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A MODEL FOR PRECIPITATION IN LITHIUM CONTAINING BRINES

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ABSTRACT

A review of the lithium industry was made and it was concluded that there is significant potential for future lithium demand. A review of the possibility of extraction of lithium by ion exchange resins from seawater and low grade brines indicated the extreme difficulty of such an undertaking due to the low selectivity of ion exchange resins for lithium and the high concentration of other cations in typical brines. A program for modeling the equilibria of the Silver Peak Brine field is provided. This program is an equilibrium model taking into consideration the effects of high ionic strength (>1.0 m),equilibria and solubility product. A dynamic representation of extent of evaporation is also included in the model. The predicted precipitations have been shown to be reasonably consistent with experimentally observed values. It is envisaged that a model of this type oould be applied to any brine as a means of predicting degree of complexation, component activities and at least the limits of precipitation.

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NOMENCLATURE

C_{ijk}	=	Complex k formed by reaction M_i with L_j
H	=	Hydrogen Ion
$K\omega$	=	Ion - product of water
L_j	=	Ligand j
M_i	=	Metal i
OH	=	Hydroxide ions
TOTM,TOTL	=	Analytical (total) concentrations of Metals and Ligands respectfully
m_i	=	molality
R	=	Gas Constant
T	=	Solution Temperature
x_i	=	Concentration moles/liter
f_i	=	Activity Coefficient
N_A	=	Avogadro's Number
e_o	=	Electronic Charge
I,Y	=	Ionic Strength ($\frac{1}{2}m_i z_i^2$)
$Z_{+,-}$	=	Absolute number of unit charges on the ion.

GREEK LETTERS

μ_i = Chemical Potential

κ = Effective diameter of the ion

γ_{12} = Mean ionic activity coefficient for the electrolyte indicated by the subscript, being for the pure solution and for the mixed solution

α_{ijk} = Stoichiometric Coefficient of M_i in C_{ijk}

β_{ijk} = Stoichiometric coefficient of L_j in C_{ijk}

ξ_{ijk} = Stoichiometric coefficient of H or OH in C_{ijk}

Γ_{12} = Reduced Activity Coefficient, namely $(\gamma_{12})^{1/z_1 z_2}$

δ = charge on metals

ζ = charge on ligands

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CHAPTER 1

INTRODUCTION

Interest in the extraction of lithium from as yet not well developed sources has increased in recent years. There are three potential sources for lithium extraction: pegmatites, brines, and certain clays.[37] Pegmatites are the traditional source and the extractive technology for these resources is well developed[38]. Brines are now receiving some attention and although processing is in existence at Silver Peak,Nevada the techniques presently employed are inadequate for the majority of brine sources.[39] The clay sources have not been considered at the present time but do represent a viable possibility should the demand for lithium increase as expected[3].

An objective of this study was to develop a computer program that could be used as a means of giving an initial evaluation of process viability(feasibility) and later for process optimization. One problem associated with high concentration, multi-ion solutions is the deviation of such solutions from ideal thermodynamic behavior. The Debye-Hückel theory and extensions are not valid above 0.5 molar[36] so some form of empirical representations

of activity coefficients must be made, for example Bromley's[27] and Meisner et al's[25] work. The occurance of high ionic strength solutions in hydrometallurgical systems is wide spread[25]. Equilibrium calculations in such systems require information on the thermodynamic activity coefficients of the dissolved species. The application of the empirical methods of Meissner et al is used in this thesis for brines, but the application is general enough to afford application to typical hydrometallurgical systems.

1.1 Aim of this Study

The objectives of this study have been:

(1) To review the lithium industry with respect to future requirements of lithium. In particular the literature associated with the extraction of lithium from brines and seawater.

(2) To review the possibility of the extraction of very dilute lithium concentrations from seawater and brines using currently available ion-exchange resins.

(3) To apply the solution theory of Meissner et al to a complex, high ionic strength brine in order to predict aqueous species in solution, and indicate the limits for lithium extraction and precipitate formation as a function

of extent of evaporation.

1.2 Organization of Thesis

The investigation is presented in Chapters 2 to 7, which follow. In Chapter 2 a literature survey is presented which is divided into four distinct sections. These are 1) Lithium Resources and Industry 2) Solar Evaporation 3) Extraction of Lithium from Seawater 4) Solution Modelling. In Chapter 3 the theoretical considerations of the thesis are presented. The emphasis in this chapter is on the methods used for calculating activity coefficients in mixed solutions. Chapter 4 is a detailed presentation of the model including an overall flowsheet. Chapter 6 deals with the application of the model to the Silver Peak brine field. In this chapter the activity coefficients and species distribution predictions are presented graphically. Also included is a comparison with the experimental work along with a discussion of the significance of the results. Experimental details and results are presented in Chapter 5. Chapter 7, the final chapter, concludes the work along with suggestions for future work.

CHAPTER 2

LITERATURE SURVEY

The review presented here has been divided into four parts. The first section deals with the lithium resources and industry. This section has been included in an attempt to show some justification for the investigation by illustrating the enormous projected future demand for lithium.

The second section concerns solar evaporation and is included as a necessary background for the model development work of chapter 4. The third section is a discussion of the literature associated with the extraction of lithium from seawater. This section is included to illustrate why a model is required to determine the limitations of lithium extraction. The fourth section deals directly with the model development.

2.1 Lithium Resources and Industry

A symposium held in January 1976 on the lithium resources and requirements by the year 2000 illuminated a difference of opinion. On the one hand an impending shortage of lithium was forecast by the U.S. Geological

Survey[1] but the representatives from industry[2] were united in their opinion that the potential increased demand for lithium suggested by the work on the development of lithium batteries could be met.

Vine[3] points out that the estimates of the availability of lithium tend to be misleading to those who plan to use this rare metal in alternative energy applications. Reasons for an overly optimistic outlook are two-fold (1) Geologic estimates of resources (for example Norton[4], 1973) summarize data on amounts of lithium in the ground without regard to recoverability and (2) All recently published estimates are biased by an unrealistic preliminary[3] forecast of lithium available from one large brine field in Nevada. It is to these two points that much of the work of this thesis is devoted.

2.1.1 Current Uses - Foote Mineral Company extracts lithium from Silver Peak, Nevada, and both Lithium Corporation and Foote Mineral Company extract lithium from spodumene concentrates in North Carolina. The U.S.S.R. is also a producer and exporter to the west.

Besides the basic producers there are several lithium chemical producers, the most important of which are, Metallgesellschaft in West Germany and Honjo Chemical in

Japan. The major lithium chemicals[7] are carbonates for use in ceramics, lithium fluoride in the aluminum industry, hydroxide in the grease industry, bromide and chloride in airconditioning, hypochlorite in sanitation, metal in pharmaceuticals, and butyllithium in synthetic rubber.

Orazem[5] has indicated that the largest potential in the next 5 years for lithium demand is the aluminum industry. The lithium battery is not expected to have a major impact on the lithium industry until the early 1980's.

2.1.2 Future Uses - Lithium Battery - As part of the energy storage program of the U.S. Energy Research and Development Administration is the development of storage batteries for load leveling on electric utilities and automotive propulsion. Lithium - aluminum/iron sulphide batteries show promise both for utility energy storage batteries and electric vehicle batteries. Landgrebe[5] points out that a high manufacturing volume may be required for these batteries, and the availability of the required raw materials is an important consideration.

The lithium-aluminum/iron sulphide batteries utilizes lithium not only as one of the active materials but also as a consituent of the LiCl-KCl molten salt electrolyte.

If the performance goals for this battery are achieved, the demand for these batteries will in turn create a greatly increased demand for lithium. Projections have been made of the quantity of lithium required for the lithium/iron sulphide batteries produced from 1985-2000. The projected lithium requirement in the year 2000 represents a substantial fraction of the present estimate of the world lithium resources and is nearly equal to the estimated economically recoverable lithium resources in the U.S.A..

2.1.3 Future Uses - Fusion Power - Fusion is the process by which the nuclei of light elements are forced to combine and form new light elements with a net yield of significant quantities of energy per reaction.

Bogart[6] suggests that the first generation fusion reactors will be based on the deuterium-tritium (D-T) reaction, within the deuterium-lithium fuel cycle.

The deuterium resource is effectively infinite, being found in one part in 6,500 in water. Commercial lithium is available in large but not unlimited quantites.

The lithium requirement for different fusion reactor concepts is strongly design dependent. When lithium is used both as a breeder and a coolant in either the metallic or the salt form, the inventories are very high. In

alternative solid breeder concepts the lithium requirements are much smaller, but this lithium must be enriched in the isotope lithium-6, and a neutron multiplying element also must be used. Because of the high burnup rate in solid breeder concepts, periodic refueling must be performed which will affect the annual net lithium requirement. This is not the case in liquid lithium breeder/coolant concepts which have such a high initial inventory of lithium-6 that the small fractional burnup per year does not mandate periodic refueling.

In conclusion fusion power may place a significant demand on what presently is thought to be economically recoverable reserves of lithium if the lithium is used for reactor cooling in addition to tritium breeding.

2.2 Solar Evaporation

One of the earliest applications of solar evaporation has been in producing sodium chloride and recently for producing products such as potash. For more complex systems such as the saline brines at Silver Peak, Nevada a more sophisticated approach is required. To this end a procedure to predict mother liquor composition and salt deposition as a function of extent of evaporation is therefore required. Some work has been done in this area but it

is generally aimed at the prediction of evaporation rates only, for example, the work of Pancharatnam[8,9] . Other work is summarized by Jacobsen and Ore[10] who also present a Solar pond model, essentially a heat balance to predict evaporation rates. They also present a procedure to predict liquor composition.

2.2.1 Solar Pond Operation - The complexity of a solar pond system is dependent upon the type of minerals to be recovered. All solar ponds are affected to some degree by the following variables[11] :

(1) Meteorology (evaporation, temperature, wind, radiation, humidity); (2) brine concentration, entering and leaving pond; (3) pond depth; (4) pond area; (5) leakage of pond liquors into the ground; (6) entrainment of pond liquors in crystallized salts; (7) type and amount of salt crystallized in the pond.

The significance of each variable is dependent upon the total amount of evaporation and the type of minerals to be crystallized. Net evaporation is a function of all meteorological conditions, the two most important being solar radiation and precipitation. Evaporation is greatest where it is hot and dry. Other factors affecting the evaporation are wind, humidity, and concentration of the

brine.

2.2.2 Practice at Silver Peak, Nevada - Since considerable attention is given to the lithium extraction from a brine similar to the Silver Peak operation in this thesis the actual operation is outlined here.

Barrett and O'Neill[12] discuss the geology and hydrology of this operation in some detail. They also present typical data from the pond system, Table 2-1 . A description of the operation is as follows:

The brines are pumped from beneath a playa surface inside a closed basin. The playa deposits consist of mixtures of clays, silts, sands, and evaporites, many of which are saturated with saline brines down to known depths of 600 feet.

The brine pumped from the wells contains 300 ppm of lithium and 10-15 wt % of other dissolved solids. The brines are pumped into a series of solar evaporation ponds and after they reach saturation a series of salts are precipitated. As a consequence of the evaporation the lithium concentration is increased to approximately 5000 ppm. Lithium is recovered from the brine by precipitation as lithium carbonate.

TABLE 2.1

SILVER PEAK POND SYSTEM. TYPICAL DATA

Pond No.	Area (Acres)	Brine Vol ('000. galls)	Li Conc (ppm)	Solid Phases	Extent of Evaporation { fraction H_2O remaining }
1	760	200,000	680	None	0.61
2	520	120,000	780	NaCl	0.53
3	90	25,000	930	NaCl	0.45
4	86	22,000	1200	NaCl	0.35
5	46	15,000	1400	NaCl, gypsum, $Mg(OH)_2$	0.30
6	41	5,500	1900	NaCl, $CaCO_3$	0.22
7	17	1,500	2400	NaCl, Glaserite	0.17
8	13	1,000	3100	NaCl, Glaserite, KCl	0.13
9	14	3,000	5000	NaCl, Glaserite, KCl	0.08

Notes: (i) Lime added to pond 4 in order to precipitate magnesium

(ii) Glaserite ($K_3Na(SO_4)_2$)

2.2.3 Review of Various Brines - Geothermal fluids from various sources in the Western United States contain quantities of lithium ranging from the low parts per million level to concentrations of hundreds of parts per million (ppm)[13] . Some of these geothermal resources can be considered to be significant, if not major, resources or reserves of lithium.

Chemical differences between evaporite basins are pronounced[14] . Great Salt Lake, Utah and the Great Salt Lake Desert to the west are characterized by high concentration of NaCl. Others such as Railroad Valley, Southwest Ely, Nevada, contain a large body of salt that includes a body of gaylussite ($Na_2Ca(CO_3)_2 \cdot 5H_2O$). Bristol Lake in California is characterized by an unusually high concentration of calcium chloride. Other basins in the Mojave Desert area in California are characterized by high concentrations of boron. Clayton Valley, southwest of Tonopah, Nevada, is characterized by a high lithium-to-sodium ratio in a chloride brine.

Once dissolved, lithium tends to remain in solution in residual brines, even after evaporative concentration and precipitation of the salts of sodium, magnesium, and potassium. Brines associated with these evaporite minerals may contain as much as 1000 times more lithium than seawater

contains.

White, Thompson, Fournier[15] present tables of lithium contents of various waters. Lithium contents of natural waters range from 0.003 ppm to more than 500 ppm. Refer to Table 2.2 for a comparison of various brine compositions.

Other brines considered of interest relative to this thesis are those of Utah and the Salars of the central Andean region of northern Chile, western Boliva, and northwestern Argentina. Eriksen, Guillermo, and Thomas[16] report that recent exploration has shown that some of the Salars contain relatively high concentrations of lithium, and it seems that this region has potentially large resources of lithium. A table of chemical compositions of some of the lithium rich brines from northern Chile are presented in Table 2-3.

Whelan and Petersen[17] consider the occurance of lithium in the Great Salt Lake brines, subsurface brines, volcanic rocks, and miscellaneous lithium bearing minerals. Subsurface brines considered to be possible sources of lithium in Utah include (1) subsurface brines of Bonneville Salt Flats in the Great Salt Lake Desert, (2) subsurface brines of Sevier Lake, (3) oil field brines, and (4) brines that may be produced incidental to geothermal development.

TABLE 2.2

LITHIUM CONTENT OF VARIOUS WATERS

In milligrams per liter

	Li	Na	Li/Na ratio	Cl	Li/Cl ratio
Ocean	0.170	10,500	0.00002	19,000	0.00001
North American Rivers	0.0003	∿9	0.00030	8	0.00400
Warm Springs, 50°C	0.040	∿30	0.00100	5	0.00800
Salton Sea Brine Calif(∿350°C)	215	50,400	0.04300	155,000	0.00140

EVAPORATE BRINES

	Li	Na	Li/Na ratio	Cl	Li/Cl ratio
Clayton Valley, Nev.	380	66,200	0.0057	95,000	0.004
Searles, Calif.	81	110,000	0.0007	121,000	0.0007

TABLE 2.3

CHEMICAL CONCENTRATIONS, IN MILLIGRAMS PER LITER, IN SELECTED LITHIUM BRINES FROM NORTHERN CHILE

Locality	Solids	Na	K	Mg	Ca	Li	Cl	SO_4	HCO_3	B
Salar de Atacama	370,000	91,100	23,600	9650	450	1570	189,500	15,900	230	440
Salar de Pujsa	89,298	28,500	1,295	653	375	137	27,660	28,110	0	675
Salar de San Martin	102,138	28,160	2,614	6252	1566	187	60,050	2,490	625	426
Salar de Lagunas	390,000	126,800	14,280	3630	110	412	176,600	47,770	406	979

Two analyses of Utah brines are presented in Table 2-4. Barrett and O'Neill[12] present an analysis of the Silver Peak brines and this is illustrated in Table 2-5. It is this chemical analysis which is used extensively for the analysis with the model as discussed in Chapter 6.

2.3 Extraction of Lithium from Seawater using Ion Exchange

It has been suggested[40] that lithium can be extracted from seawater or lowgrade brines with ion exchange resins. The following brief examination of the literature highlights some of the associated problems. Little information pertaining to lithium extraction from brines appears in the literature, therefore most of the information was gained by communicating directly with the ion exchange resin manufactures and water treatment companies.

2.3.1 Methods of Extraction - The low concentration of lithium in seawater, 180 ppb[41] compared to the high concentration of other more common cations creates an immediate problem for any extraction procedure. Several possible routes for lithium extraction are considered in the literature[40,42]. The various procedures considered for the concentration of dilute species include adsorption, solvent extraction, ion exchange, evaporation, precipitation and

TABLE 2.4

(A) ANALYSIS OF SHALLOW AQUIFER BRINES

GREAT SALT LAKE DESERT

Ion	Grams/Liter	Ion	Grams/Liter
Cl^-	139.630	Ca^{++}	1.25
Br^-	0.038	Sr^{++}	0.057
I^-	N.D	Mg^{++}	1.730
$SO_4^=$	4.240	SiO_2	0.0087
$CO_3^=$	0.000	HCO_3^-	0.041
$BO_3^=$	0.023	Al^{+++}	0.0018
Na^+	76.700	F^-	0.0013
K^+	4.430	NO_3^-	0.0048
Li^+	0.003		

Total dissolved solids	228.28
Specific Gravity	1.150
pH	7.1 @ 25°C

Notes: (i) N.D., Not determined

TABLE 2.4 cont'd.

(B) MEAN ANALYSIS OF 10 SHALLOW SUBSURFACE BRINES, SOUTHERN HALF OF SEVIER LAKE, UTAH

Ion	Value in Grams per Liter
Cl^-	92.4000
Mg^{++}	3.4400
Ca^{++}	0.6000
Na^+	64.3700
K^+	2.5400
$SO_4^=$	21.6600
Br^-	0.0540
Li^+	0.0225
B	0.0350

Total dissolved solids (g/l)	185.14
Specific Gravity	1.126

TABLE 2.5

SILVER PEAK BRINE ANALYSIS

Ion	Well Brine wt %
Na^+	6.20
K^+	0.80
Mg^{++}	0.04
Li^+	0.04
Ca^{++}	0.05
$SO^=$	0.71
Cl^-	10.10

electrochemical separation. Due to the low concentration of lithium in seawater preliminary investigations indicate that an extraction process involving a preconcentration step is required, for example solar evaporation.

2.3.2 Use of Ion Exchange Resins - Stenberg and Dang[40] present a preliminary design and analyis for the extraction of lithium from seawater based on solar evaporation and ion exchange. Although the analysis sounds promising there is considerable uncertainty as to the liquid-solid equilibrium during evaporation and the capability of ion exchange resins in separating the various cations.

It is these assumptions that throw doubt on the analysis, although they themselves point out the need for an experimental study in this area. Kunin[43] regards the low selectivity of ion exchange resins for lithium and the high concentration of other cations in the solution to be the major problem for the extraction of lithium from seawater.

Jouy and Coursier[44] have established the ability of ion exchange resins to separate lithium from other cations, however their work concerns solutions of Li/Na ratio of 2.3:1 . Lithium has a lower affinity for the typical cation site than H, Na, K, Mg, Ca. However the affinity for the

site (as compared to other ions) decreases with increase in degree of crosslinking within the resin. Refer to Table 2-6. With this in mind Higgens[45] suggests a possibility for lithium extraction would be via ion exclusion. McGarvey[46] suggests that lithium recovery development should involve the removal of divalent cations (calcium and magnesium) on a primary cation exchanger. Once the initial condition is achieved he suggests that lithium complexes be formed in order for a separation to be made from the remaining cations.

In conclusion, from the literature and communications with the industry it would appear that the extraction of lithium from sources with low lithium values and massive amounts of other cations is an extremely difficult undertaking, it is therefore unlikely that a straight cation process can be used for lithium recovery. Further, the work of this thesis has illustrated a problem for ion exchange due to the highly complexed nature of lithium in high ionic strength solutions.

2.4 Solution Modelling

This section relates to the identification of species in solutions and representation of such solutions by equilibrium models. An equilibrium model is considered appropriate as opposed to a rate model due to the high residence

TABLE 2-6

EFFECT OF DEGREE OF CROSSLINKING ON

RELATIVE AFFINITIES FOR POLYSTYRENE CATION-EXCHANGE RESINS

	% Divinylbenzene		
	4	8	12
H^+	1.00	1.00	1.00
Li^+	0.90	0.85	0.81
Na^+	1.30	1.50	1.70
K^+	1.75	2.50	3.05
Mg^{++}	2.40	2.50	2.60
Ca++	3.40	3.90	4.60

times associated with solar evaporation ponds and the relatively slow evaporation rates.

2.4.1 Equilibrium Models - Equilibrium models require the computation of the composition of systems containing numerous species which may be distributed between aqueous, gaseous, and solid phases.

To solve the chemical equilibrium problem, two principle techniques can be distinguished[18]. First the so-called equilibrium constant approach which consists of simultaneous solution of the set of nonlinear equations provided by the mass law and the mole balance equations. This method was pioneered by such workers as Brinkley[19] and has found one of its best known applications to aqueous systems through the HALTAFALL program. This program was developed by Sillén and his co-workers (Ingri et al)[20].

The second technique was first proposed by Dantzig[21] and his co-workers and consists of directly minimizing the Gibbs free energy function subject to the constraint of the mole balance equations. Sturm [22] indicates that this method has been applied to large multiphase systems by Shapiro. A complete review of the theory and applications of the two methods is given by Zeleznik and Gordon[23].

Morel and Morgan[18] have developed a general purpose program especially adapted to the study of coordinative

interactions and dissolution and precipitation in aqueous systems. The program uses the stability constant approach and the Newton-Raphson method for digital computation of equilibria. It is this approach that has been adapted for use in this thesis.

2.4.2 Calculations of Activity Coefficients in High Ionic Strength Solutions - Aqueous systems dealt with in hydrometallurgy usually involve solutions of strong electrolytes. Equilibrium calculations in such systems require information on the thermodynamic activity coefficients of the dissolved species. Little experimental information on these activity coefficients has been available, especially in more concentrated multi-ion solutions commonly encountered in hydrometallurgy. However in recent years empirical methods for the prediction of activity coefficients has appeared[24-33].

