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### Title

ESTABLISHMENT OF A COMPUTER DATA BASE ON GEOTHERMAL PROPERTIES OF AQUEOUS NaCl, KCl AND CaCl<sub>2</sub> SOLUTIONS

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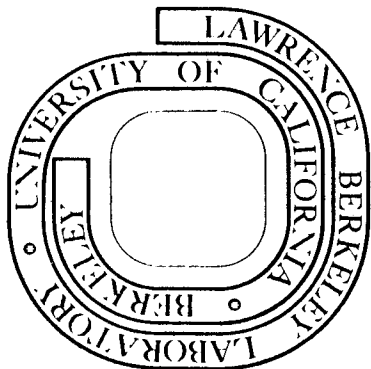
James A. Fair and Sidney L. Phillips

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Establishment of a Computer Data Base on  
Geothermal Properties of Aqueous  
NaCl, KCl and CaCl<sub>2</sub> Solutions

by

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The increased recognition over the past fifteen years that the petroleum resources of the United States were finite and being exhausted at an ever increasing rate, resulted in the current unprecedented research and development program to utilize other domestic energy resources. The question has been raised, whether domestic energy resources such as geothermal can contribute to those U.S. energy needs which are so essential to our health and economic well-being, without at the same time degrading our environment to unacceptable levels. The need for collecting and disseminating evaluated data on a timely basis is obvious.

It is the case in geothermal energy--and understandably so because this area is experiencing so rapid a growth--that there are many gaps in what is commonly termed "public knowledge" about basic and applied research data. New techniques have been developed for research that should be widely applied to exploration and utilization; basic research data by engineers are needed for predictive modeling, thereby saving much time and expense; some geothermal resources may not be made productive by current technology, thus indicating the need for additional research; other resources may be quickly utilized without the need for further development work. To fill these information gaps by providing evaluated data is both necessary and urgent. If the gaps are not filled, there is the penalty of unnecessary duplication and expense in research and the additional expense, not often measurable in monetary terms, that needed domestic geothermal energy resources cannot be exploited.

The Lawrence Berkeley Laboratory is sponsored by the U.S. Energy Research and Development Administration to establish a National Geothermal Information Resource (GRID) (Ref. 1). The objective of GRID is mainly

to compile and disseminate evaluated data on geothermal science and technology. For this purpose, we have found it convenient to classify geothermal information into the following six major categories: (1) exploration, (2) utilization, (3) institutional considerations, (4) environmental aspects, (5) reservoir characteristics, and (6) physical chemistry. The major emphasis of this paper is on the physical chemistry category which contains the GRID file on geothermal basic scientific data. For completeness, the data content of the other five categories is also briefly discussed in the following sections.

### Exploration

Geothermal resource exploration and evaluation activities center around the methodology used to locate and evaluate geothermal hydrothermal, geopressured, hot dry rock and magma resources covering the following principal categories: (1) geology, (2) geochemistry, (3) geophysics, (4) drilling, (5) hydrology, (6) land-use factors, and (7) resource assessment.

These techniques are used to: (1) locate subsurface regions which contain a high temperature anomaly, and (2) estimate the extent of the reservoir, its useful lifetime, and potential for use for either power production or non-electrical applications.

### Environmental

The GRID compilation of the environmental aspects of geothermal energy currently covers any effects to the air, water, and land compartments of the environment due to the exploration and utilization of geothermal energy (e.g., subsidence, H<sub>2</sub>S). Generally, this centers on the following information: (1) statement of the problems, (2) the effects of the environmental

quality parameters to the air, water, or land, (3) methods used for control and abatement, (4) mechanisms and pathways of the pollutant, (5) instrumentation for monitoring and measuring the environmental effect, and (6) recommendations in areas where additional data are needed.

#### Utilization

This category contains information on the current and expected electrical and non-electrical uses of geothermal energy including the following: hot-water (brine) transport; space, process, agricultural heating; power generation; binary cycle power generation; corrosion; erosion and scaling; resource reservoir evaluation; brine treatment.

