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THERMOCHEMICAL PROPERTIES OF GIBBSITE, BAYERITE, BOEHMITE, DIASPORE AND THE ALUMINATE ION BETWEEN 0 AND 350°C

by

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ABSTRACT

A requirement for modelling the chemical behavior of groundwater in a nuclear waste repository is accurate thermodynamic data pertaining to the participating minerals and aqueous species. In particular, it is important that the thermodynamic properties of the aluminate ion be accurately determined, because most rock forming minerals in the earth's crust are aluminosilicates, and most groundwaters are neutral to slightly alkaline, where the aluminate ion is the predominant aluminum species in solution. Without a precise knowledge of the thermodynamic properties of the aluminate ion, aluminosilicate mineral solubilities cannot be determined.

The thermochemical properties $\overline{C^{o}_{p,298}}$, $\overline{S^{o}_{298}}$ and $\Delta\overline{H^{o}_{f,298}}$ and $\Delta\overline{G^{o}_{f,298}}$ of the aluminate ion have been determined from the solubilities of the aluminum hydroxides and oxyhydroxides in alkaline solutions between 20 and 350°C. An internally consistent set of thermodynamic properties, C^{o}_{p} , S^{o}_{298} , $\Delta H^{o}_{f,298}$ and $\Delta G^{o}_{f,298}$ have been determined for gibbsite, boehmite, diaspore and corundum. The thermodynamic properties of bayerite have been provisionally estimated and a preliminary value for $\Delta G^{o}_{f,298}$ of nordstrandite has been determined.

A NOTE ON NOTATION

The notation in this report generally follows conventional usage. Terms and symbols are identified and defined as they occur. However, the use of thermodynamic equilibrium constants, expressed with a K, or reaction quotients, expressed with a Q, may, in places differ from conventional usage.

K	refers to the equilibrium constant of a reaction, determined either by thermodynamic calculation, or from observation, after all corrections for nonstandard state conditions have been applied.
K'	refers to the equilibrium constant of a reaction, usually a solubility reaction, in which corrections have been applied to reduce it to standard state conditions, but, by virtue of deficiencies in the thermodynamic model applied, further empirical corrections are needed to attain true standard state conditions.
Q	refers to a standard state reaction product in which a system has not attained equilibrium.
Q'	is analogous to K' in that model corrections are not adequate to permit correction to true standard state conditions.
$\log(Q/K)$	Occasionally, a solubility product, determined from a solubility measurement, Q, is compared with the corresponding solubility product, K, determined from other thermodynamic data sources. This is conveniently expressed as the logarithm of the ratio of the two constants. On rare occasions, an equilibrium constant, K, derived from solubility data in one part of the text, will be redefined as Q when compared with K derived from independent sources. It is here that Q refers to the ion activity product (I.A.P.) as conventionally used in the literature.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

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Numerous scientists have contributed in various ways through fruitful discussions, technical suggestions, making available computer codes, unpublished data or preprints, or encouragement in general. Among these, we would particularly like to acknowledge the following: Professor Hubert L. Barnes, Pennsylvania State University; Dr. Robert R. Berman, University of British Columbia. Professors Ian S.E. Carmichael, and Harold C. Helgeson, University of California, Berkeley; Dr. Bruce Hemingway, U.S.G.S., Reston; Dr. J.K. Hovey, University of Alberta; Professor John H. Weare, University of California, San Diego; Drs. William L. Bourcier, Kenneth Jackson and Kevin Knauss, Lawrence Livermore National Laboratory; Dr. G. Michel Lafon, Exxon Production Research Company; Dr. Donald C. Langmuir, Colorado School of Mines; Professor Gil Michard, University of Paris; Professor Kenneth S. Pitzer, and Mr. Everett Shock, University of California, Berkeley; Dr. Leonard Silvester, Lawrence Berkeley Laboratory, Dr. John Tanger, University of California, Berkeley; Dr. Karl Wefers, Alcoa Laboratories, and Dr. Thomas J. Wolery, Lawrence Livermore National Laboratory.

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The senior author would like to thank Mr. James Landers for conducting an exploratory study on diaspore dissolution kinetics, which was incorporated in this report at the last moment, and Mr. Tri Tran, Ms. Lidia Liu, and Ms. Nancy Chuma for performing some of the calculations.

EXECUTIVE SUMMARY

This report was prepared by staff of the Lawrence Berkeley Laboratory on behalf of the U.S. Nuclear Regulatory Commission (NRC) through NRC FIN NO B3040-6 under Interagency Agreement DOE-5O-80-97, through U.S. Department of Energy Contract No. DE-AC03-76SF00098. The specific goal of the project was to identify the geochemical phenomena which control radionuclide migration in the thermally perturbed area adjacent to a high level waste repository. In order to accomplish this, precise modelling of water rock interactions is required. Water-rock interaction modelling requires accurate thermodynamic data for all participating aqueous species and particularly those of major elements such as aluminum. For nearly two decades, there have been questions regarding the validity of the thermodynamic properties of gibbsite, ($Al(OH)_3$), and corundum, (Al_2O_3), and the aqueous solubilities of the aluminum hydroxide minerals, gibbsite, bayerite ($Al(OH)_3$), boehmite ($AlOOH$), and diaspore ($AlOOH$). This makes it difficult to estimate accurately the thermodynamic properties of aqueous aluminum species, and consequently makes current water-rock interaction modelling a questionable endeavor.

The heat capacity, $C_p^o(T)$, entropy, S_{298}^o, and heat of formation, $\Delta H_{f,298}^o$, of gibbsite and corundum, which have been obtained by calorimetric measurements, were tentatively accepted as correct. $\Delta H_{f,298}^o$ of diaspore was calculated from phase equilibrium data by Haas (1972) and the calorimetrically derived $C_p^o(T)$ and S_{298}^o for diaspore by Perkins et al. (1969). Using only the high temperature heat capacity data by Mukaibo et al. (1969), S_{298}^o and $\Delta H_{f,298}^o$ of boehmite were refined through a comparison of the overlapping aqueous alkaline solubilities of gibbsite, boehmite and diaspore along the water saturation surface between 20 and 350°C. The solubility measurements for these three minerals were obtained from both published and unpublished sources.

The foregoing analysis reconciles the calorimetrically derived thermodynamic properties of gibbsite with those of corundum, but it appears that the S_{298}^o, of $Al_2O_3 \cdot H_2O$ published by Shomate and Cook (1946) cannot be attributed to boehmite, as is commonly assumed.

The refined thermodynamic properties of boehmite and the accepted thermodynamic properties of gibbsite and diaspore were used with selected solubility measurements for these minerals in aqueous alkaline solutions to compute the Gibbs free energy of formation, ΔG_f^o, of the aluminate ion between 0 and 350°C, assuming the reactions:

$$Al(OH)_3 + OH = Al(OH)_4^-$$

gibbsite

$$AlOOH + H_2O + OH^- = Al(OH)_4^-$$

boehmite
diaspore

Preliminary estimates of $\overline{C^o_{p,298}}$, $\overline{S^o_{298}}$ and $\Delta\overline{H^o_{f,298}}$ for $Al(OH)_4^-$ were calculated from predicted gibbsite solubility data between 20 and 70°C. These values were used together with $\overline{V^o}$ ($Al(OH)_4^-$) from Hovey and Hepler (1987) to calculate the Born coefficient, $\omega_{Pr,Tr}$ and the a_1, a_2, a_3, a_4, c_1 and c_2 parameters of the AlO_2^- species for the modified HKF equation of state for ionic and molecular species in aqueous electrolytes (Tanger and Helgeson, 1988; Shock and Helgeson, 1988). Agreement between the HKF model prediction of $\Delta G_{f,T}^o(AlO_2^-)$ with that obtained from gibbsite, boehmite and diaspore solubilities along the water saturation surface between 20 and 350°C is excellent.

Published information on the solubility of bayerite in alkaline aqueous solutions, and heats of decomposition and solution of bayerite and gibbsite, permitted an estimate to be made of the ΔS^o_{298} and $\Delta H^o_{f,298}$ of bayerite, assuming that $C^o_p(T)$ is the same as that of gibbsite. Solubility data indicate that bayerite is only twice as soluble as gibbsite at 25°C. With increasing temperature, this difference becomes even smaller. A preliminary estimate of $\Delta H^o_{f,298}$ of nordstrandite was attempted.

A summary of refined thermodynamic data derived from the evaluation conducted in this report is given in the following tables.

TABLE I
SUMMARY OF THERMODYNAMIC PROPERTIES OF ALUMINUM HYDROXIDES AND OXYHYDROXIDES, AND CORUNDUM

Mineral	Formula	$C^o_{p,298}$	Maier-Kelley Function parameters			S^o_{298}	$\Delta H^o_{f,298}$	$\Delta G^o_{f,298}$	$\log K^o_{f,298}$
		$cal.gfw^{-1}.K^{-1}$	a	$b \times 10^3$	$c \times 10^{-5}$	$cal.gfw^{-1}.K^{-1}$	$kcal.gfw^{-1}$	$kcal.gfw^{-1}$	–
Bayerite	$Al(OH)_3$	23.005	8.650	45.60	0.0	18.97	–307.829	–275.570	201.995
Gibbsite	$Al(OH)_3$	23.005	8.650	45.60	0.0	16.36 ± 0.08	–309.065 ± 1.284	–276.025	202.329
Nordstrandite	$Al(OH)_3$	–	–	–	–	–	–	–275.826	202.183
Boehmite	AlOOH		12.905	20.70	–3.005	8.99 ± 0.19	–237.893	–219.289	160.741 ± 0.26
Diaspore	AlOOH		14.430	0.780	0.120	8.446 ± 0.02	–238.827	–220.082	161.322
Corundum	Al_2O_3	18.889	27.490	2.820	–8.380	12.176 ± 0.03	–400.510 ± 0.300	–378.184	277.217

TABLE II
SUMMARY OF THERMODYNAMIC PROPERTIES OF THE ALUMINATE ION

Formula	$\overline{C^o_{p,298}}$	$\overline{S^o_{298}}$	$\Delta\overline{H^o_{f,298}}$	$\Delta\overline{G^o_{f,298}}$	$\log\overline{K^o_{f,298}}$	$\overline{V^o}$
	$cal.gfw^{-1}.K^{-1}$	$cal.gfw^{-1}.K^{-1}$	$kcal.gfw^{-1}$	$kcal.gfw^{-1}$	–	$cm^3.gfw^{-1}$
$Al(OH)_4^-$	+21.08	+29.59	–357.56	–311.88	+228.611	+46.22
AlO_2^-	–14.89	–3.81	–220.93	–198.506	+145.507	+10.08

HKF Equation of State Parameters

Formula	$a_1 \times 10^1$ $cal.gfw^{-1}.bar^{-1}$	$a_2 \times 10^{-2}$ $cal.gfw^{-1}$	a_3 $cal.K.gfw^{-1}.bar^{-1}$	$a_4 \times 10^{-4}$ $cal.K.gfw^{-1}$	c_1 $cal.gfw^{-1}.K^{-1}$	$c_2 \times 10^{-4}$ $cal.K.gfw^{-1}$	$\omega \times 10^{-5}$ $cal.gfw^{-1}$
AlO_2^-	0.31586	3.0566	–2.1559	–2.9054	13.331	–6.075	1.6866

TABLE III

LOG K_{s4} FOR ALUMINUM HYDROXIDES, OXYHYDROXIDES AND CORUNDUM TAKEN ALONG THE WATER SATURATION SURFACE

T,°C			$\text{Log}K_{s4}$[1]		
	Gibbsite	**Bayerite**	**Boehmite**	**Diaspore**	**0.5 Corundum**
0	−1.679	−1.263	−1.462	−2.108	+0.127
25	−1.276	−0.943	−1.240	−1.821	+0.119
50	−0.889	−0.626	−1.022	−1.548	+0.138
60	−0.740	−0.502	−0.937	−1.445	+0.149
100	−0.184	−0.032	−0.623	−1.059	+0.210
150	+0.433	+0.499	−0.279	−0.638	+0.298
200			+0.018	−0.269	+0.391
250			+0.276	+0.257	+0.481
300			+0.500	+0.348	+0.568
350			+0.689	+0.604	+0.642

[1] Values are based on HKF Equation of state prediction of AlO_2^- thermodynamic properties, and differ slightly from those obtained from an empirical fit of gibbsite, boehmite and diaspore solubility data, given in Table 12.

TABLE IV

ESTIMATED VALUES OF LOG K_4^{-1} FOR THE REACTION $Al(OH)_4^- = Al(OH)_3^0 + OH^-$

T,°C	1/T, $K^{-1} \times 10^3$	log K_4^{-1}
0	3.661	−9.088
25	3.354	−8.517
50	3.095	−8.034
60	3.002	−7.861
100	2.680	−7.262
150	2.363	−6.673
200	2.133	−6.208
250	1.911	−5.832
300	1.745	−5.522
350	1.605	−5.261

FOREWORD

This report is an outgrowth of other research being conducted for the United States Nuclear Regulatory Commission. One of the major concerns regarding the deep burial of high level radioactive waste, is its potential to be leached after burial, and be transported by groundwaters to the earth's surface. How radioactive waste constituents migrate in groundwater is an issue that must be understood before safe burial can be ensured. Herein lies the justification for this study. Present attempts to model groundwater transport of radioelements depend on a quantitative understanding of how rock-forming minerals react and equilibrate with the groundwater, and how radioelements will behave in this environment. Because most important rock-forming minerals are aluminosilicates, an essential part of the modelling process is our knowledge of the behavior of aluminum in solution. Unfortunately, the senior author found serious discrepancies in the literature regarding the thermodynamic properties of aluminum species in aqueous solution, which raised questions as to the validity of current attempts to model groundwater compositions. Before further research could be conducted, the matter of quantifying the aluminum speciation in solution had to be resolved.

At first, this seemed to be a relatively easy problem. In many groundwaters, the dominant aluminum species is the aluminate ion, $Al(OH)_4^-$. The thermodynamic properties of this species could, in principle, be determined quite easily from the solubilities of the aluminum hydroxides, gibbsite, boehmite and diaspore. Although only the thermochemical properties of gibbsite are fully determined, it seemed a relatively easy matter to cross-correlate the thermochemical properties of boehmite and diaspore with gibbsite, and with corundum, a mineral that is also completely characterized thermodynamically. Although questions have been raised over the last seventeen years regarding possible errors in the thermodynamic properties of either gibbsite or corundum, this did not appear to be a major problem. However, reconciling the disparate sources of information and establishing consistency between the calorimetrically determined thermodynamic properties of gibbsite and corundum proved to be yet another uncertainty complicating the ensuing analysis.

A large number of papers describing the solubility of gibbsite, bayerite, boehmite, and diaspore as well as previously unpublished solubility measurements on gibbsite, boehmite and diaspore, were reviewed and the available data subjected to systematic evaluation. Data sources required close scrutiny in order to establish which set of data represented a closer approach to the true solubility of a given mineral. Furthermore, the ensuing analysis proved to be unexpectedly sensitive to small errors in the collected data. Thus, the substitution of one data set over another could lead to a wholly different albeit potentially unrealistic interpretation. The interpretation given here is believed to be the best compromise of all sources of data evaluated. Deviations from the authors' assigned values of the solubilities of gibbsite, bayerite, boehmite and diaspore in alkaline solutions, can for the most part be explained satisfactorily.

The authors conclude that the calorimetrically determined thermochemical properties of gibbsite and corundum are internally consistent to within experimental error. Of the four aluminum hydroxide and oxyhydroxide minerals, diaspore is the most stable over the whole range between 0 and 350°C. The standard enthalpy of formation $\Delta H^o_{f,298}$, of bayerite, boehmite and diaspore, have been determined from solubility, phase equilibrium and calorimetric data. A critical error in the published entropy, S^o_{298}, of boehmite has been identified, and a more realistic value was computed. Recent unpublished calorimetric studies by Bruce Hemingway, USGS, confirm the discrepancy in the published entropy of boehmite.

The satisfactory reconciliation of the thermochemical properties of gibbsite, boehmite, diaspore and corundum permitted calculation of $\log K^o_{f,T}(Al(OH)_4^-)$ and the corresponding $\Delta\overline{G^o_{f,T}}\,(Al(OH)_4^-)$. The authors were not confident they could calculate the remaining thermochemical properties for $Al(OH)_4^-$. However, these were determined using $\log K_{s4}$(gibbsite) between 20 and 70°C. The value of the conventional standard partial molar heat capacity was found to be in excellent agreement with that measured independently by J.K. Hovey at the University of Alberta.

The derived thermodynamic properties of $Al(OH)_4^-$ at 25°C were used to calculate HKF equation of state parameters for the corresponding ionic species, AlO_2^-. The HKF equation of state, developed by Helgeson and his students and coworkers at the University of California, Berkeley, now demonstrates a remarkable ability to predict the standard state of thermodynamic properties of ionic species over a wide range of temperatures and pressures. Comparison of the predicted $\Delta\overline{G}_f^o$ (AlO_2^-) with that determined from solubility measurements in this report, shows excellent agreement over the temperature range 20°C to 350°C. The difference never exceeds 0.17 $kcal.gfw^{-1}$.

An evaluation of measured solubilities of bayerite in alkaline media, and scattered measurements of the heats of decomposition of bayerite and gibbsite, and the heats of dissolution of bayerite and gibbsite in hydrofluoric acid, allowed for an internally consistent set of thermodynamic data to be obtained for this mineral. These results demonstrate that bayerite is less stable than gibbsite over the range of temperatures and pressures over which solubilities measurements were made.

Many of the previously unpublished experimental results presented in this report are exploratory in nature, being attempts to define an approach to the problem. Although preliminary, they provide the basis for more rigorous studies. While the results presented here are believed to be as accurate as is presently achievable with available information, several critical studies should be conducted to verify the findings. These include an independent determination of the low temperature heat capacity of boehmite to compute S_{298}^o, which is presently underway at the USGS, Reston, and more precise low and high temperature solubility determinations of boehmite and diaspore in the alkaline region.