Meissner and Tester [24] present a method where $\gamma\pm$, the mean activity coefficient of an electrolyte in aqueous solution, can be determined knowing a single experimental value of $\gamma\pm$ at a known ionic strength. The known value of $\gamma\pm$ must be at a concentration well above those to which Debye-Hückel equation applies, that is greater than ionic strength of 1.0. When such an experimental value is not available, a procedure for predicting $\gamma\pm$ at a known concentration is

presented. This procedure appears applicable to chlorides, bromides, iodides, acetates, nitrates, chlorates, and hydroxides. In combination, these relationships make it possible to predict $\gamma\pm$ values at any concentration for a number of pure electrolytes in aqueous solution at 25°C.

Meissner et al[25] extend the graphical representation presented above to propose a general method whereby values of $\gamma\pm$ for any strong electrolyte in aqueous solution over temperatures ranging from 0°C to 150°C can be predicted. An equation for calculating $\gamma\pm$ at various temperatures is also suggested by Cobble [26]. In this equation the mean activity coefficient at a particular temperature is required along with a temperature dependent parameter tabulated by Cobble over the range 25°C to 250°C.

Bromley[27] takes the graphically correlated work done by Meissner et al and presents a generalized analytic correlation to predict activity coefficients. His single parameter equation is well correlated to an ionic strength of about 6 . The data used for the correlations of both Bromley and Meissner was obtained from the data of Robinson and Stokes[28], Harned and Owen[29] and Wu and Hamer[30].

In Kusik and Meissner's recent work[31,32] culminating in their paper presented at the 1977 Annual AIME meeting[33] they present a method for calculating the activity coeffic-

ient in mixed solutions. The calculation involves determining a reduced activity coefficient and then allowance is made for the various cation-anion pairs. This procedure was used in this thesis.

CHAPTER 3

THEORETICAL CONSIDERATIONS

This chapter deals with the thermodynamic considerations appropriate to this investigation. The method used for calculating pure activity coeffficients and the allowance for high ionic strength and multi-ion solutions are also reviewed.

3.1 Activity Coefficients

Activity coefficients give a measure of the deviation from ideality. Bockris et al[34] explains the physical significance of activity coefficients as follows: For a hypothetical system of ideal(noninteracting) particles, the chemical potential has been defined as:

$$\mu_i(\text{ideal}) = \mu_i^0 + RT\ln X_i \qquad 3.1$$

for a real system

$$\mu_i(\text{real}) = \mu_i^0 + RT\ln X_i + RT\ln f_i \qquad 3.2$$

Subtracting 3.1 from 3.2

then $$\Delta\mu_{i-I} = RT\ln f_i \qquad 3.3$$

Thus the activity coefficient is a measure of the chemical-potential change arising from ion-ion interactions.

3.1.1 Debye-Hückel Theory - According to the Debye-Hückel theory the chemical-potential change $\Delta\mu_{i-I}$ arising from ion-ion interaction has been shown to be given by

$$\Delta\mu_{i-I} = -\frac{N_A(Z_i e_o)^2}{Z\varepsilon\kappa^{-1}} \qquad 3.4$$

The Debye-Hückel relationship can be written in terms of the ionic strength* and applied to solutions below an ionic strength of 0.001 molar.

$$\log\gamma_i = \frac{AZ_i{}^2 I^{\frac{1}{2}}}{1+a^0 BI^{\frac{1}{2}}} \qquad 3.5$$

A and B are constants characteristic of the solvent (water) at the specified temperature. The quantity a_i^0 has a value dependent upon the 'effective diameter' of the ion in solution. However, the assumption of the smoothed out charge surrounding a central ion is not correct at high ion concentrations.

* Concept developed by Lewis and Randall, defined as $I=\frac{1}{2}\Sigma m_i Z_i^2$

In the brines under consideration in this thesis the dissolved ions are in close proximity, the distance of separation being 10 Å or less[22]. Under these conditions the approximations underlying the Debye-Hückel ion interaction theory are no longer valid, and the mutual attractive energy of oppositely charged ions will be comparable with or greater than the thermal energy which tends to maintain a random distribution.

3.1.2 Extensions to Debye-Hückel Theory - An attempt to overcome the limitations of the Debye-Hückel theory are illustrated by the empirical expression proposed by Davies[35], that is

$$\log\gamma_i = AZ_i^2\left(\frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}} - 0.2I\right) \qquad 3.6$$

This expression has validity up to 0.5 molar. In more concentrated solutions the work of Kusik, Meissner, Tester, and Bromley are applicable to activity coefficient determination.

3.2 Activity Coefficients of Strong Electrolytes

Empirical correlations to predict activity coefficients in strong electrolytes have been developed by Meissner et

al[24,25]. Graphical manipulation is required to apply the work of Meissner et al. Bromley[27] presented an analytic correlation and it is his equation that is applied in this thesis.

3.2.1 Bromley's Correlation - The activity coefficients of strong aqueous electrolytes are well correlated by the single parameter equation developed by Bromley.

$$\log\gamma_{\pm i} = \frac{-0.511|Z_+Z_-|I^{\frac{1}{2}}}{1+\rho I^{\frac{1}{2}}} + \frac{(0.06+0.6B)|Z_+Z_-|I}{\left(1+\frac{1.5}{|Z_+Z_-|}I\right)^2} + BI \qquad 3.7$$

This correlation is valid to an ionic strength of 6.

A complete set of B values at 25°C with ρ set equal to 1.0 are found in the tables of reference 27.

3.2.2 Activity Coefficients in Multicomponent Solutions - Kusik and Meissner's[33] paper was applied in this thesis to the determination of activity coefficients of electrolytes in a multicomponent aqueous solution.

Kusik and Meissner define a reduced activity coefficient Γ^0_{12} and Γ_{12} as follows:

$$\Gamma^0_{12} = (\gamma^0_{12})^{1/Z_1Z_2} \qquad \text{Pure Solution}$$

$$\Gamma_{12} = (\gamma_{12})1/Z_1Z_2 \qquad \text{Mixed Solution}$$

Further, the reduced activity coefficient of electrolyte 12 in a multicomponent (mixed) aqueous solution, namely Γ_{12}, is usually different from its pure solution value. Kusik and Meissner present a method for determining Γ_{12} from pure solution values of Γ^0 for the various cation-anion pairs that can be formed. All the Γ^0 values are determined at the temperature and total ionic strength of the mixture. Then,

$$\log\Gamma_{ij} = \frac{Z_i}{Z_i+Z_j}(V_{i2}I_2\log\Gamma^0_{i2} + V_{i4}I_4\log\Gamma_{i4} + \ldots)/I_T + \frac{Z_j}{Z_i+Z_j}(V_{j1}I_1\log\Gamma^0_{j1} + V_{j3}I_3\log\Gamma^0_{j3} + \ldots)/I_T \qquad 3.8$$

where the cations i have odd subscripts and the anions j have even subscripts. I_i and I_j are the ionic strengths of the individual ions.

$$V_{ij} = \text{weighting factor } 0.5(Z_i + Z_j)^2/(Z_iZ_j)$$

3.2.3 Activity coefficients as a function of Temperature - Activity coefficients change with temperature. In this

work the equation developed by Cobble [26] is used.

$$\log\gamma_{\pm}^{T_1} = \log\gamma_{\pm}^{25} - \frac{I^{\frac{1}{2}}}{1+I^{\frac{1}{2}}}(A_{\gamma}^{T_1} - A_{\gamma}^{25}) \qquad 3.9$$

$A_{\gamma}^{T_1}$ is the major temperature dependent variable and is tabulated over the range, 25°C to 250°C. The mean activity coefficient must be known at a particular temperature in order to estimate the activity coefficient at any other temperature up to 250°C.

3.2.4 Individual Ion Activity Coefficients - It is not possible to measure directly individual ion activity coefficients. In order to calculate these values the assumption that $\gamma_+ = \gamma_-$ for a standard uni-univalent electrolyte over the ionic strength range of interest must be made. To this end the behavior of KCl in solution is the standard for obtaining individual ion activities, hence as an approximation:

$$\gamma_{\pm KCl} = \{(\gamma_{K^+})(\gamma_{Cl^-})\}^{\frac{1}{2}} = \gamma_{K^+} = \gamma_{Cl^-} \qquad 3.10$$

This assumption is often called the MacInnes assumption[36]. Details of the application of this method, known as the mean salt method, are given in Garrels and Christ[36].

CHAPTER 4

DETAILS OF COMPUTER MODEL

This chapter is concerned with the detailed development and formulation of a model to represent the equilibrium precipitation of salts from a brine and the species distribution in such a brine. The model takes into consideration the effects of high ionic strength, equilibria and solubility product. A dynamic representation of extent of evaporation is included by making step decreases in solution volume and adjusting the concentrations accordingly.

4.1 Description of the System

A general method of computation and a systematic notation describing the chemical system in algebraic terms were adopted. This systematic approach to chemical equilibrium is based on the work of Morel and Morgan[18].

The notation chosen differentiates metals and ligands and represents the chemical system in a tableau format. An example of the tableau representation is made in table 4.1. The complex formation, C_{ijk} is represented as

$$C_{ijk} \equiv (M_i)_\alpha (L_i)_\beta (H) \qquad 4.1$$

TABLE 4.1

GENERAL REPRESENTATION OF AQUEOUS SPECIES

IN TERMS OF METALS M_i, LIGANDS L_j, H IONS AND OH IONS

	L_1	L_2	$L_3(OH)$
M_1	$C_{111} \equiv (M_1)(L_1)$ $C_{112} \equiv (M_1)(L_1)H$	$C_{121} \equiv (M_1)(L_2)H$	$C_{131} \equiv (M_1)(L_3)$
M_2		$C_{221} \equiv (M_2)(L_2)H$	$C_{231} \equiv (M_2)(L_3)$ $C_{232} \equiv (M_2)(L_3)_2$ $C_{233} \equiv (M_2)(L_3)_4$
$M_3(H)$	$C_{311} \equiv (M_3)(L_1)$ $C_{312} \equiv (M_3)_2(L_1)$	$C_{321} \equiv (M_3)(L_2)$ $C_{323} \equiv (M_3)_2(L_2)$ $C_{323} \equiv (M_3)_3(L_2)$	

where i is an index specifying the metal, j is an index specifying the ligand, k is an index specifying the various M_i - L_j complexes in an arbitrary order, α(in fact, α_{ijk}) is the stoichiometric coefficient of the metal in the formula of C_{ijk}, equation 4.1, β(in fact, β_{ijk}) is the stoichiometric coefficient of the ligand in the formula of C_{ijk}, and ε(in fact, ε_{ijk}) is the stoichiometric coefficient of the hydrogen ion, H^+, in the formula of C_{ijk}.

For example: the complex $Ca(OH)^+$ is specified as follows: $C_{5,3,1} = Ca^1(OH)^{+1}H^0$

where i = 5 specifying the metal
j = 3 specifying the ligand
ε = 0 since no hydrogen ion
k = 1 index specifying the particular complex
α,β = 1

Further details of the above example can be seen in the tables of Appendix III, Input Matrices.

Other values for k, that is, 2,3,4 etc. would be used if other complexes of Ca^+ and OH^- ions existed. Only one combination of a particular metal and ligand are considered in this thesis, therefore only two dimensional arrays need be considered here. However, the programme

can easily be expanded to accomodate three dimensional arrays if other complexes need to be considered.

Using the definition of the stability constant, K_{ijk}, the mass action law can be written

$$C_{ijk} = K_{ijk} \cdot \left[M_i\right]^{\alpha} \cdot \left[L_j\right]^{\beta} \cdot \left[H\right]^{\varepsilon} \qquad 4.2$$

This formula implicitly contains the result $\left[OH\right] = K\omega/H$ in the case where $\left[H\right]$ in the above formula is replaced by $\left[OH\right]$.

In the tableau form the arrays of numbers $K, \alpha, \beta,$ and ε completly describe the general chemical properties of the system (Refer to Appendix III for the input arrays for the model of the Silver Peak Brine system). The program is written such that the arrays are the general input to the program for any system under consideration. In order to solve the set of nonlinear equations as many equations as unknowns are required. It is convenient to consider the concentrations of complexes as secondary unknowns, that is dependent relations, given the principle unknowns M_i, L_j, and H by equation 4.1.

H^+ and OH^- ion concentrations are at least seven orders of magnitude smaller in value compared to the other ion concentrations in the brine considered in this thesis.

As a result, problems associated with the convergence of the numerical solution were found. In particular, the correction to H^+ ion concentration was of the same order as the H^+ ion concentration itself and so no convergence was observed. Hence the charge balance was adopted in place of a proton balance.

4.1.1 Descriptrion of General Balances - In general terms, the mole balances can be written as follows:

$$TOTM_i = \left(M_i\right) + \sum^{*}_{j,k} \alpha_{ijk}\left(C_{ijk}\right) \qquad 4.3$$

that is sum on line i of Table 4.1

$$TOTL_j = \left(L_j\right) + \sum^{*}_{i,k} \beta_{ijk}\left(C_{ijk}\right) \qquad 4.4$$

that is sum on column j of Table 4.1

where $TOTM_i$ and $TOTL_j$ are the analytical or total concentrations of metal M_i and ligand L_j, respectively.

The final equation is the charge balance expressing the electroneutrality of the system. That is the sum of the negative charges on the anions must exactly balance the sum of the positive charges on the cations.

Then,

$$YC = \Sigma\delta\left(M_i\right) - \Sigma\zeta\left(L_j\right) + \Sigma^{\text{cationic}}_{\text{complexes}} - \Sigma^{\text{anionic}}_{\text{complexes}} \qquad 4.5$$

This equation has not been generalized in the program

*$\Sigma_{j,k}$ a double summation and order unimportant

and must be evaluated for each case under consideration. However, if the proton balance was applicable a general equation could be adopted similar to equations 4.3 and 4.4.

4.1.2 Newton-Raphson method - This derived system of n independent equations containing n unknowns is generally nonlinear, therefore a numerical iterative solution is required. Normally a reduction of the number of equations which have to be solved numerically is attempted. In this study, this was not done in order to maintain the general tableau presentation. To solve the equation set, a Newton-Raphson method was applied. In order to use this method, expressions for the derivatives of the general equations 4.3, 4.4, and 4.5 with respect to the principle variables M_i, L_j, and H are required. A generalized set of the derivatives is presented in Appendix I.

4.2 Ionic Strength Calculations

An estimate of the ionic strength has to be made before the ionic strength is calculated accurately. This is required since initially the species distribution and the activity coefficients are not known. This initial estimate of the ionic strength is made by calculating its value based on the contribution of metals and ligands alone.

This will not be far in error since the species concentration is small relative to the metal and ligand concentrations. Further calculations of ionic strength are based on all the considered charged ion species.

4.2.1 Activity Coefficient Calculations - The activity coefficients are a function of the solution ionic strength. The ionic strength is calculated as described above, then the emperical relations of Bromley[27] and Meissner et al[24,25] are used to predict the mean activity coefficients. The recent work of Meissner and Kusik[33] is then applied in order to allow for any interactions between ions. Finally the individual activity coefficients are determined via the mean salt method.

4.3 Precipitation Calculations

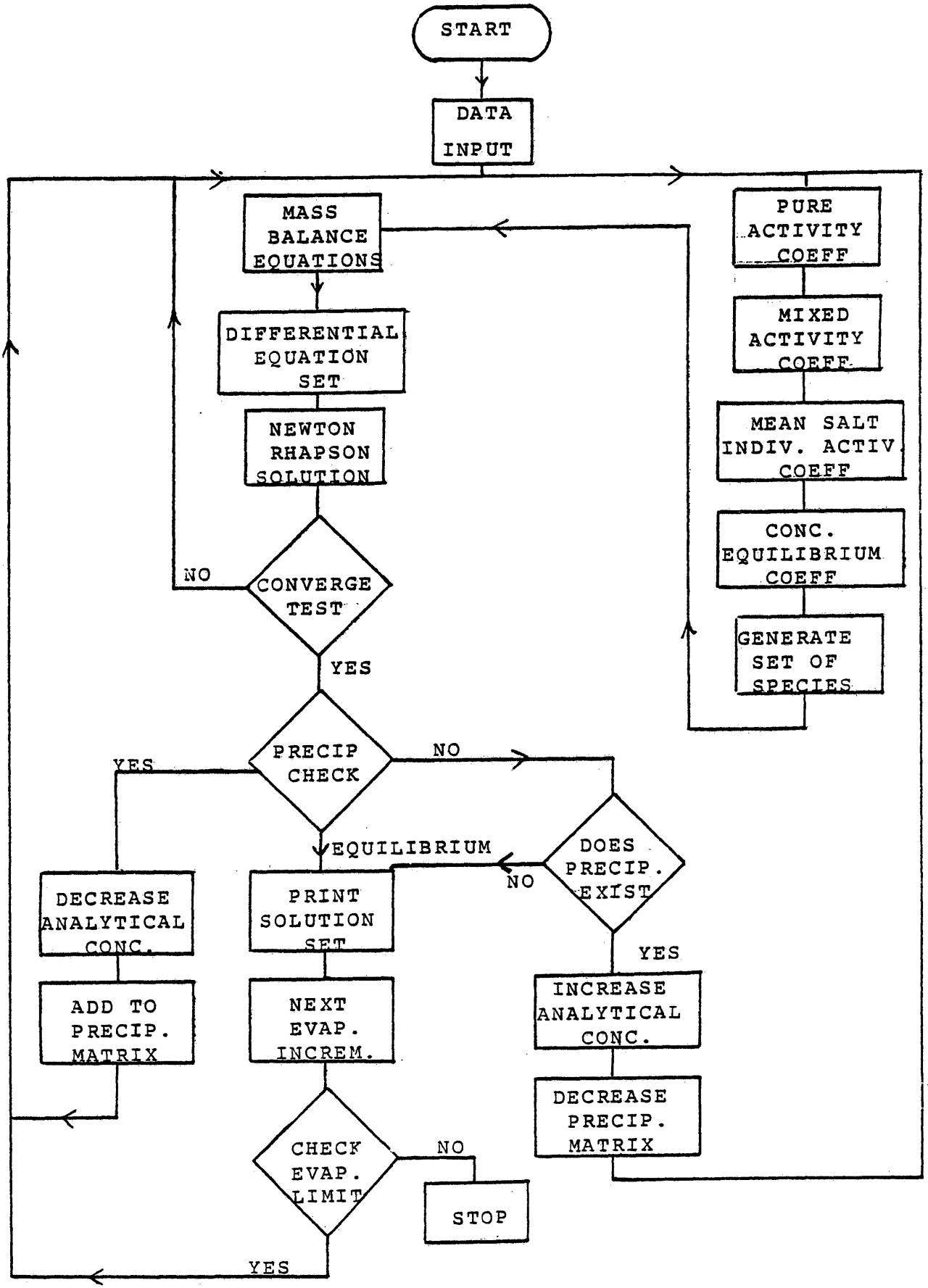
Once equilibrium has been established in the solution the possibility of precipitation is then considered. No consideration is given to kinetics nor co-precipitation. The absence of a kinetics consideration is a reasonable assumption when considered relative to the residence times, on the order of one year, involved in solar evaporation ponds. However, coprecipitation does occur, for example, glaserite, $K_3Na(SO_4)_2$ is observed in the solid products at

Silver Peak.

In the programme, precipitation is deemed to occur when the ion product is found to exceed the solubility product. When this occurs the total analytical concentration is decreased by a small increment. The program also makes allowance for the possibility of a solid redissolving. With these corrected values the solution equilibrium is again determined and the procedure is repeated until the solution equilibria and the solid-liquid equilibria are satisfied. At this point the next evaporation increment is considered. Refer to Table II-3 in Appendix II for solubility product data.

A flow chart of the above description is given in figure 4.1 and a computer listing for the Silver Peak Case is presented in Appendix IV.

FIGURE 4.1 GENERAL FLOWSHEET OF EQUILIBRIUM MODEL



CHAPTER 5

EXPERIMENTAL DETAILS

This chapter is concerned with the experimental confirmation of the model. Attempts at direct confirmation are impossible. It is not feasible to measure the species in solution in a quantitative manner at all. All that can be done experimentally is to measure the total analytical concentration in solution and hence determine the fraction of water evaporated before the commencement of precipitation.

This section of the thesis is brief due to the simple nature of the experimental work. As a result, the equipment used and procedure followed are presented in a brief manner. Some discussion of the analytical procedures is also made.

5.1 Experimental Equipment and Procedure

Equipment - The equipment used in this thesis consists of a flask immersed in a constant temperature bath. Air was bubbled into the flask in order to stir the mixture and aid evaporation. The solution volume was monitored by measuring the ullage.

Procedure - The starting point for the experimental work was a 50% water evaporated solution of synthetic Silver Peak Brine. The concentrations given in Table 2-5 of the Silver Peak Brine were doubled in order to represent the 50% water evaporated situation.

Two liters of the solution were prepared and agitated vigorously for 12 hours in a closed container. At this point a sample was taken, sample #1, and the flask was opened to the atmosphere to allow the solution to evaporate. The temperature bath was maintained at 40°C.

Samples of the solution were taken at approximately 24 hour intervals for the chemical analysis. The samples taken were immediately filtered in preheated glassware. Evaporation was continued to dryness at which point a sample of the precipitate was taken for solid identification via x-ray analysis.

5.2 Results

The results of the chemical analysis for this experiment are presented in Table 5-1 through Table 5-7. A discussion of the experimental results in comparison with the model predictions are made in Chapter 6, in particular, figures 6-1 through 6-7.

X-ray analysis of the solids was performed and positive

identification of NaCl, KCl, and $(K,Na)SO_4$ were made. It is possible that other mixed salts were present but these were not identified.

5.3 Analysis

The analysis procedure was as follows:

Na^+	Flame emission
K^+	Flame emission
Mg^{++}	Atomic Absorption Spectroscopy
Ca^{++}	Atomic Absorption Spectroscopy
Li^+	Atomic Absorption Spectroscopy
Cl^-	Mohr's method(50)
$SO_4^=$	Spectrophotometric technique

Flame emission and atomic absorption analysis were performed on a Perkin-Elmer Model 306 atomic absorption unit. $SO_4^=$ analysis was performed using the Sulver IV procedure of the HACH model DR-E42 portable laboratory. Mohr's(50) method for the determination of Cl^- is a titrametric procedure where the chlorides are precipitated as insoluable silver salts. The end point is indicated by the formation of Ag_2CrO_4, a dark colored insoluable salt.