#### Institutional

Included here are the federal, state, local, organizational, legal and regulatory considerations in the development of geothermal energy: land-use; exploration and production; operating regulations; industry financial incentives; sale of geothermal power; fluid transport.

#### Reservoir Characterization

Reviews and evaluation of data relevant to the development and production of wells covering: porosity, artificial stimulation, natural recharge, modeling, well tests and logging measurements.

#### Physical Chemistry

Geothermal physical chemistry, as used here, is defined as laboratory measurements and theoretical calculations of basic scientific data on gases, solutions, and rocks at elevated temperatures and pressures (500°C, 500 bars). Table 1 lists typical areas where needs for basic scientific data have been

Table 1. Geothermal Physical Chemistry

Basic numerical data covering temperatures to 500°C and pressures to 500 bars:

- A. Aqueous Solutions
- B. Rocks and Minerals
- C. Rock-Solution Interactions
- D. Secondary Fluids
- E. Corrosion and Scaling
- F. Other



identified (Ref. 2,3). Such data are needed, for example, in the intelligent design of geothermal power plants, and to predict and understand the behavior which may be used for either electrical or other applications, (e.g., process heat). While the larger GRID compilation includes gases and rocks, this report is limited to aqueous solutions.

In high temperature aqueous chemistry and in the geological sciences there is a wealth of poorly organized and evaluated experimental data. While a number of excellent compilations of data currently are available, they have one or both of the following shortcomings: (1) no single compilation contains all of the data needed for efficient utilization of the U.S. geothermal potential, and (2) they contain data of only limited geothermal interest, e.g., 25°C and 1 atm pressure. A major goal of this project is to provide from a single source evaluated data on aqueous solutions that are of geothermal interest with respect to physical property, concentration, temperature, and pressure. This goal includes formulating the data into forms most useful to geothermal scientists and engineers, e.g., tables, graphs and analytical expressions.

The following is an example of a calculation that illustrates the importance of using the correct physical properties of aqueous solutions (e.g., NaCl, KCl) solutions. (See Ref. 4 for details.)

Consider the design of a pumping station designed to pump a geothermal brine through a vertical pipe 15 cm in diameter at a flow rate of 3 m/sec. The brine consists of 3.5 molal NaCl aqueous solution at 150°C along the vapor saturation curve. A knowledge of the viscosity and density of the brine is needed to calculate the electric power required to drive the pump. As in any calculation, one starts with a certain set of basic assumptions concerning the operating parameters of the system under

consideration. Because of the current lack of readily available data on the basic properties of sodium chloride solutions, the approximation generally made is to assume that the brine fluid is pure water instead of 3.5 molal NaCl. This approximation leads to an error of about 20% in the power required to drive the pump, because at a given flow rate, more power is required to pump sodium chloride solutions than to pump pure water. The effect becomes larger as both the temperature and concentration of NaCl are increased. A 3.5 molal solution was chosen because viscosity data above 150°C and 3.5 molal do not currently exist. However, concentrations in naturally occurring geothermal brines may exceed 6 molal (e.g., Salton Sea) and temperatures may exceed 300°C. The situation is further complicated because geothermal brines generally contain significant amounts of calcium chloride and potassium chloride, as well as minor amounts of many other constituents (e.g., silica).

As shown in the example, a real saving in both time and effort is achieved by using basic data to predict the behavior of geothermal systems. With this objective in mind, a compilation of the important properties for aqueous sodium, potassium, and calcium chloride solutions was initiated, and the current status is described in the following sections.

#### Bibliographic Compilation

Our selection of properties important to geothermal science and technology is based on those listed in the report on the results of the meeting on Geothermal Chemistry (Ref. 2), and include, for example the following: enthalpy, heat capacity, activity coefficient, osmotic coefficient,  $\rho V T X$ , viscosity, thermal conductivity, and electrical conductivity. We have compiled a bibliography of literature references to this data which currently contains

about 1100 citations. This bibliography is annotated and is stored on magnetic tape for quick retrieval.