Finally, it should be noted, that this report is intended to be a working document designed to be modified and updated with the acquisition of new information as it becomes available. For this reason, the procedures used in the calculations are described in greater detail than is customary. Also, some sections still need further development. Estimates of the errors of some parameters have been omitted, primarily because to have taken them into account would have hindered progress towards finding a satisfactory interpretation while not contributing significantly towards discriminating between correct and incorrect data.

The senior author would be most grateful to receive comments and criticisms of this report. He alone accepts responsibility for errors and omissions. He would like to emphasize, however, that whatever success this report will have in leading to more precise computations of groundwater chemistry, it is the cumulative effort of many scientists over many years that makes this possible.

1. INTRODUCTION

1.1 Background

In recent years, internally consistent thermodynamic data of mineral phases have been compiled and evaluated, using information derived both from calorimetric and from phase equilibrium measurements. (Zen, 1972; Thompson, 1974; Ulbrich and Merino, 1974; Day, 1976; Helgeson et al., 1978; Perkins et al., 1979; Hemley et al., 1980; Chatterjee et al. 1984; Halbach and Chatterjee, 1982, 1984; Wood and Holloway, 1984; Berman et al., 1985; Berman, 1988). These evaluations serve to highlight inconsistencies between independent sets of experimental data, and to influence the direction of further research towards resolving them. This continuing process is leading to a progressive refinement of the thermodynamic data.

Internally consistent data bases are needed to compute the composition of the aqueous phase coexisting with various mineral assemblages. However, few mineral solubilities have been measured with sufficient precision over the wide range of temperatures, pressures and supporting electrolyte concentrations necessary to validate either the mineral thermodynamic data bases, or to test electrolyte models used to relate species concentrations with the chemical components of participating minerals.

A notable exception is the silica polymorphs, quartz, cristobalite and amorphous silica. The abundant solubility data of these polymorphs have been carefully reviewed by Walther and Helgeson (1977) and by Fournier and Potter (1982).

Most of the common rock-forming minerals are aluminosilicates. Their aqueous solubilities can be estimated only if the thermodynamic properties of the alumina component in the aqueous phase is well established over the geologically significant range of temperatures, pressures and electrolyte concentrations. Unfortunately, considerable uncertainty attends this matter, as can be noted from discussions in several recent papers. (Arnorssen et al., 1982, 1983; Hemingway, 1982; Apps and Neil, 1982; Kuyunko et al., 1983; Reed and Spycher, 1984).

A substantial body of literature describing the alkaline aqueous solubility of alumina hydrates, and a few papers on the aqueous solubility of corundum have been published during the last sixty years, in support of the development of the Bayer process for refining bauxitic aluminum ores. These papers, and several others unrelated to the aluminum industry, provide a wealth of information suitable for evaluating the thermodynamic properties of the aluminate ion between 0 and 350°C when used in conjunction with the thermodynamic properties of gibbsite, boehmite, diaspore and corundum.

This opportunity has not been missed by Russian workers who have conducted comprehensive reviews of the literature and published several papers summarizing their estimates of thermochemical properties of aluminum species in solution. (Sokolova and Khodakovskiy 1977; Khodakovskiy et al., 1980; Kuyunko, et al., 1983). Recent work by the senior author, requiring an accurate interpretation of the experimental dissolution of basalt in groundwater at elevated temperature, highlighted the need for a reinterpretation of the literature data and earlier solubility measurements on gibbsite, boehmite and diaspore by the senior author (Apps, 1970), together with more recent hitherto unpublished reconnaissance measurements of diaspore solubility by Apps, Neil, and Landers. The purpose of this paper, then, is to reevaluate available data on alumina hydrate aqueous solubilities, to reconcile the thermodynamic properties of gibbsite, bayerite, boehmite, diaspore and corundum, and to present thermodynamic data on the aluminate ion, which can be used in modelling aqueous solubilities of aluminosilicates up to 350°C.

2. APPROACH

Estimation of the thermodynamic properties of minerals and aqueous species normally requires the construction of ''cycles'' (Robinson et al., 1982) or paths for constructing internally consistent thermodynamic data sets, which can be linked to reference phases whose properties have universal acceptance. Calculation of thermodynamic properties from raw data requires the use of equations and models containing a number of assumptions. The thermodynamic cycle evaluated in this report is outlined schematically in Figure 1. It incorporates two reference phases, corundum and gibbsite, both of which have been used as primary or secondary standards, and relates the properties of these two phases with bayerite, boehmite and diaspore through aqueous solubility and phase equilibrium measurements.

The currently available data for this cycle fall into three categories:

1. Calorimetric measurements.
2. Solubility measurements.
3. Phase equilibrium measurements.

In the following sections, we will summarize each of these categories in turn. Then conduct the necessary calculations to reconcile and extract thermodynamic parameters as appropriate.

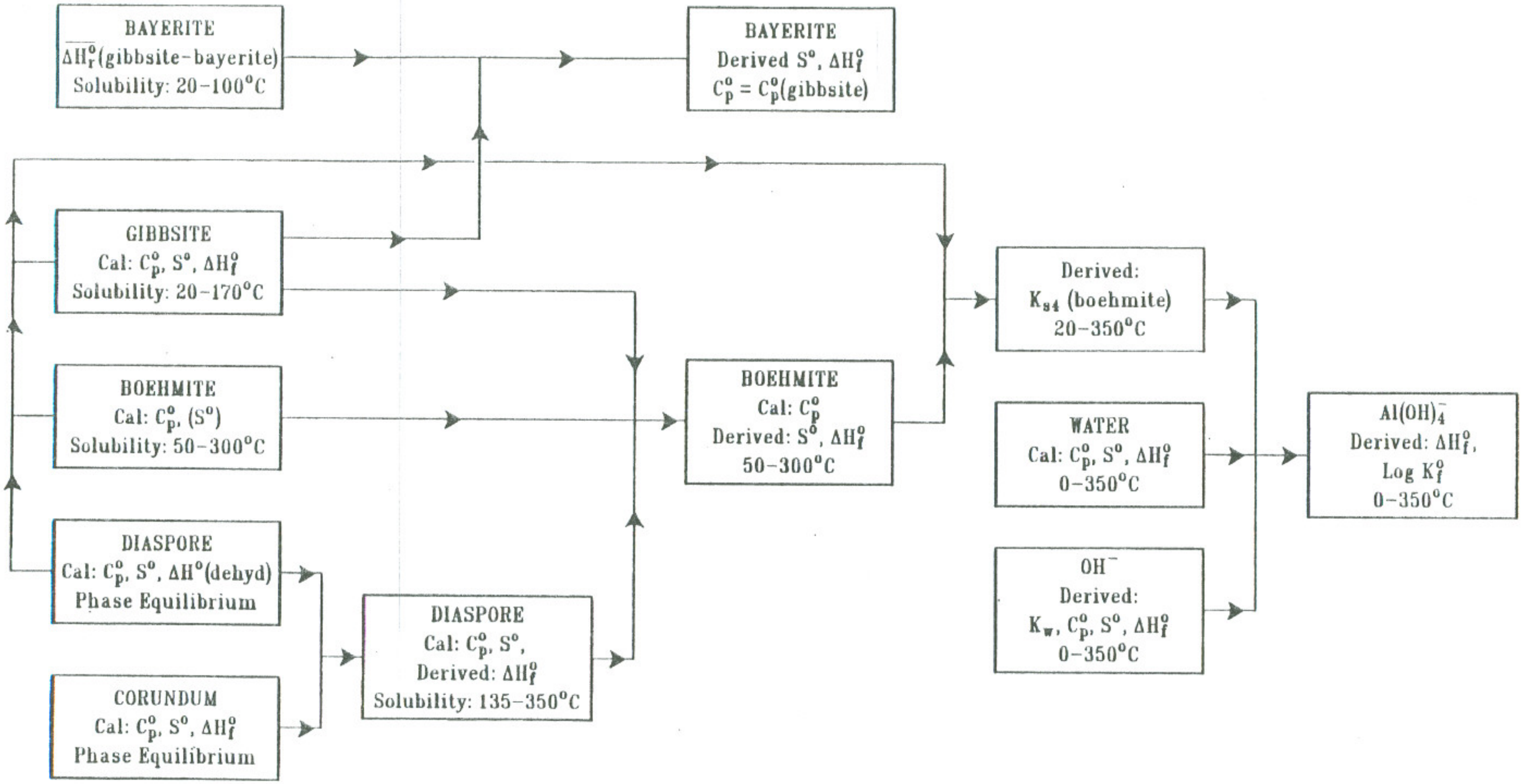

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Figure 1. Cycle for the calculation of some thermodynamic properties of aluminum hydroxides, oxyhydroxides, and the aluminate ion, $Al(OH)_4^-$.

3. AVAILABLE THERMODYNAMIC DATA FOR THE ALUMINUM HYDROXIDES, OXYHYDROXIDES AND CORUNDUM

The thermodynamic data used in this study is summarized in Table 1. A discussion of these data follows:

TABLE 1

THERMODYNAMIC DATA FOR ALUMINUM OXIDES AND HYDROXIDES
AT 25°C AND 1 ATMOSPHERE PRESSURE

Mineral	formula	Measured range of C_p^o, K	S^o, $\mathrm{cal.gfw^{-1}.K^{-1}}$	ΔH_f^o, $\mathrm{kcal.gfw^{-1}}$
Gibbsite	$Al(OH)_3$	13-480	16.36±0.08[1)]	−309.065 ± 1.284[1]
Bayerite	$Al(OH)_3$	—	—	—
Boehmite	AlOOH	53-586	11.58±0.12[2)]	—
Diaspore	AlOOH	5-520	8.446±0.02[3)]	−238.827[4)]
Corundum	Al_2O_3	13-2257	12.176±0.03[5)]	−400.510±0.300[5)]

[1)] Hemingway and Robie (1977a) and Hemingway et al. (1978)

[2)] Shomate and Cook (1946)

[3)] Perkins et al. (1979)

[4)] Calculated from 5) using phase equilibrium data from Haas (1972) as interpreted by Helgeson et al. (1978)

[5)] Robinson et al. (1982)

3.1 Gibbsite

Heat capacity measurements on gibbsite have been made by Shomate and Cook (1946) between 53 and 297 K, by Hemingway et al. (1977) between 13 and 480 K, and by Mukaibo et al. (1969) between 313 and 450 K. All measurements are in substantial concordance. In addition, Shomate and Cook measured the heat content of gibbsite between 322 and 424 K. The entropy, S_{298}^o, has been computed by Shomate and Cook (1946) and by Hemingway et al. (1977). Agreement between the two determinations is close. The value, 16.36 ± 0.03 $\mathrm{cal.gfw^{-1}.K^{-1}}$, by Hemingway et al. (1977) was chosen. Because of difficulties reconciling thermodynamic data based on Barany and Kelley's determination of the heat of formation of gibbsite, $\Delta H_{f,298}^o$, (Barany and Kelley, 1961), Hemingway and Robie (1977a) redetermined $\Delta H_{f,298}^o$(gibbsite) using a different reaction scheme. Their revised value for $\Delta H_{f,298}^o$, 309.065 ± 0.285 $\mathrm{kcal.gfw^{-1}}$, was used in this study.

3.2 Bayerite

No standard state thermodynamic data have been computed for bayerite from calorimetric measurements. Some heats of decomposition and heats of solution have been made. Their evaluation depends on comparable data for gibbsite. Section 7 is devoted to this analysis.

3.3 Boehmite

Heat capacity measurements have been made by Shomate and Cook (1946) between 53 and 296 K on an aluminum monohydrate giving an X-ray pattern described as "dehydrated bayerite". Subsequently, Mukaibo et al. (1969) made measurements on an impure boehmite between 313 and 586 K. The quality of both sets of measurements is questioned by Robinson et al. (1982), who prefer the estimated values of Haas et al. (1981). Shomate and Cook used their heat capacity data on "dehydrated bayerite" to calculate an entropy, S^o_{298}, that has been reported subsequently by Kelley and King (1961), Robie and Waldbaum (1968), Robie et al. (1978), Robinson et al. (1982), Helgeson et al. (1978) and Berman et al. (1985) for boehmite.

Kennedy (1959) mentioned that Barany and Kelley had determined the S^o_{298} on a sample of boehmite that he prepared, and cites a value identical with that given by Shomate and Cook (1946). However, there appears to be no other report of this determination. In the absence of confirmatory data, the published determination must be considered suspect. No determination has been made of the heat of formation of boehmite.

3.4 Diaspore

Heat capacity measurements have been made by King and Weller (1961) between 51 and 296 K, by Perkins et al. (1979) between 5 and 520 K, and by Mukaibo et al. (1969), between and 313 and 586 K. All measurements are in reasonable agreement.

Entropy determinations by King and Weller (1961) and by Perkins et al. (1979) yielded 8.43 ± 0.04 and 8.446 ± 0.02 cal.gfw^{-1}.K^{-1} respectively. The more recent value by Perkins et al. (1979) was chosen for this study. No heat of formation data have been reported, although Mukaibo et al. (1969) give the enthalpy of dehydration of diaspore according to the reaction

$$2\ \mathrm{AlOOH} = \alpha\mathrm{Al_2O_3} + \mathrm{H_2O(v)}$$

as 19.9±0.3 kcal.gfw^{-1} ($Al_2O_3.H_2O$). This value is consistent within analytical error with the value determined from phase equilibrium measurements.

3.5 Corundum

The generally accepted values of heat capacity are derived from Ditmars and Douglas (1971), who tabulated functions between 0 and 1200 K, based on data between 13 and 380 K by Furukawa et al. (1956), and measurements by Ditmars and Douglas between 323 and 1173 K. Above 1175 K, the high temperature enthalpy data between 1173 and 2257 K by West and Ishihara (1970) were used. These data were compared with some 20 earlier studies on Cp or ΔH^o measurements above room temperature. Ditmars and Douglas' values have been incorporated in the JANAF tables with slight modification by Chase et al. (1978).

Many calorimetric measurements of the heat of formation of corundum have been made (Holley and Huber, 1951; Mah, 1957; Schneider and Gattow, 1954; Snyder and Seltz, 1945; Zenkov, 1981). All involved burning aluminum metal in an oxygen atmosphere, because of the near insolubility of corundum in hydrofluoric acid, and the difficulty of measuring the heat of solution of aluminum in acid.

The most recent studies give closely consistent values, e.g. −400.29±0.31, (Holley and Huber, 1951), −400.48±0.25, (Mah, 1957) and −399.90±0.12, (Zenkov, 1981) (values given in kcal.gfw^{-1}). Although Holley and Huber (1951) report that corundum (αAl_2O_3) was the only reaction product, Schneider and Gattow (1954) and Zenkov (1981) note the presence of other polymorphs. Schneider and Gattow (1954) identified $\chi\ Al_2O_3$, which has a ΔH^o_f that is up to 10 kcal. gfw^{-1} less stable than αAl_2O_3 (Carniglia, 1983). Chase et al. (1978) have chosen a value of 400.50±0.300 kcal.gfw^{-1} for $\Delta H^o_{f,298}$, but are uncertain as to how close this is to the true value. They note that the reactions:

$$Al_2O_3(c) + 6HCl(g) = 2AlCl_3(g) + 3H_2O(g)$$

and

$$Al_2O_3(c) + 6HF(g) = 2AlF_3(c) + 3H_2O(g)$$

yield −401.8±1.5 and −405.2±1.5 kcal.gfw^{-1}, respectively for $\Delta H^{o}_{f,298}$(corundum). They point out, however, that the reaction involving HF may be biased by the formation of aluminum oxyfluoride.

An alternative, but less direct way of verifying $\Delta H^{o}_{f,298}$(corundum) is to utilize information derived from a combination of calorimetric and phase equilibrium data for reactions involving the formation of corundum.

Examples include the reactions:

$$\underset{\text{muscovite}}{KAl_3Si_3O_{10}(OH)_2} = \underset{\text{sanidine}}{KAlSi_3O_8} + \underset{\text{corundum}}{Al_2O_3} + \underset{\text{water}}{H_2O}$$

or

$$\underset{\text{paragonite}}{NaAl_3Si_3O_{10}(OH)_2} = \underset{\text{analbite}}{NaAlSi_3O_8} + \underset{\text{corundum}}{Al_2O_3} + \underset{\text{water}}{H_2O}$$

In the first case, sufficient information is available to compute $\Delta H^{o}_{f,298}$ (corundum) independently as was done by Chatterjee and Johannes (1974) using $\Delta H^{o}_{f,298}$ (muscovite) from Barany (1964), S^{o}_{298} (muscovite) from Weller and King (1963), $\Delta H^{o}_{f,298}$ (sanidine) from Waldbaum (1968) and Waldbaum and Robie (1971), and S^{o}_{298} (sanidine) from low temperature heat capacity data by Kelley et al. (1953). Chatterjee and Johannes (1974) show that the $\Delta H^{o}_{f,298}$ (corundum), when compared with that cited in Robie and Waldbaum (1986), must be correct to within one kilocalorie. However, problems in interpreting the degree of ordering in muscovite, and more recent high temperature heat capacity data made it difficult for Krupka et al. (1979) to reconcile the phase equilibrium data of Chatterjee and Johannes (1974) with calorimetric values. Berman et al. (1985) were more successful in reconciling the same data by assuming a totally disordered sanidine, again suggesting the validity of the currently accepted $\Delta H^{o}_{f,298}$ (corundum), given by Chase et al. (1978).