5.3.1 Discussion of Analysis Procedures - Due to the high concentrations of the samples significant dilutions for

analysis were required. The samples for atomic absorption analysis, Mg^{++}, Ca^{++}, and Li^{+}, required on the average 1:2000 dilutions. The other ions Na^{+},K^{+}, $Cl^{-}$and $SO_4^{=}$ required dilutions ranging from 1:100 to 1:1000.

The analytical results for magnesium, lithium and potassium offer no definite trends but have still been included in the presentation of results, figure 6-1 through 6-7. The only explanation that can be offered for this randomness is the analytical technique itself along with the error introduced by the high dilutions. A detailed study of the matrix effects in high concentration multi-ion solutions of this type is required before any confidence can be expressed in the analytical results.

TABLE 5-1

EXPERIMENTAL RESULTS FOR POTASSIUM

	Concentration mg/l	Volume of liquor (ml)	Fraction water Evaporated	Mass Balance Total (mg)	Balance fraction
#1	14,000	2000	0.5	28,000	0.87
#2	15,000	--	--	--	--
#3	19,000	1834	0.54	34,846	1.08
#4	21,000	1607	0.60	33,747	1.05
#5	29,000	1260	0.69	36,540	1.14
#6	57,000	854	0.79	32,452	1.01
#7	57,000	706	0.83	40,242	--
#8	65,000	418	0.91	27,170	0.85

TABLE 5-2

EXPERIMENTAL RESULTS FOR MAGNESIUM

	Concentration mg/l	Volume of liquor (ml)	Fraction water Evaporated	Mass Total (mg)	Balance fraction
#1	720	2000	0.5	1440	1.00
#2	480	--	--	--	--
#3	650	1834	0.54	1192	0.83
#4	740	1607	0.60	1189	0.83
#5	890	1260	0.69	1122	0.78
#6	1200	854	0.79	1024	0.71
#7	1700	706	0.83	1200	0.83
#8	3400	418	0.91	1421	0.99

TABLE 5-3

EXPERIMENTAL RESULTS FOR CALCIUM

	Concentration mg/l	Volume of liquor (ml)	Fraction water Evaporated	Mass Total (mg)	Balance fraction
#1	1300	2000	0.5	2600	1.0
#2	1000	--	--	--	--
#3	1100	1834	0.54	2017	0.78
#4	1100	1607	0.60	1767	0.68
#5	1100	1260	0.69	1386	0.53
#6	1000	854	0.79	854	0.33
#7	570	706	0.83	402	0.15
#8	500	418	0.91	209	0.08

TABLE 5-4

EXPERIMENTAL RESULTS FOR LITHIUM

	Concentration mg/l	Volume of liquor (ml)	Fraction water Evaporated	Mass Balance Total (mg)	Fraction
#1	700	2000	0.5	1400	0.81
#2	800	--	--	--	--
#3	1100	1834	0.54	2017	1.16
#4	1100	1607	0.60	1767	1.02
#5	1400	1260	0.69	1764	1.02
#6	2000	854	0.79	1708	0.98
#7	3100	706	0.83	2188	1.26
#8	5800	418	0.91	2424	1.40

TABLE 5-5

EXPERIMENTAL RESULTS FOR SODIUM

	Concentration mg/l	Volume of liquor (ml)	Fraction water Evaporated	Mass Total (mg)	Balance Fraction
#1	100,000	2000	0.5	200,000	0.82
#2	130,000	--	--	--	--
#3	160,000	1834	0.54	293,440	1.20
#4	150,000	1607	0.60	241,050	0.99
#5	130,000	1260	0.69	163,800	0.67
#6	120,000	854	0.79	102,480	0.42
#7	91,000	706	0.83	64,246	0.26
#8	89,000	418	0.91	37,202	0.15

TABLE 5-6

EXPERIMENTAL RESULTS FOR CHLORIDES

	Concentration moles/liter	Volume of liquor (ml)	Fraction water Evaporated	Mass Balance Total moles	Fraction
#1	5.0	2000	0.5	10.00	0.99
#2	5.5	--	--	--	--
#3	5.6	1834	0.54	10.27	1.01
#4	5.4	1607	0.60	8.68	0.86
#5	5.3	1260	0.69	6.68	0.66
#6	5.4	854	0.79	4.61	0.45
#7	10.9	706	0.83	--	--
#8	5.4	418	0.91	2.26	0.22

TABLE 5-7

EXPERIMENTAL RESULTS FOR SULFATE

	Concentration mg/l	Volume of liquor (ml)	Fraction water Evaporated	Mass Balance Total (mg)	Fraction
#1	1850	2000	0.5	3700	1.0
#2	1900	--	--	--	--
#3	2000	1834	0.54	3680	0.99
#4	1900	1607	0.60	3053	0.83
#5	1950	1260	0.69	2457	0.66
#6	2050	854	0.79	1750	0.47
#7	2100	706	0.83	1482	0.40
#8	2100	418	0.91	877	0.24

CHAPTER 6

MODEL APPLICATION TO SILVER PEAK BRINE

This chapter is concerned with the specific case of the Silver Peak Brine. The assumptions involved in applying the model are discussed along with the values predicted by the model. Some discussion of experimental values is also included although the presentation of the experimental results is made in Chapter 5.

6.1 Details of the Calculation Procedures

This section is divided into two parts, (1) Species Determination and Equilibrium constants and (2) Activity coefficients.

6.1.1 Species Determination and Equilibrium Constants - An analysis of a typical well brine[12] was used as the starting point in determining the possible species that were to be considered. The tableau approach was again used here, as presented in Table 6-7, because in this way such a presentation has a pedagogic and practiacl value in pointing out the possible complex formations. In this case the primary metal variables, Na^+, K^+, Mg^{++}, Li^+,

Ca^{++}, H^+ and ligands, $SO_4^=$, Cl^-, and OH^- are considered. Reference was made to the appendices of Garrels and Christ[36] in determining these species.

For the H^+ and $SO_4^=$ combination two species are feasible, HSO_4^-aq., and $H_2SO_4^0$aq.. Examination of the equilibrium constants at 40°C:

$$HSO_4^- = H^+ + SO_4^= \qquad \log_{10}k = -1.815 \qquad 6.1$$

$$H_2SO_4^0 = H^+ + HSO_4^- \qquad \log_{10}k = 1.815 \qquad 6.2$$

leads to the conclusion that $H_2SO_4^0$aq. will be small relative to HSO_4^- due to the higher dissociation constant associated with the second equilibria, equation 6.2. Hence only HSO_4^- aq. is considered in the program.

The equilibrium constants determined for the species in Table 5-1 were calculated from ΔG_f^0 data and the equation:

$$-RT\ln K_T = \Sigma \nu_i \mu_i^0 = \Delta G_T^0 \qquad 6.3$$

The values of ΔG_f^0 came from several sources, these sources along with the values are detailed in Table II-5 of Appendix II. For calculation purposes a temperature of 40°C was chosen. Experimental studies were also performed at this temperature.

In Pancharatnam's[8] model of solar pond evaporation rates he presents typical values for brine temperatures

TABLE 6-1

SPECIES CONSIDERATION IN SILVER PEAK BRINE

	$SO_4^=$	Cl^-	OH^-
Na^+	$NaSO_4^-$ aq.	$NaCl^0$	$NaOH^0$
K^+	KSO_4^- aq.	KCl	KOH
Mg^{++}	$MgSO_4^0$	--	$MgOH^+$
Li^+	$Li_2SO_4^0$	$LiCl^0$	$LiOH^0$
Ca^{++}	$CaSO_4^0$	--	$CaOH^+$
H^+	HSO_4^- aq.	HCl	Water

and evaporation rates under meteorological conditions similar to those occuring during a tropical summer. His brine temperatures range from 78 to 92°F and air temperatures from 78 to 90°F over a typical day. Hence the temperature of 40°C (94°F) chosen for calculation purposes is on the high side for a solar pond operation. However in the southwest U.S. during summer air temperatures of 37°C (100°F) are not uncommon. So it is not unreasonable to assume that liquid temperatues could approach 40°C.

6.1.2 Activity Coefficients - As was previously discussed in Chapter 4 the mass balance and dissociation constants are required in order to calculate the species distribution. However to use these thermodynamic expressions the activity coefficients are required in order to convert molalities to activities. Hence the activity of the neutral species $CaSO_4^0$, $MgSO_4^0$, the charged species $MgOH^+$, $NaSO_4^-$ and for the various ions Na^+,K^+, Cl^-etc. are required. The activities of free ions are calculated via the procedure outlined in Chapter 4. The complex species cause additional problems for activity coefficient determination and the discussion following outlines the assumptions used in this thesis.

Uncharged Species - Reliable information on the activity coefficients of neutral ion pairs such as $CaSO_4^0$, $MgSO_4^0$ is not available.(36)

However the values that are presented in the literature are somewhat controversial because it is not possible to put accurate limits of error on these numbers. The values presented are as follows; Garrels and Thomson(51) used 1.13 and it has been suggested by other authors(36) that the correct value is 1.0 or a few percent less. Therefore it seems best simply to assume activity coefficients of unity for these species. In view of the various uncertainties entering the calculations in which these activity coefficients are used, this assumption probably does not greatly affect the final results.

Charged Species - Calculations of individual ion activity coefficients has been discussed in Chapter 4. Garrels and Christ(36) argue that the activity coefficients of charged species such as KSO_4^- and $NaSO_4^-$ can be considered the same as HCO_3^-. They argue that similar activity coefficients would be expected for all singly charged species of about the same size. This assumption is also made in this thesis.

Experimental values of $\gamma_{HCO_3^-}$ have been presented by Walker et al(47). It is from this work that the value 0.68

was chosen for the charged species. The observed changes in activity coefficient as a funciton of ionic strength are small at ionic strengths in the range of this thesis, 3.9 to 6.0m. The curves presented by Walker et al[47] are based on their experimental work in the range 0.01 to 3.0m. Extrapolation of these curves to 6.0m is still consistent with the form of the theoretical curves presented by Garrels and Christ[36].

Individual Ions - The mean salt method was applied in order that individual activity coefficients could be determined. The assumption that $\gamma^+ = \gamma^-$ for KCl, as discussed in Chapter 3, was made in order to determine the free ion activity coefficients. The bridge salts and associated equations are detailed in Appendix III.

Water - The activity coefficient of water was assumed to be one for this thesis. This is clearly not correct as is evidenced by the work of Robinson and Stokes[28] where they present plots of activity of water versus concentration for various electrolytes. Meissner and Kusik[32] discuss a method for determining vapour pressure of water over aqueous solutions containing more than one strong electrolyte. Knowing the vapour pressure of water the activity can, as a consequence, be determined.

This method could be applied in this thesis to allow

TABLE 6-2

ACTIVITY COEFFICIENTS OF SPECIES

Dissolved Species		Activity Coefficient
$NaSO_4^-$	(1,1)*	0.68
$NaCl^0$	(1,2)	1.00
$NaOH^0$	(1,3)	1.00
KSO_4^-	(2,1)	0.68
KCl^0	(2,2)	1.00
KOH^0	(2,3)	1.00
$Li_2SO_4^0$	(4,1)	1.00
$LiCl^0$	(4,2)	1.00
$LiOH^0$	(4,3)	1.00
$CaSO_4^0$	(5,1)	1.00
$CaOH^+$	(5,3)	0.68
HSO_4^-	(6,1)	0.68
HCl^0	(6,2)	1.00
$MgSO_4^0$	(3,1)	1.00
Mg(OH+)	(3,3)	0.68
H_2O	(6,3)	1.00

* Matrix identifiers to be used in conjunction with Appendix III.

for changes in activity coefficient as a function of ionic strength but at this stage is only considered for future work.

Table 6-2 summarizes the values chosen for activity coefficients in the above discussion.

6.2 Discussion of Simulation using the Program

Two simulations were performed for the examination of the Silver Peak Brine. The first case included the species $NaCl^0$, and the second case did not. There is some doubt expressed in the literature as to the existence of the $NaCl^0$ species. Garrels and Christ[36] in their seawater model ignore any Na^+ and Cl^- ion associations, however, a dissociation constant is presented by Rosini, Wagman, and Evans[49].

For the case where no $NaCl^0$ species was considered the program predicted NaCl precipitaition at 0.60 fraction evaporated and this compares favorably with the experimental results. Refer to figure 6.1 and 6.2. For the $NaCl^0$ species case the program predicts no precipitation until over 90% of the water has evaporated and then the first salt to precipitate is Na_2SO_4 followed by KCl. However NaCl does not precipate until later since Na^+ and Cl^- ions are tied up as $NaCl^0$.

As a result more consistent results, as compared with

experimental observation, were obtained for the no $NaCl^0$ species assumption. The figures and discussion presented in this chapter are therefore all based on the predictions of the no $NaCl^0$ case.

6.2.1 Species Distribution - Using the program listed in Appendix IV, the species distribution and activity coefficients were calculated at extents of evaporation in the range 0 - 60%. The results are plotted in figures 6-7 to 6-13 and the computer printout from which these data are plotted is presented in Appendix V.

The Newton-Raphson solution in the program requires an initial guess close to the solution before it will converge. An initial guess is made at the beginning of the programme and for subsequent evaporation steps the solution for the previous increment is used as the first guess. Above a fraction evaporated of 0.6 the program fails to converge. This is due to the fact that previous increment guesses are no longer valid because of the large changes in solution composition above fraction evaporated of 0.6. A decrease in increment value offered no relief as the problem again occured at slightly higher concentrations. The main reason for this behavior is attributed to the increasing activity coefficients as a function of ionic strength. Note in figures 6-8 to 6-11

the increasing slope as a function of increasing ionic strength.

The most striking feature of the computer analysis is the extent to which the cation Li^+ is complexed relative to the other cations, in particular the more numerous Na^+, refer to figure 6-13. In figure 6-14 a plot of concentrations of species are presented as a function of ionic strength (extent of evaporation) and from here it would appear that most of the Li^+ ion exists as the complex LiCl.

6.2.2 Activity Coefficients - There is no way of checking the predicted species nor the correctness of the activity values. However comparison with curves produced in the literature, of single ion activity coefficients versus ionic strength, for example Garrels and Christ[36] can be made. These plots are determined by the mean salt method and although they do not take into account the various ion -ion interactions, for example Na^+-Mg^{++}, etc, the general form is consistent with the values predicted in this work. A physical explanation of the consistency of these results can also be made.

At low concentrations, <~0.01M, the Debye-Hückel theory adequately explains activities as a function of ionic stremgth. With this theory the activities decrease as a

function of ionic strength due to the increasing interionic forces. However, the Debye-Hückel theory ignores the withdrawal of solvent from solution (solvation) as the electrolyte concentration increases. Hence as a function of increasing ionic strength the activity decreases due to increasing interionic forces and the solvation increases. Therefore, a plot of activity coefficient versus ionic strength should pass through a minimum and then start to rise as is experimentally observed. Since the work in this thesis is at such a high ionic strength, 3-6m, the increasing section of the curve discussed above is the only section observed, refer to figures 6-7 to 6-10. For the $SO_4^=$ situation the minimum has yet to be reached (figure 6-12).

6.2.3 Formation of Carbonates - No allowance for the formation of carbonates was made in this thesis. However, the Silver Peak operation[12] reports that most of the calcium precipitates in the ponds due to the adsorption of CO_2. Experimental work in this thesis indicated precipitataion of calcium began at a fraction evaporated of 0.5 (refer to Figure 6-3). However no calcium carbonate was observed in the x-ray study. It is possible that some mixed salt, for example ($(Na,Ca)CO_3$) formed. A future modification to the program would be to include gas/solid equilibria and

the accompanying carbonate chemistry. The appropriate set of equations would comprise an additional three considerations; hydration equilibria of CO_2 ($H_2CO_3 = CO_2(aq) + H_2O$) and the first and second equilibrium constants of H_2CO_3, that is the equilibria containing H^+ and HCO_3^- respectfully.

6.2.4 Comparison with Silver Peak - The only information available from the Silver Peak Pond system is the value of the extent of evaporation at which the various salts begin to precipitate. This point of precipitation is indicated on figures 6.1 to 6.7. The agreement between the point of precipiation for the Silver Peak operation and the model is not as good as the experimental work and the model.

The difference could be explained by the presence of other ions in the brine that were not reported in the brine analysis given by the Silver Peak Operation. Another explanation could be the shortcomings of the model itself. For example, the activity coefficients predicted by the model may not be representative of the actual situation.

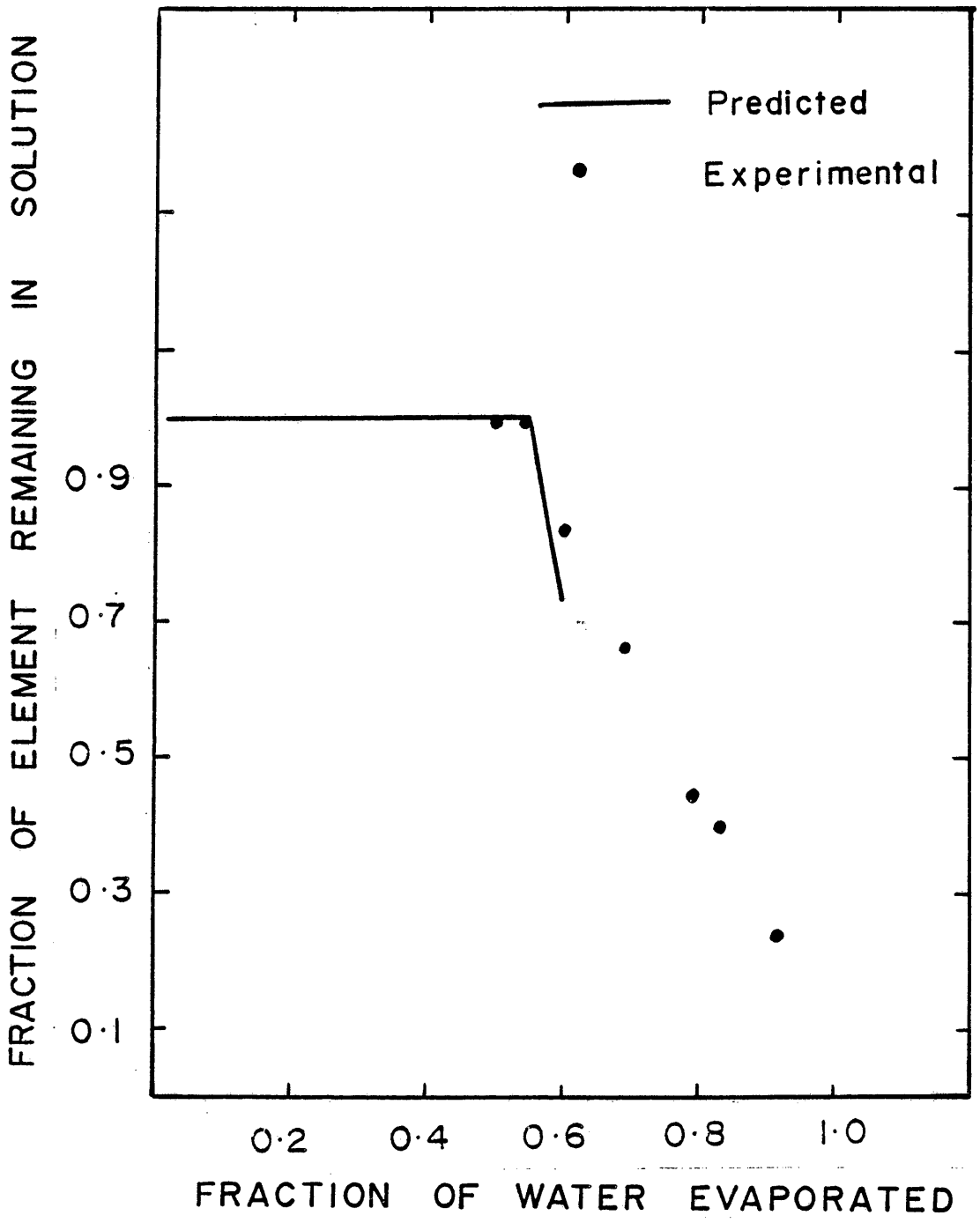


Figure 6.1 Comparison of Experimental with Predicted Value in Solution for Chlorides

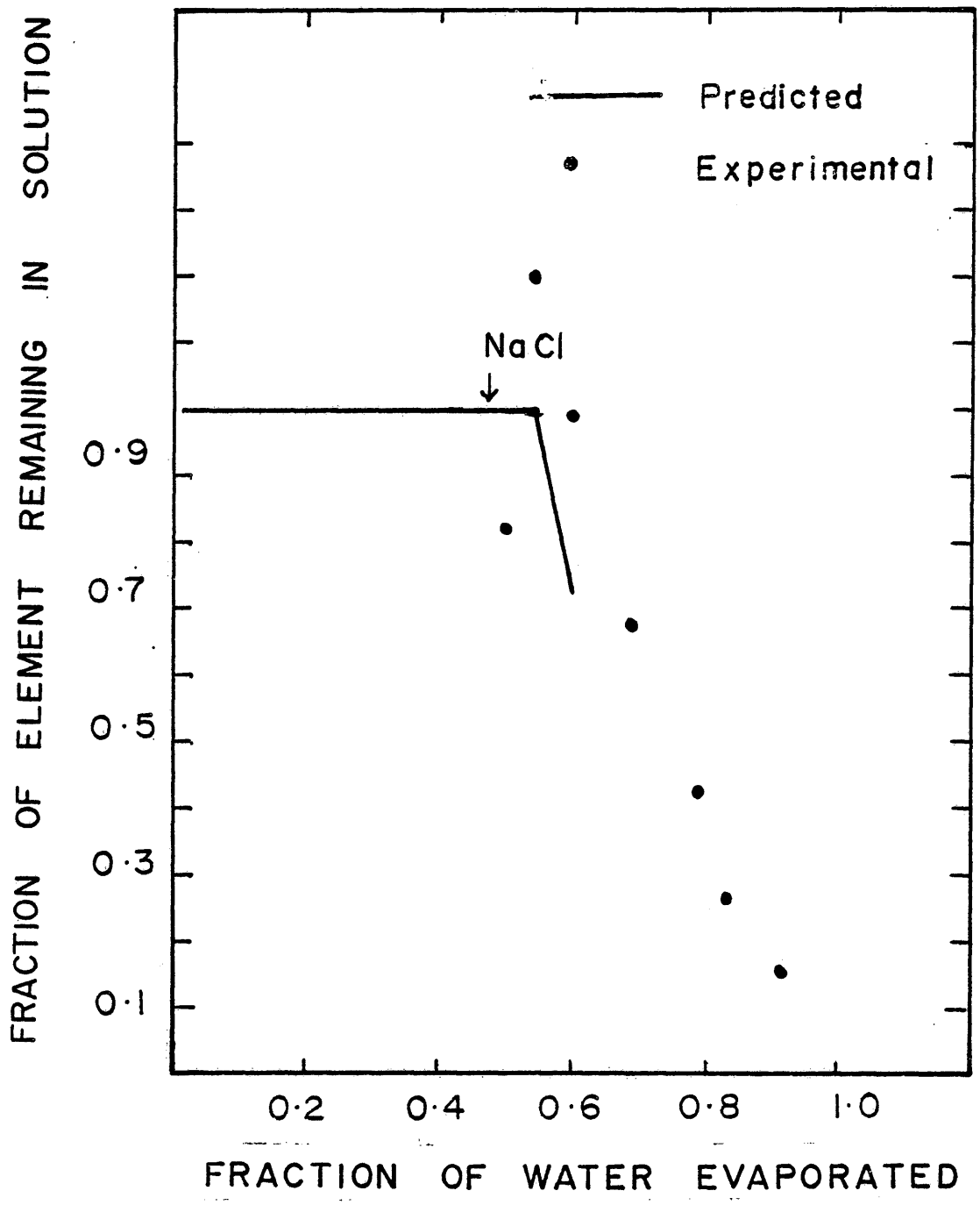


Figure 6.2 Comparison of Experimental with Predicted Value in solution for Sodium