The bibliography covers the properties of aqueous solutions of sodium chloride, potassium chloride, and calcium chloride from 1965 to January 1976. The initial work is mostly limited to the last ten years; however, retrospective literature searches are planned. To the extent possible, we obtain copies of each document referenced in the bibliography for the follow-on data extraction and data evaluation. Each document is categorized according to geothermal property, composition, temperature, and pressure.

We have found it most efficient for organizing our bibliography file to input the citations into a hierarchically structured computerized data base, as described in the following section.

#### Documentation File (GEODOC)

The GRID documentation file, GEODOC, is a computer-based file which contains descriptive cataloging and indexing rules for all GRID documents (Ref. 5). This file (along with other GRID files) is managed by the Berkeley Data Base Management System (BDMS) (Ref. 6).

Each record in the GEODOC file contains descriptive cataloging, abstracting, and indexing information corresponding to a single document. The information within a given record is subdivided into computer retrievable "data elements". Table 2 lists the definition of all the data elements which may appear in a GEODOC record. Some data elements, e.g., Author's Name, can occur repeatedly within a record and an "m" in the third column of Table 2 indicates that such multiple occurrences are allowed. The "LBL Tag" for each data element is shown in the left hand column of Table 2. These tags are used to label the data elements within a record.

Table 2. OEODOC Data Elements

LBL Tag	INIS Tag	m*	n*	Data Element Definition
SC	008			document short code: unique identifier for document
TY				type of document/bibliographic levels/literary indicator
DES-CAT		m	n	delineates information for one bibliographic level
BL	009			bibliographic level indicator
PT	200			primary title (translated into English if necessary)
PS	201			primary subtitle (translated into English if necessary)
TA	620			title augmentation
L	600			language (for non-English document)
OT	230			original title (non-English) or journal/series title
OS	231			original subtitle (non-English) or journal/series subtitle
ED	250			edition
CODEN				journal CODEN
AUTHORS		m	n	delineates author-affiliation group
AU	100	m		author's name
AN	100			author note (ed., comp., eds., comps.)
AA	100	m		author's affiliation
AC	700			affiliation code
CE	110	m		corporate entry
CC	710			corporate code
DG	111			academic degree
SPO		m		sponsor
SPC				sponsor code
SCN		m		sponsor contract number
RN	300			report or patent number
SN	310	m		secondary numbers
INT	320			International Standard Book Number or Patent Code
PUB	402			publisher
PUP	401			place of publication
PUD	403			publication date
COL	500			collation (volume, issue, page)
N	610			note
COT	210			conference title
COP	211			conference place
COD	213			conference date
AV				availability and price

Continued on next page.

Table 2. GEODOC Data Elements (Continued)

LBL Tag	INIS Tag	m*	n	Data Element Definition
REL-REF		m	n	delineates information for one related reference.
RL				relator
RLR				relationship and reference
RSC				related short code
ABSTRACT		m	n	delineates one abstract
ABS				abstract
ABS0		m		abstract source
INDEX		m	n	INDEX.1 general indexing. INDEX.2, 3,...N splits
CQ		m		category/qualifier
TICC		m		TIC category
DE	800	m		descriptor from thesaurus
DD	800	m		data descriptor from thesaurus
ID	m			identifier
PD	810	m		proposed descriptor
CONTROL			n	internal LBL data elements
LA		m		local availability
BR				borrow/return
DCSO		m		descriptive catalogers initials, date and comment
AISO		m		abstractor-indexers initials, date and comment
DATA-FILE		m		data file name
POT		m		data descriptor for potential data
IN		m		data descriptor for included data

\*m-This data element may have multiple entries

\*n-This data element contains no value and need not be entered on input. It serves to delineate a group of data elements.