In the case of the reaction involving the decomposition of paragonite, phase equilibrium measurements were made by Chatterjee (1970). Calorimetric data for all other phases are available except for $\Delta H^{o}_{f,298}$(paragonite). Robie and Hemingway (1984) attempted to calculate $\Delta H^{o}_{f,298}$(paragonite) from several independent reactions involving paragonite, including that given above, and obtained values consistent to within ±1.1 kcal.gfw^{-1}. This again suggests that the accepted value for $\Delta H^{o}_{f,298}$(corundum) by Chase et al. (1978), and used by these workers, cannot be substantially in error.

For the purposes of this evaluation, the authors have selected the thermodynamic parameters for corundum from the compilation by Robinson et al. (1982), which were taken from Chase et al. (1978) and are almost identical with their values. They are summarized in Table 1.

4. EVALUATION OF SOLUBILITY DATA IN ALKALINE SOLUTIONS

4.1 Introduction

As mentioned in the introduction, most measurements of aluminum hydroxide solubilities have been conducted in support of the Bayer process for treating bauxitic aluminum ores. In this process, bauxite, which usually consists of a mixture of aluminum hydroxides with impurities such as kaolinite and iron oxides, is digested in a concentrated aqueous solution of sodium hydroxide (≤ 200 g.$l^{-1}Na_2O$) at temperatures as high as 250°C. The alumina and silica dissolve, leaving a residue of iron oxides or "red mud". Subsequent cooling of the pregnant liquor to 50–60°C and seeding with gibbsite leads to precipitation of a relatively pure coarsely crystalline gibbsite product that is easily separated from the liquor by settling and filtration. Most solubility measurements of gibbsite, boehmite and diaspore, reported in the literature, have therefore been made in highly caustic sodium hydroxide solutions to temperatures as high as 350°C.

Table 2 lists the sources of data used in the present evaluation of alkaline solubilities of gibbsite, boehmite and diaspore. A few oft quoted papers, e.g, Gayer et al. (1958) and Raupach (1963) been omitted from the initial evaluation, because their results are quite discordant with those of the majority of other investigators. Their results are interpreted in Section 7. The alkaline solubility measurements of a synthetic gibbsite by May et al. (1979) are included in the initial evaluation in spite of the discordance of their results. Their research merits careful analysis because of the meticulous care with which their experiments were conducted, and the insight the research provides in interpreting the results of other investigators.

Although solubility data on corundum exists, for example, Yalman et al. (1960), Yamaguchi et al. (1962), Levinson et al. (1963), Anderson and Burnham (1967), Ostapenko and Arapova (1971), Ganeev and Rumyantsev (1974), and Ganeev et al. (1974) and Ragnarsdottir and Walther (1985), these data were not evaluated in the present study owing to difficulties associated with the use of the electrolyte model embodied in the EQ3 code at temperatures above 350°C, and at supercritical pressures.

A large body of literature also reports on various studies involving the precipitation of gels and finely crystalline products from supersaturated solutions of aluminum. Most of the resulting precipitates are poorly characterized and frequently involve crystallization of metastable phases. Hemingway (1982) gives an excellent discussion of this subject. Such studies are of interest in resolving questions relating to the interpretation of experimental solubility measurements and to the persistence of metastable phases in nature. A brief review of this subject is given in Section 7.

Aluminum hydroxides are amphoteric compounds, which dissolve in solution to produce positively or negatively charged ions, depending on the pH of the solution. The distribution of these species in relation to pH and total aluminum concentration has been evaluated and summarized by Katorcha (1972), Khodakovskiy (1975) and Baes and Mesmer (1976), the first two investigators also predicting species distribution as a function of temperature. Figure 2, taken from Baes and Mesmer (1976) illustrates their interpretation of the saturation surface of gibbsite at 25°C in relation to the participating aqueous aluminum species. It is generally believed that over most of the alkaline region beyond neutral pH, only one aluminum species dominates in solution; the aluminate ion $Al(OH)_4^-$. However, considerable diversity of opinion exists as to its state of hydration, and whether it is tetrahedrally or octahedrally coordinated with surrounding oxygens. It could be described as $Al^{VI}(OH)_4 . 2H_2O^-$, $Al^{IV}(OH)_4^-$, $Al^{IV}O(OH)_2^-$, $Al^{IV}O_2^-$, or in other less likely octahedral coordinations. For the purposes of this paper, the commonly accepted tetrahadral configuration, $Al(OH)_4^-$, will be used, although arguments in support of the progressive dehydration of the $Al(OH)_4^-$ ion with increasing temperature and ionic strength (e.g., Dibrov et al., 1964a, Hemingway, 1982) are quite persuasive. Furthermore, if an electrolyte model is used which includes the effect of solvation, e.g. Tanger and Helgeson (1988), then it becomes necessary to describe the species as AlO_2^-. The existence of polynuclear complexes in alkaline solution is more tenuous. From the evidence of Dibrov et al. (1964) and Szita and Berecz (1975), we have decided initially to omit them from consideration in this analysis.

TABLE 2

SOURCES OF SOLUBILITY MEASUREMENTS FOR ALUMINUM HYDROXIDES AND OXYHYDROXIDES IN ALKALINE SOLUTIONS

Mineral	Source	Temperature Range, °C
Gibbsite	Apps (1970)	24.0-92.8
	Berecz and Szita (1970) and Szita and Berecz (1970)	25-60
	Fricke and Jucaitis (1930)	30,60
	Fulda and Ginsberg (1951)	40-100
	Ikkatai and Okada (1962)	40-130
	Kittrick (1966)	25
	Kuznetsov (1952)	25-140
	Lyapunov et al. (1964)	60, (95)
	May, Helmke and Jackson (1979)	25
	Packter (1979)	20-80
	Russell et al. (1955)	40-170
	Sato (1954)	30-70
	Tsirlina (1936)	60, 80, 95
	Wefers (1967b)	60,105
Bayerite	Chistyakova (1964)	20
	Fricke (1928)	3
	Fricke (1929)	30
	Hem and Roberson (1967)	25
	Herrmann and Stipetić (1950)	25, 28.5
	Lyapunov et al. (1973)	40-60
	Russell et al. (1955)	40-100
	Sanjuan and Michard (1987)	50
Boehmite	Apps (1970)	49.65, 70.05, 90.05; 121-225
	Bernshtein and Matsenok (1961)	250, 300
	Kuyunko et al. (1983)	200, 250
	Magarshak (1938)	150, 200
	Russell et al. (1955)	80-170
	Wefers (1967b)	95,105
Diaspore	Apps (1970)	29-93.5; 124-260
	Apps and Neil (this report)	175, 250, 325; 100-350
	Apps and Landers (this report)	197
	Bernshtein and Matsenok (1965)	250, 300
	Chang, Pak and Li (1979)	250-325
	Druzhinina (1955)	200, 220
	Wefers (1967b)	135-350

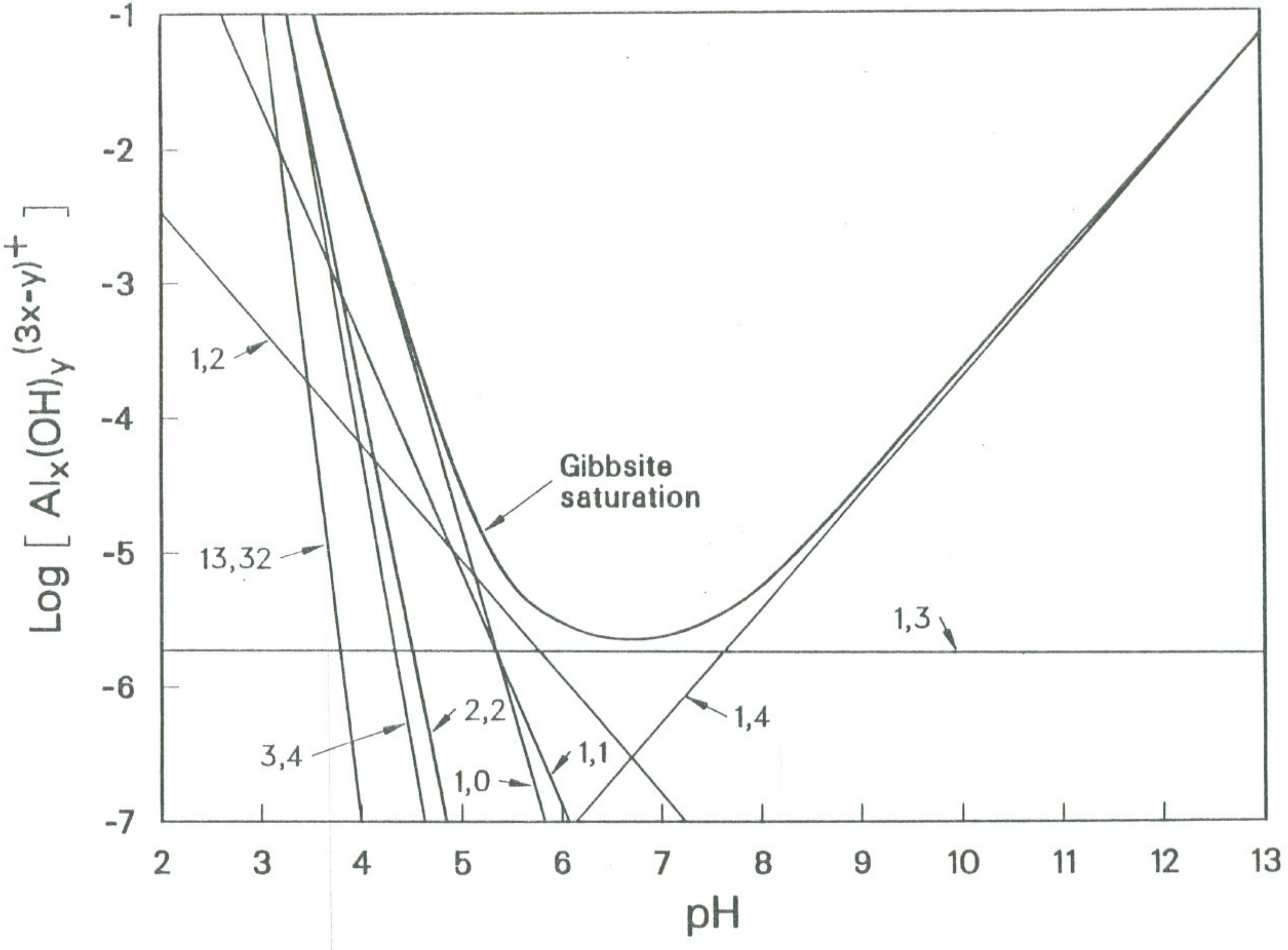

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Figure 2. The saturation surface of gibbsite at 25°C estimated by Baes and Mesmer (1976). Aqueous species designated by numbers represents respectively the stoichiometry of Al^{+++} and OH^{-}.

We assume that gibbsite dissolves in alkaline solution according to the reaction:

$$Al(OH)_3 + OH^- \;=\; Al(OH)_4^-$$

for which the solubility product is:-

$$K_{s4}(\text{gibbsite})(T) \;=\; \frac{[Al(OH)_4^-]}{[OH^-]}$$

where [ ] denote activities.

Similarly:

$$AlOOH + OH^- + H_2O \;=\; Al(OH)_4^-$$

for which:

$$K_{s4}(\text{boehmite/diaspore})(T) \;=\; \frac{[Al(OH)_4^-]}{[OH^-][H_2O]}$$

Calculation of K_{s4}[1] for all three aluminum hydroxides requires the computation of the distribution of aqueous species based on available chemical analyses of solutions coexisting with the solid phases, calculation of ionic and neutral species activity coefficients, and calculation of the activity of water. This was done using a computer code, EQ3, developed by T.J. Wolery at the Lawrence Livermore National Laboratory (Wolery, 1983). This particular code was chosen because it is very thoroughly documented, and because it continues to be supported and improved through DOE funding. It also has great flexibility in accepting data in a variety of forms. In addition, it incorporates an extensive data base, most of which is derived from a critical evaluation of the thermodynamic properties of minerals by Helgeson et al. (1978). The thermodynamic properties of many of the aqueous species have also been evaluated and computed using a solvent interaction model, also developed by Helgeson and his coworkers (1974a,b, 1976, 1981). Since the EQ3 code will be the vehicle for conducting analyses of aqueous fluids in repository environments, it was felt that it should also serve to evaluate the thermodynamic properties of minerals that will eventually be incorporated in its database. It should be emphasized, however, that much of the data reduction in this report involves solutions whose ionic strengths fall outside the range considered acceptable for the simple electrolytic model incorporated in the EQ3 code. More sophisticated models will eventually be needed for a more refined data reduction.

Although the authors have extended the use of EQ3 algorithms beyond their designed limits, it was felt that this was justified, especially because more sophisticated models are not readily available, and because much of the evaluation involved comparisons of the relative agreement of different data sets.

The EQ3 code uses the generally accepted relations for the computation of activities of aqueous species in solution

$$a_i = m_i \gamma_i$$

where a_i = the thermodynamic activity ($mole.kg^{-1}$)
m_i = concentration of species i ($mole.kg^{-1}$)
γ_i = activity coefficient (-)

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[1] Note that for the designation of reaction constants in this report, the nomenclature of Sillen and Martell (1964) is followed.

and where

$$\log \gamma_i = \frac{-A(z_i)^2\sqrt{I}}{(1 + \overset{o}{a}_i B\sqrt{I}} + \dot{B} I$$

A, B = Debye Huckel parameters
$\overset{o}{a}_i$ = ionic radius (m^{-9})
z_i = ionic charge (−)
I = ionic strength
= $\frac{1}{2}\sum_{i=1}^{i} m_i z_i^2$ ($mol.kg^{-1}$)
$\dot{B}$ = an adjustable parameter to ensure a proper fit.

This extension of the Debye-Huckel equation, used by Helgeson (1969) and derived from earlier studies by Pitzer and Brewer (Lewis and Randall, 1961), has been found useful in analyzing solutions of ionic strength less than one molal. In the EQ3 code, the B parameter is assigned values so that activity coefficients in aqueous NaCl solutions can be computed. The B parameter differs only slightly from that required to replicate NaOH solutions (Robinson and Stokes, 1959, p. 492) so it was deemed unnecessary to modify B , particularly when other uncertainties may affect the calculation of species distribution to an even greater degree.

In general, EQ3 sets the activity coefficient of neutral species to unity, i.e.

$$\log \gamma_i = 0$$

The activity of water can be calculated by means of the Gibbs-Duhem equation once the activities of all aqueous species are known. However, EQ3 uses instead an approximation from Helgeson (1969) where

$$\log a_{H_2O} = -2I\phi'/(2.303\omega)$$

where $\phi' = 1 - D'J' + \frac{w_2 I_E}{2} + 2\frac{w_3 I_E^2}{3} + 3\frac{w_3 I_E^3}{4}$
and I_E = stoichiometric ionic strength of sodium chloride solution
$D' = 2.303A/(w_1^3 I_E)$
$J' = B' - 2\ln B' - 1/B'$
$B' = 1 + w_1 I_E$

where w_1, w_2, w_3, w_4 are constants adjusted to fit experimental data.
Also,

ω = 1000/molecular wt of water
ϕ' = osmotic coefficient of water

This equation, according to Wolery (1983), is valid for up to 2 molal stoichiometric ionic strength sodium chloride solution.

The approach taken in calculating the solubility products of gibbsite, boehmite and diaspore is in most cases as follows:

1. Data from the literature and unpublished sources were recalculated into a form suitable for acceptance by EQ3.

2. The distribution of species was computed using EQ3 at the appropriate temperature, and assuming the total pressure to be equal to the vapor pressure of water at that temperature. In most cases, when only Na and Al concentrations were given, electrical neutrality was assumed by balancing the system with the addition or subtraction of $(OH)^-$
3. The logarithms of the apparent solubility products were calculated on the basis of the computed activities of $Al(OH)_4^-$, OH^- and H_2O, as appropriate. By apparent solubility product, the authors mean the solubility product calculated by the EQ3 code at the ionic strength of the solution, but without graphical extrapolation to $I = 0$ as may be done in the following step.
4. When appropriate, the logarithms of the apparent solubility products were plotted against "true" ionic strength, as calculated by the EQ3 code, and extrapolated to zero ionic strength by fairing a continuous line through the available data. Such extrapolations had to be congruent with other data sets.
5. The resulting logarithms of the solubility products were plotted against $\frac{1}{T}$, (K^{-1}) and compared.

Solubility measurements reported in the literature generally fall into one of three categories

(1) Those conducted at low ionic strength, i.e. less than 0.1 *m* total ionic strength.

(2) Those whose solution components are reported in weight percent Na_2O and Al_2O_3, or as molal quantities, (*m*).

(3) Those whose solution components are reported in $g.l^{-1}Na_2O$ or Al_2O_3 or as molar quantities, (M).

In order to compute the appropriate solubility products, all solution concentration data had to be converted to molalities. In the case of data reported in $g.l^{-1}$, the corresponding densities of the solutions are required. These were determined using an empirical equation based on the published data on solution densities in the system $Na_2O–Al_2O_3–H_2O$ by Dibrov et al. (1964b). The procedures used are more fully described in Appendix H.

Some investigators made their own data reductions and reported the solubility product, K_{s4}. Such results were used in this report when the data reduction method was consistent with that used in this report, or where the raw data were not published.

In the following sections, we will compare the calculated solubility products for gibbsite, boehmite and diaspore from our own experiments and from those reported in the literature.

4.2 Gibbsite

The data from twelve published investigations of gibbsite solubilities in alkaline media were compiled and evaluated. The pertinent data and calculated apparent solubility products are tabulated in Appendix A. In addition, previously unpublished solubility measurements on gibbsite in dilute sodium hydroxide solutions between 24 and 93°C, described by the senior author in his Ph.D. thesis, are reported and reevaluated in Appendix B. The gibbsite solubility measurements range from 20 to 170°C.