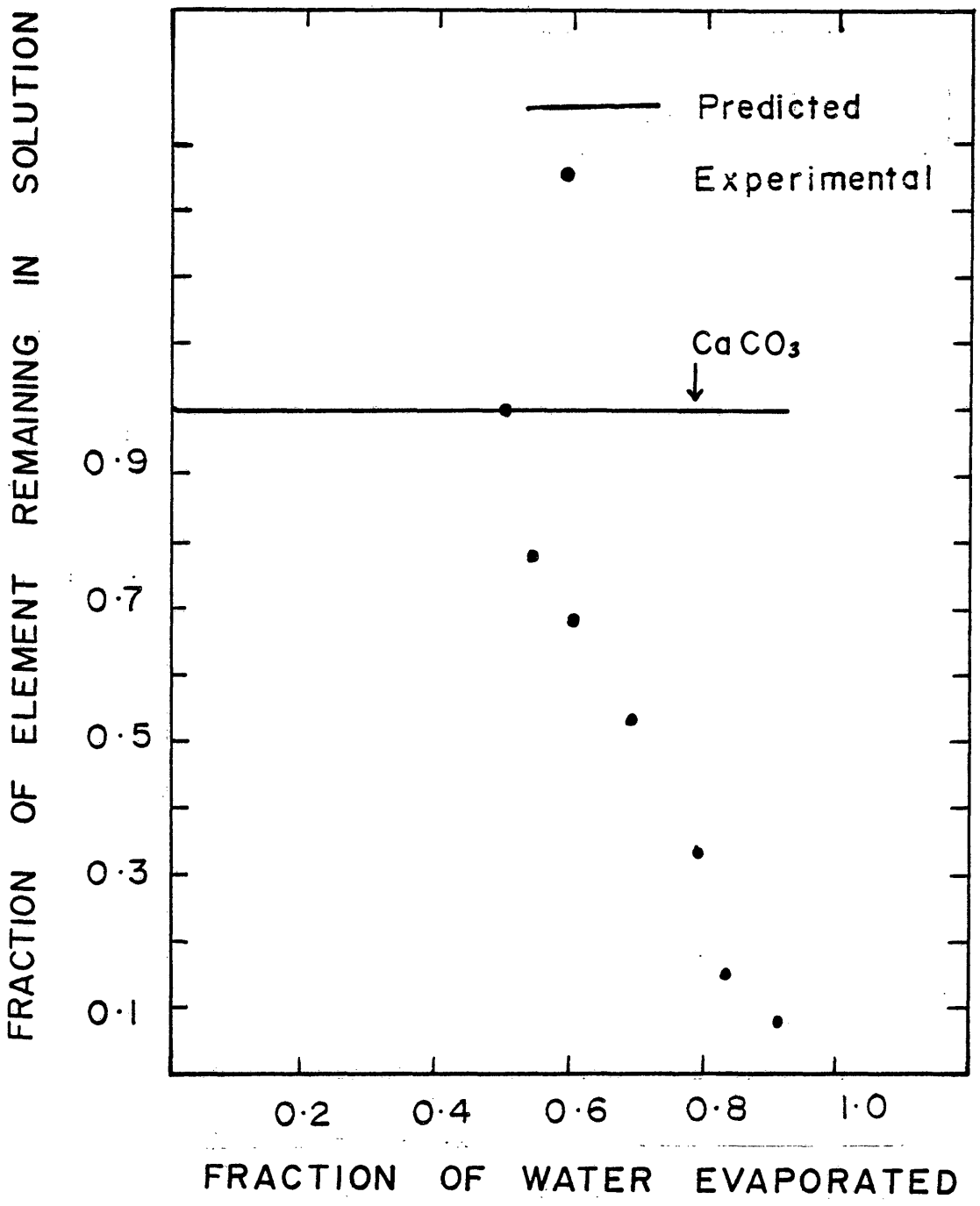


Figure 6.3 Comparison of Experimental with Predicted Value in solution for Calcium

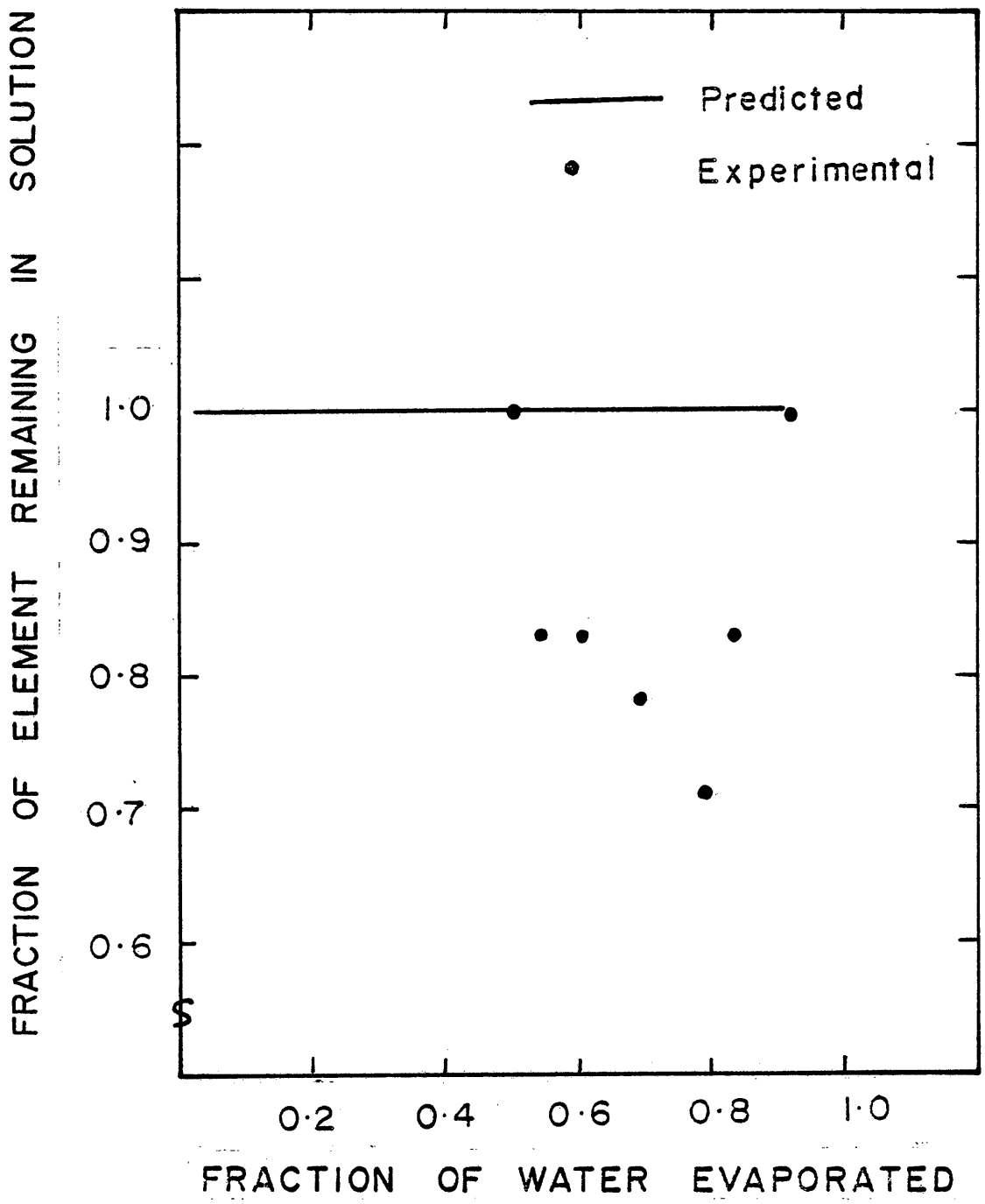


Figure 6.4 Comparison of Experimental with Predicted Value in solution for Magnesium

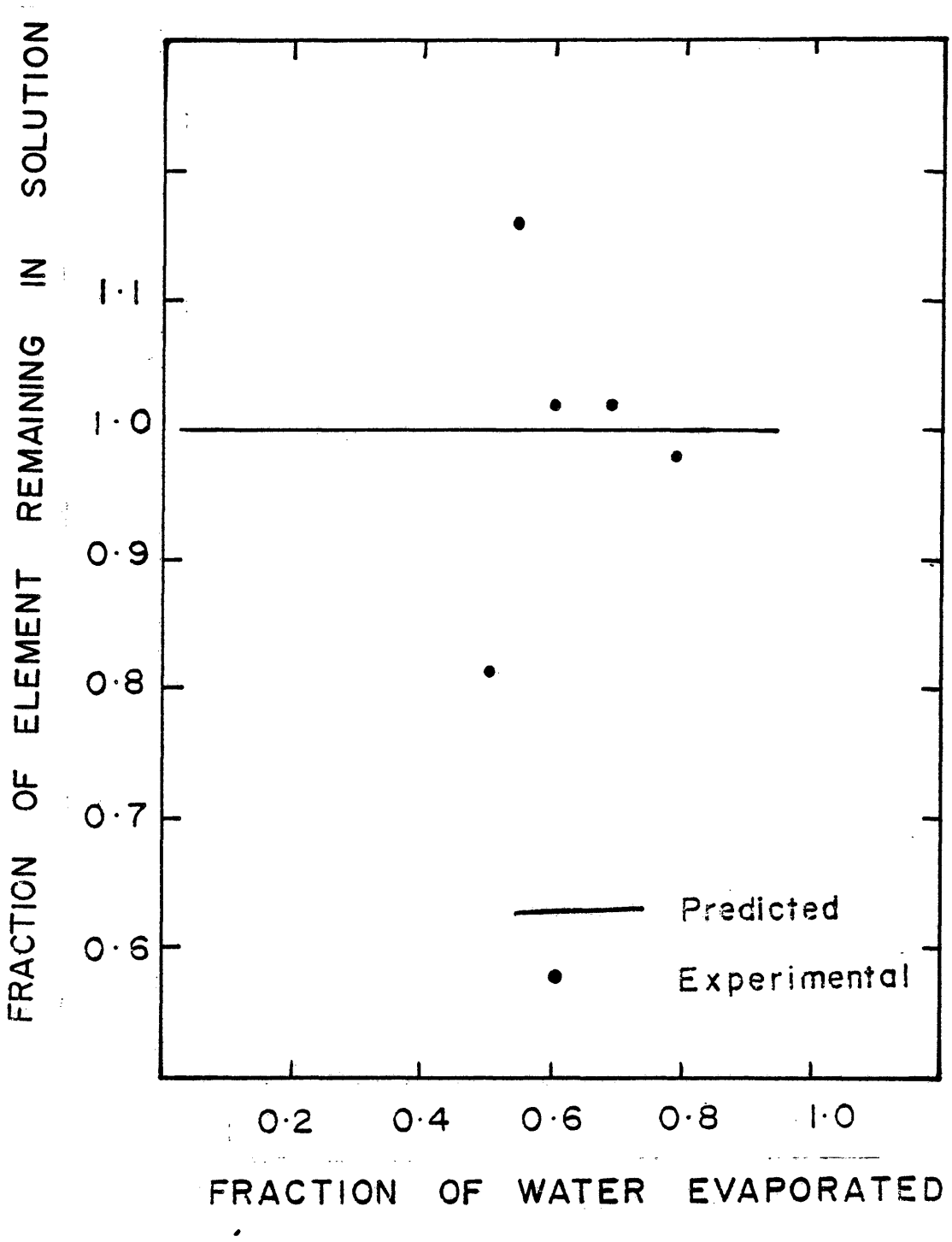


Figure 6.5 Comparison of Experimental with Predicted Value in solution for Lithium

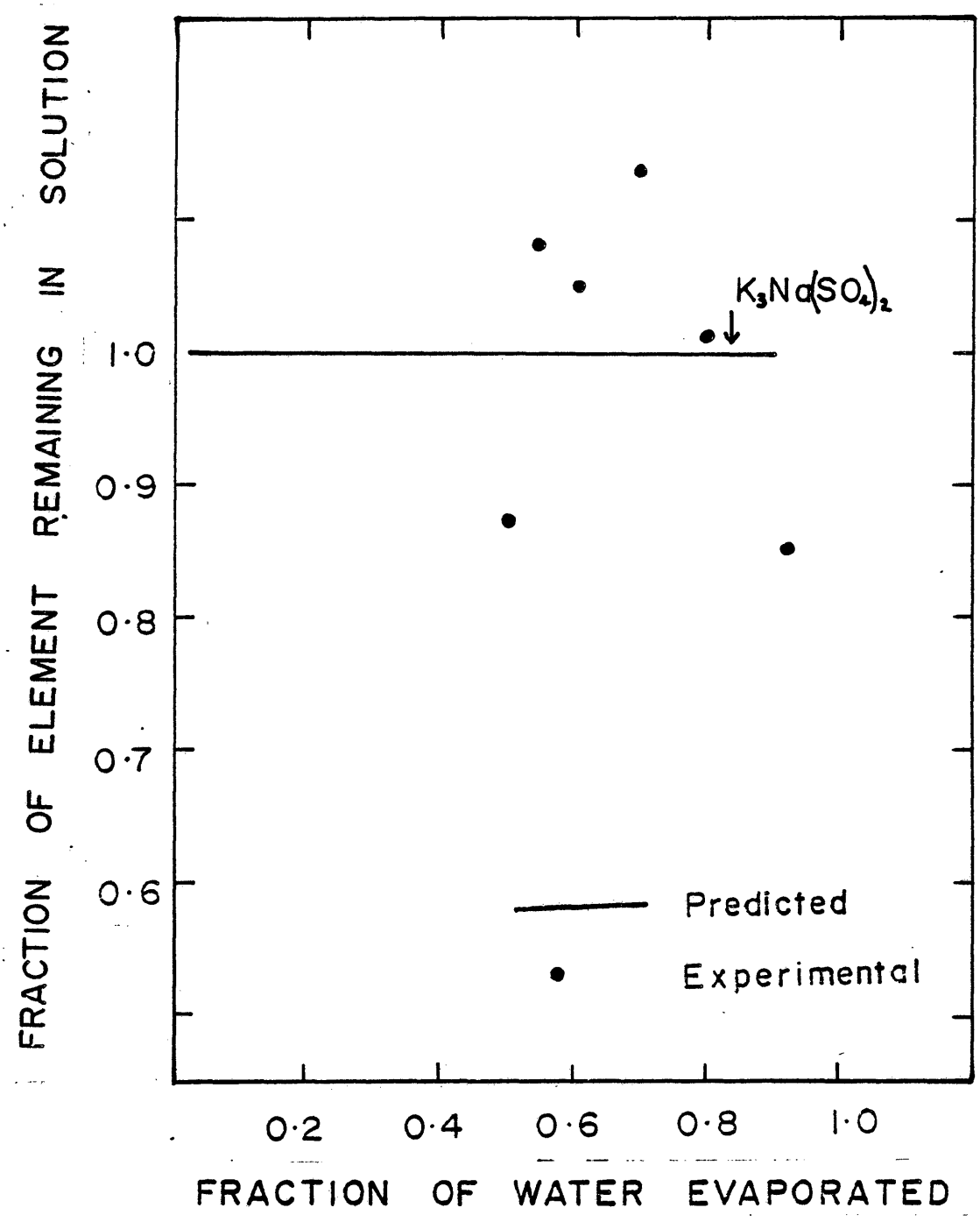


Figure 6.6 Comparison of Experimental with Predicted Value in solution for Potassium

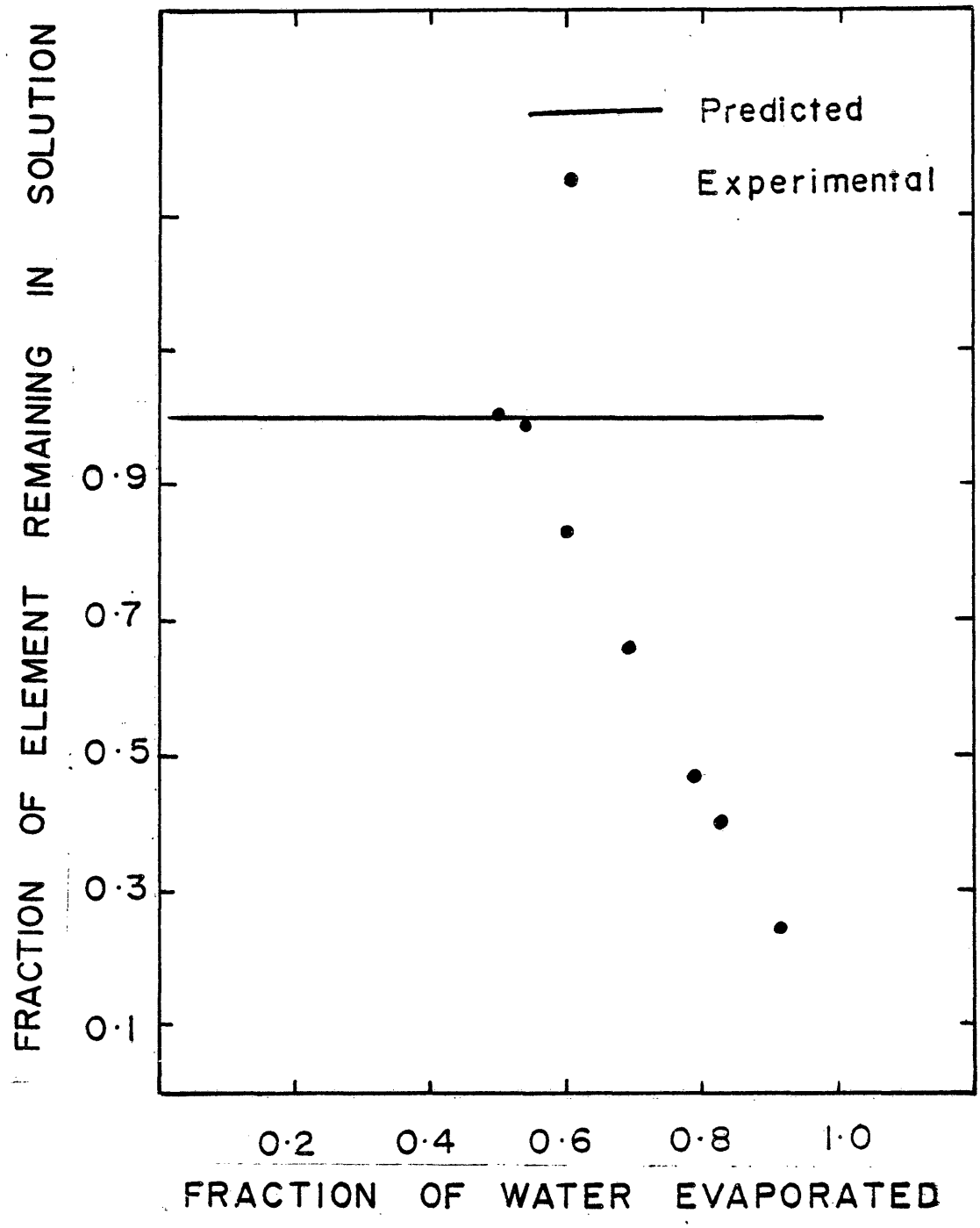


Figure 6.7 Comparison of Experimental with Predicted Value in solution for Sulfates