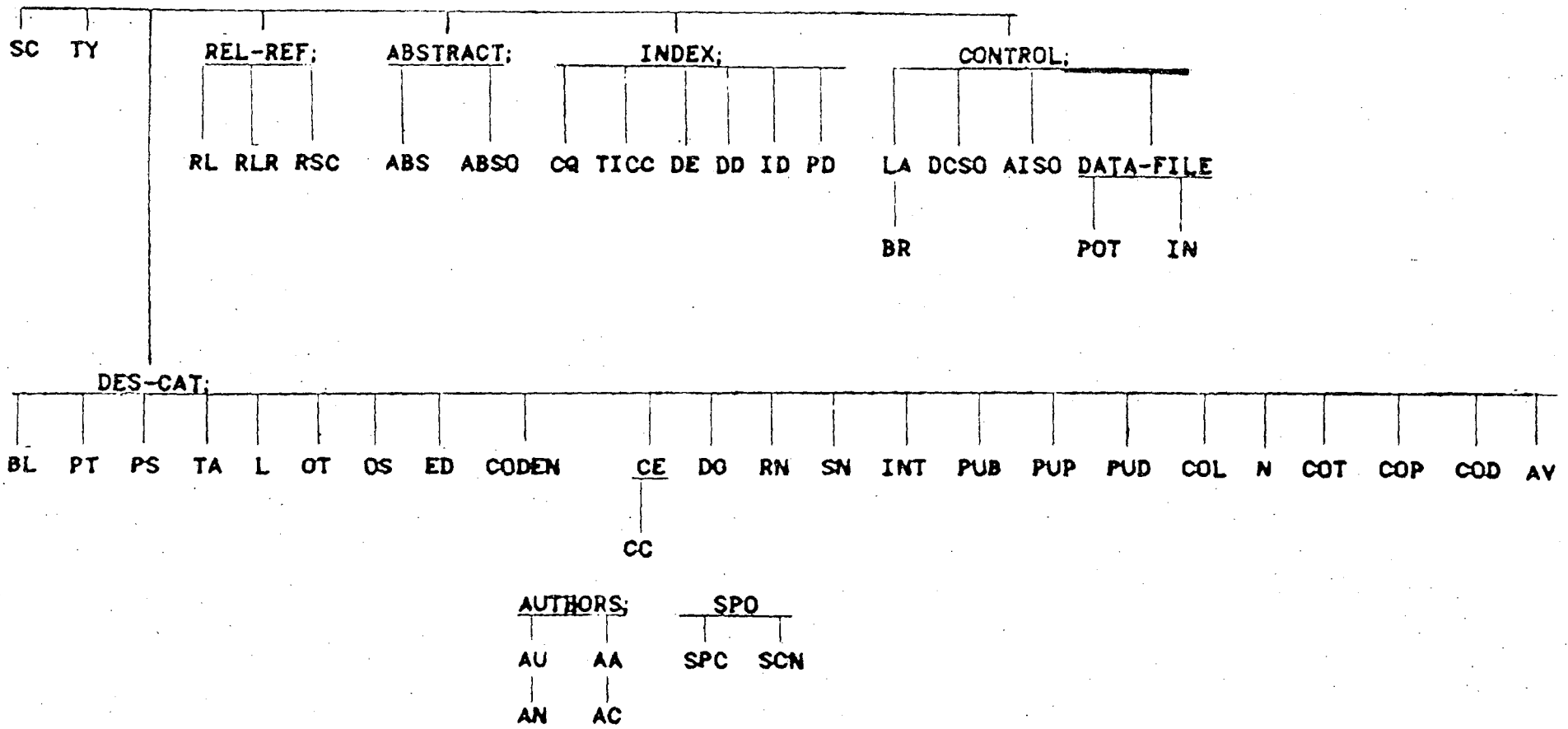
The data elements bear certain hierarchical relations to each other; that is, some data elements are subordinate to, or conversely, are parents of others. Figure 1 is a diagram of the hierarchical structure. This structure is also indicated in Table 2 by indenting the tag names of subordinate data elements and placing them after their parents. The data elements may be input to the system in any order except that subordinate data elements must follow the occurrence of the parent with which they are associated.