The logarithms of the apparent solubility products, K'_{s4}, computed from the data of Fricke and Jucaitis (1930), Fulda and Ginsberg (1951), Ikkatai and Okada (1962), Lyapunov et al. (1964), Russell et al. (1955), Szita and Berecz (1970), and Tsirlina (1936) are plotted against ionic strength, as illustrated in Figures 3a, b, c. Those by Wefers (1967b) are similarly treated in Appendix G.

Log K'_{s4} values are not independent of ionic strength, but show smooth trends towards higher values with increasing ionic strength. This may be attributed to failure of the model embodied in the EQ3 code and its data base to correct adequately for ionic strength, complexing and the activity of water. A smaller variation with ionic strength is obtained if the presence of the dehydrated aluminate ion, AlO_2^-, is assumed instead of $Al(OH)_4^-$. However, such a correction, even if substantiated by independent spectroscopic evidence (Eremin et al. 1974) was not incorporated, as it would have constituted an ad hoc correction without correcting for the errors introduced by inappropriate use of other parameters referred to above. It should be reemphasized at this point, that the model embodied in EQ3 was never intended to be used for solutions with ionic strength greater than 1.0, (Wolery 1983). However, as noted earlier, the model is a useful means of extrapolating log K'_{s4} to infinite dilution, and of comparing the relative precision and accuracy of data from different investigators.

The graphical extrapolation of log K'_{s4} to infinite dilution as shown in Figures 3a, b and c was carried out with data from the various investigations. The resulting log K_{s4} values are summarized in Table 3, together with the results of Apps (1970) from Appendix B., and the log K_{s4} values from Kittrick (1966), Kuznetsov (1951), May et al. (1979) and Packter (1979).

4.2.1. Comparison of the Calculated Results of Gibbsite Solubility Measurements by Various Investigators

When the derived log K_{s4} values from Apps (1970), Fricke and Jucaitis (1930), Fulda and Ginsberg (1951), Ikkatai and Okada (1962), Kittrick (1966), Kuznetsov (1952), Lyapunov et al. (1964), May et al. (1979), Packter, (1979), Russell et al. (1955), Szita and Berecz (1970), Tsirlina (1936) and Wefers (1967b) are plotted versus the reciprocal temperature ($\frac{1}{T}$, $K^{-1} \times 10^3$) as illustrated in Figure 4, it is immediately apparent that relatively close agreement exists between all investigators except for the results of Kuznetsov (1952), and May et al. (1979). The deviations of the former might be attributed to the non-attainment of equilibrium at 25°C, and to possible recrystallization to boehmite in measurements at 100, 120 and 140°C. However, the brevity of Kuznetsov's communication makes it impossible to provide a definite explanation. The results given by May et al. (1979) for both synthetic and natural gibbsite have been carefully examined by Hemingway (1982) in the light of other solubility studies on gibbsite and aluminum hydroxide precipitates, mainly in the 25°C temperature range. Hemingway believes that the experimental conditions, which included the use of TRIS buffers to control pH in alkaline solutions, induced equilibration with respect to the metastable nordstrandite form of $Al(OH)_3$ rather than the synthetic gibbsite that May et al. (1979) employed. This interpretation has not been independently verified. The authors believe that other interpretations might be placed on the experimental results of May et al. (1979), and these are discussed in Section 7.

Minor systematic differences between the results of the remaining investigators can be observed. Thus, the solubility of gibbsite determined by Apps (1970) at 24°C appears to be high. The starting material for his experiments was similar to that of Kittrick (1966) who noted that it appeared to contain traces of included sodium aluminate, which caused supersaturation of the solution with respect to gibbsite under his experimental conditions. This has been challenged subsequently by Bloom and Weaver (1982) who believe that the synthetic gibbsite used was coated with a poorly crystalline surface layer. Kittrick's experiments at 25°C show quite clearly that in excess of 400 days are required for a dilute alkaline solution to attain substantial equilibrium with respect to gibbsite. The authors' investigation of alkaline solubilities of aluminum hydroxide polymorphs in Section 7 suggests that gibbsite crystal aggregates synthesized in the Bayer process may be coated with bayerite. This bayerite is assumed to dissolve and progressively recrystallize to gibbsite. It may not be surprising that many solubility measurements made with Bayer process gibbsite display a range of "solubilities" between gibbsite and bayerite. The time for alkaline solutions to equilibrate with respect to gibbsite at temperatures around 25°C may take years. The gibbsite solubility results obtained by Apps (1970) are consistent with this interpretation.

Packter's solubility measurements on 0.54 micrometer material also appear to be high. The small particle size suggests that the equilibrium solubility of this material would be somewhat higher than coarsely crystalline material supposedly used by most other investigators. This is examined more closely in Section 7. The measurements of Fricke and Jucaitis (1930), Ikkatai and Okada (1962) and Tsirlina (1936), all lead to calculated solubilities slightly higher than those determined from the precise measurements of Szita and Berecz (1970) and Russell et al. (1955). The results of these latter investigations generally show less scatter in their data than those of other investigators, and a substantial number of measurements were made

TABLE 3

SUMMARY OF SOLUBILITY PRODUCT CONSTANTS, K_{s4} FOR GIBBSITE

Source	Derivation	T, °C	Log K_{s4}	Comments
Apps (1970)	Calculated with EQ 3 using 0.001 or greater NaOH	24.0	−1.03	Average of 3 measurements
		29.7	−0.99	Average of 8 measurements
		49.7	−0.73	Average of 6 measurements
		69.6	−0.59	Average of 6 measurements
		92.8	−0.20	Average of 7 measurements
Fricke and Jucaitis (1930)	Extrapolation	30	−1.06	
			−1.06	KOH electrolyte
		60	−0.71	
Fulda and Ginsberg (1951)	Extrapolation	74	−0.49	
		79	−0.44	
		84	−0.38	
		89	−0.32	
		94	−0.27	
		100	−0.18	
Ikkatai and Okada (1962)	Extrapolation	40	−0.93	Dissolution reaction
		70	−0.49	
		100	−0.14	
		130	+0.14	
		40	−0.87	Precitation reaction
		70	−0.46	
		100	−0.18	
Kittrick (1966)	Recomputed from source	25	−1.31	Average of 4 data sets
Kuznetsov (1952)	Taken directly from the reference	25	−1.94	
		30	−1.37	
		45	−0.83	
		60	−0.64	
		80	−0.47	
		100	−0.29	
		120	−0.28	
		140	−0.27	
Lyapunov et al. (1964)	Extrapolation	60	−0.70	
May et al. (1979)	Taken from the reference	25	−0.63	Synthetic gibbsite

TABLE 3 (Continued)

SUMMARY OF SOLUBILITY PRODUCT CONSTANTS, K_{s4} FOR GIBBSITE (Continued)

Source	Derivation	T, °C	Log K_{s4}	Comments
Packter (1979)	Taken from the reference	20	−1.187	0.54 micron particles
		35	−0.959	
		50	−0.733	
		65	−0.553	
		80	−0.319	
Russell et al. (1955)	Extrapolation	40	−1.02	
		50	−0.87	
		60	−0.73	
		70	−0.57	
		80	−0.43	
		90	−0.32	
		100	−0.16	
		110	−0.06	
		120	+0.03	
		130	+0.11	
		140	+0.20	
		150	+0.30	
		160	+0.39	
		170	+0.50	
Szita and Berecz (1970)	Extrapolation	25	−1.25	
		35	−1.04	
		50	−0.77	
		60	−0.62	
Tsirlina (1936)	Extrapolation	95	−0.19	
Wefers (1967b)	Extrapolation	60	−0.53	Values are approximate
		80	−0.5	
		90	−0.4	
		105	−0.35	

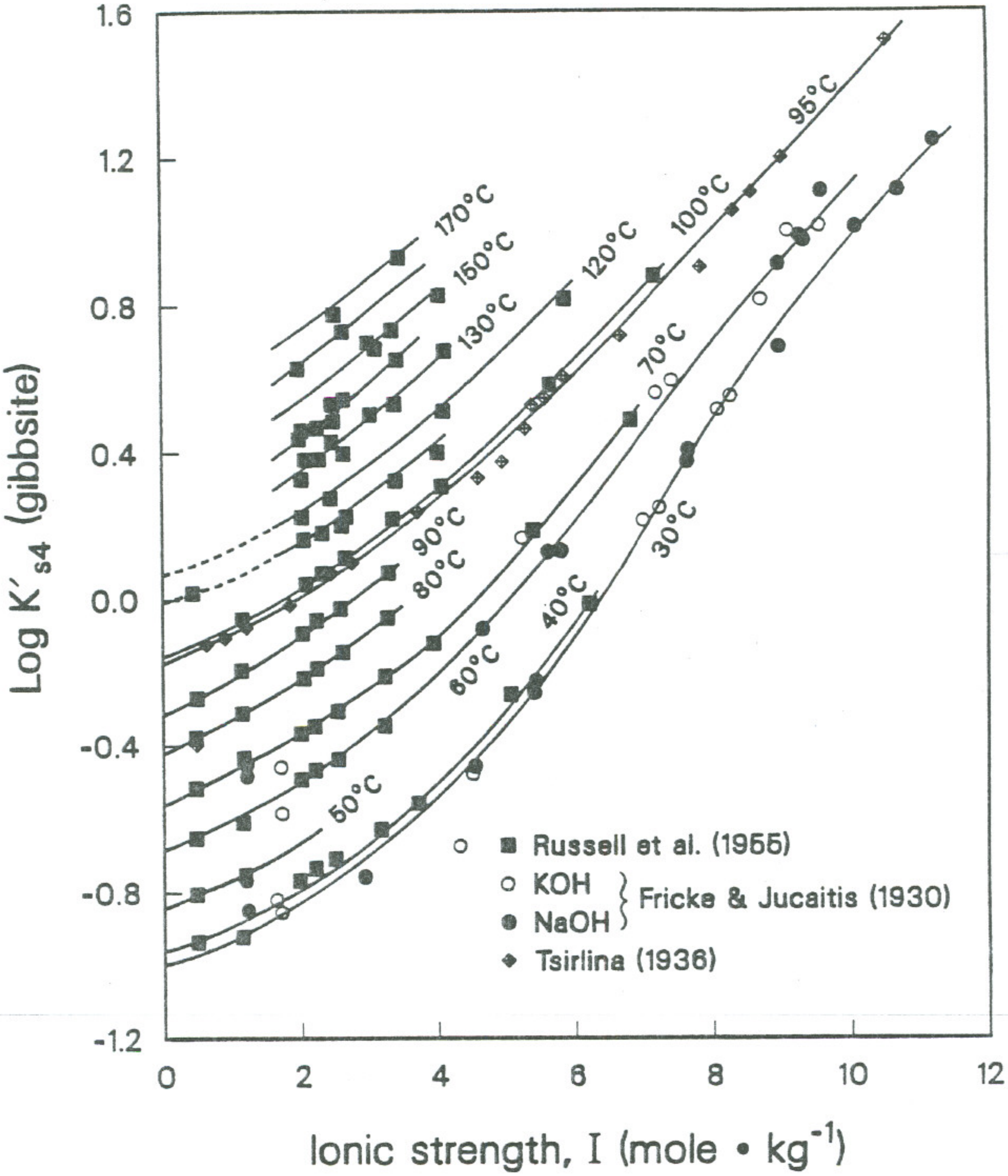

Figure 3a. The apparent solubility products, K'_{s4}(gibbsite), plotted against ionic strength. (a) Fricke and Jucaitis (1930), Russell et al. (1955) and Tsirlina (1936).

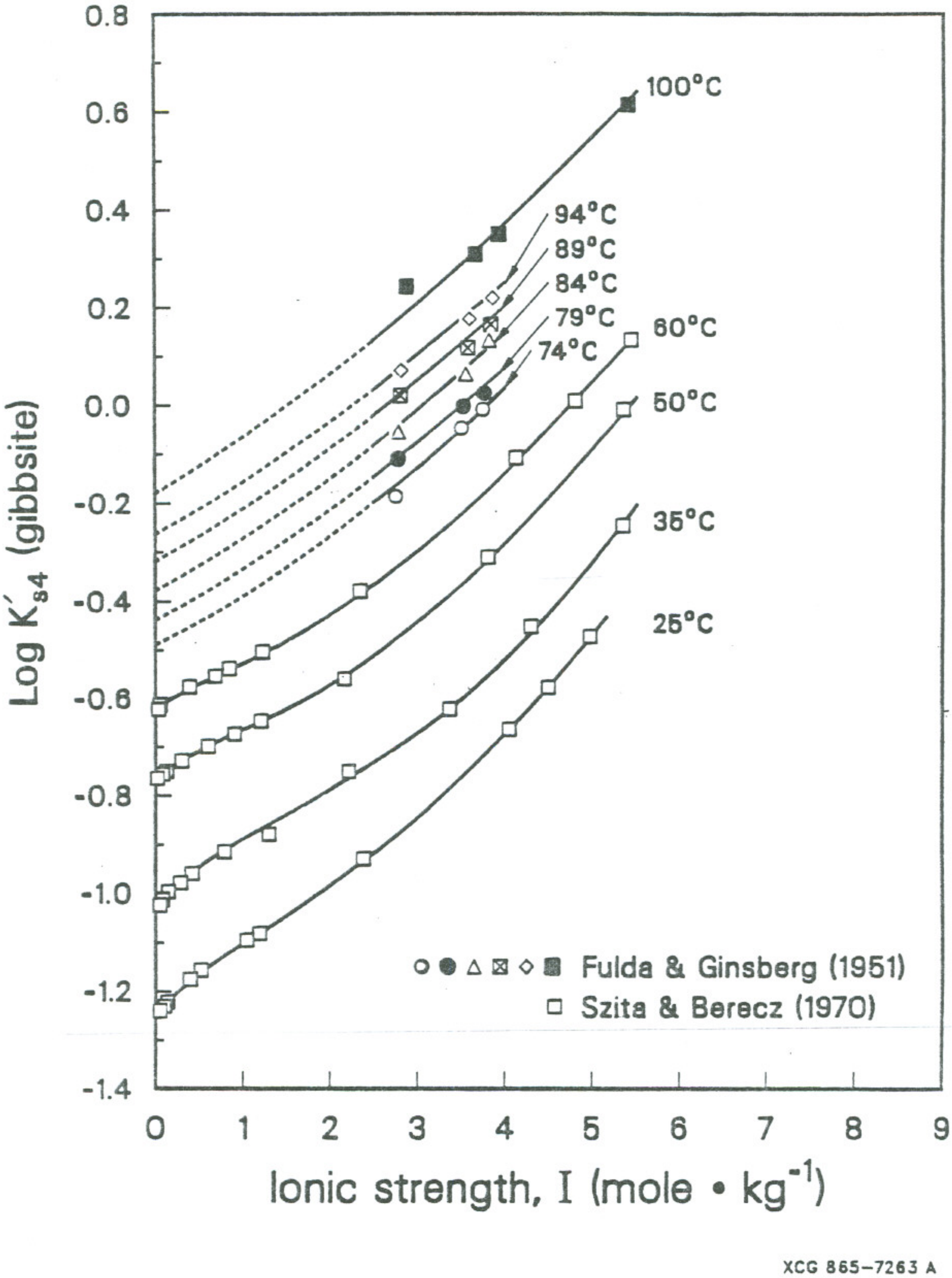

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Figure 3b. The apparent solubility products, K'_{s4}(gibbsite), plotted against ionic strength. (b) Fulda and Ginsberg (1951) and Szita and Berecz (1970).

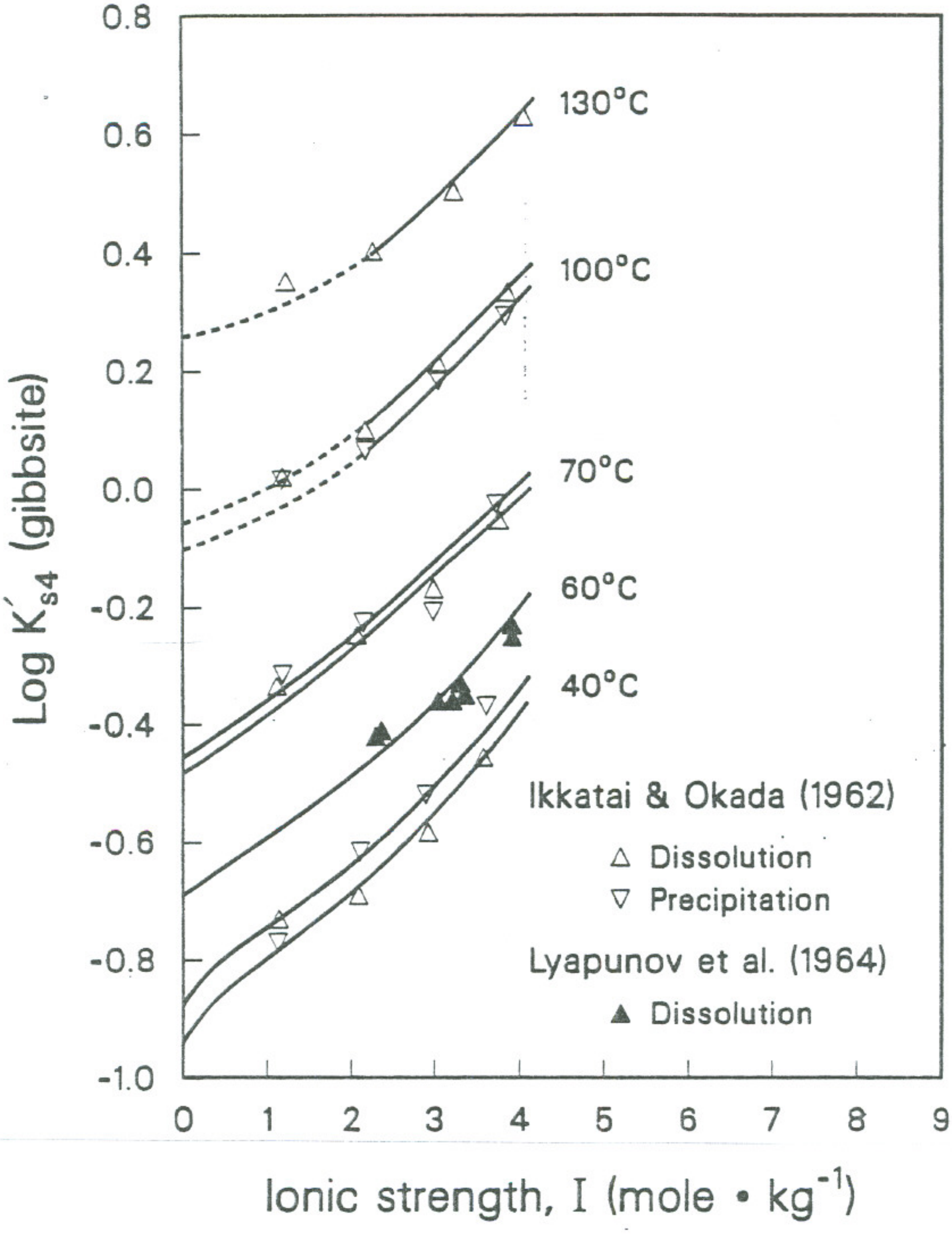

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Figure 3c. The apparent solubility products, K'_{s4}(gibbsite), plotted against ionic strength. (c) Ikkatai and Okada (1962) and Lyapunov et al. (1964).