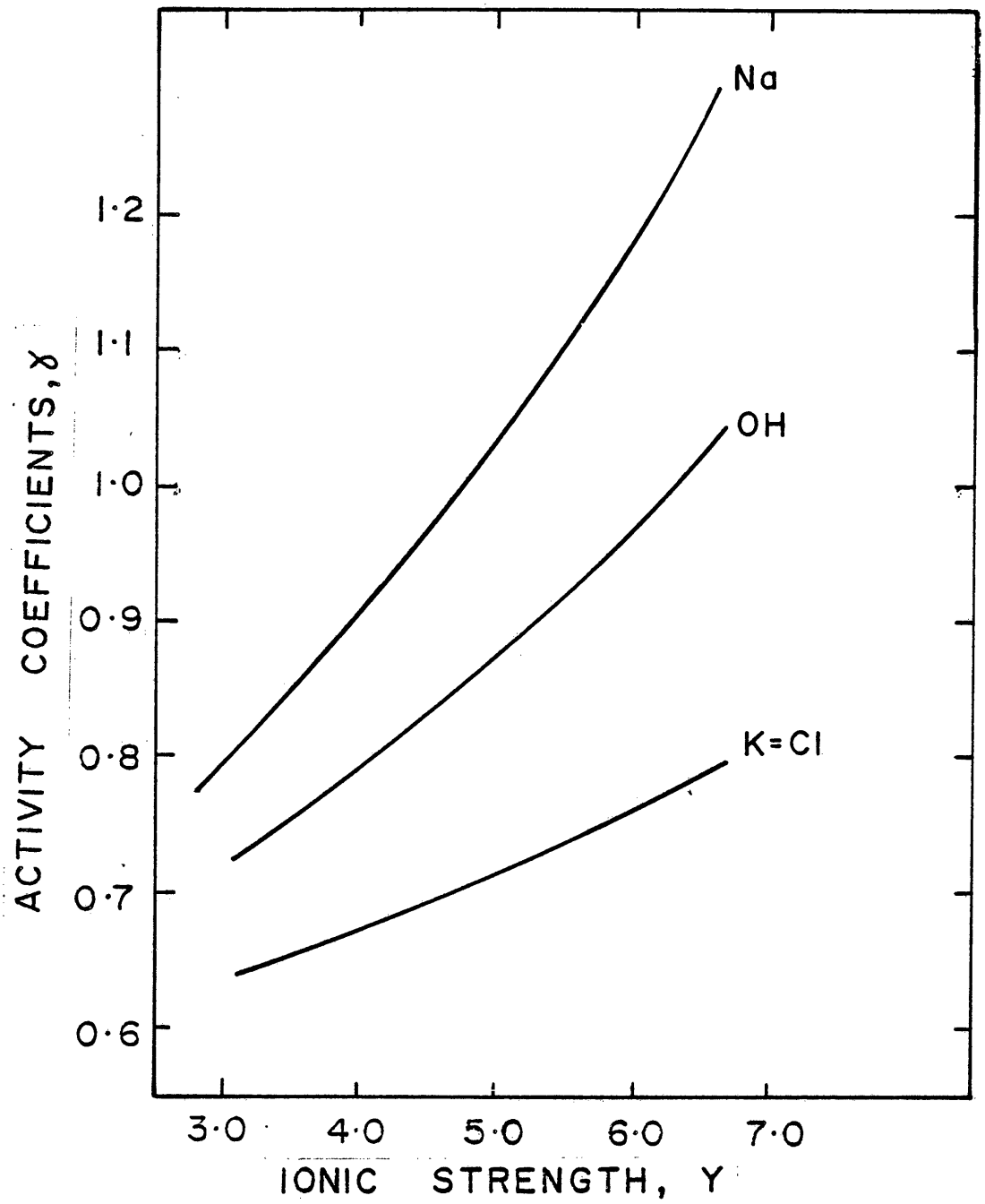


Figure 6.8 Predicted values of Activity Coefficient as a function of Ionic Strength, Na^+, OH^-, K^+, and Cl^-

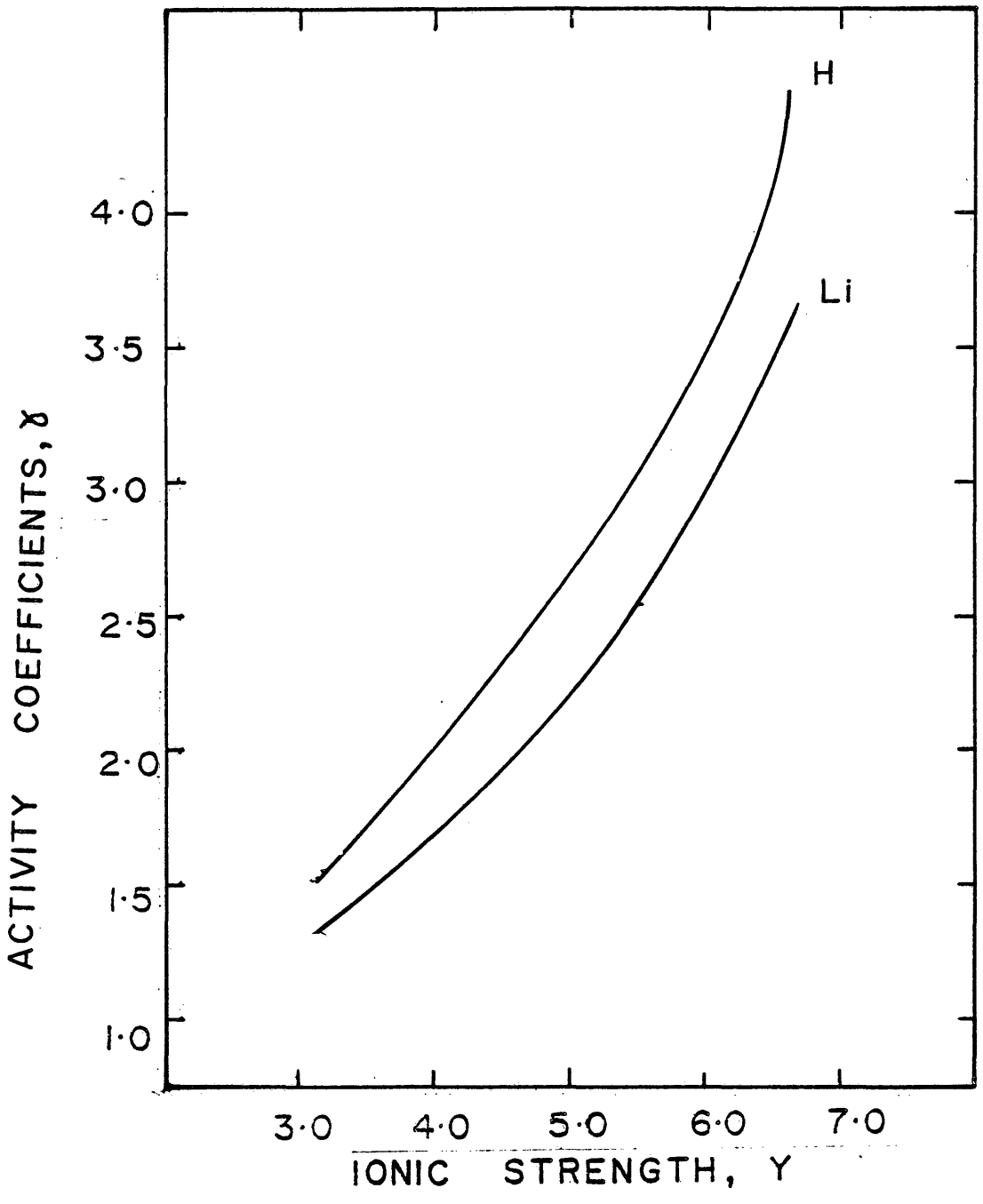


Figure 6.9 Predicted Values of Activity Coefficient as a Function of Ionic Strength, H^+ and Li^+

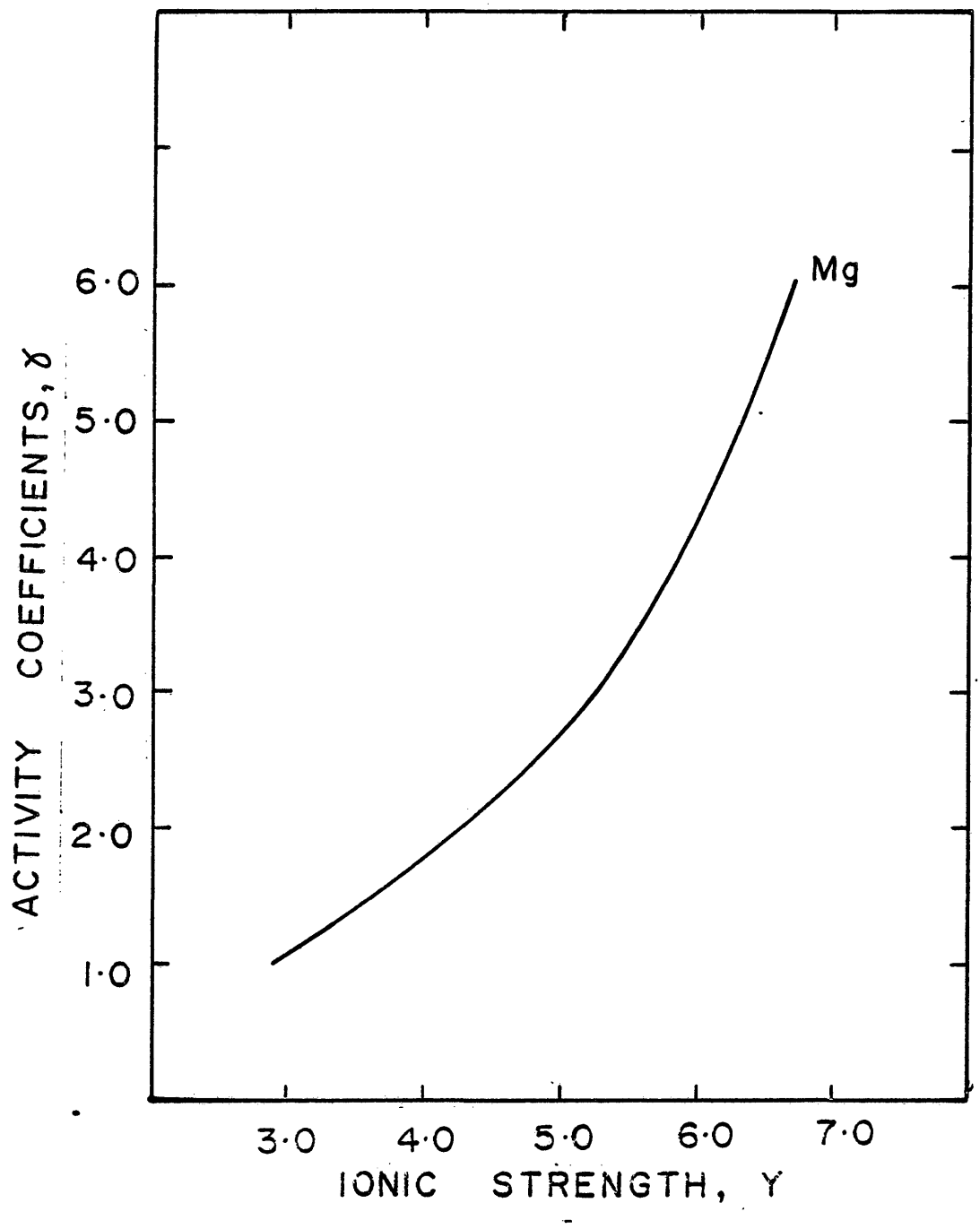


Figure 6.10 Predicted Values of Activity Coefficient as a Function of Ionic Strength, Mg^{++}

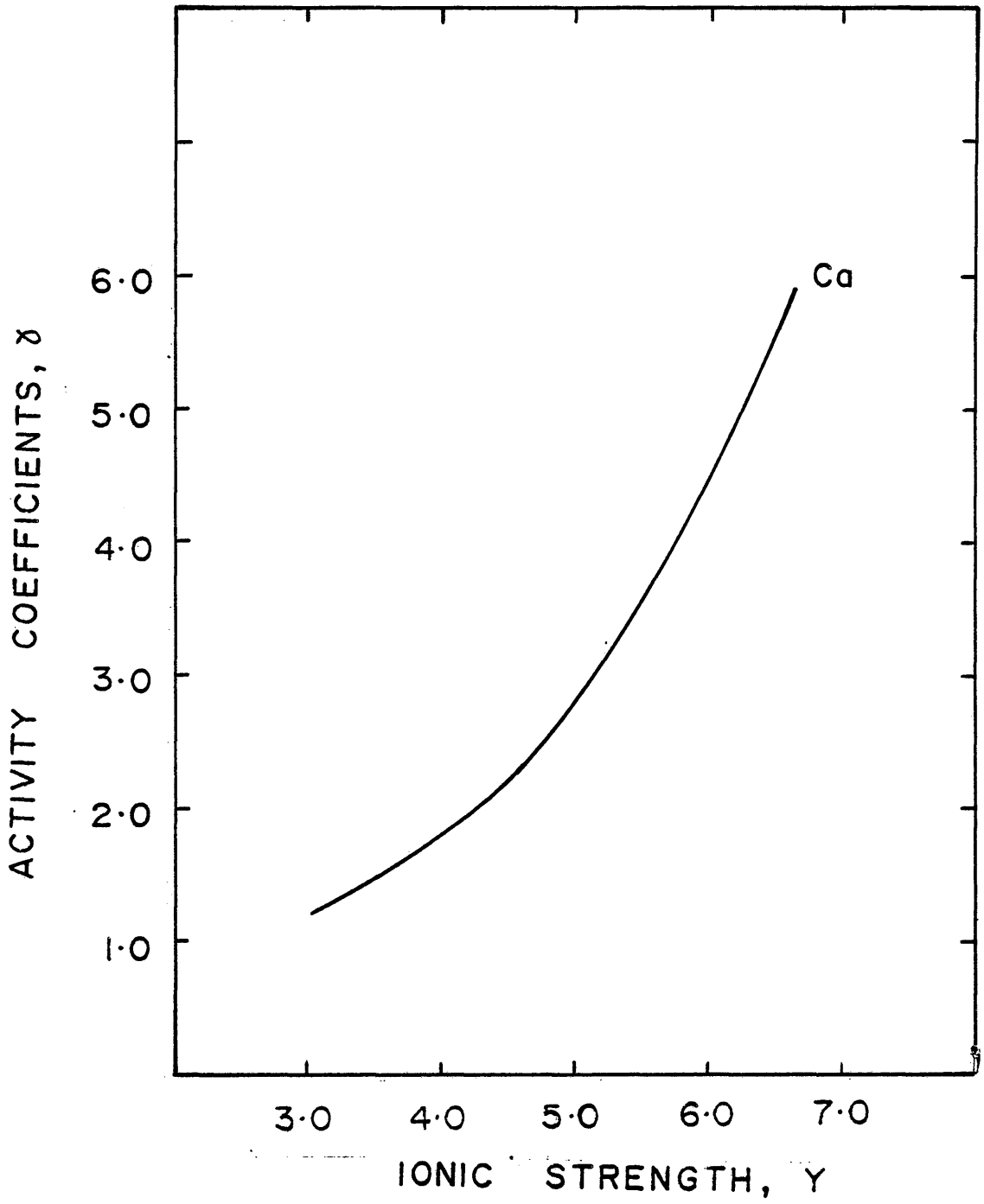


Figure 6.11 Predicted values of Activity Coefficient as a Function of Ionic Strength, Ca^{++}

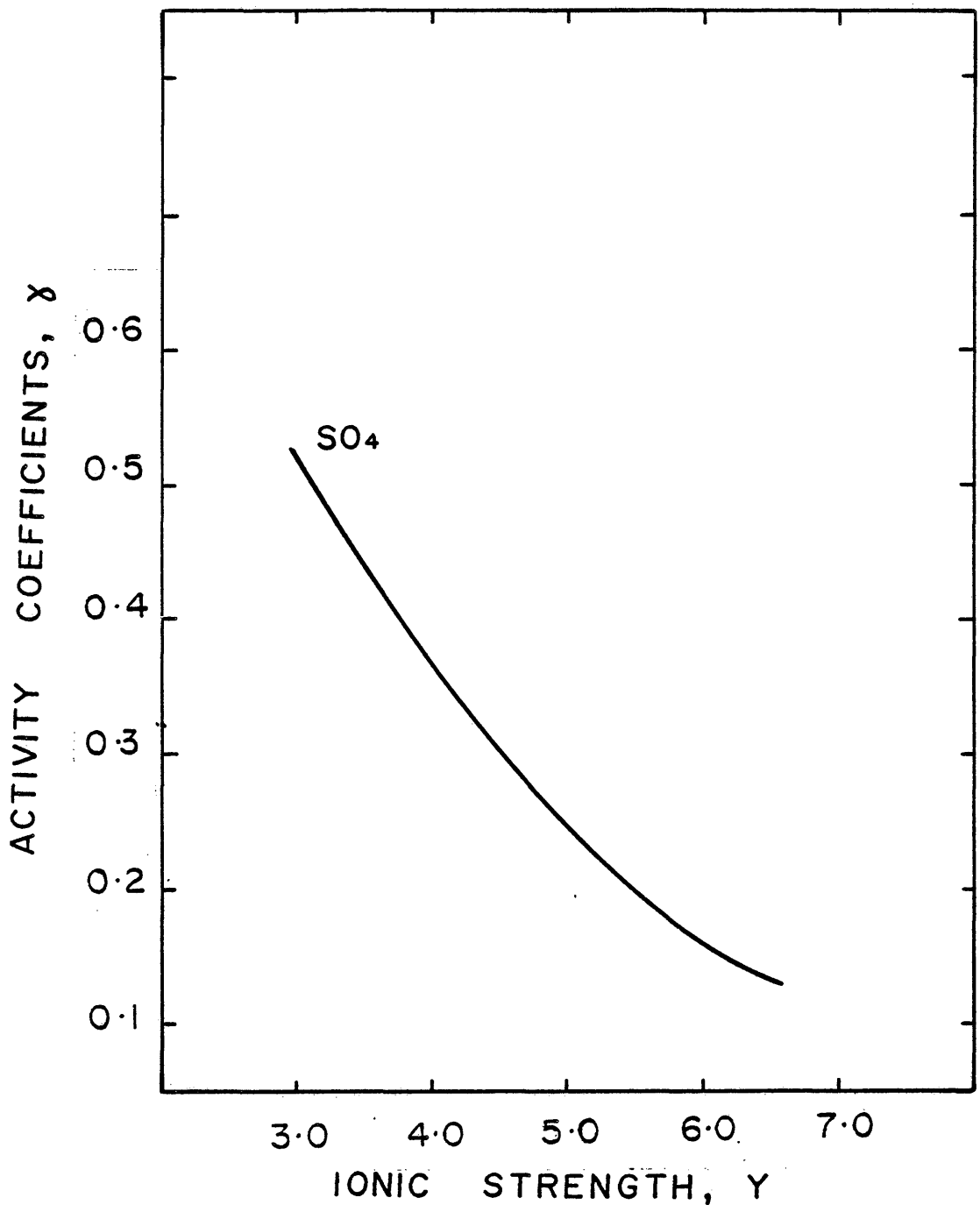


Figure 6.12 Predicted Values of Activity Coefficient as a Function of Ionic Strength, $SO_4^=$

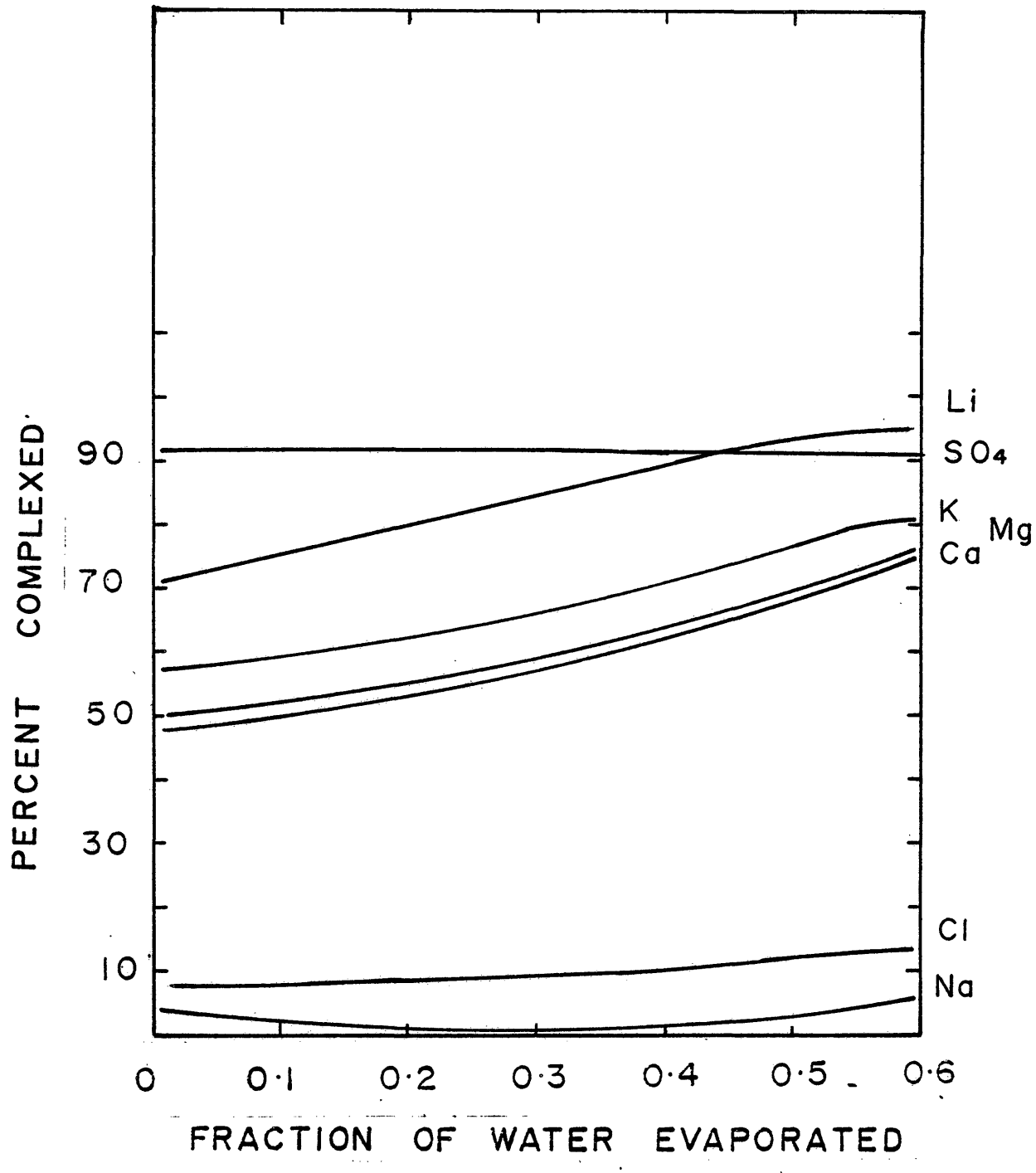


Figure 6.13 Percent Complexed versus Fraction Water Evaporated based on Predicted Values