The GEODOC cataloging rules are standardized and are modeled after those of the International Nuclear Information System (INIS) of the International Atomic Energy Agency (Ref. 7). The data elements have been chosen to correspond as closely as possible to those used by INIS to facilitate information exchange with other data bases using INIS rules. See Table 2 where an INIS tag is shown for those data elements whose internal format is identical to the GEODOC format.

The GRID records are permanently stored on magnetic tape; temporary storage on disc files is also utilized for faster access than tape. Multiple copies of the data are stored on back-up tapes to provide for possible computer system crashes or failure of the storage medium, e.g., breakage of magnetic tape.

We have found that a computerized data base has numerous advantages in the manipulation of large amounts of data. For example, selective retrieval and editing of bibliographic citations is made trivial through the use of BDMS. Several of the data elements are keys (indexes) which can be searched for a specific topic, e.g., Author's Name, thus facilitating the generation of various quick indexes to the citations.

Fig. 1 GEODOC Record Structure



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-II-

Essentially all the records have a category called "Descriptors" which contains key words to describe the data content of the article. This enables one to retrieve all the citations that deal with a particular property; for example, one may retrieve all the records that deal with density. At the present time, searches are allowed on only one descriptor at a time; later we expect to have the capability of performing a Boolean search. This will permit a file search with a string of operations, e.g., to find all the stored citations that deal with density and sodium chloride solutions at 25°C and pressures greater than 100 bars. All "Descriptors" used are listed in a thesaurus of controlled terms (Ref. 8). Other data elements, e.g., OT and AA, also are derived from controlled authority files (Ref. 5).

A printed list of references is available quickly after entering the information on the keyboard. Figure 2 is an example of a typical citation in the standard BDMS output format which indicates the data structure. Figure 3 is an optional output format which presents the bibliographic citation in a more customary form, as a convenience to users.

Besides brine data, the GRID data base system currently consists of two other separate files: environmental and exploration. Each of these files may be loaded by a monitor and searched one at a time. As work progresses, other files differentiated by structure and content will be added.

#### Aqueous Electrolyte Data

The properties for which bibliographic data on sodium chloride, potassium chloride, and calcium chloride have been collected by GRID are listed in Table 3. It should be remembered that these properties are not



Figure 2

RECORD 146

SC = O'REILLY 70;

TY = J/AS;

DES-CAT.1;

BL = A;

PT = ROTATIONAL CORRELATION TIMES AND COEFFICIENTS OF VISCOSITY OF ELECTROLYTIC SOLUTIONS;

AUTHORS;

AU.1 = O'REILLY, D.E.;

AU.2 = PETERSON, E.M.;

AA = ARGONNE NATIONAL LAB., ILL. (USA);

AC = 0 448 000 US;

DES-CAT.2;

BL = S;

OT = J. PHYS. CHEM.;

PUD = 1970;

COL = V. 74 (17), P. 3280-3285;

INDEX;

CQ.1 = SOLUTIONS/MISC.;

CQ.2 = SOLUTIONS/VOLUMETRIC;

DE.1 = EMPIRICAL EQUATIONS;

DE.2 = APPARENT MOLAL VOLUME;

DE.3 = DIFFUSION;

DE.4 = VISCOSITY;

DE.5 = RELAXATION TIME;

DE.6 = LOW TEMPERATURE;

DE.7 = STANDARD TEMPERATURE;

DE.8 = ELECTROLYTES;

DE.9 = CESIUM CHLORIDES;

DE.10 = HEAVY WATER;

DE.11 = LITHIUM CHLORIDES;

DE.12 = MAGNESIUM CHLORIDES;

DE.13 = POTASSIUM CHLORIDES;

DE.14 = SODIUM CHLORIDES;

PD = COPY;

CONTROL;

DCSO = JAF;

Figure 3

O'REILLY 70  
SOLUTIONS/MISC.  
SOLUTIONS/VOLUMETRIC

TITLE- ROTATIONAL CORRELATION TIMES AND COEFFICIENTS  
OF VISCOSITY OF ELECTROLYTIC SOLUTIONS.