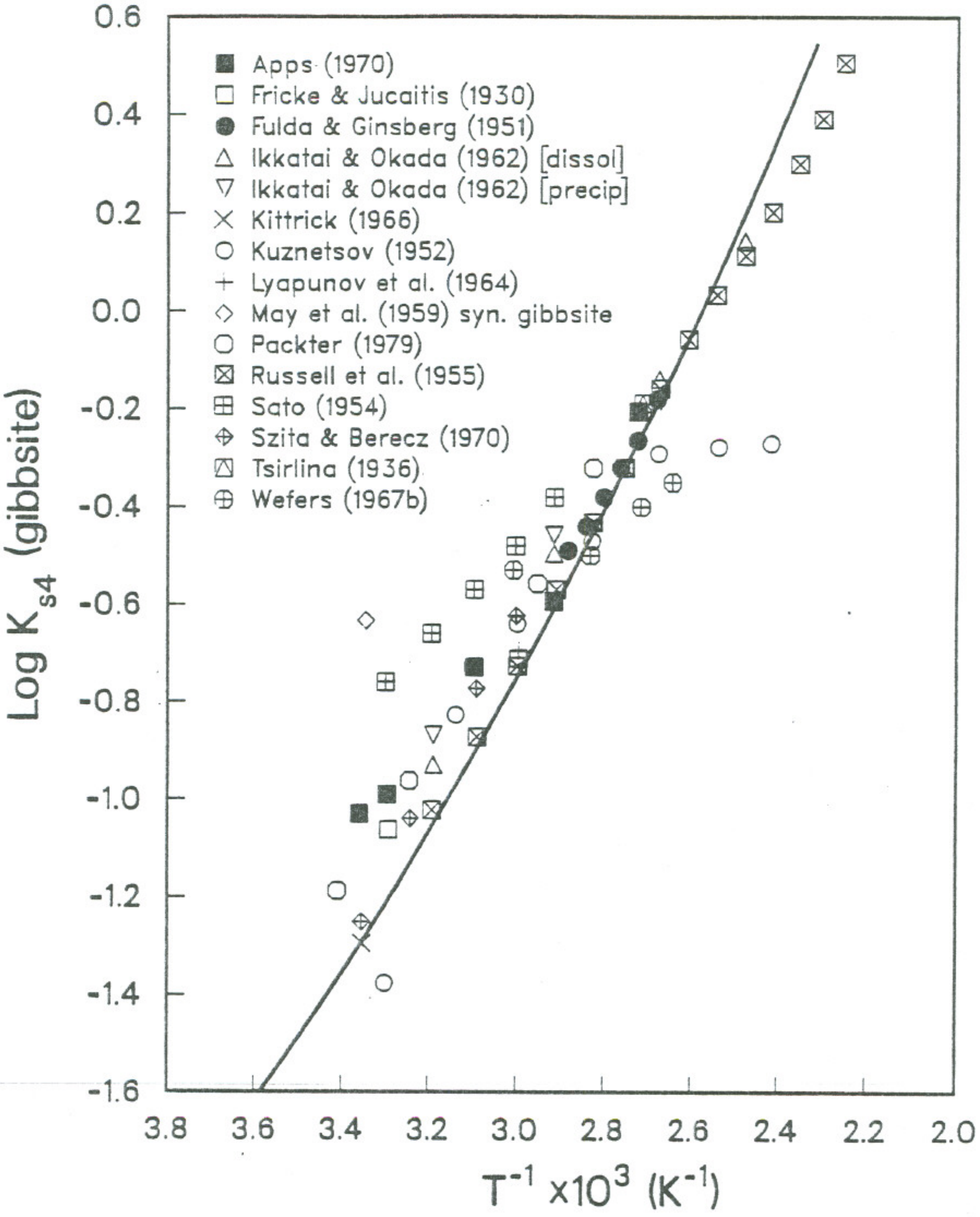

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Figure 4. The solubility product, K_{s4}, of gibbsite as a function of reciprocal temperature.

at each temperature investigated. Their results are therefore preferred. These investigators also were fully conscious of the need to monitor either the approach to equilibrium, or to ensure sufficient time for equilibrium to be attained.

It should be noted that the scatter in the Russell et al. data becomes appreciable at temperatures above 120°C due to the difficulty in measuring the solubility of gibbsite in the short period prior to its decomposition to boehmite. Their results above 120°C (i.e. at 130, 140, 150, 160 and 170°C) should therefore be considered minimal values of gibbsite solubility at those temperatures.

4.3 Boehmite

Fewer measurements of boehmite solubility have been reported in the literature than for gibbsite. They include those in studies by Bernshtein and Matsenok (1961); Fulda and Ginsberg (1951), Kuyunko et al. (1983), Magarshak (1938), and Russell et al. (1955). In addition, there are two hitherto unpublished solubility studies by Apps (1970) as well as some solubility measurements by Wefers (1967b) on diaspore where supersaturation appears to have lead to the precipitation of boehmite. The solubility measurements of these investigations span a temperature range from 50 to 300°C, overlapping the gibbsite solubility measurements for 120°C.

The initial data from the published literature, and calculated apparent solubility products, log K'_{s4}(boehmite), for all investigators except Wefers (1967b) are tabulated in Appendix C. The data by Wefers (1967b) together with calculated apparent solubility products, log K'_{s4}(boehmite), are given in Appendix G. In addition, the previously unpublished solubility measurements on boehmite in dilute sodium hydroxide solutions between 50 and 255°C, described by the senior author in his Ph.D. thesis, (Apps, 1970), are reported and reevaluated in Appendix D.

Log K'_{s4} values from all the investigators cited above, except those from Apps (1970) and Wefers (1967b) are plotted against ionic strength in Figures 5a, b, and c, and the observed trends extrapolated to infinite dilution. Only the log K'_{s4} values obtained from the data of Kuyunko et al. (1983) at 200 and 250°C and Magarshak (1938) at 200°C permit extrapolation to infinite dilution with reasonable confidence. The remaining data either require lengthy extrapolation, as is the case with the values derived from Russell et al. (1955) and Fulda and Ginsberg (1951), or show considerable scatter such as those by Fulda and Ginsberg (1951), and by Wefers (1967b) from Appendix G. Calculation of log K_{s4} at zero ionic strength was facilitated at temperatures between 80 and 120°C, by recomputing gibbsite solubility data in the same form as log K'_{s4}(boehmite), i.e.,

$$\log K_{s4} = \frac{[\mathrm{Al(OH]}_4^-]}{[\mathrm{OH}^-][\mathrm{H_2O}]}$$

and using the resulting trends to extrapolate the boehmite data to infinite dilution with subparallel lines. This somewhat empirical procedure improves the confidence in the final log K_{s4} value, although it is clear that a more rigorous model for the electrolyte solution is required. It should be noted, however, that even a linear approximation will lead to a maximum deviation in log K_{s4} of only about 0.1 unit.

All the resulting values of log K_{s4}(boehmite) are summarized in Table 4 and plotted in Figure 6 versus reciprocal temperature ($\frac{1}{T}$, K^{-1} x 10^3).

4.3.1 Comparison of the Calculated Results of Boehmite Solubility Measurements by Various Investigators

The log K_{s4} (boehmite) values by Apps (1970), Russell et al. (1955), Kuyunko et al. (1983) and Bernshtein and Matsenok (1961), all fall on a coherent trend as a function of reciprocal temperature. Log K_{s4}(boehmite), determined from the data by Magarshak (1938) at 200°C, is in excellent agreement with that of Kuyunko et al. (1983) at the same temperature. However, the log K'_{s4} values derived from the data

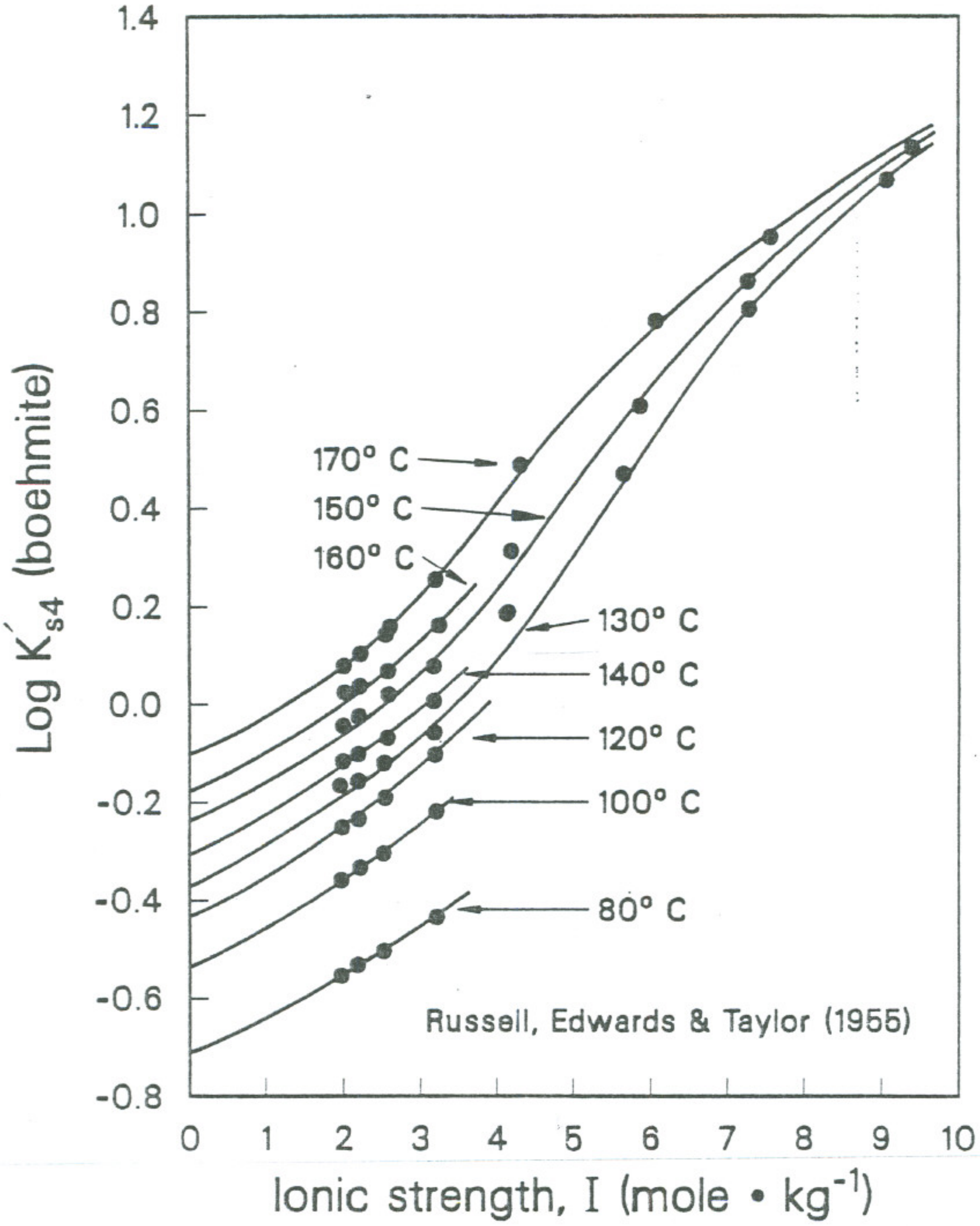

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Figure 5a. The apparent solubility products, K'_{s4}(boehmite), plotted against ionic strength. (a) Russell et al. (1955).

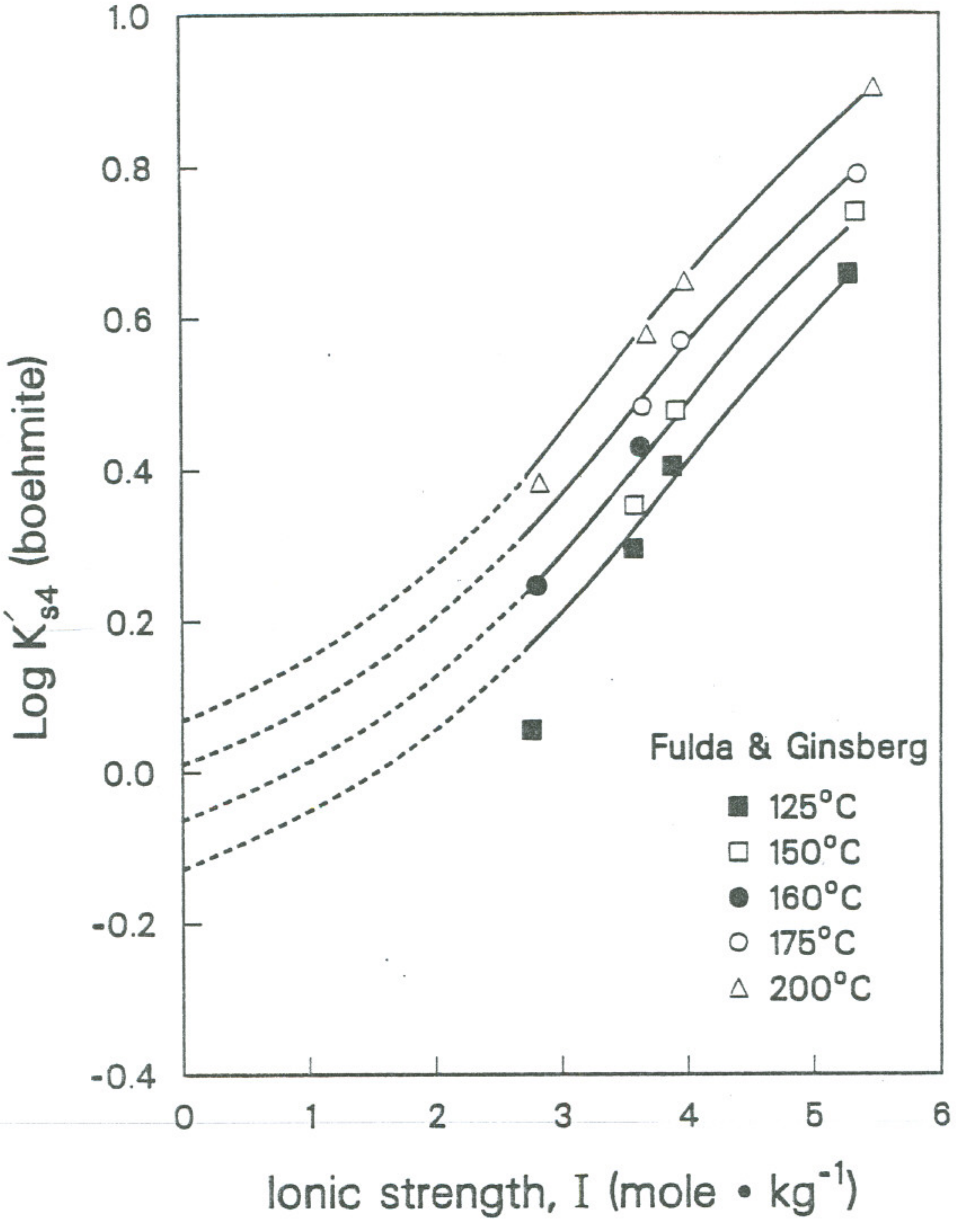

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Figure 5b. The apparent solubility products, K'_{s4}(boehmite), plotted against ionic strength. (b) Fulda and Ginsberg (1951).