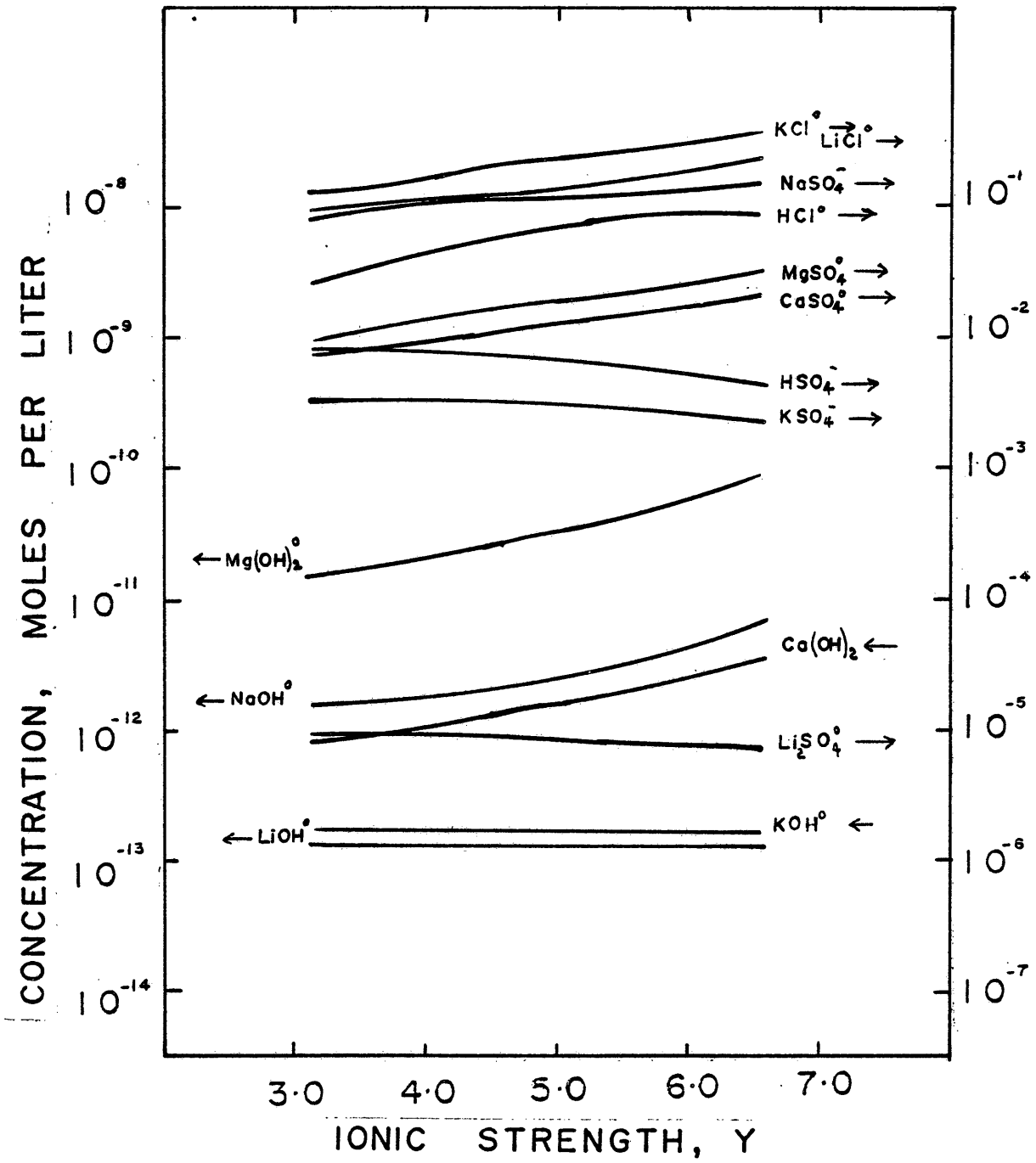


Figure 6.14 Species Concentration as a Function of Ionic Strength

CHAPTER 7

CONCLUSION

A final overall discussion of this study and the conclusions drawn are presented in this final chapter.

7.1 Discussion and Conclusions

The discussion and conclusions presented in this section are enumerated according to the aims of the study as outlined in the Introduction.

1) 'A review of the lithium industry was made and it was concluded that there was significant potential for future lithium demand. In the short term the demand for lithium will be for use in the lithium battery and in the longer term, for use in fusion power.

A review of the brine resources available indicate the existence of extensive deposits but no literature concerned with the extraction of lithium from these resources is available. The industry recognizes the availability of the new resources, brines compared to pegmatites etc, but little development work in lithium extraction from these resources is being attempted.

2) A review of the possibility of extraction of lithium from seawater and low grade brines using ion exchange was made. Little information pertaining to lithium extraction from brines appears in the literature, therefore most of the information was obtained from the resin manufacturers and water treatment companies. It was concluded that the extraction of low values of lithium from massive amounts of other cations is an extremely difficult undertaking. It is therefore unlikely that a straight cation process can be used for lithium recovery due to the low selectivity of ion exchange resins for lithium and the high concentrations of other cations.

3) An equilibria model for a brine was successfully developed based on the solution theory of Meissner et al[31-33]. The model takes into consideration the effects of high ionic strength, equilibria and solubility product. A dynamic representation of extent of evaporation is included by making step decreases in solution volume and adjusting the concentrations accordingly.

The model was used to give an indication of the extent of complexation as the solution evaporated and also to predict the onset of precipitation. This objective was achieved, however the program does not have the capability

to determine the equilibria above an ionic strength of 6. This problem is due to the rapidly changing solution concentrations at high ionic strength and the inability of the Newton-Raphson technique to converge unless the initial guess is close to the problem solution.

In summary, it can be concluded from the review on ion exchange separation in Chapter 2 that some form of pre-concentration step is required before lithium can be separated from the other cations. It is envisaged that a model of this type could be applied to any brine as a means of predicting at least the limits of the various salt precipiiations.

Experimental work is still required to determine if Li can be separated from the concentrated mix. The predicted high degree of complexation of lithium in such a mix could be a means of aiding this separation. This can only be confirmed by experimental work involving concentrated solutions and ion exchange resins.

7.1.1 Additional Conclusions - The following conclusions are made in addition to the original aims of the thesis as expressed in Chapter 1.

1) The predictions of the model were more consistent with experimental observation when the $NaCl^0$ species was ignored. There is some doubt expressed in the literature as to the

existence of the $NaCl^0$ species. The work of this thesis would also indicate that the $NaCl^0$ species is not important.

2) The Silver Peak Operation reports the precipitation of Ca as $CaCO_3$. The experimental work of this thesis did indicate the removal of Ca from solution but no direct evidence of $CaCO_3$ precipitation was found. It is postulated that the calcium precipitates as some mixed salt, for example $((Na,Ca)CO_3)$.

3) The model predicts the equilibrium H^+ concentration to range from 1.02×10^{-2} mole/liter to 1.81×10^{-3} mole/liter. The pH of such a solution, calculated form $pH = -\log_{10} a_{H^+}$ ranges from 1.82 to 2.09 whereas the information from the Silver Peak operation is for a pH of 6.9. No explanation can be offered for this large difference other than the possibility of error in the models prediction due to the low concentration of H^+ compared to other ions, for example $H^+ = 1 \times 10^{-7}$ mole/liter and Na^+ = 3 mole/liter.

7.2 Recomendations for Further Work

1) Extend the present model to include adsorption from a gas phase. In particular the inclusion of adsorption

of CO_2 and the associated carbonate chemistry.

2) Extend the present model to include the variation in the activity of water as a function of ionic strength.

3) To now pursue an investigation of the ion exchange resins available as a means of lithium extraction, knowing the types of feed solution after preconcentration that could be available.

APPENDIX I

DERIVITIVE OF THE GENERAL BALANCE EQUATIONS

Mass Balances

$$\text{Let } YM_i = \left(M_i\right) + \sum_{j,k}^{*} \alpha \left(C_{ijk}\right) - \text{Tot } M_i \quad (= 0 \text{ from Eq 4.3})$$

$$YM_i = \left(L_j\right) + \Sigma\beta\left(C_{ijk}\right) - \text{Tot } L_j \quad (=0 \text{ from Eq 4.4})$$

Charge Balances

$$YC = \Sigma\delta\left(M_i\right) - \Sigma\zeta\left(L_j\right) + \Sigma_{\text{complexes}}^{\text{cationic}} - \Sigma_{\text{complexes}}^{\text{anionic}} (=0 \text{ from Eq 4.5})$$

Using Equation 4.2:

$$C_{ijk} = K_{ijk} \cdot \left(M_i\right)^{\alpha}\left(L_j\right)^{\beta}\left(H\right)^{\varepsilon}$$

Then:

$$\frac{\partial YM_i}{\partial\left(M_k\right)} = 0 \quad \text{for } i \neq k$$

$$\frac{\partial YL_j}{\partial\left(L_k\right)} = 0 \quad \text{for } j \neq k$$

$$\frac{\partial YM_i}{\partial M_i} = 1 + \sum_{j,k}^{*2}\left(C_{ijk}\right)/\left(M_i\right)$$

* Σ a double summation and order unimportant. Equivalent to $\Sigma\Sigma$ or $\Sigma\Sigma$
j,k jk kj

$$\frac{\partial YL_j}{\partial L_j} = 1 + \sum_{i,k} \beta^2 \left(C_{ijk}\right) / \left(L_j\right)$$

$$\frac{\partial YM_i}{\partial \left(L_j\right)} = \sum_{k} \alpha\beta \left(C_{ijk}\right) / \left(L_j\right)$$

$$\frac{\partial YL_j}{\partial \left(M_i\right)} = \sum_{k} \alpha\beta \left(C_{ijk}\right) / \left(M_i\right)$$

$$\frac{\partial YM_i}{\partial \left(H\right)} = \sum_{j,k} \alpha\varepsilon \left(C_{ijk}\right) / \left(H\right) - \sum \alpha\beta \left(C_{ijk}\right) / \left(H\right)$$

$$\frac{\partial YL_j}{\partial \left(H\right)} = \sum_{i,k} \beta\varepsilon \left(C_{ijk}\right) / \left(H\right) + \sum_{\substack{\text{last} \\ \text{row}}} \alpha\beta \left(C_{ijk}\right) / \left(H\right)$$

No general expressions for the derivations of the charge balance with respect to the principle variables were made. However the derivatives of the charge balance equation presented in Appendix II explain the requirements.

APPENDIX II

CHARGE BALANCE AND DERIVATIVES FOR SILVER PEAK BRINE CASE

Charge Balance from equation 4.5

$$YC = \left[H^+\right]+\left[Na^+\right]+\left[K^+\right]+2\left[Mg^{++}\right]+\left[Li^+\right]+2\left[Ca^{++}\right]+\left[CaOH^+\right]+\left[MgOH^+\right]-\left[NaSO_4^-\right]-\left[HSO_4^-\right]-\left[OH^-\right]-\left[Cl^-\right]-2\left[SO_4^=\right]-\left[KSO_4^-\right] = 0$$

$$\frac{\partial YC}{\partial Na^+} = 1 - \left[NaSO_4^-\right]/\left[Na^+\right]$$

$$\frac{\partial YC}{\partial K^+} = 1 - \left[KSO_4^-\right]/\left[K^+\right]$$

$$\frac{\partial YC}{\partial Mg^{++}} = 2 + \left[Mg(OH)^+\right]/\left[Mg^{++}\right]$$

$$\frac{\partial YC}{\partial Li^+} = 1$$

$$\frac{\partial YC}{\partial Ca^{++}} = 2 + \left[CaOH^+\right]/\left[Ca^{++}\right]$$

$$\frac{\partial YC}{\partial H} = 1 - \left[HSO_4^-\right]/\left[H^+\right]+\left[OH^-\right]/\left[H^+\right]-\left[CaOH^+\right]/\left[H^+\right]-\left[MgOH^+\right]/\left[H^+\right]$$

$$\frac{\partial YC}{\partial SO_4^=} = -\left[NaSO_4^-\right]/\left[SO_4^=\right]-\left[HSO_4^-\right]/\left[So_4^=\right]-2-\left[KSO_4^-\right]/\left[SO_4^=\right]$$

APPENDIX II cont'd

$$\frac{\partial YC}{\partial Cl^-} = -1$$

APPENDIX II

TABLE II-1 DERIVATIVE MATRIX FOR SILVER PEAK BRINE CASE PRINCIPLE VARIABLES, M_1 to M_6 and L_1, L_2 HENCE 8X8 MATRIX

$\frac{\partial(YM_1)}{\partial M_1}$	$\frac{\partial(YM_1)}{\partial M_2}$	$\frac{\partial(YM_1)}{\partial M_3}$	$\frac{\partial(YM_1)}{\partial M_4}$	$\frac{\partial(YM_1)}{\partial M_5}$	$\frac{\partial(YM_1)}{\partial M_6}$	$\frac{\partial(YM_1)}{\partial L_1}$	$\frac{\partial(YM_1)}{\partial L_2}$
$\frac{\partial(YM_2)}{\partial M_1}$	$\frac{\partial(YM_2)}{\partial M_2}$	$\frac{\partial(YM_2)}{\partial M_3}$	$\frac{\partial(YM_2)}{\partial M_4}$	$\frac{\partial(YM_2)}{\partial M_5}$	$\frac{\partial(YM_2)}{\partial M_6}$	$\frac{\partial(YM_2)}{\partial L_1}$	$\frac{\partial(YM_2)}{\partial L_2}$
$\frac{\partial(YM_3)}{\partial M_1}$	$\frac{\partial(YM_3)}{\partial M_2}$	$\frac{\partial(YM_3)}{\partial M_3}$	$\frac{\partial(YM_3)}{\partial M_4}$	$\frac{\partial(YM_3)}{\partial M_5}$	$\frac{\partial(YM_3)}{\partial M_6}$	$\frac{\partial(YM_3)}{\partial L_1}$	$\frac{\partial(YM_3)}{\partial L_2}$
$\frac{\partial(YM_4)}{\partial M_1}$	$\frac{\partial(YM_4)}{\partial M_2}$	$\frac{\partial(YM_4)}{\partial M_3}$	$\frac{\partial(YM_4)}{\partial M_4}$	$\frac{\partial(YM_4)}{\partial M_5}$	$\frac{\partial(YM_4)}{\partial M_6}$	$\frac{\partial(YM_4)}{\partial L_1}$	$\frac{\partial(YM_4)}{\partial L_2}$
$\frac{\partial(YM_5)}{\partial M_1}$	$\frac{\partial(YM_5)}{\partial M_2}$	$\frac{\partial(YM_5)}{\partial M_3}$	$\frac{\partial(YM_5)}{\partial M_4}$	$\frac{\partial(YM_5)}{\partial M_5}$	$\frac{\partial(YM_5)}{\partial M_6}$	$\frac{\partial(YM_5)}{\partial L_1}$	$\frac{\partial(YM_5)}{\partial L_2}$
$\frac{\partial(YC)}{\partial M_1}$	$\frac{\partial(YC)}{\partial M_2}$	$\frac{\partial(YC)}{\partial M_3}$	$\frac{\partial(YC)}{\partial M_4}$	$\frac{\partial(YC)}{\partial M_5}$	$\frac{\partial(YC)}{\partial M_6}$	$\frac{\partial(YC)}{\partial L_1}$	$\frac{\partial(YC)}{\partial L_2}$
$\frac{\partial(YL_1)}{\partial M_1}$	$\frac{\partial(YL_1)}{\partial M_2}$	$\frac{\partial(YL_1)}{\partial M_3}$	$\frac{\partial(YL_1)}{\partial M_4}$	$\frac{\partial(YL_1)}{\partial M_5}$	$\frac{\partial(YL_1)}{\partial M_6}$	$\frac{\partial(YL_1)}{\partial L_1}$	$\frac{\partial(YL_1)}{\partial L_2}$
$\frac{\partial(YL_2)}{\partial M_1}$	$\frac{\partial(YL_2)}{\partial M_2}$	$\frac{\partial(YL_2)}{\partial M_3}$	$\frac{\partial(YL_2)}{\partial M_4}$	$\frac{\partial(YL_2)}{\partial M_5}$	$\frac{\partial(YL_2)}{\partial M_6}$	$\frac{\partial(YL_2)}{\partial L_1}$	$\frac{\partial(YL_2)}{\partial L_2}$

$$
\begin{bmatrix}
1+\sum_{j,k}\alpha^2\left(C_{ijk}\right)/\left(M_i\right) & 0 & 0 & 0 & 0 & \left(\sum_{j,k}\alpha\epsilon\left(C_{ijk}\right)/H-\Sigma\alpha\beta C_{ij}/H\right) & \left(\Sigma\alpha\beta\left(C_{ijk}\right)/L_j\right) & \Sigma\alpha\beta\left(C_{ijk}\right)/L_j \\
0 & 1+\sum_{j,k}\alpha^2\left(C_{ijk}\right)/\left(M_i\right) & 0 & 0 & 0 & " & " & " \\
0 & 0 & 1+\sum_{j,k}\alpha^2\left(C_{ijk}\right)/\left(M_i\right) & 0 & 0 & " & " & " \\
0 & 0 & 0 & 1+\Sigma\alpha^2\left(C_{ijk}\right)/\left(M_i\right) & 0 & " & " & " \\
0 & 0 & 0 & 0 & 1+\Sigma\alpha^2\left(C_{ijk}\right)/\left(M_i\right) & " & " & " \\
1-\dfrac{\left(NaSO_4^-\right)}{\left(Na^+\right)} & 1-\dfrac{\left(KSO_4^-\right)}{\left(K^+\right)} & 2+\dfrac{\left(Mg(OH)^+\right)}{\left(Mg^{++}\right)} & 1 & 2+\dfrac{\left(CaOH^+\right)}{\left(Ca^{++}\right)} & * & -\left(\dfrac{NaSO_4^-}{SO_4^=}-\dfrac{HSO_4^-}{SO_4^=}-2-\dfrac{KSO_4^-}{SO_4^=}\right)-1 & \\
\sum_k\alpha\beta\left(C_{ijk}\right)/M_i & \sum_k\alpha\beta\left(C_{ijk}\right)/M_i & \sum_k\alpha\beta\left(C_{ijk}\right)/M_i & \sum_k\alpha\beta\left(C_{ijk}\right)/M_i & \sum_k\alpha\beta\left(C_{ijk}\right)/M_i & ** & 1+\sum_{i,k}\beta^2 C_{ijk}/L_j & 0 \\
\Sigma\alpha\beta\left(C_{ijk}\right)/M_i & \Sigma\alpha\beta\left(C_{ijk}\right)/M_i & \Sigma\alpha\beta\left(C_{ijk}\right)/M_i & \Sigma\alpha\beta\left(C_{ijk}\right)/M_i & \Sigma\alpha\beta\left(C_{ijk}\right)/M_i & " & 0 & 1+\Sigma\beta^2\left(C_{ijk}\right)/L_j
\end{bmatrix}
$$

* $\dfrac{\partial YC}{\partial H} = 1-\dfrac{HSO_4^-}{H^+}+\dfrac{OH^-}{H^+}-\dfrac{CaOH^+}{H^+}-\dfrac{MgOH^+}{H^+}$

** $\dfrac{\partial YL_i}{\partial H} = \Sigma\beta_j\left(C_{ijk}\right)/H+\Sigma\alpha\beta\left(C_{ijk}\right)/H$

TABLE II-2 DERIVATIVE FUNCTION MATRIX FOR SILVER PEAK BRINE

TABLE II - 3

SOLUBILITY PRODUCT DATA FOR SILVER PEAK BRINE CASE

Salt	Source	Equation	$Log_{10}K_{sp}$ at 40°C
$Ca(OH)_2$	48	$Ca(OH) = Ca^{++} + 2OH^-$	- 4.780
$CaCl_2$	48	$CaCl = Ca^{++} + 2Cl^-$	10.878
$CaSO_4$	48	$CaSO = Ca^{++} + SO^=$	- 2.050
LiOH	48	$LiOH = Li^+ + OH^-$	1.201
LiCl	48	$LiCl = Li^+ + Cl^-$	6.990
NaCl	48	$NaCl = Na^+ + Cl^-$	1.610
NaOH	49	$NaOH = Na^+ + OH^-$	7.037
Na_2SO_4	48	$Na\ SO = 2Na^+ + SO^=$	- 0.1815
KCl	48	$KCl = K^+ + Cl^-$	0.855
KOH	49	$KOH = K^+ + OH^-$	10.860
$MgSO_4$	48	$MgSO = Mg^{++} + SO^=$	4.070
$MgCl_2$	48	$MgCl = Mg^{++} + 2Cl^-$	21.030
$Mg(OH)_2$	48	$Mg(OH) = Mg^{++} + 2OH^-$	-10.530

TABLE II-4

EQUILIBRIUM CONSTANTS FOR SPECIES CONSIDERATION

SILVER PEAK BRINE CASE

Species	Equation	$\log_{10}k$ at 40°C	Source
$CaOH^+_{(aq)}$	$CaOH^+ = Ca^{++} + OH^-$	-1.243	48
$CaSO_4{}^0_{(aq)}$	$CaSO_4{}^0 = Ca^{++} + SO_4^=$	-2.199	48
$Li_2SO_4{}^0_{(aq)}$	$LiSO_4{}^0 = 2Li^+ + SO_4^=$	0.00	49
$LiCl^0_{(aq)}$	$LiCl^0 = Li^+ + Cl^-$	0.00	49
$LiOH^0_{(aq)}$	$LiOH^0 = Li^+ + OH^-$	0.00	49
$NaCl_{(aq)}$	$NaCl^0 = Na^+ + Cl^-$	0.105	49
$NaOH^0_{(aq)}$	$NaOH^0 = Na^+ + OH^-$	0.663	48
$NaSO_4{}^-_{(aq)}$	$NaSO_4{}^- = Na^+ + SO_4^=$	0.684	48
$KSO_4{}^-_{(aq)}$	$KSO_4{}^- = K^+ + SO_4^=$	-0.908	48
$KCL^0_{(aq)}$	$KCl^0 = K^+ + Cl^-$	0.00	49
$KOH^0_{(aq)}$	$KOH^0 = K^+ + OH^-$	0.00	49
$MgSO_4{}^0_{(aq)}$	$MgSO_4{}^0 = Mg^{++} + SO_4^=$	-2.248	48
$MgOH^+_{(aq)}$	$MgOH^+ = Mg^{++} + OH^-$	-2.458	48
$HSO_4{}^-_{(aq)}$	$HSO_4{}^- = H^+ + SO_4^=$	-1.815	49

TABLE II-4 cont'd

Species	Equation	$\log_{10}k$ at 40°C	Source
$H_2SO_4{}^0{}_{(aq)}$	$H_2SO_4{}^0 = H^+ + HSO^-$	1.815	49
$HCl^0{}_{(aq)}$	$HCl^0 = H^+ + Cl^-$	0.00	49

Sources:

48 Calculated from dissociation constants in Table 4.1 of Garrels & Christ. These values are taken from the book by, Jannik Bjerrum, Gerold Schwarzenbach, and Lars Gunnar Sillén, 'Stability constants, Part II: Inorganic Ligands. London, The Chemical Society, 1958.