AUTHOR- O'REILLY, D.E.; PETERSON, E.M. [ARGONNE  
NATIONAL LAB., ILL. (USA)].

REFERENCE- J. PHYS. CHEM., V. 74 (17), P.  
3280-3285 (1970).

DESCRIPTORS- EMPIRICAL EQUATIONS; APPARENT MOLAL  
VOLUME; DIFFUSION; VISCOSITY; RELAXATION TIME;  
LOW TEMPERATURE; STANDARD TEMPERATURE;  
ELECTROLYTES; CESIUM CHLORIDES; HEAVY WATER;  
LITHIUM CHLORIDES; MAGNESIUM CHLORIDES;  
POTASSIUM CHLORIDES; SODIUM CHLORIDES.

Table 3. Typical Geothermal Aqueous Solution  
Properties for each Concentration and Composition

Thermodynamic Properties

Heat Capacity

Free Energy

Enthalpy

Entropy

Activity Coefficient

Osmotic Coefficient

Other

Physical Properties

Viscosity

Density

Vapor Pressure

Electrical Conductivity

Thermal Conductivity

Other

totally independent functions, and frequently one property may be calculated from another; for example, some thermodynamic properties may be derived from vapor pressure measurements.

The task of extracting and evaluating numerical data from our stored literature references is currently in progress. Figures 4-7 indicate some areas where experimental measurements have been made. Each X indicates one reference to original experimental data that has been published. Figures 4-7 illustrate the current status of geothermal aqueous solution data, and show areas where additional experimental work is needed.

#### Typical Brine Data

While the overall compilation of evaluated brine properties includes those listed above in the section on "Bibliographic Compilation," our current activities center around density, heat capacity, and viscosity. The National Bureau of Standards, U.S. Geological Survey, U.S. Energy Research and Development Administration, Office of Saline Water, and other organizations have been active in supporting data evaluation in areas which also may be relevant to geothermal brine properties. For example, see References 2, 3, 9-12.

A recent and very comprehensive compilation on the density of sodium chloride solutions has been published by Potter and Brown (Ref. 10). This report contains a least squares regression analysis of the available data covering temperature to 500°C, pressures to 2000 bars, and concentrations to 7.0 molal in tabular form. A remaining task is to develop a satisfactory equation of state to represent the data.

Data on the variation in viscosity (and density) of vapor saturated aqueous NaCl and KCl solutions has been reported by Korosi and Fabuss to

Figure 4

DENSITY

		TEMPERATURE (°C)					
		< 25	25	26-100	101-200	201-300	> 300
CONCENTRATION	< 0.1 m	X X X X	X X X X X X X X	X X X X X X X X	X X X X X X X X X	X X X X X X X X X	X X
	0.11-1.0 m	X X X X X X X X	X X X X X X X X X X	X X X X X X X X X	X X X X X X X X X X	X X X X X X X X X	X X X
	1.01-3.0 m	X X X X	X X X X X X X X	X X X X X X X X	X X X X X X X X X X	X X X X X X X X X X	X X X X
	> 3.0 m	X X X X	X X X X X X X X	X X X X X X X X	X X X X X X X X X X	X X X X X X X X X X	X X X X

NaCl

Figure 5

DENSITY

		TEMPERATURE (°C)					
		< 25	25	26-100	101-200	201-300	> 300
CONCENTRATION	< 0.1 m	X X X X X X X X X X X X X X X	X X X X X X X X X X X X X X X	X X X X X X X X X X	X X X X X	X	X
	0.11-1.0 m	X X X X X X X X X X X X X X X	X X	X X X X X X X X X X X X X X X	X X X X X	X X X	X X X
	1.01-3.0 m	X X X	X X X X X X X X X X X X X X X X X X X X	X X X X X	X X X X X	X	X
	> 3.0 m	X X X X X	X X X X X X X X X X X X X X X	X X X X X	X		