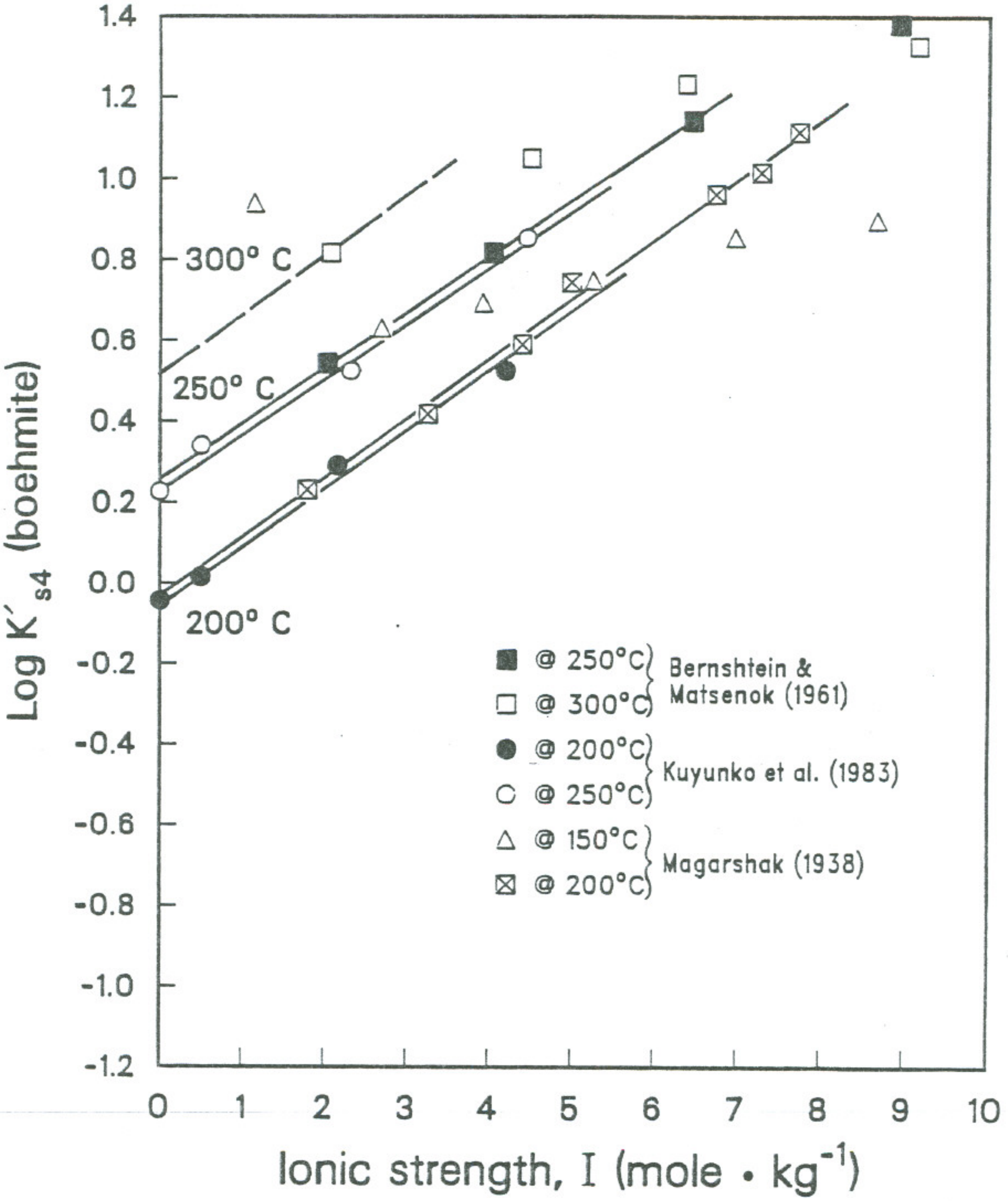

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Figure 5c. The apparent solubility products, K'_{s4} (boehmite), plotted against ionic strength. (c) Bernshtein and Matsenok (1961), Kuyunko et al. (1983) and Magarshak (1938).

TABLE 4

SUMMARY OF SOLUBILITY PRODUCT CONSTANTS, K_{s4}, FOR BOEHMITE

Source	Derivation	T, °C	Log K_{s4}	Comments
Apps (1970)	Revised using EQ 3	49.6	−1.04	
		70.0	−0.87	
		90.0	−0.76	
		121.0	−0.48	
		123.2	−0.45	
		153.8	−0.22	
		184.0	−0.02	
		217.6	+0.28	
		241.8	+0.35	
		256.0	+0.40	
		255.0	+0.35	
Bernshtein and Matsenok (1961)	Extrapolation	250	+0.30	One data point used
		300	+0.55	Value is approximate
Fulda and Ginsberg (1951)	Extrapolation	125	−0.12	Values are approximate
		150	−0.06	
		160	−0.05	
		175	+0.01	
		200	+0.07	
Kuyunko et al. (1983)	Extrapolation	200	0.00	
		250	+0.27	
Magarshak (1938)	Extrapolation	150	–	Equilibrium apparently not attained
		200	+0.03	
Druzhinina (1955)	Extrapolation	200	−0.06	Revised data from Magarshak, above
Russell et al. (1955)	Extrapolation	80	−0.73	
		100	−0.55	
		120	−0.45	
		130	−0.38	
		140	−0.32	
		150	−0.25	
		160	−0.18	
		170	−0.11	
Wefers (1967b)	Extrapolation	105	−0.35	Values are approximate
		135	−0.25	
		150	−0.10	

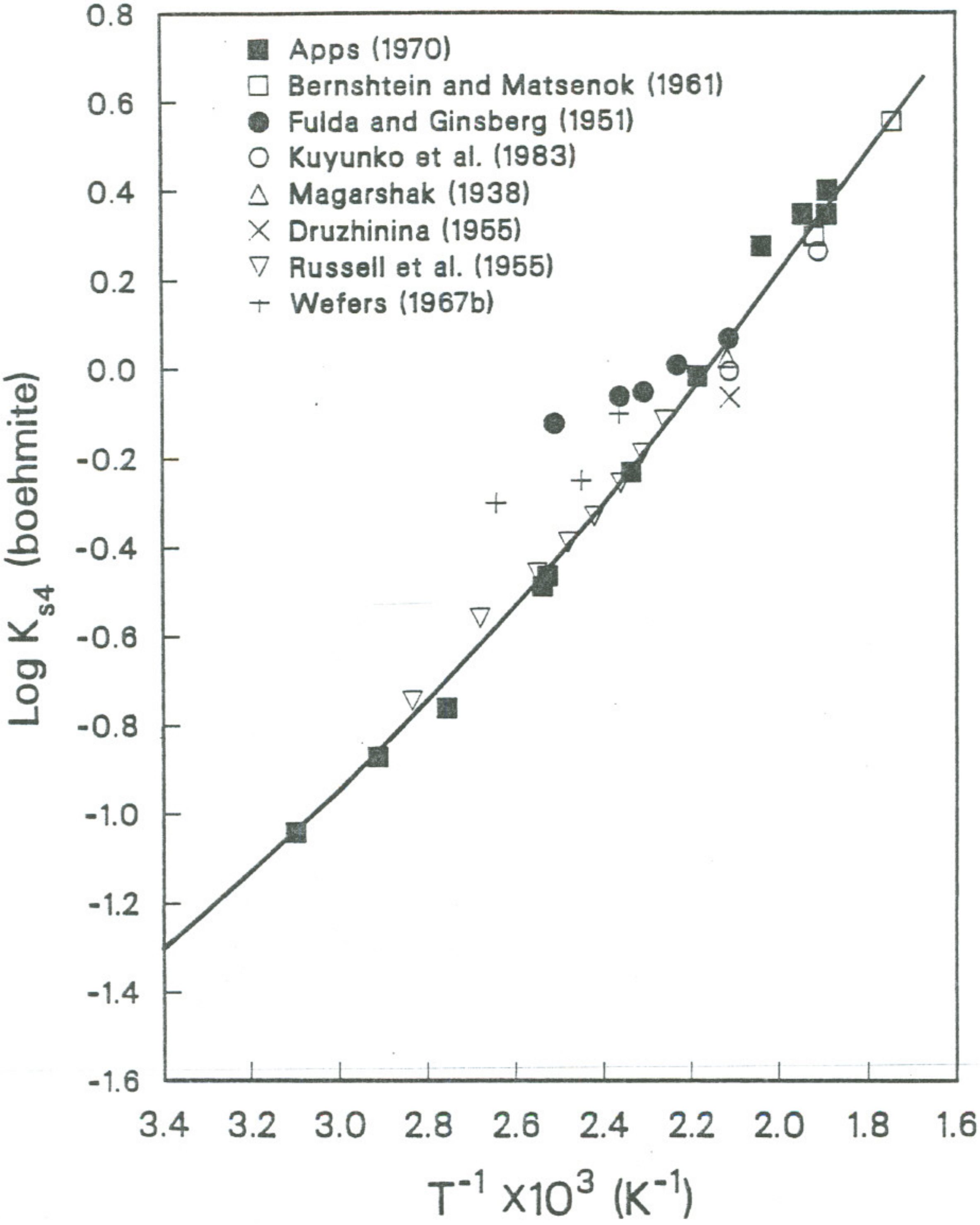

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Figure 6. The solubility product, K_{s4}, of boehmite as a function of reciprocal temperature.

by Magarshak (1938) at 150°C do not show coherence with those derived from Russell et al. (1955) in the same temperature region, and are therefore suspect. The log K'_{s4} values derived from Fulda and Ginsberg (1951) and Wefers (1967b) also show substantially less coherence than those derived from Russell et al. (1955). For this reason, log K_{s4} values derived from Fulda and Ginsberg (1951), Magarshak (1938) and Wefers (1967b) at 150°C, were not included in subsequent calculations of the thermodynamic properties of boehmite and the aluminate ion.

4.4 Diaspore

Because of the difficulty in achieving reversible equilibrium with respect to diaspore in alkaline solutions, most diaspore solubility measurements have been conducted at temperatures greater than 200°C. The data of Bernstein and Matsenok (1965), Chang et al. (1979), Druzhinina (1955), and Wefers (1967b), and one measurement of the solubility of "diaspore clay" from Taylor et al. (1927) were evaluated for the purposes of this investigation. Their measurements cover a range of temperatures from 150 to 350°C. The pertinent initial data and calculated apparent solubility products, log K_{s4}, are summarized in Appendices E and G. The preliminary measurements of diaspore solubility by Apps (1970), Apps and Neil (this report) and Apps and Landers (this report) are evaluated in Appendix F. Attempts by Apps and Neil (See Appendix F) to measure diaspore solubilities in dilute sodium hydroxide solutions below 200°C were unsuccessful. Autoclave studies using sodium aluminate solutions seeded with diaspore, and conducted at 135 and 150°C by Wefers (1967b), appear to have equilibrated with respect to boehmite.

Log K'_{s4} values from all the investigators cited above, except for those obtained from measurements in dilute sodium hydroxide solutions by Apps and Neil and Apps and Landers (Appendix F), are plotted versus ionic strength in Figures 7a,b and c, and the observed trends extrapolated to infinite dilution as for boehmite. Because even greater uncertainty attends data resulting from extrapolation of log K'_{s4}(diaspore) to infinite dilution, the corresponding trends observed in extrapolating log K'_{s4}(boehmite) were used as a guide for the diaspore data.

A noticeable feature of the data obtained by Bernshtein and Matsenok (1965) and by Wefers (1967b) above 300°C is the tendency for log K'_{s4} values for the high ionic strength solutions to fall below the trend expected on the basis of boehmite measurements at 200 and 250°C. This behavior is not observed in log K'_{s4} values obtained from the data by Chang et al. (1979), leading to the suspicion that the former measurements may reflect either initial non-attainment of equilibrium, or that reprecipitation of insoluble products occurred during quenching of the autoclave prior to sampling. Evidence provided by Wefers (1967b) suggests that the latter explanation may be correct, (See Appendix G). The interpolated trends of log K'_{s4} values derived from the data by Chang et al. (1979) are steeper than anticipated. Furthermore, the log K'_{s4} (diaspore) values derived from Bernshtein and Matsenok (1965), are almost coincident with log K'_{s4}(boehmite) derived from these authors' 1961 paper, as may be observed in Figure 7c, suggesting that their diaspore sample may have been contaminated with or reflect short term equilibration with respect to boehmite.

Log K_{s4} values obtained by extrapolation of log K'_{s4} to infinite dilution from the data of the pertinent papers, are summarized in Table 5 together with those of Apps (1970), Apps and Neil, and Apps and Landers from Appendix F.

4.4.1 Comparison of the Calculated Results of Diaspore Solubility Measurements by Various Investigators

The log K_{s4} data summarized in Table 5 is plotted versus reciprocal temperature ($\frac{1}{T}$, $K^{-1} \times 10^3$) in Figure 8. A trend is observed showing general consistency between investigators, with the exception of solubility measurements by Chang et al. (1979), which are significantly lower. Variation in log K_{s4} between investigators ranges up to ±0.1. This is somewhat larger than that of corresponding gibbsite or boehmite values.

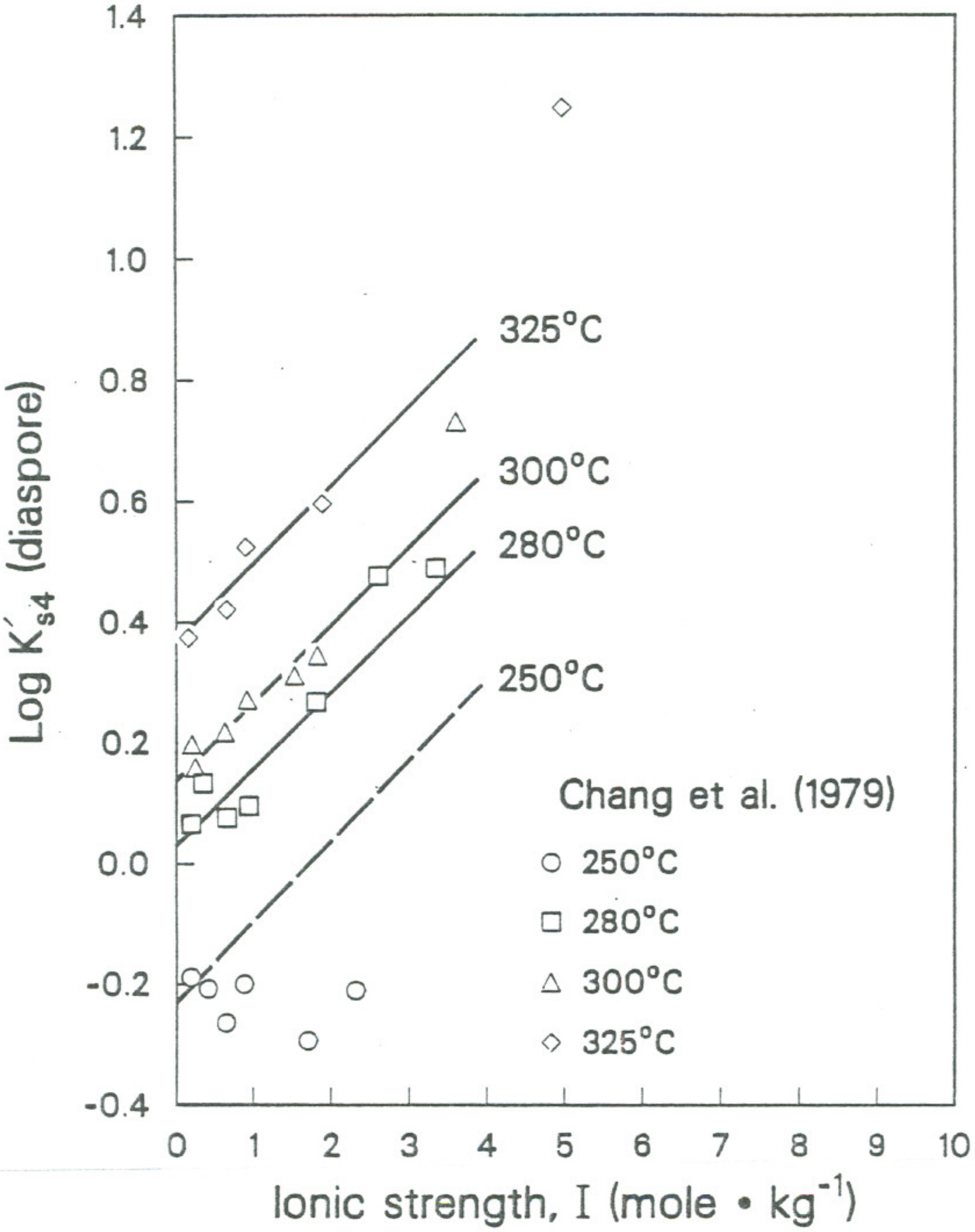

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Figure 7a. The apparent solubility products, K'_{s4}(diaspore), plotted against ionic strength. (a) Chang et al. (1979).