49 Rossini, F.D., Wagman, D.D., Evans, W.H., Samuel Levine, and Irving Jaffee, Selected values of Chemical Thermodynamic Properties: Natl. Bur. Standards Circ. 500, U.S. Dept. Commerce (1952).

APPENDIX III

INPUT MATRICES TO PROGRAM

1. Equilibrium constants

$$\begin{bmatrix} 0.68 & 0 & -0.66 \\ 0.91 & 0 & 0.00 \\ 2.25 & 0 & 2.46 \\ 0.00 & 0 & 0.00 \\ 2.20 & 0 & 1.24 \\ 1.82 & 0 & 13.33 \end{bmatrix}$$

2. Solubility Products

$$\begin{bmatrix} -0.18 & 1.61 & 7.04 \\ 0.00 & 0.855 & 10.86 \\ 4.07 & 21.03 & -10.54 \\ 0.00 & 6.99 & 1.20 \\ -2.05 & 10.88 & -4.78 \\ 0.00 & 0.00 & 0.00 \end{bmatrix}$$

APPENDIX III cont'd

3. Stoichiometric coefficient, α

$$\begin{bmatrix} 1 & 0 & 1 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \\ 2 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 1 \end{bmatrix}$$

4. Stoichiometric coefficient, β

$$\begin{bmatrix} 1 & 0 & 1 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 1 \\ 1 & 0 & 1 \\ 1 & 1 & 1 \end{bmatrix}$$

APPENDIX IV

NOMENCLATURE FOR BASIC PROGRAM LISTING

A(I,J) = Log K

B(I,J) = α

C(I,J) = β

D(I,J) = ε

E1(I,J) = Log K_s (solubility product)

F(I,J) = δ

G(I,J) = η

H1(I,J) = λ

I = number of metals

J = number of ligands

O(I) = total concentration of metals from analysis

P(J) = total concentration of ligands from analysis

Q(I) = charge on metal ions

J(I) = charge on ligand ions

Y = total ionic strength

Z(P,Q) = Mean activity coefficient via Bromley's formula

V(P) = Reduced activity coefficient, Kusik & Meissner's definition

W(M,B) = Mixed solution activity coefficient

APPENDIX IV

PROGRAM LISTING

```
10 REM ***PROGRAMME TO CALCULATE EQUILIBRIA BETWEEN SPECIES GIVEN
 TOTAL
20 REM    METAL AND LIGAND CONCENTRATIONS FOR BRINE SYSTEMS CONTA
INING LITHIUM
40 REM  ##########################################################
########
50 REM    INPUT DATA MATRICES
60 REM ***DATA MATRICES CONTAIN ,GENERAL STOICHIOMETRIC AND THERM
ODYNAMIC
70 REM    DATA,TOTAL CONCENTRATIONS OF METALS AND LIGANDS, GUESSE
S FOR THE
80 REM   FREE METALS AND LIGANDS
90 REM ***A(I,J)=LOGK,B(I,J)=ALPHA,C(I,J)=BETA,D(I,J)=GAMMA,E1(I,
J)=LOGKS
100 REM     F(I,J)=DELTA,G(I,J)=NETA ,H1(I,J)=LAMDA
110 REM ****INPUT NUMBER OF METALS,I,LIGANDS,J
120 READ I,J
130 DATA 6,3
140 DIM A(6,3),B(6,3),C(6,3),D(6,3),Z(6,3),S(6,3),K(6,3),V(6,3),U
(6,3)
150 DIM N(8,8),I(8,8),O(6),P(3),M(6),L(3),Q(6),J(3),T(8),X(9),R(9
),H(8)
160 DIM B1(6,3),W(6,3),F1(6,3),Y(9)
170 DIM E2(6,3),E3(6,3),E1(6,3),F(6,3),G(6,3),H1(6,3),D1(6,3)
180 REM *****INPUT THERMO. DATA ANDSTOICIOMETRIC COEFFICIENTS
190 MAT READ A,B,C,D
200 DATA 0.68,0,-.66,.91,0,0,2.25,0,2.46,0,0,0,2.20,0,1.24,1.82,0
,13.33,1,0,1,1,1,1
210 DATA 1,0,1,2,1,1,1,0,1,1,1,1,1,0,1,1,1,1,1,0,1,1,1,1,1,0,1,1,
1,1,0,0,0
220 DATA 0,0,0,0,0,0,0,0,0,0,0,0,0,0,0
221 MAT PRINT A,B,C,D
230 REM***INPUT THERMO. DATA AND STOICHIOMETRIC COEFFICIENTS FOR
240 REM     PRECIPITATED MATERIAL
250 MAT READ E1,F,G,H1
251 DATA -.18,1.61,7.04,0,.855,10.86,4.07,21.03,-10.54
252 DATA 0,6.99,1.20,-2.05,10.88,-4.78,0,0,0
260 DATA 2,1,1,0,1,1,1,1,1,0,1,1,1,1,1,0,0,0,1,1,1,0,1,1
270 DATA 1,2,2,0,1,1,1,2,2,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,0,
0,0
280 REM ****INPUT TOTAL CONCENTRATIONS FROM ANALYSIS, O(I)=METALS
, P(J)=LIGANDS
290 MAT READ O,P
300 DATA 3.01,0.22,0.019,0.111,0.014,4.6458E-8,0.111,3.231,3.98E-
07
```

```
310 REM***INPUT INITIAL GUESS, METALS M(I);LIGANDS L(J)
320 MAT READ M,L
330 DATA 2.93559,9.59862E-02,8.8358E-03,3.08435E-02,6.88739E-03,6
.88728E-03,7.93356E-03,2.99909,5.4E-12
340 REM INPUT UNIT CHARGE ON ION METALS,Q(I),LIGANDS J(I)
350 MAT READ Q,J
360 DATA 1,1,2,1,2,1,2,1,1
370 MAT D1=ZER(6,3)
371 Z9=1
372 PRINT "SIMULATION DOES NOT INCLUDE AQUEOUS SPECIES NACL"
390 Z4=1
391 MATA =(-1)*A
398 Z=0
399 A7=0
400 REM ##########################################################
##########
410 REM           IONIC STRENGTHS
420 REM  ##########################################################
##########
430 REM Y(P), IONIC STRENGTHS OF METALS, Y(A),IONIC STRENGTHS OF
LIGANDS
440 REM            ***FOR METALS***
450 FOR P=1 TO I
460 Y(P)=0.5*M(P)*Q(P)^2
470 NEXT P
471 REM ***FOR LIGANDS ***
480 FOR Q=1 TO J
490 A=I+Q
500 Y(A)=0.5*L(Q)*J(Q)^2
510 NEXT Q
520 REM TOTAL IONIC STRENGTH, Y
530 Y=0
540 FOR P=1 TO I+J
550 A=Y(P)
560 Y=Y+A
570 NEXT P
571 REM *** FOR SPECIES****
572 IF Z9= 1 THEN 575
573 B=0.5*(S(1,1)+S(2,1)+S(3,3)+S(5,3)+S(6,1))
574  GO TO 576
575 B=0
576 Y=Y+B
577 Z9=2
580 REM ***PURE COMPONENT ACTIVITY COEFFICIENTS***
590 REM    MEAN ACTIVITY COEFFICIENTS DETERMINED VIA FORMULA DERI
VED
600 REM BY BROMLEY
```

```
610 MAT B1=ZER(6,3)
620 B1(1,2)=0.0574
630B1(1,3)=0.0747
640 B1(2,2)=0.0240
650 B1(2,3)=0.1131
660 B1(3,1)=-0.0153
670 B1(4,1)=0.0207
680 B1(4,2)=0.1283
690 B1(4,3)=-0.0097
700 B1(6,2)=0.1433
710 FOR P=1 TO I
720 FOR Q=1 TO J
730 IF B1(P,Q)=0 THEN 800
740 A1=(-0.511*Q(P)*J(Q)*Y^0.5)/(1+Y^0.5)
750 A2=((0.06+0.6*B1(P,Q))*Q(P)*J(Q)*Y)/(1+(1.5*Y)/(Q(P)*J(Q)))^2
760 A3=B1(P,Q)*Y
770 A4=A1+A2+A3
780 Z(P,Q)=10^A4
790 GO TO 810
800 Z(P,Q)=0
810 NEXT Q
820 NEXT P
830 REM   ##########################################################
#########
840 REM REDUCED ACTIVITY COEFFICIENTS
850 REM  ##########################################################
#########
860 REM  CALCULATE REDUCED PURE COMPONENT ACTIVITY COEFFICIENTS A
CCORDING
870 REM TO KUSIKS AND MEISSENERS DEFINATION
880 FOR P=1 TO I
890 FOR Q=1 TO J
900 V(P,Q)=Z(P,Q)^(1/(Q(P)*J(Q)))
910 IF (V(P,Q))=0 THEN 930
920 V(P,Q)=LOG10(V(P,Q))
930 NEXT Q
940 NEXT P
950 REM   ##########################################################
##########
960 REM MIXED SOLUTION ACTIVITY COEFFICIENTS
```

```
970 REM   ##########################################################
#########
980 REM CALCULATION OF ACTIVITY COEFFICIENTS FOR MIXED SOLUTIONS
VIA
990 REM METHOD DESCRIBED BY KUSIK AND MEISSENER
1000 REM  WEIGHTING FACTOR CALCULATION
1010 FOR B=1 TO J
1020 FOR M=1 TO I
1030 FOR N=1 TO J
1040 U(M,N)=0.5*(Q(M)+J(N))^2/(Q(M)*J(N))
1050 NEXT N
1060 E=0
1070 FOR Q=1 TO J
1080 L=I+Q
1090 A=U(M,Q)*Y(L)*V(M,Q)
1100 E=E+A
1110 NEXT Q
1120 F=0
1130 FOR A=1 TO I
1140 D=U(A,B)*Y(A)*V(A,B)
1150 F=F+D
1160 NEXT A
1170 W(M,B)=(Q(M)/(Q(M)+J(B)))*E/Y+(J(B)/(J(B)+Q(M)))*F/Y
1180 W(M,B)=10^(W(M,B))
1190 NEXT M
1200 NEXT B
1201 REM TEMPERATURE CORRECTION VIA COBBLES METHOD
1202 FOR B=1 TO J
1203 FOR M=1 TO I
1204 W(M,B)=LOG10(W(M,B))-((Y^0.5)/(1+Y^0.5))*0.015
1205 W(M,B)=10^W(M,B)
1206 NEXT M
1207 NEXT B
1210 REM ##########################################################
##########
1220 REM INDIVIDUAL ACTIVITY COEFFICIENTS
1230 REM  ##########################################################
#########
1240 REM ***ACTIVITY COEFFICIENTS OF METALS AND LIGANDS VIA MEAN
SALT
1250 REM METHOD, MATRIX X --METALS ,MATRIX R --LIGANDS
```

```
1260 X(1)=W(1,2)^2/W(2,2)
1270 X(2)=W(2,2)
1280 X(3)=W(3,1)^2*W(6,2)^4/W(4,1)^3/W(2,2)
1290 X(4)=W(4,2)^2/W(2,2)
1300 X(5)=W(5,1)^2*W(6,2)^4/W(4,1)^3/W(2,2)
1310 X(6)=W(6,2)^2/W(2,2)
1320 R(1)=W(4,1)^3*W(2,2)^2/W(6,2)^4
1330 R(2)=W(2,2)
1340 R(3)=(W(2,3)^2)/W(2,2)
1350 REM    ##########################################################
###########
1360 REM CONCENTRATION EQUILIBRIUM CONSTANTS
1370 REM ##########################################################
#######
1380 F1(1,1)=F1(2,1)=F1(6,1)=F1(3,3)=F1(5,3)=0.68
1390 F1(3,2)=F1(5,2)=F1(1,2)=8
1400 F1(2,2)=F1(2,3)=F1(3,1)=F1(4,1)=F1(4,2)=F1(4,3)=F1(5,1)=F1(6
,2)=1.0
1410 F1(6,3)=F1(1,3)=1.0
1420 REM  CALCULATION OF CONCENTRATION EQUILIBRIUM CONSTANTS
1430 REM K(P,Q) --CONCENTRATION EQUILIBRIA MATRIX
1440 FOR Q=1 TO J
1450 FOR P=1 TO I
1460 IF F1(P,Q)=8 THEN 1490
1470 K(P,Q)=10^(A(P,Q))*F1(P,Q)/(X(P)^B(P,Q))/(R(Q)^C(P,Q))/(X(I)
^D(P,Q))
1480 GO TO 1500
1490 K(P,Q)=0
1500 NEXT P
1510 NEXT Q
1520 REM GENERATE SET OF SPECIES CONCENTRATION
1530 FOR Q=1 TO J
1540 FOR P=1 TO I
1550 IF K(P,Q)=0 THEN1580
1560 S(P,Q)=M(P)^B(P,Q)*L(Q)^C(P,Q)*M(I)^D(P,Q)/K(P,Q)
1570 GO TO 1590
1580 S(P,Q)=0
1590 NEXT P
1600 NEXT Q
```

```
1601 REM ##############################################################
##################
1910 REM                          MASS BALANCE EQUATIONS
1920 REM ##############################################################
##########
1930REM MASS BALANCE SET ON METALS NOT INCLUDING H AND MASS BALAN
CE ON
1940 REM LIGANDS NOT INCLUDING OH. PROTON BALANCE KEPT EXTERNAL T
O ITERATION
1950 REM SET FOR NEWTON-RHAPSON SOLUTION
1960 REM BALANCE EQUATIONS TO MATRIX T(K)
1970 REM        ########################
1980 REM           **METALS BALANCE **
1990 REM        ########################
2000 FOR P=1 TOI-1
2010 T(P)=0
2020 FOR Q=1 TO J
2030 A=B(P,Q)*S(P,Q)
2040 T(P)=T(P)+A
2050 NEXT Q
2060 T(P)=T(P)+M(P)-O(P)
2070 NEXT P
2080 REM       ########################
2090 REM             **LIGANDS BALANCE **
2100 REM           ########################
2110FOR Q=1 TOJ-1
2120 X=Q+I
2130 T(X)=0
2140 FOR P=1 TO I
2150 A=C(P,Q)*S(P,Q)
2160 T(X)=T(X)+A
2170 NEXT P
2180 T(X)=T(X)+L(Q)-P(Q)
2190 NEXT Q
2191 REM ***CHARGE BALANCE ***
2192 T(I)=0
2193 FOR P=1 TO I
2194 X1= M(P)*Q(P)
2195 T(I)=T(I)+X1
2196 NEXT P
2197 FOR Q= 1 TO J
2198 X2=L(Q)*J(Q)
2199 T(I)=T(I)-X2
2200 NEXT Q
2201 T(I)=T(I)+S(3,3)+S(5,3)-S(1,1)-S(2,1)-S(6,1)
2202 REM ##############################################################
##########################
```

```
2203 REM DIFFERENTIAL MATRIX
2204 REM ##########################################################
#################
2220 REM   ##########################################################
###########
2230 REM   MATRIX NAME N(P,T)
2240 FOR P=1 TO I-1
2250 FOR T=1 TO I-1
2260 S1=0
2270 IF T=P THEN 2310
2280 N(P,T)=0
2290 GO TO2370
2300 GOTO 2380
2310 FOR Q=1 TO J
2320 A=B(P,Q)^2*S(P,Q)
2330 S1=S1+A
2340 NEXT Q
2350 X1=1+S1/M(P)
2360 N(P,T)=X1
2370 NEXT T
2380 NEXT P
2390 FOR Q=1 TO J-1
2400 FOR P=1 TO I-1
2410 S3=B(P,Q)*C(P,Q)*S(P,Q)
2420 S=Q+I
2430 T=P
2440 X1=S3/M(P)
2450 N(S,T)=X1
2460 NEXT P
2470 NEXT Q
2480 FOR Q=1 TO J-1
2490 FOR T=1 TO J-1
2500 M=I+Q
2510 N=I+T
2520 S4=0
2530 IF M=N THEN 2570
2540 N(M,N)=0
2550 GO TO 2630
```

```
2560 GOTO 2640
2570 FOR P=1 TO I
2580 A=C(P,Q)^2*S(P,Q)
2590 S4=S4+A
2600 NEXT P
2610 X1=1+S4/L(Q)
2620 N(M,N)=X1
2630 NEXT T
2640 NEXT Q
2650 FOR Q=1 TO J-1
2660 FOR P=1 TO I-1
2670 S5=B(P,Q)*C(P,Q)*S(P,Q)
2680 S=Q+I
2690 X1=S5/L(Q)
2700 N(P,S)=X1
2710 NEXT P
2720 NEXT Q
2730 G4=1-S(6,1)/M(I)+L(J)/M(I)-S(5,3)/M(I)-S(3,3)/M(I)
2940 N(I,I)=G4
2950 N(6,1)=1-S(1,1)/M(1)
2960 N(6,2)=1-S(2,1)/M(2)
2970 N(6,3)=2+S(3,3)/M(3)
2980 N(6,4)=1
2990 N(6,5)=2+S(5,3)/M(5)
3000 N(6,7)=-2-S(1,1)/L(1)-S(6,1)/L(1)-S(2,1)/L(1)
3010 N(6,8)=-1
3050 W2=0
3060  FOR P=1 TO I-1
3070 FOR Q=1 TO J
3080 A=B(P,Q)*D(P,Q)*S(P,Q)/M(I)
3090 W2=W2+A
3100 NEXT Q
3110 B=B(P,J)*C(P,J)*S(P,J)/M(I)
3120 W2=W2-B
3130 N(P,I)=W2
3140 NEXTP
3150 W3=0
3160 FOR Q=1 TO J-1
3170 FOR P=1 TO I
3180 V=I+Q
3190 A=C(P,Q)*D(P,Q)*S(P,Q)/M(I)
3200 W3=W3+A
```

```
3210 NEXT P
3220 B=B(I,Q)*C(I,Q)*S(I,Q)/M(I)
3230 W3=W3+B
3240 N(V,I)=W3
3250 NEXT Q
4000 REM ##########################################################
##########
4010 REM    NEWTON-RHAPSON SOLUTION
4020 REM  ##########################################################
#########
4030 MAT T=(-1)*T
4040 MAT I=INV(N)
4050 MAT H=I*T
4060 K=0
4070 FOR Q=1 TO I+J-1
4080 IF Q>I THEN 4120
4090 IF ABS(H(Q)/M(Q))<1E-04 THEN 4160
4091 IF Q=I THEN 4102
4100 M(Q)=M(Q)+H(Q)
4101 GO TO 4105
4102 M(Q)=M(Q)+H(Q)
4105 IFM(Q)<0THEN 4108
4106 GO TO 4180
4108 M(Q)=M(Q)-H(Q)/2
4109 PRINT"H GOES NEG"
4110 GO TO 4180
4120 A=Q-I
4130 IF ABS(H(Q)/L(A))< 1E-04 THEN 4160
4140 L(A)=L(A)+H(Q)
4141 IF L(A)<0 THEN 4143
4142 GO TO 4180
4143 L(A)=1E-8
4150 GOTO 4180
4160 K=K+1
4170 IFK=I+J-1 THEN 4360
4180 NEXT Q
4194 IF Z=50 THEN 4340
4200 Z=Z+1
4201 L(J)=K(I,J)/M(I)
4214 C1=0
4220 FOR P=1 TO I
4230 X1=M(P)*Q(P)
4240 C1=C1+X1
```

```
4250 NEXT P
4260 C2=0
4270 FOR Q=1 TO J
4280 X2=L(Q)*J(Q)
4290 C2=C2+X2
4300 NEXT Q
4310 C3=C1-C2+S(3,3)+S(5,3)-S(1,1)-S(2,1)-S(6,1)
4332 GO TO 400
4340 PRINT "NUMBER  OF ITERATIONS EXCEEDS 15"
4350 STOP
4360 REM ***** CONCENTRATION SOLUBILITY PRODUCT
4380 FOR Q=1 TO J
4390 FOR P=1 TO I
4391 IF E1(P,Q)=0 THEN 4420
4400 E2(P,Q)=10^(E1(P,Q))/(X(P)^F(P,Q))/(R(Q)^G(P,Q))/(X(I)^H1(P,
Q))
4410 GO TO 4430
4420 E2(P,Q)=0
4430 NEXT P
4440 NEXT Q
4460 REM CONCENTRATION SOLUBILITY CHECK,E3(P,Q) IS PRODUCT OF FRE
E IONS
4470 K=0
4480 FOR Q=1 TO J
4490 FOR P=1 TO I
4500 E3(P,Q)=(M(P)^F(P,Q))*(L(Q)^G(P,Q))*(M(I)^H1(P,Q))
4530 IF E2(P,Q)=0 THEN 4680
4531 A=ABS(E3(P,Q)-E2(P,Q))
4532 IF A/E2(P,Q) >0.1 THEN 4538
4533 IF A/E2(P,Q) >0.05 THEN 4540
4534 IF A/E2(P,Q) >0.01 THEN 4542
4535 IF A/E2(P,Q) >0.005 THEN 4544
4536 A7=4
4537 GO TO 4545
4538 A7=0
4539 GO TO 4545
4540 A7=1
4541 GO TO 4545
4542 A7=3
4543 GO TO4545
4544 A7=4
4545 B7= 0.1/(4^A7)
4546 IF A/E2(P,Q)<1E-02 THEN 4680
4560 IF E3(P,Q)<E2(P,Q) THEN 4620
```

```
4570 REM PRECIPITATE SPECIES
4580 O(P)=O(P)-B7*O(P)*F(P,Q)
4590 P(Q)=P(Q)-B7*P(Q)*G(P,Q)
4600 D1(P,Q)=D1(P,Q)+B7*O(P)
4610 GO TO 4700
4620 IF D1(P,Q)>0 THEN 4640
4630 GO TO 4680
4640 O(P)=O(P)+B7*O(P)*F(P,Q)
4650 P(Q)=P(Q)+B7*P(Q)*G(P,Q)
4660 D1(P,Q)=D1(P,Q)-B7*O(P)
4670 GO TO 4700
4680 K=K+1
4690 IF K=I*J THEN 4730
4700 NEXT P
4710 NEXT Q
4720 GO TO 400
4730 REM ***PRINT OUT RESULTS ****
4740 PRINT "#####################################################"
4750 PRINT"SOLUTION VOLUME=";Z4
4760 PRINT
4770 PRINT
4780 PRINT "METAL CONCENTRATIONS"
4790 PRINT
4800 PRINT
4810 FOR Q=1 TO I
4820 PRINT M(Q)
4830 NEXT Q
4840 PRINT "LIGAND CONCENTRATION"
4850 PRINT
4860 PRINT
4870 FOR Q=1 TO J
4880 PRINT L(Q)
4890 NEXT Q
4891 PRINT
4892 PRINT   "    ACTIVITY COEFFICENTS"
4893PRINT "  METALS  "
4894 FOR P=1 TO I
4895 PRINT X(P)
4896 NEXTP
4897 PRINT   "LIGANDS"
4898 FOR Q=1 TO J
4899 PRINT R(Q)
4900 NEXT Q
```

```
4901 PRINT
4902 PRINT
4910 PRINT "SPECIES CONCENTRATION"
4920 MAT PRINT S
4930 PRINT
4940 PRINT
4950 PRINT "PRECIPITATE MATRIX"
4960 MAT PRINT D1
4961 PRINT"IONIC STRENGTH=";Y
4962 PRINT
4963 PRINT "CHARGE BALANCE =";C3
4970 PRINT "NUMBER OF ITERATIONS=";Z
4980 REM ##########################################################
########
4990 REM       EVAPORATION INCREMENT
5000 REM ##########################################################
########
5010 REM EVAPORATION SIMULATED BY STEP DECREASE IN VOLUME
5011 IF Z4<0.40 THEN 5015
5012 Y=0.05
5013 GO TO 5020
5015 Y=0.01
5016 GO TO 5020
5018 Y=0.005
5020 FOR P=1 TO I
5030 O(P)=O(P)*Z4/(Z4-Y)
5040 NEXT P
5050 FOR Q=1 TO J
5060 P(Q)=P(Q)*Z4/(Z4-Y)
5070 NEXT Q
5080 Z4=Z4-Y
5101 IF Z4<0.39 THEN 5110
5102 GO TO398
5110 PRINT"EVAPORATION INCREMENT COMPLETE "
5111 STOP
5120 END
```

