$

$VAR(\gamma) = 2.43 \times 10^{-7}$

$\sigma^{*}(\phi) = 0.00066$

$\sigma^{*}(\gamma) = 0.00068$

From Robinson and Stokes (12) and Harned and Owen (13), mean activity coefficients can be calculated over the temperature range 0-100°C using an equation of the form:

$$\log \gamma_{\pm} = A - \frac{B}{T} - C \log T$$

Table 9 illustrates these results.

TABLE 9. MEAN ACTIVITY COEFFICIENTS

Temp. (°C)	Molality 0.1	0.2	0.5	1.0	2.0	3.0	4.0
0	0.781	0.731	0.671	0.637	0.630	0.660	0.717
20	.779	.733	.679	.654	.665	.712	.783
40	.774	.728	.678	.657	.678	.728	.802
60	.766	.721	.671	.654	.676	.726	.799
80	.757	.711	.660	.641	.663	.712	.777
100	.746	.698	.644	.622	.641	.687	.746

Liu and Lindsay (9) have recently reported activity coefficients at high temperatures as illustrated in Table 10.

Table 10. Smoothed Activity Coefficients for NaCl

	Temperature, °C									
Molality	75	100	125	150	175	200	225	250	275	300
0.05	0.804	0.794	0.780	0.764	0.746	0.725	0.702	0.673	0.638	0.592
0.10	0.757	0.746	0.729	0.709	0.687	0.662	0.633	0.599	0.559	0.506
0.20	0.711	0.698	0.677	0.653	0.626	0.597	0.563	0.525	0.479	0.422
0.40	0.669	0.655	0.631	0.602	0.571	0.536	0.498	0.454	0.404	0.345
0.60	0.651	0.637	0.610	0.578	0.543	0.505	0.464	0.418	0.366	0.3[illegible]8
0.80	0.643	0.628	0.599	0.564	0.527	0.486	0.442	0.394	0.340	0.2[illegible]7
1.00	0.640	0.624	0.594	0.557	0.517	0.474	0.428	0.378	0.323	0.261
1.50	0.645	0.627	0.592	0.550	0.505	0.457	0.406	0.352	0.294	0.231
2.00	0.661	0.641	0.601	0.553	0.503	0.450	0.394	0.337	0.276	0.212
2.50	0.682	0.659	0.615	0.562	0.506	0.448	0.388	0.327	0.264	0.20[illegible]
3.00	0.709	0.682	0.632	0.573	0.512	0.449	0.385	0.321	0.256	0.19[illegible]
3.50	0.740	0.708	0.652	0.587	0.520	0.452	0.384	0.316	0.249	0.182
4.00	0.774	0.737	0.674	0.602	0.529	0.456	0.384	0.313	0.244	0.176
4.50	0.812	0.769	0.698	0.619	0.539	0.461	0.385	0.311	0.239	0.171
5.00	0.853	0.803	0.724	0.636	0.550	0.466	0.386	0.309	0.236	0.167
5.50	0.898	0.839	0.750	0.655	0.562	0.472	0.387	0.308	0.233	0.163
6.00	0.947	0.878	0.779	0.674	0.573	0.478	0.389	0.307	0.230	0.16[illegible]
6.50	–	0.919	0.808	0.693	0.585	0.484	0.391	0.306	0.228	0.157
7.00	–	–	–	0.713	0.597	0.490	0.393	0.305	0.226	0.155
8.00	–	–	–	–	–	–	0.396	0.304	0.223	0.151
9.00	–	–	–	–	–	–	–	–	0.220	0.148
10.00	–	–	–	–	–	–	–	–	–	0.145

h. Osmotic coefficients

Values of the osmotic coefficients taken from references 11, 12, 13, 9, above have been listed in Table 8 (25°C) and Table 11 (75-300°C).