KCL

Figure 6

DENSITY

		TEMPERATURE (°C)					
		< 25	25	26-100	101-200	201-300	> 300
CONCENTRATION	< 0.1 m	X X	X X X X	X			
	0.11-1.0 m	X X	X X X X X X	X			
	1.01-3.0 m	X X	X X X	X			
	> 3.0 m	X	X X	X			

CaCl<sub>2</sub>

Figure 7

VISCOSITY

CONCENTRATION	TEMPERATURE (°C)					
	< 25	25	26-100	101-200	201-300	> 300
< 0.1 m	XX	XXXX	XXXXX			
0.11-1.0 m	XXXXXX	XXXXXX	XXXXXX	XXX		
1.01-3.0 m	XXX	XXXXXX	XXX	XX		
> 3.0 m	X	XXX	XXX	XXX		

NaCl



150°C and 3.5 molal concentration (Ref. 11). Measurements were made using a Cannon master glass capillary instrument. The viscosimeters were closed end, and pressurized with hydrogen for measurements above 75°C to avoid liquid evaporation and boiling. At 150°C, the relative viscosity was 1.024 for a 0.1020 m NaCl solution, as compared to 1.010 for a 0.0999 m NaCl solution at 25°C. For 3.5345 m NaCl, the relative viscosity was 1.432 at 25°C versus 1.571 at 150°C for a 3.6024 m solution (Ref. 11). The measured viscosities for KCl solutions were generally 1-10% lower than those for comparable NaCl solutions at all temperatures.

A third example of brine data relevant to geothermal chemistry is the partial evaluation of thermodynamic properties of vapor saturated NaCl solutions by Silvester and Pitzer (Ref. 12). The work covers osmotic and activity coefficient data, enthalpy data, and heat capacity data on aqueous sodium chloride solutions. The data from the various sources were fitted to a thirteen parameter equation which reproduces the osmotic coefficient data to  $\pm 0.005$  over the composition range 0-6M and temperature range 0-300°C, enthalpy data to  $\pm 5-10$  cal/mole for compositions of 0-5M at temperatures from 25-100°C, heat capacity data to  $\pm 0.5$  cal/°K for compositions of 0-2M at temperatures from 25-200°C. Tabulated values of the total Gibbs energy, enthalpy, and heat capacity, plus partial molal and excess thermodynamic quantities of sodium chloride solutions for compositions of 0-6M at 25°C intervals from 0-300°C are given along with the same quantities in graphical form for compositions of 0-6M at temperatures of 100-350°C (Ref. 12).

### Theoretical Modeling

Success in theoretical modeling of electrolyte solutions leaves something to be desired. Part of the problem originates from the lack of sufficiently reliable experimental data at elevated temperatures. Most of the modeling of electrolyte solutions, except for infinitely dilute solutions, consists of curve fitting the experimental data (generally to a power series). Curve fitting is a viable technique for interpolation but not for extrapolation. For example, as the temperature increases the rate of change of a physical property may increase markedly until a singularity is reached at the critical point, e.g., the heat capacity of NaCl solutions becomes infinite at the critical point. See Ref. 12.

### Conclusion

Areas where future effort in basic geothermal NaCl data evaluation might be directed include the following: (1) development of numerical data formats for computer storage, (2) compilation of all the available data into a numerical data base listing values in an internally consistent set of standard units (e.g., SI units), (3) evaluation of numerical data to obtain a set of internally consistent recommended best values, (4) development of an equation of state or similar analytical expression for the relevant geothermal property, (5) generation of a set of tables (perhaps in the style of the ASME steam tables, Ref. 13) that would enable one to look up values of the individual properties quickly.

### Acknowledgment

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