APPENDIX V

RESULTS OF SIMULATION ON SILVER PEAK BRINE - COMPUTER PRINTOUT

```
SIMULATION DOES NOT INCLUDE AQUEOUS SPECIES NACL
**************************************************
SOLUTION VOLUME= 1

METAL CONCENTRATIONS

 2.93405
 9.72117E-2
 9.64922E-3
 3.13567E-2
 7.48352E-3
 1.02220E-2
LIGAND CONCENTRATION

 9.12067E-3
 3.00301
 4.24756E-12

    ACTIVITY COEFFICENTS
  METALS
 0.809177
 0.639574
 1.19916
 1.32221
 1.20901
 1.48172
LIGANDS
 0.498257
 0.639574
 0.727036

SPECIES CONCENTRATION

 7.59422E-2     0              1.60401E-12

 3.37739E-3     0.119414       1.92002E-13

 9.35086E-3     0              1.51551E-11

 7.81166E-6     7.96304E-2     1.28034E-13

 6.51650E-3     0              7.14038E-13

 6.68764E-3     2.90904E-2     0.999993
```

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 3.13344

CHARGE BALANCE =-1.45624E-4
NUMBER OF ITERATIONS= 4
****
SOLUTION VOLUME= 0.95

METAL CONCENTRATIONS

3.08842
9.88594E-2
9.91627E-3
3.07187E-2
7.70042E-3
1.00214E-2

LIGAND CONCENTRATION

9.50352E-3
3.15407
4.07460E-12

ACTIVITY COEFFICENTS

METALS
0.824192
0.644003
1.27988
1.38
1.29042
1.55445

LIGANDS
0.470116
0.644003
0.736886

SPECIES CONCENTRATION

8.00470E-2	0	1.67205E-12
3.40006E-3	0.12932	1.91157E-13
1.00834E-2	0	1.61619E-11
8.02886E-6	8.61077E-2	1.27282E-13
7.03616E-3	0	7.62470E-13
6.76217E-3	3.16421E-2	0.999978

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 3.29039

CHARGE BALANCE =-3.77392E-5
NUMBER OF ITERATIONS= 4
##
SOLUTION VOLUME= 0.9

METAL CONCENTRATIONS

3.25991
0.100426
1.01851E-2
2.99173E-2
7.92026E-3
9.76467E-3

LIGAND CONCENTRATION

9.94362E-3
3.32155
3.90296E-12

ACTIVITY COEFFICENTS
METALS
0.841548
0.64924
1.37704
1.44769
1.38846
1.64006
LIGANDS
0.440546
0.64924
0.748305

SPECIES CONCENTRATION

8.45886E-2	0	1.75290E-12
3.41412E-3	0.140604	1.90425E-13
1.09256E-2	0	1.73730E-11
8.21738E-6	9.33997E-2	1.26494E-13
7.63499E-3	0	8.20798E-13
6.81621E-3	3.45353E-2	0.999974

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 3.4643

CHARGE BALANCE =-3.35086E-5
NUMBER OF ITERATIONS= 4
##

SOLUTION VOLUME= 0.85

METAL CONCENTRATIONS

3.45161
0.101867
1.04515E-2
2.89296E-2
8.14012E-3
9.44492E-3

LIGAND CONCENTRATION

1.04537E-2
3.50826
3.73242E-12

ACTIVITY COEFFICENTS

METALS
0.861775
0.655462
1.4957
1.52788
1.50821
1.74201

LIGANDS
0.409532
0.655462
0.761637

SPECIES CONCENTRATION

8.96323E-2	0	1.84993E-12
3.41688E-3	0.153539	1.89810E-13
1.19009E-2	0	1.88475E-11
8.36419E-6	0.101642	1.25653E-13
8.33010E-3	0	8.91914E-13
6.84379E-3	3.78344E-2	0.99997

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 3.6581

CHARGE BALANCE =-2.62597E-5
NUMBER OF ITERATIONS= 4
##
SOLUTION VOLUME= 0.8

METAL CONCENTRATIONS

3.66732
0.103123
1.07094E-2
2.77318E-2
8.35543E-3
9.05359E-3

LIGAND CONCENTRATION

1.10517E-2
3.71776
3.56331E-12

ACTIVITY COEFFICENTS
METALS
0.885569
0.662894
1.64309
1.62413
1.657
1.86512
LIGANDS
0.377071
0.662894
0.777329

SPECIES CONCENTRATION

9.52610E-2	0	1.96802E-12
3.40520E-3	0.168471	1.89347E-13
1.30400E-2	0	2.06716E-11
8.45379E-6	0.111001	1.24755E-13
9.14413E-3	0	9.80031E-13
6.83707E-3	4.16152E-2	0.999966

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 3.87549

CHARGE BALANCE =-1.55811E-5
NUMBER OF ITERATIONS= 4
****
SOLUTION VOLUME= 0.75

METAL CONCENTRATIONS

3.91186
0.104115
1.09497E-2
2.62998E-2
8.55942E-3
8.58189E-3

LIGAND CONCENTRATION

1.17622E-2
3.95461
3.39598E-12

ACTIVITY COEFFICENTS
METALS
0.91387
0.671837
1.82985
1.74144
1.84559
2.01621
LIGANDS
0.343196
0.671837
0.795973

SPECIES CONCENTRATION

0.101575	0	2.11413E-12
3.37517E-3	0.185841	1.89077E-13
1.43829E-2	0	2.29706E-11
8.46736E-6	0.121682	1.23801E-13
1.01067E-2	0	1.09128E-12
6.78641E-3	4.59713E-2	0.999961

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 4.12115

CHARGE BALANCE =-3.55416E-7
NUMBER OF ITERATIONS= 4

****
SOLUTION VOLUME= 0.7

METAL CONCENTRATIONS

4.19143
0.104737
1.11593E-2
2.46108E-2
8.74219E-3
8.02159E-3

LIGAND CONCENTRATION

1.26194E-2
4.22463
3.23083E-12

ACTIVITY COEFFICENTS
METALS
0.947968
0.682694
2.07221
1.88701
2.09041
2.20525

LIGANDS
0.307992
0.682694
0.818368

SPECIES CONCENTRATION

0.108699	0	2.29836E-12
3.32194E-3	0.206224	1.89054E-13
1.59826E-2	0	2.59313E-11
8.38262E-6	0.133942	1.22790E-13
1.12572E-2	0	1.23482E-12
6.68015E-3	5.10191E-2	0.999955

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 4.40111

CHARGE BALANCE = 2.08321E-5
NUMBER OF ITERATIONS= 4
****
SOLUTION VOLUME= 0.65

METAL CONCENTRATIONS

4.51415
0.104848
1.13195E-2
2.26469E-2
8.88928E-3
7.36608E-3

LIGAND CONCENTRATION

1.36727E-2
4.5355
3.06824E-12

ACTIVITY COEFFICENTS

METALS
0.989685
0.696018
2.39582
2.07162
2.41743
2.44722

LIGANDS
0.271617
0.696018
0.845629

SPECIES CONCENTRATION

0.116782	0	2.53596E-12
3.23954E-3	0.23037	1.89343E-13
1.79100E-2	0	2.98431E-11
8.17427E-6	0.148103	1.21727E-13
1.26483E-2	0	1.42489E-12
6.50449E-3	5.69056E-2	0.999949

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 4.72329

CHARGE BALANCE = 4.98042E-5
NUMBER OF ITERATIONS= 4

```
##################################################
SOLUTION VOLUME= 0.6

METAL CONCENTRATIONS

 4.89087
 0.104259
 1.14037E-2
 2.03989E-2
 8.97975E-3
 6.61209E-3
LIGAND CONCENTRATION

 1.49957E-2
 4.89743
 2.90860E-12

    ACTIVITY COEFFICENTS
  METALS
 1.04167
 0.712594
 2.84325
 2.31187
 2.8698
 2.76563
LIGANDS
 0.234339
 0.712594
 0.879343

SPECIES CONCENTRATION

  0.126014       0              2.85073E-12

  3.12076E-3     0.25928        1.90020E-13

  2.02615E-2     0              3.51716E-11

  7.81541E-6     0.164582       1.20618E-13

  1.43525E-2     0              1.68441E-12

  6.24361E-3     6.38181E-2     0.999942
```

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 5.09824

CHARGE BALANCE = 8.90575E-5
NUMBER OF ITERATIONS= 4
****
SOLUTION VOLUME= 0.55

METAL CONCENTRATIONS

5.33638
0.102722
1.13737E-2
1.78730E-2
8.98344E-3
5.76225E-3

LIGAND CONCENTRATION

1.67022E-2
5.32443
2.75219E-12

ACTIVITY COEFFICENTS

METALS
1.10791
0.733562
3.48923
2.63473
3.52331
3.19917

LIGANDS
0.19657
0.733562
0.92186

SPECIES CONCENTRATION

0.136625	0	3.28165E-12
2.95720E-3	0.294313	1.91180E-13
2.31697E-2	0	4.27035E-11
7.28041E-6	0.183926	1.19475E-13
1.64696E-2	0	2.05224E-12
5.88045E-3	7.20011E-2	0.999935

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 5.54044

CHARGE BALANCE = 1.42415E-4
NUMBER OF ITERATIONS= 4
##
SOLUTION VOLUME= 0.5

METAL CONCENTRATIONS

5.87147
9.99056E-2
1.11765E-2
1.51001E-2
8.85754E-3
4.82862E-3

LIGAND CONCENTRATION

1.89773E-2
5.83615
2.59910E-12

ACTIVITY COEFFICENTS
METALS
1.19468
0.760642
4.4744
3.0863
4.52076
3.81525
LIGANDS
0.158925
0.760642
0.97679

SPECIES CONCENTRATION

0.148907	0	3.89604E-12
2.73960E-3	0.337346	1.92927E-13
2.68205E-2	0	5.38463E-11
6.55025E-6	0.206882	1.18315E-13
1.91403E-2	0	2.59800E-12
5.39837E-3	8.17809E-2	0.999929

PRECIPITATE MATRIX

0	0	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 6.07028

CHARGE BALANCE = 2.16493E-4
NUMBER OF ITERATIONS= 4
****
SOLUTION VOLUME= 0.45

METAL CONCENTRATIONS

6.35777
9.91515E-2
1.09451E-2
1.32044E-2
8.70109E-3
3.67658E-3

LIGAND CONCENTRATION

2.18467E-2
6.29832
2.75286E-12

ACTIVITY COEFFICENTS
METALS
1.28109
0.787298
5.62152
3.36552
5.68481
4.48096

LIGANDS
0.130848
0.787298
1.03137

SPECIES CONCENTRATION

0.16388	0	5.05919E-12
2.66735E-3	0.387081	2.21634E-13
3.12770E-2	0	7.40905E-11
6.33629E-6	0.233456	1.33672E-13
2.24099E-2	0	3.58904E-12
4.57571E-3	0.081692	1.00003

PRECIPITATE MATRIX

0	0.163042	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 6.55461

CHARGE BALANCE =-4.30612E-5
NUMBER OF ITERATIONS= 8
##
SOLUTION VOLUME= 0.4

METAL CONCENTRATIONS

6.38772
0.110583
1.12292E-2
1.46754E-2
8.93939E-3
1.80577E-3

LIGAND CONCENTRATION

2.46443E-2
6.31503
5.51898E-12

ACTIVITY COEFFICENTS
METALS
1.28747
5.390124
3.58863
5.76613
4.51792
LIGANDS
0.12944
0.790224
1.03878

SPECIES CONCENTRATION

0.184655	0	1.03149E-11
3.33210E-3	0.43608	5.00982E-13
3.62713E-2	0	1.55471E-10
8.84752E-6	0.262811	3.01925E-13
2.60603E-2	0	7.55205E-12
2.52859E-3	4.07123E-2	0.999958

PRECIPITATE MATRIX

0	0.854216	0
0	0	0
0	0	0
0	0	0
0	0	0
0	0	0

IONIC STRENGTH= 6.59979

CHARGE BALANCE = 2.80713E-4
NUMBER OF ITERATIONS= 18
EVAPORATION INCREMENT COMPLETE

REFERENCES

1. Norton, J.J., Lithium Resource Estimates - What do they mean: Lithium Resources and Requirements by the year 2000, James D. Vine Editor Geological Survey Professional Paper 1005. "A collection of papers presented at a symposium held in Golden, Colorado, January 22-24, 1976.

2. Kunasz, I.A., Lithium Resources - Prospects for the future: as for reference 1.

3. Vine, J.D., The Lithium Resource Enigma: as for reference 1.

4. Norton, J.J., 1973, Lithium, cesium, and rubidium - the rare alkali metals, in Brobst, d.A., and Pratt, W.P.,eds., United States Mineral Resources: U.S. Geol. Survey Prof. Paper 820, p.365-398.

5. Landgrebe, A.A., Battery Research sponsored by the U.S. Energy Research and Development Administration: as for reference 1.

6. Bogart, S.L., Fusion power and the potential Lithium Requirement: as for reference 1.

7. Hader, R.N., Nielsen, R.L., Herre, M.G., Lithium and its compound: Industrial and Engineering Chemistry, Vol. 43, No.12,2636.

8. Pancharatnam, S., Transient Behavior of a Solar Pond and Prediction of Evaporation Rates: Ind. Eng. Chem. Process Des. Develop., Vol. 11, No. 2, 1972.

9. Pancharatnam, S., Transient Behavior of Solar Pond through Fourier Analysis: Ind. Eng. Chem. Process Des. Develop., Vol. 11, No. 4, 1972.

10. Jacobsen, R.N. and Ore, F., Solar Pond Modeling: Symp. on Salt, 4th Proc. Houston, Tex., April 8-12 1973, v.2.

11. Kirk-Othmer, Chemical Encyclopedia.

12. Barrett, W. T. and O'Neill, B.J., Recovery of Lithium from Saline Brines using Solar Evaporation: Symp. on Salt, 4th Proc. Houston, Tex., April 8-12 1973, v.2.

13. Berthold, C.E. and Baker, D.H., Lithium Recovery from Geothermal Fluids: as for reference 1.

14. Vine, J.D., Nonpegmatite Lithium Resoure Potential: as for reference 1.

15. White, D.E., Thompson, J.M. and Fournier, R.O., Lithium contents of Thermal and Mineral Waters: as for reference 1.

16. Ericksen, G.E. and Guillermo Chong, D. and Tomás Vila, G., Lithium Resources of Salars in the Central Andes: as for reference 1.

17. Whelan, J.A. and Petersen, C.A., Lithium Resources of Utah: as for reference 1.

18. Morel, F. and Morgan, J., A Numerical Method for Computing Equilibria in Aqueous Chemical Systems: Environ. Sci. and Tech. v.6, No. 1, Jan 1972.

19. Brinkley, S.R., Calculation of the Equilibrium Composition of Systems of many constituents: J. Chem. Phys. v. 15, 107, Feb. 1947.

20. Ingri, N., Kakolowicz, W., Sillen, L.G., and Warnquist, B., Talanta, v.14, 1261 (1967).

21. White, W.B., Johnson, S.M., and Dantzig, G.B., Chemical Equilibrium in Complex Mixtures: J. Chem. Phys. v. 28, 751 May 1958.

22. Sturm, W., Chapt. 3 of Riley, J.P. and Skirrow: Chemical Oceanography, 2nd Ed. Acad. Press, 1975.

23. Zeleznik, F.J. and Gordon, S., Calculation of Complex Chemical Equilibria: Ind. Eng. Chem., v.60, 27, June 1968.

24. Meissner, H.P. and Tester, J.W., Activity Coefficients of Strong Electolytes in Aqueous Solutions: Ind. Eng. Chem. Process Des. Develop., vol 11, No. 1, 1972.

25. Meissner, H.P., Kusik, C.L., and Tester, J. W., Activity Coefficients of Strong Electrolytes in Aqueous Solution - Effect of Temperature: A.I.Ch.E. Journal V. 118, No. 3, p. 661, May, 1972.

26. Cobble, J. W., Thermodynamic Properties of High Temperature Aqueous Solutions VI: J. Am. Chem. Soc., 86: 5394-5401.

27. Bromley, L.A., Thermodynamic Properties of Strong Electrolytes in Aqueous Solutions: A.I.Ch.E. Journal, vol. 19, No. 2, March, 1973.

28. Robinson, R.A., and Stokes, R.H., Electrolyte Solutions: 2nd Ed., Butterworths, London, 1968.

29. Harned, H.S. and Owen, B.B., The Physical Chemistry of Electrolytic Solutions: A.C.S. Monograph Series No. 137, 3rd Ed., Reinhold, New York, 1958.

30. Wu, Y.C. and Hamer, W.J., Osmotic Coefficients and Mean Activity Coefficients of a Series of Uni-Univalent Electrolytes in Aqueous solutions at 25°C: N.B.S. Report 10002, Geb. 10, 1969.

31. Kusik, C.L. and Meissner, H.P., Vapor Pressures of Water over Aqueous Solutions of Strong Electrolytes: Ind. Eng. Chem. Process Des. Develop., Vol.12, No.1, 1973.

32. Meissner, H.P. and Kusik, C.L., Aqueous Solutions of Two or More Strong Electrolytes: Ind. Eng. Chem. Process Des. Develop., Vol. 12, No. 2, 1973.

33. Kusik, C.L. and Meissner, H.P., Activity Coefficients in Hydrometallurgy Presented at 106th A.I.M.E. Meeting: Atlanta, Georgia.

34. Bockris, J.M. and Reddy, A.K.N., Modern Electrochemistry: Voll, Plenum Press, New York, 1970.

35. Butler, J.N., Ionic Equilibrium - A mathematical approach: Addison-Wesley Publishing Co., Inc. , 1964.

36. Garrels, R.M. and Christ, C.L., Solutions, Minerals, and Equilibria: Freeman, Cooper & Co., San Francisco, 1965.

37. Kuncast, I.A., Lithium Raw Materials: Industrial Rocks and Minerals, S.J. Lefond, Ed., A.I.M.E., pp. 791-803 (1975).

38. Wyman, R.A., Laboratory Investigation of Spodumene Floatation: Canadian Mining and Metallurgy Bulletin, 49 (532), August, pp.562-565 (1956).

39. Averill, W.A. and Olsen, D.L., A review of the extractive porcesses for Lithium from ores and brines.

40. Steinberg, M. and Dang, Vi-Duong, Preliminary design and analysis of a process for the extraction of lithium from seawater.

41. Brewer, P.G., Minor Elements in Seawater: Chapt. 7, of Riley,J.P. and Skirrow, Chemical Oceanography, 2nd Ed., Acad. Press, 1975.

42. Goodenough, R.D., Recovery of Lithium: U.S. Patent # 2,964,381, filed Jan 29, 1957.

43. Kunin, R. and Lane, M., Personal Communication: Ecodyne, Graver water Division, January 24, 1978.

44. Jouy, A.D. and Coursier, J., Separation of Lithium and sodium by displacement development on Ion Exchangers, Bull. Soc. Chim. Grance, 1958, p. 323, paper #42.

45. Higgens, I.R., Personal communication: Chemical Separations Corporation, Jan. 19, 1978.

46. McGavey, F.X., Personal communication: Sybron/Ionac, Feb. 1, 1978.

47. Walker, A.C., Bray, U.B., and Johnston, J., J. Am. Chem. Soc., 49, 1255 (1927).

48. Bjerrum, J., Schwarzenbach, G., and Sillén, L.G., Stability Constants Part II: Inorganic Ligands, London, The Chemical Society, 1958.

49. Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S., Jaffe, I., Selected values of Chemical Thermodynamic Properties, Natl. Bur. Standards Circ. 500, U.S. Dept. Commerce (1952).

50. Willard - Furman, Elementry Quantitative Analysis

51. Garrels, R.M. and Thompson, M.E., Am. J. Sci, 260, 57 (1962).