Table 11. Smoothed Osmotic Coefficients for NaCl (Ref. 9)

	Temperature, °C									
Molality	75	100	125	150	175	200	225	250	275	300
0.05	0.938	0.934	0.929	0.923	0.915	0.907	0.897	0.884	0.868	0.846
0.10	0.926	0.922	0.915	0.907	0.897	0.886	0.873	0.857	0.837	0.809
0.20	0.917	0.913	0.904	0.894	0.882	0.868	0.852	0.832	0.806	0.772
0.40	0.916	0.912	0.902	0.889	0.874	0.857	0.837	0.812	0.781	0.740
0.60	0.922	0.917	0.907	0.892	0.876	0.856	0.833	0.806	0.771	0.725
0.80	0.930	0.926	0.914	0.899	0.880	0.859	0.834	0.804	0.766	0.717
1.00	0.940	0.936	0.923	0.907	0.887	0.864	0.837	0.805	0.765	0.713
1.50	0.967	0.962	0.948	0.929	0.906	0.879	0.848	0.812	0.767	0.709
2.00	0.996	0.990	0.974	0.952	0.926	0.896	0.862	0.821	0.772	0.709
2.50	1.026	1.018	1.000	0.975	0.947	0.914	0.876	0.831	0.778	0.711
3.00	1.057	1.046	1.025	0.998	0.967	0.930	0.889	0.841	0.784	0.714
3.50	1.088	1.075	1.051	1.020	0.986	0.946	0.902	0.851	0.791	0.718
4.00	1.120	1.103	1.076	1.042	1.004	0.962	0.914	0.860	0.797	0.721
4.50	1.152	1.131	1.100	1.063	1.022	0.976	0.925	0.868	0.803	0.725
5.00	1.184	1.159	1.124	1.083	1.038	0.990	0.936	0.876	0.809	0.728
5.50	1.216	1.187	1.147	1.103	1.054	1.002	0.946	0.884	0.814	0.732
6.00	1.249	1.215	1.170	1.121	1.069	1.014	0.955	0.890	0.819	0.736
6.50	–	1.242	1.193	1.139	1.083	1.025	0.963	0.896	0.823	0.739
7.00	–	–	–	1.157	1.097	1.035	0.970	0.901	0.827	0.743
8.00	–	–	–	–	–	–	0.982	0.910	0.834	0.750
9.00	–	–	–	–	–	–	–	–	0.839	0.757
10.00	–	–	–	–	–	–	–	–	–	0.76[illegible]

i. Vapor pressures taken from the International Critical Tables (3) are shown in Table 12.

12

Table [illegible]. Vapor Pressures of Aqueous Solutions in mm Hg

Temp. (C)	Per Cent NaCl in Solution											
	0.0	2.5	5	7.5	10	12.5	15.0	17.5	20.0	22.5	25.0	27.5
0	4.579	4.5	4.4	4.4	4.3	4.2	4.1	4.0	3.8	3.7	3.5	
10	9.21	9.1	8.9	8.8	8.6	8.4	8.2	8.0	7.7	7.4	7.1	
20	17.54	17 3	17.0	16.7	16.4	16.1	15.7	15.3	14.8	14.2	13.6	
30	31.83	31.4	30.9	30.4	29.8	29.2	28.5	27.7	26.8	25.8	24.7	
40	55.34	54.5	53.6	52.7	51.7	50.7	49.5	48.1	46.6	44.9	43.0	
50	92.54	91.2	89.7	88.1	86.4	84.7	82.8	80.5	78.1	75.3	72.2	
60	149.46	147.2	144.8	142.3	139.7	136.8	133.7	130.0	126.0	121.7	116.8	
70	233.79	230.2	226.4	222.4	218.3	213.9	208.9	203.5	197.5	190.7	183.1	
80	355.47	350	344	338	332	325	318	309.5	300.5	290.2	278.9	266
90	526.00	517	509	500	491	481	470	458	445.1	430	414	395
100	760.00	748	736	723	710	695	680	665	643	622	599	572
110	1074.5	1057	1040	1022	1003	983	961	936	911	881	849	810
B P.,°C	100.0	100.44	100.90	101.40	101.93	102.51	103.16	103.89	104.72	105.68	106.78	108.12

j. Apparent molal volumes are given in Table 13 as determined by Wade (14).

Table 13. Apparent Molal Volume in Aqueous Solution

Molality	Apparent Molal Volume ϕ in cm^3
0	16.40*
0.1	16.68
0.2	16.88
0.3	17.05
0.4	17.20
0.5	17.35
0.75	17.67
1.0	17.97

* This extrapolated value also gives the partial molal volume in infinitely dilute solution.

k. Partial molal volumes recently reported by Millero (15) are shown in Table 14.