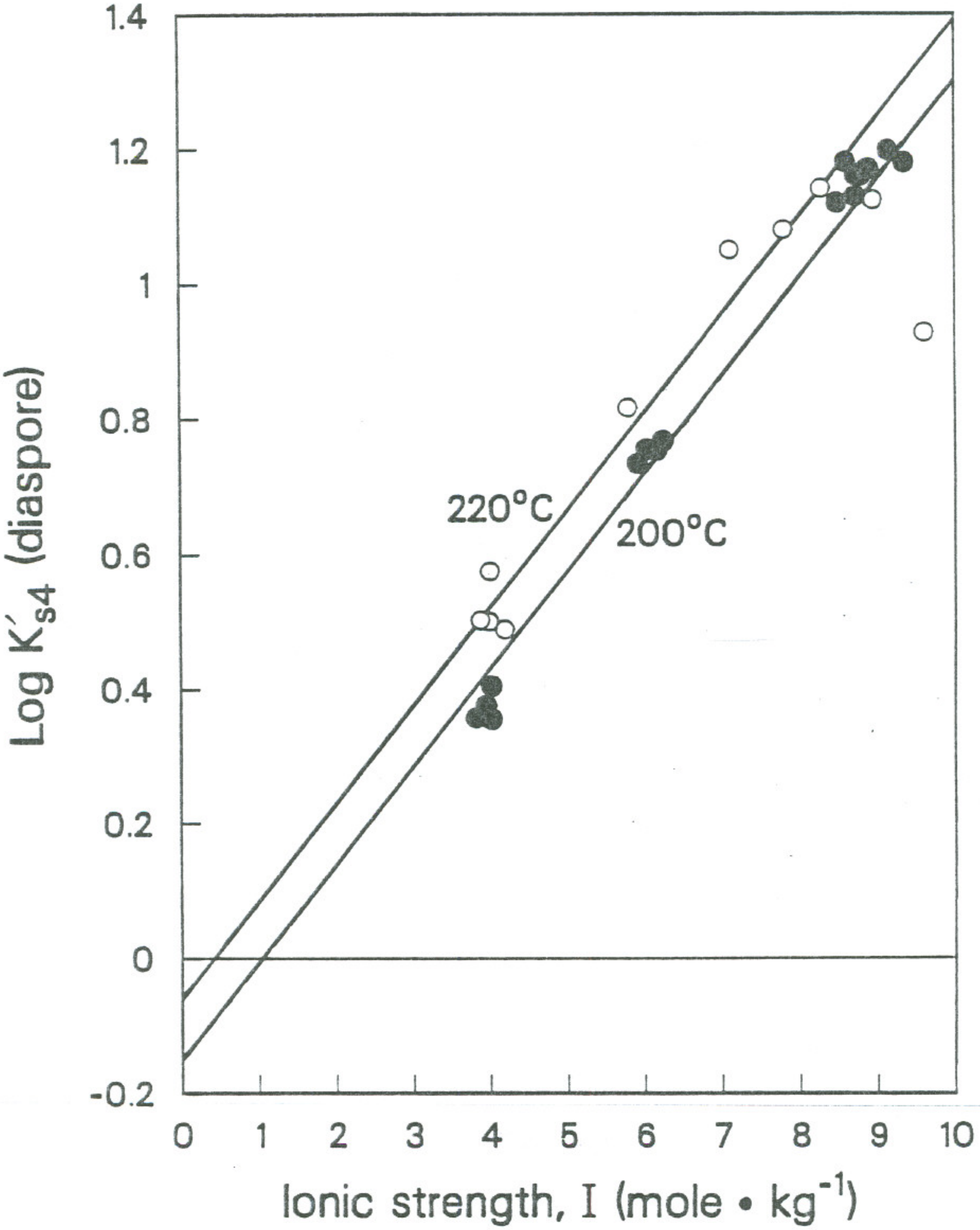

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Figure 7b. The apparent solubility products, K'_{s4} (diaspore), plotted against ionic strength. (b) Druzhininia (1955).

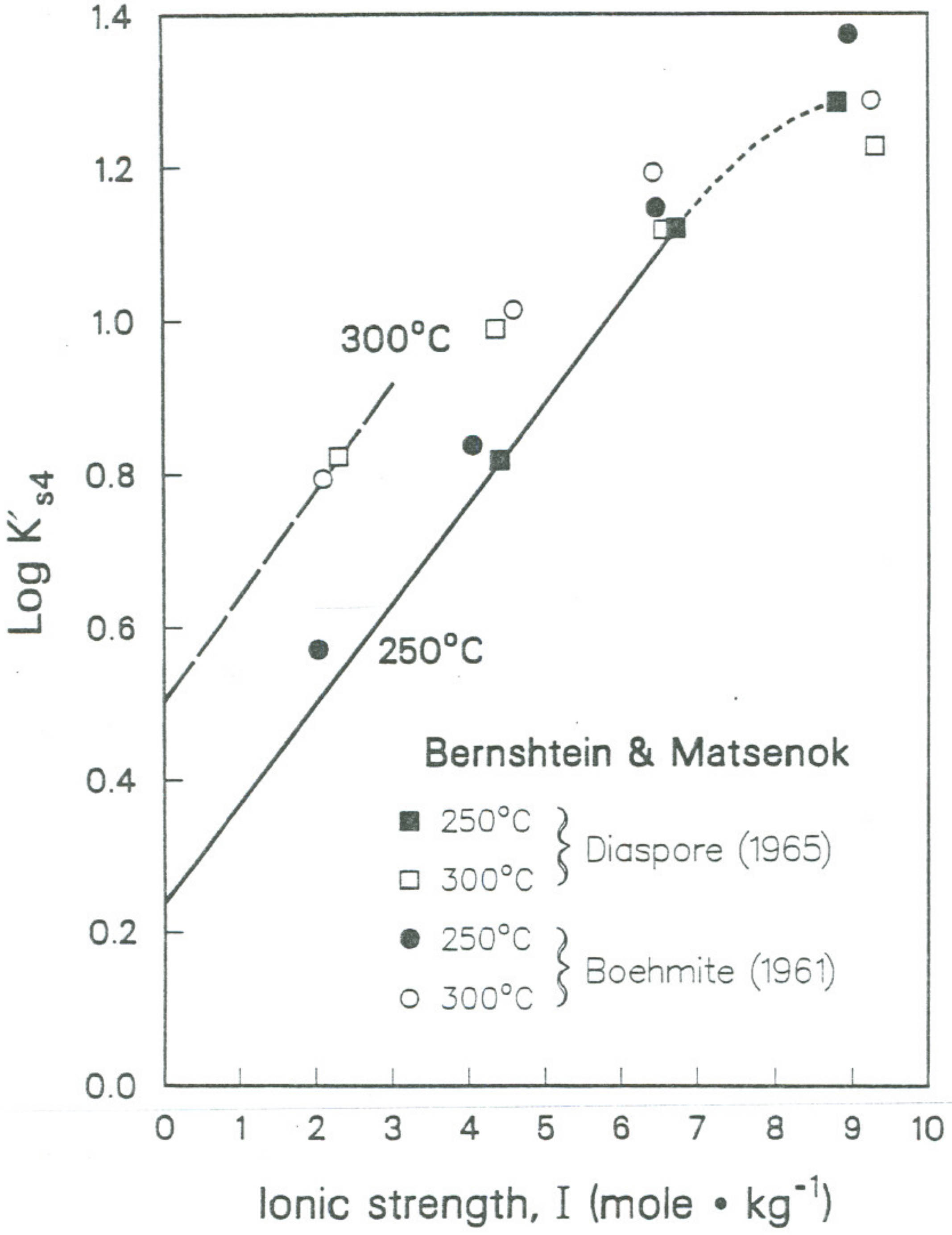

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Figure 7c. The apparent solubility products, K'_{s4}(boehmite, diaspore), plotted against ionic strength. (c) Bernshtein and Matsenok (1961, 1965).

TABLE 5

SUMMARY OF SOLUBILITY PRODUCT CONSTANTS, K_{s4}, FOR DIASPORE

Source	Derivation	T, °C	Log K_{s4}	Comments
Apps (1970)	Calculated using EQ 3	226.5	−0.07	
		259.0	+0.23	
		260.0	+0.21	
Apps and Neil (this work)	As above	200	−0.25	Ascending temperature intervals
		225	−0.04	
		250	+0.05	
		275	+0.26	
		300	+0.30	
		325	+0.57	
		350	+0.60	
		350	+0.66	
		350	+0.68	
		325	+0.50	Descending temperature intervals
		300	+0.43	
		275	+0.25	
		250	+0.18	
		225	+0.04	
		200	−0.14	
Apps and Landers (this work)		197	−0.28	
Bernshtein and Matsenok (1965)	Extrapolation	250	+0.24	Boehmite solubility?
		300	+0.50	
Chang et. al. (1979)	Extrapolation	250	−0.25	
		280	+0.01	
		300	+0.12	
		325	+0.36	
Druzhinina (1955)	Extrapolation	200	−0.15	
		200	−0.15	
		220	−0.06	
Taylor et al. (1927)	Extrapolation	150	−0.85	Diaspore clay
Wefers (1967b)		250	+0.36	
		300	+0.54	
		330	+0.48	
		350	+0.66	

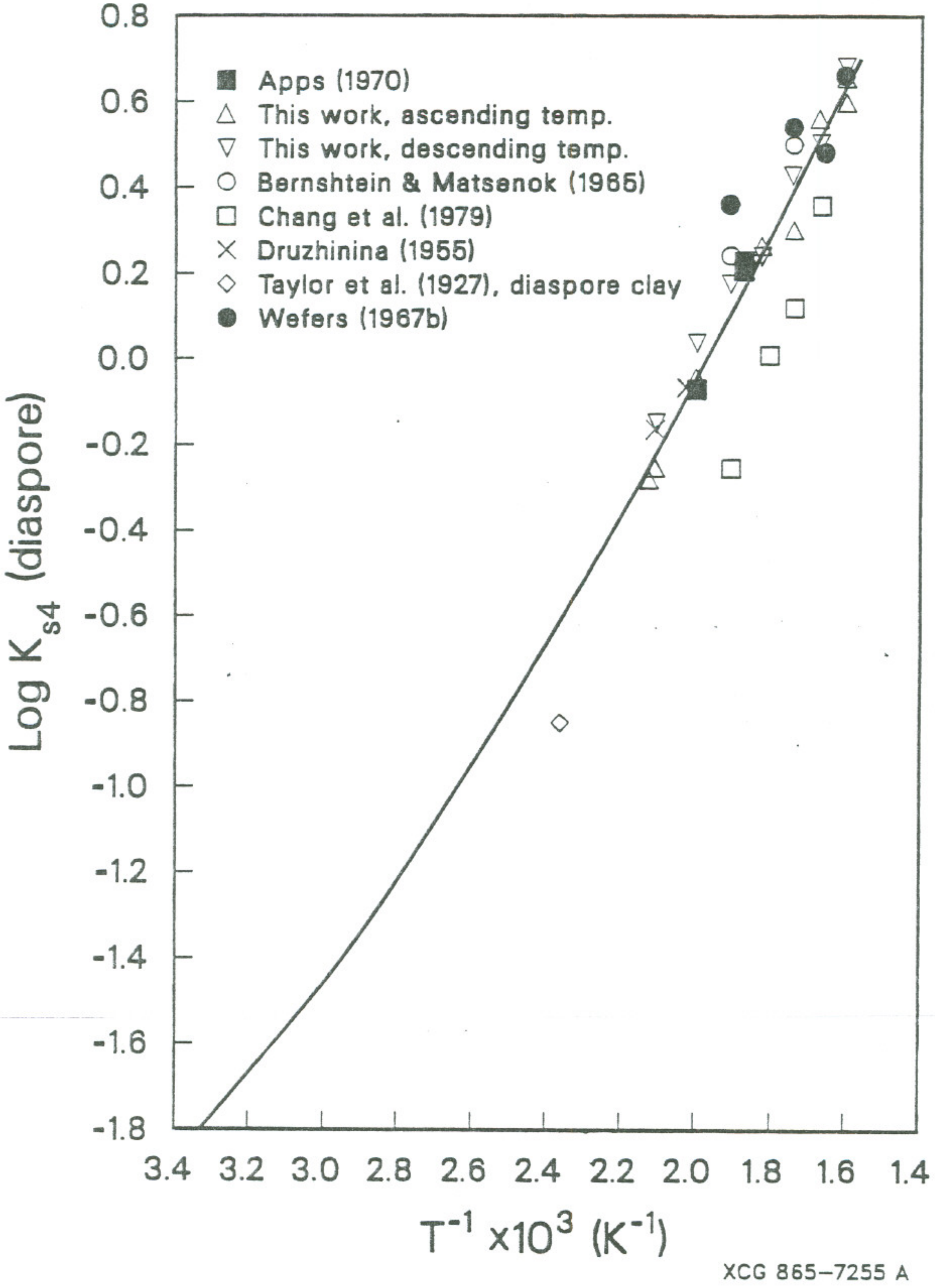

Figure 8. The solubility product, K_{s4}, of diaspore as a function of reciprocal temperature.

5. COMPARISON OF THE THERMODYNAMIC PROPERTIES OF GIBBSITE, BOEHMITE AND DIASPORE

5.1 Reconciliation of log K_r for the Reaction Gibbsite = Boehmite + Water, Based on Solubility Measurements, with that Based on Calorimetric Measurements

Different methods may be used to compare the thermodynamic properties of gibbsite, boehmite and diaspore. That adopted in this study is initially to compute the heterogeneous equilibria between the phases over the temperature ranges where solubility measurements overlap, thereby eliminating, the need to consider the thermodynamic properties of the aluminate ion, which are an additional source of uncertainty. For example, Dibrov et al. (1964a), Eremin (1974a), and Hemingway (1982) provide evidence that the aluminate ion may change its hydration state within the temperature range under consideration. Gibbsite and boehmite solubility measurements overlap between 50 and 170°C, whereas those for boehmite and diaspore overlap between 150 and 300°C. The logarithm of the equilibrium constants K_{r1} and K_{r2} may be computed from the difference of the respective solubility products, thus:

$$\begin{array}{llll}
\underset{\text{gibbsite}}{Al(OH)_3 + OH^-} & = & Al(OH)_4^- & K_{s4}(\text{gibbsite}) \\
\underset{\text{boehmite}}{AlOOH + OH^- + H_2O} & = & Al(OH)_4^- & K_{s4}(\text{boehmite}) \\
\hline
\underset{\text{gibbsite}}{Al(OH)_3} & = & \underset{\text{boehmite water}}{AlOOH + H_2O} & K_{r1} \\
\hline
\end{array}$$

where

$$\log K_{r1} = \log K_{s4}(\text{gibbsite}) - \log K_{s4}(\text{boehmite})$$

Similarly

$$\begin{array}{llll}
\underset{\text{boehmite}}{AlOOH + OH^- + H_2O} & = & Al(OH)_4^- & K_{s4}(\text{boehmite}) \\
\underset{\text{diaspore}}{AlOOH + OH^- + H_2O} & = & Al(OH)_4^- & K_{s4}(\text{diaspore}) \\
\hline
\underset{\text{boehmite}}{AlOOH} & = & \underset{\text{diaspore}}{AlOOH} & K_{r2} \\
\hline
\end{array}$$

where

$$\log K_{r2} = \log K_{s4}(\text{boehmite}) - K_{s4}(\text{diaspore}).$$

The experimentally determined estimates of the respective reaction constants are summarized in Table 6. Because of the spread in reported values of the solubility constant, log K_{s4}(gibbsite), two sets of data are given in Table 6 for temperatures below 100°C. The lower solubility set is in response to observations by

TABLE 6

CALCULATION OF THE EQUILIBRIUM CONSTANTS K_{r1} AND K_{r2}, RESPECTIVELY FOR THE REACTIONS: GIBBSITE = BOEHMITE + WATER AND BOEHMITE = DIASPORE, AND OF log K_f^o(BOEHMITE)

					log K_{r1}		log K_{r2}	log K_f^o(boehmite)	
T, °C	log K_{s4}(gibbsite) average values	log K_{s4}(gibbsite) low values	log K_{s4}(boehmite) average values	log K_{s4}(diaspore) average values	K_{s4}(gibbsite) average values	K_{s4}(gibbsite) low values		average values	low values
50	−0.78	−0.87	−1.00		+0.22	0.13		147.34	147.25
70	−0.52	−0.57	−0.88		+0.36	0.31		137.97	137.92
80	−0.38	−0.43	−0.73		+0.35	0.30		133.61	133.55
90	−0.27	−0.32	−0.74		+0.47	0.42		129.62	129.57
100	−0.15	−0.12	−0.59		+0.44	0.43		125.69	125.68
120	+0.03		−0.47		+0.50			118.56	
130	+0.13		−0.38		+0.51			115.23	
140	+0.20		−0.32		+0.52			112.07	
150	+0.30		−0.25		+0.55			109.08	
150				−0.85			+0.20		109.27
160	+0.39		−0.18		+0.57			106.21	
170	+0.50		−0.11		+0.61			103.49	
200			+0.01	−0.22			+0.27	96.34	
250			+0.33	+0.11			+0.22	85.78	
300			+0.55	+0.38			+0.17	77.12	

Kittrick (1966), who found evidence that synthetic gibbsite initially tends to supersaturate in solution at 25°C, and requires hundreds of days to reach equilibrium. His predicted solubility product for gibbsite at 25°C is consistent with the solubility data by Russell et al. (1955) when extrapolated 25°C. These investigators were careful to ensure that saturation equilibrium had been attained with respect to gibbsite. In contrast, other solubility measurements on synthetic gibbsite below 100°C, e.g. those by Apps (1970) are probably in a region of supersaturation because of a previously unsuspected active surface layer or contamination by bayerite. Gibbsite solubility measurements reported by Packter (1979) are on fine (0.54 μm) particles whose solubility would be enhanced over that of coarsely crystalline gibbsite. Thus the results of these two authors represent an upper bound to gibbsite solubility. The 25°C and 35°C solubility measurements by Szita and Berecz (1970) are also closely concordant with those by Kittrick and by Russell et al. However, their measurements at 50 and 60°C are higher than those of the latter investigators at the same temperature. No satisfactory explanation for this discrepancy can be found at present. For the reasons elaborated on above, the low values of log K_{s4} (gibbsite) were chosen for calculation of log K_{r1}, at temperatures below 100°C. Log K_{r1} and log K_{r2} are plotted in Figure 9 versus $\frac{1}{T} \times 10^3$ (K^{-1}). The thermodynamic parameters for the reactions, gibbsite = boehmite + water, and boehmite = diaspore can be recovered by linear regression of an equation that defines the values of the standard state thermodynamic properties, ΔS°_θ, ΔH°_θ, $\Delta C^\circ_{p,\theta}$, $\Delta C^{\circ\prime}_{p,\theta}$....., thus:

$$R\ln K(T) = \Delta S^\circ_\theta\,(Pa(1)) - \Delta H^\circ_\theta\,(Pa(2)) + \Delta C^\circ_{p,\theta}\,(Pa(3)) + d\Delta C^\circ_{p,\theta}/dT\,(Pa(4))\ ....$$

where $Pa(1) = 1.0$

$Pa(2) = 1.0/T$

$Pa(3) = [1.0/\theta - 1.0/T]$

$Pa(4) = [\theta/T - 1 + \ln(T/\theta)]$

and where θ is the reference temperature, 298.15 K.