Table 14

Salt	$\bar{V}^\circ$ (cm^3/mole)	b_V [cm^3 liter mole^{-2}]	S_V* [cm^3 liter$^{1/2}$ mole$^{-3/2}$]	References
NaCl	*16.61*	0.018		20,55,104
	16.62	0.048		22
	16.62	−0.03		16
	16.63	(0.003)		50
	16.61			56
	16.65			34
	16.64			57
	16.60			58
	16.6			5
	16.67			45
	16.62		1.884, 1.853	26,113
	16.61			51
	16.8			9
	15.9			9
	17.03			59
	16.54			43
	16.8			52
	16.28		2.22	53
	16.28			2
	16.40		2.153	3
	16.35			60
	16.44			61
	16.3			6
	16.56		1.945	62
	16.78			111
	16.45	1.693^a	0.405^a	100

l. Compressibility has been investigated by Gibson (16) and is illustrated by Table 15.

TABLE 15. COMPRESSIBILITY OF SOLUTIONS

Weight Per Cent in Soln	$\beta \times 10^6$ From Compressions at 1000 Bars	$\beta \times 10^6$ From Sound Velocities at 1 Bar
6	40.6	40.4
10	37.6	37.5
16	33.2	33.4
20	30.7	31.0
24	28.4	28.8

m. <u>Eutectic of solution</u>. The eutectic composition is 30.4 g NaCl(anhyd.) per 100 g H_2O, with the temperature being -21.12°C, Rodebush (17).

n. <u>Freezing point lowering</u> from International Critical Tables (3) are presented in Table 16.

TABLE 16. FREEZING POINT LOWERING OF SODIUM CHLORIDE SOLUTIONS

Molality	Grams Anhydrous Salt per 1000 g Water	Molal F.P. Lowering	F.P. Lowering (°C)
0.001	0.0585	3.66	0.004
.002	.1169	3.65_5	.007
.004	.2338	3.642	.015
.007	.4091	3.620	.025
.01	.5845	3.604	.036
.02	1.1690	3.570	.071
.04	2.3379	3.530	.141
.07	4.0914	3.498	.245
.10	5.8448	3.478	.348
.20	11.6896	3.424	.685
.40	23.3792	3.38	1.35
.70	40.9136	3.36	2.35
1.0	58.448	3.37	3.37
2.0	116.896	3.45	6.90
3.0	175.344	3.60_5	10.82
4.0	233.792	3.78_5	15.14
5.20*	303.9296	4.061	21.12

* Eutectic.

o. A phase diagram taken from Kaufmann (18) is shown as Figure 1.

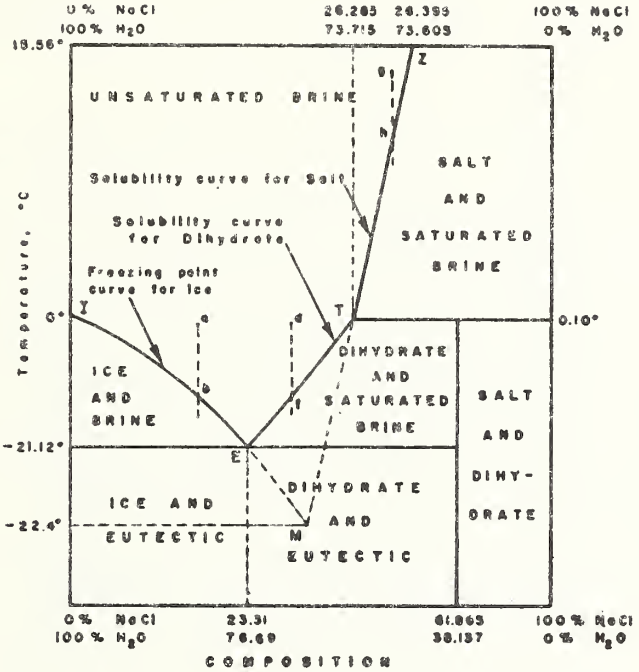

Figure 1. The system sodium chloride-water (Not to scale)

p. Density of solutions from 0 to 100°C are available from the International Critical Tables (3) and are illustrated in Table 17.

Table 17. Density of Sodium Chloride Solutions

Per Cent by Weight in Soln	Temp.									
	0°C	10°C	20°C	25°C	30°C	40°C	50°C	60°C	80°C	100°C
1	1.00747	1.00707	1.00534	1.00409	1.00261	0.99908	0.99482	0.9900	0.9785	0.9651
2	1.01509	1.01442	1.01246	1.01112	1.00957	1.00593	1.00161	0.9967	0.9852	0.9719
4	1.03038	1.02920	1.02680	1.02530	1.02361	1.01977	1.01531	1.0103	0.9988	0.9855
6	1.04575	1.04408	1.04127	1.03963	1.03731	1.03378	1.02919	1.0241	1.0125	0.9994
8	1.06121	1.05907	1.05589	1.05412	1.05219	1.04798	1.04326	1.0381	1.0264	1.0134
10	1.07677	1.07419	1.07068	1.06879	1.06676	1.06238	1.05753	1.0523	1.0405	1.0276
12	1.09244	1.08946	1.08566	1.08365	1.08153	1.07699	1.07202	1.0667	1.0549	1.0420
14	1.10824	1.10491	1.10085	1.09872	1.09651	1.09182	1.08674	1.0813	1.0694	1.0565
16	1.12419	1.12056	1.11621	1.11401	1.11171	1.10688	1.10170	1.0962	1.0842	1.0713
18	1.14031	1.13643	1.13190	1.12954	1.12715	1.12218	1.11691	1.1113	1.0993	1.0864
20	1.15663	1.15254	1.14779	1.14533	1.14285	1.13774	1.13238	1.1268	1.1146	1.1017
22	1.17318	1.16891	1.16395	1.16140	1.15883	1.15358	1.14812	1.1425	1.1303	1.1172
24	1.18999	1.18557	1.18040	1.17776	1.17511	1.16971	1.16414	1.1584	1.1463	1.1331
26	1.20709	1.20254	1.19717	1.19443	1.19170	1.18614	1.18045	1.1747	1.1626	1.1492

3. Transport and Other Properties

A listing of transport and other properties which should be included in such a monograph on aqueous sodium chloride is shown for completeness. Whether these properties can be included, will depend on the manpower available for such a task.

Boiling points of saturated solutions 760 mm.
Conductivity
Decomposition potential
Density
Density of saturated solutions
Dielectric constant at low temperatures
Diffusion coefficient
Ionic conductance
Refractive Index
Surface Tension
Thermal conductivity
Transference number
Velocity of sound
Viscosity

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Appendix 4.

Scope of Current Literature on Electrolyte Data

Several surveys of the literature on electrolyte data were made in order to adequately assess the extent and types of data on electrolyte solutions available in primary and secondary reference sources.

A number of different approaches were used to obtain a good estimate of the types and amount of data appearing in the current literature. The Bulletin of Thermodynamics and Thermochemistry (1971) was one source of information using articles on inorganic compounds only. Another source was the Chemical Abstracts, Physical Sections only (1971). Issues covering a two month period were scanned as part of an abstracting process. A third source was Chemical Titles (1972). Here, only entries with "Solution" contained in the title, were scanned. From these three different types of literature scanning the total number of articles currently appearing per year were estimated to be nearly 500 articles that dealt with electrolyte solutions of all types.

Three broad categories could be discerned from the collection of current literature: (1) Single electrolytes in water, (2) Ternary and mixed electrolytes in water, and (3) Non-aqueous systems, including single and mixed electrolytes. Properties of the single electrolytes in water were further subdivided into the thermodynamic properties and the transport properties. This was not done for the other categories. Table I depicts the approximate annual rate of appearance of current literature for electrolyte solutions.

Table I. Rate of Appearance of Current Literature for Electrolyte Solutions

Single electrolytes in pure water including				
transport properties	200	articles	per	year
without transport properties	125	"	"	"
Mixed electrolytes	200	"	"	"
Non-aqueous solutions	80	"	"	"


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