This equation, originally derived by Clarke and Glew (1966) in slightly modified form, may be expanded to any number of derivatives of $C^\circ_{p,\theta}$ with respect to temperature, the accuracy of the data, limiting the number of terms. Calculations may be performed in which any one or more parameters can be fixed and regressed values obtained for the remainder. Because calorimetrically determined entropies and heat capacities have supposedly been determined for all participating phases, fixing these parameters decreases the number of degrees of freedom required for analysis. The Clarke and Glew equation does not incorporate pressure correction terms, which vary as a function of temperature, as all measurements were effectively taken along the water saturation surface. However, the correction is exceedingly small (Δ log K_{r2} is 0.001 at 300°C). Partial compensation for pressure is applied through application of the SUPCRT code (Kirkham et al. 1978) to compute preliminary thermodynamic parameters of the participating phases along the water saturation surface.

The SUPCRT code can calculate the thermodynamic properties of minerals at any given temperature and pressure between 0 and 1000°C and between 0 and 100 kbar. The temperature dependence on heat capacity is calculated using the Maier-Kelley heat capacity power function for minerals, (Maier and Kelley, 1932):-

$$C^\circ_{P_r} = a + bT - cT^{-2}$$

to compute the temperature dependence of S°, H° and C°_p of participating minerals. A pressure correction for the Gibbs free energy term of the solid phases is made by assuming a simple linear dependence in pressure and constant volume. The coefficients a, b, and c are empirical constants characteristic of each mineral species. The Keenan et al. (1969) equation of state is used to calculate the thermodynamic properties of water (Helgeson and Kirkham, 1964). The relevant equations for minerals (Delany and Helgeson, 1978) are given below:

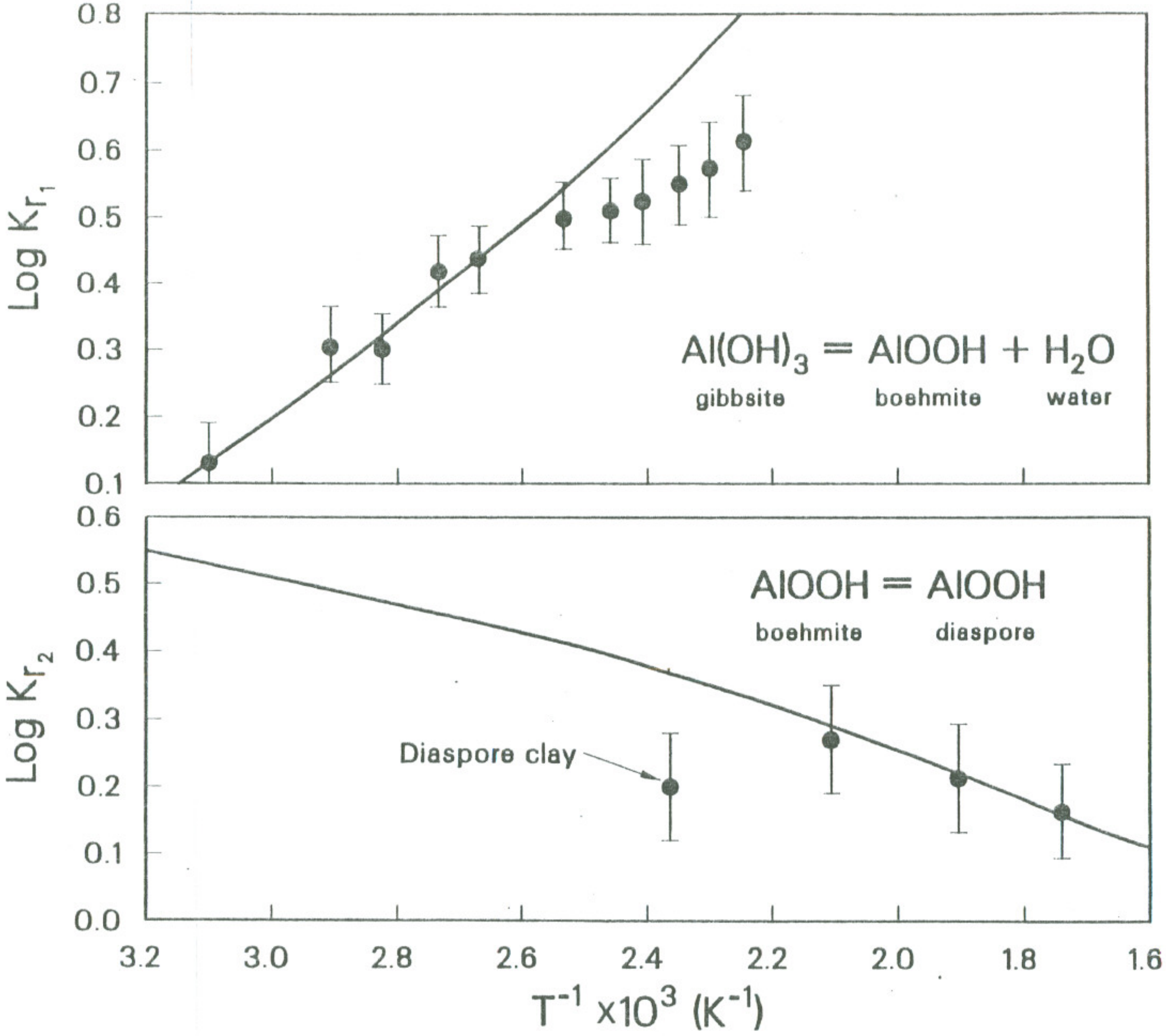

Figure 9. Experimentally determined values of log K_{r1} and log K_{r2} respectively for the reactions: (a) gibbsite = boehmite + water and (b) boehmite = diaspore, compared with logK_{r1} and logK_{r2} determined from a linear regression of the solubility measurements of gibbsite, boehmite and diaspore (continuous line).

$$S^{o}_{P,T,i} - S^{o}_{P_r,T_r,i} = a_i \ln(T/T_r) + b_i(T - T_r) - \frac{c_i}{2}\left[\frac{1}{T^2} - \frac{1}{T_r^2}\right] .$$

$$H^{o}_{P,T,i} - H^{o}_{P_r,T_r,i} = a_i\left[T - T_r\right] + \frac{b_i}{2}(T^2 - T_r^2)$$

$$- c_i\left[\frac{1}{T} - \frac{1}{T_r}\right] + V^{o}_{P_r,T_r,i}(P - P_r) ,$$

and

$$G^{o}_{P,T,i} - G^{o}_{P_r,T_r,i} = - S^{o}_{P_r,T_r,i}\,(T - T_r) + a_i(T - T_r - T \ln (T/T_r))$$

$$- \frac{(b_i T T_r^2 + c_i)\,(T - T_r)^2}{2\,T_r^2 T} + V^{o}_{P_r,T_r,i}(P - P_r) ,$$

where the subscript, i, refers to a given mineral. Log K^{o}_{f} values of gibbsite, boehmite, diaspore and water, computed using the SUPCRT code, with available entropy, enthalpy and heat capacity data, were then regressed using the Clarke and Glew equation and thermodynamic parameters recovered in a ''pressure independent'' form. In all cases, this lead to only trivial changes in heat capacity, entropy and enthalpy at 25°C. Values used in the initial calculations are given in Table 7.

TABLE 7
TABULATION OF INITIAL VALUES OF THE THERMODYNAMIC PROPERTIES OF PARTICIPATING PHASES IN REACTIONS r1 AND r2

$\Delta\Xi^{o}_{f,\theta}$	$H_2O(l)$	gibbsite	boehmite	diaspore
$\Delta S^{o}_{f,\theta}$ (cal.gfw^{-1}.K^{-1})	−38.996	−110.800	−59.807	−62.963
$\Delta H^{o}_{f,\theta}$ (kcal.gfw^{-1})	−68.315	−309.067	—	−238.861
$\Delta Cp^{o}_{f,\theta}$ (cal.gfw^{-1}.K^{-1})	+7.578	−3.705	-1.765×10^{-1}	-3.352×10^{-1}
$\Delta Cp^{o\prime}_{f,\theta}$ (cal.gfw^{-1}.K^{-2})	-2.048×10^{-3}	$+2.545\times10^{-2}$	1.826×10^{-2}	$1{-}6.241\times10^{-3}$
$\log K^{o}_{f,\theta}$ (−)	+41.552	+202.329	—	+161.322

Attempts to regress the values of log K_{r1} derived from the average value of log K_{s4}(gibbsite), given in Table 6, and fixing either the entropy of reaction and/or the heat capacity of reaction and its derivatives, resulted in a very poor fit as illustrated in Figure 10. Regression of the log K_{r1} data without restrictions lead to entropies and heat capacities of reaction that differ markedly from those calculated from published values for the participating phases. A number of possibilities exist for the very poor fit. These are summarized in Table 8 together with the resulting conclusions. After careful consideration of the alternatives, the following tentative assumptions regarding gibbsite-boehmite equilibrium were reached as a basis for further calculation.

(1) The published entropy, $S^{o}_{298}(Al_2O_3.H_2O)$, by Shomate and Cook (1946) is questionable, and, therefore, should not be used in calculations of the thermodynamic properties of boehmite. However, the consequences of assuming this value should be considered in an alternative calculation.

(2) The gibbsite solubility data above 130°C by Russell et al., (1955) should be rejected because of their cited difficulties in measuring gibbsite solubilities in that range due to its decomposition to boehmite.

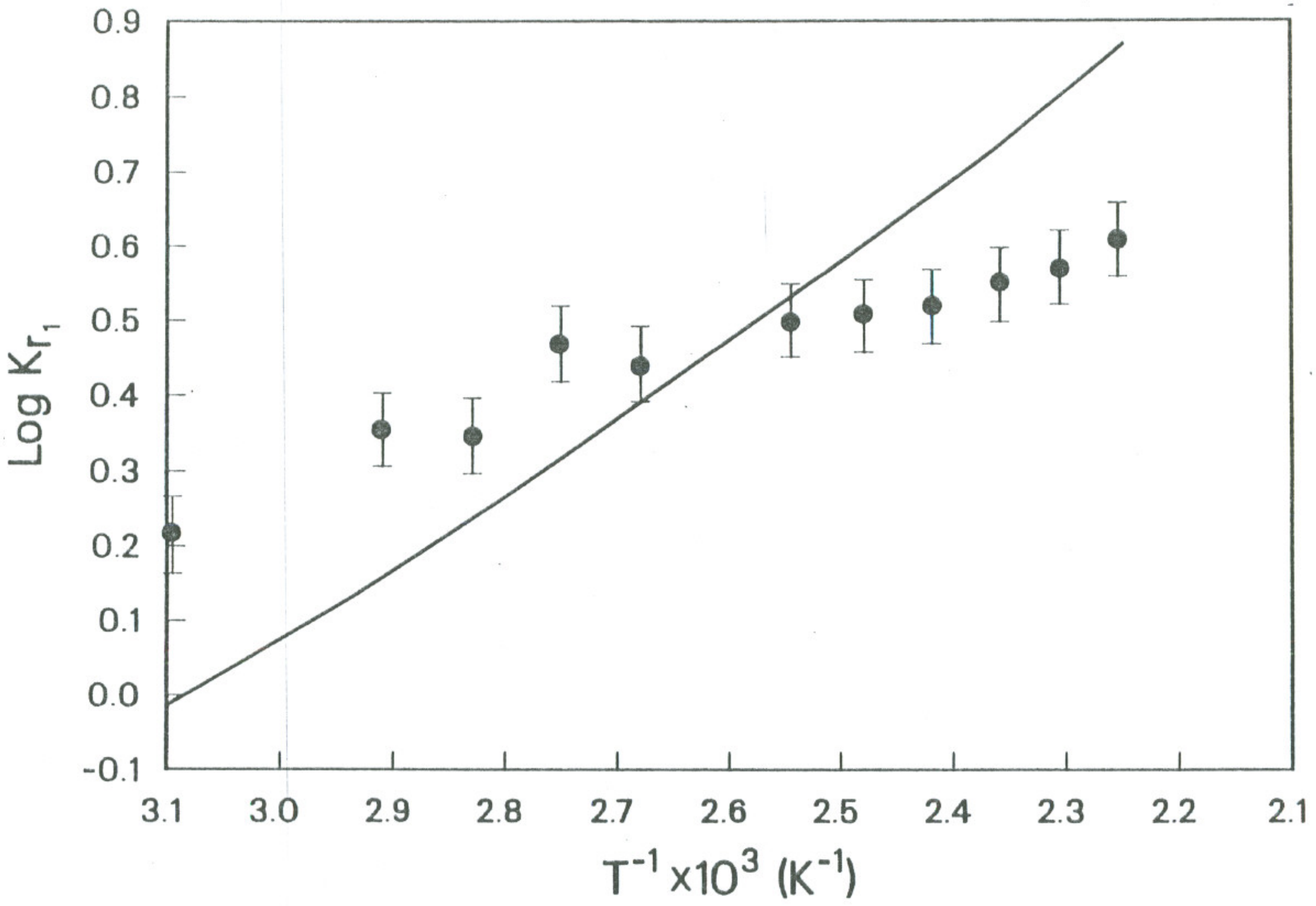

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Figure 10. Initial comparison of log K_{r1} values based respectively on solubility (data points) and calorimetric measurements (continuous line).

TABLE 8

POSSIBLE ERRORS CAUSING INCONSISTENCIES IN THE THERMODYNAMIC PROPERTIES OF EITHER GIBBSITE OR BOEHMITE

Argument	Response	Conclusion
Errors in S^o_{298}(gibbsite) C^o_p(T)(gibbsite) ΔH^o_f(gibbsite)	S^o_{298}(gibbsite) has been determined by Shomate and Cook (1946) and by Hemingway et al. (1977), and are consistent. C^o_p(T) has been measured by Mukaibo et al. (1969) and is consistent with heat content measurements by Shomate and Cook (1946). ΔH^o_f(gibbsite) was redetermined and thoroughly evaluated by Hemingway and Robie (1977a). No errors are the discernible.	No significant errors are likely in the calorimetrically determined thermodynamic properties of gibbsite.
Errors in S^o_{298}(boehmite) C^o_p(T)(boehmite)	S^o_{298} frequently reported in the literature as 11.58 $cal.gfw^{-1}.K^{-1}$ is derived from the low temperature heat capacity study by Shomate and Cook (1946) who referred to the material used as having an X-ray structure similar to dehydrated bayerite. High temperature heat capacity measurements of boehmite and diaspore were made by Mukaibo et al. (1969) The diaspore heat capacity is consistent with that measured by Perkins et al. (1979).	The low temperature heat capacity data and entropy of boehmite derived from Shomate and Cook (1946) should be treated with extreme caution.

TABLE 8 (Continued)

POSSIBLE ERRORS CAUSING INCONSISTENCIES IN THE THERMODYNAMIC PROPERTIES OF EITHER GIBBSITE OR BOEHMITE

Argument	Response	Conclusion
Incorrect solubilities of gibbsite due to non attainment of equilibrium, the formation of metastable surface phases, misidentification of the crystalline solid or excessively high solubility due to the finely crystalline nature of the material.	Russell et al. (1955) had difficulty measuring the true solubility of gibbsite above 120°C due to its rapid decomposition to boehmite. At 25°C, Kittrick found that synthetic gibbsite tends to supersaturate in solution and can require in the excess of 400 days to equilibrate. Some measurements, e.g., Packter (1979) were made on very fine grained material, which could be more soluble than a coarsely crystalline product.	Treat gibbsite data above 120°C with caution. Be conscious of potential supersaturation at lower temperatures.
As above, but for boehmite.	At temperatures greater than 150°C, boehmite may recrystallize to diaspore. At temperatures less than 100°C, the rate of dissolution of boehmite becomes increasingly slow making attainment of equilibrium very difficult, as noted by Apps (1970). Synthesized boehmite, particularly at temperatures less than 250°C, may be very finely crystalline and therefore may be more soluble than a coarsely crystalline product.	Treat all boehmite solubility data with caution.
Changing hydration state of the aluminate ion.	By determining the difference in solubilities between gibbsite and boehmite, and boehmite and diaspore, respectively, the effect of varying hydration state may be minimized if not eliminated from consideration.	This is not an important issue in reconciling the thermodynamic properties of gibbsite, boehmite, and diaspore.

(3) The gibbsite solubility measurements by Kittrick (1966) are more nearly correct than those of other investigators circa 25°C. However, both the average gibbsite solubility values for all data sets as well as minimum solubilities consistent with the findings of Kittrick (1966) should be considered as alternatives.

A major reason for the poor fit shown in Figure 10 appears to be the published entropy of boehmite. As noted earlier, the material upon which heat capacity and heat content measurements were made by Shomate and Cook (1946), gave an X-ray powder pattern similar to bayerite but differing from it principally in the intensities of the lines. However, with the exception of Parks (1972) and Hemingway et al. (1978), all subsequent compilations of thermodynamic data have attributed Shomate and Cook's entropy and heat capacity determinations on the monohydrate, $Al_2O_3.H_2O$, to boehmite. Several investigators have noted difficulties in reconciling the published heat capacity data of boehmite with independent determinations of boehmite thermochemical properties. Others have assumed that the heat capacity of boehmite is similar to that of diaspore (Helgeson et al., 1978) or have estimated the heat capacity using the corresponding states principle (Haas et al., 1981). Robinson et al. (1982) note that the high temperature heat content data of Shomate and Cook's sample of "boehmite" did not connect smoothly with the low temperature data. They also note that the heat capacity of boehmite measured by Mukaibo et al. (1969) is 1.3 percent lower than the estimated values of Haas et al. (1981). They attribute this to one percent excess water, "probably present as admixed gibbsite". Berman et al. (1985) also after noting the discrepancy in Shomate and Cook's heat content and heat capacity measurements, found that the solubility data of Hemley et al. (1980) for the reaction;

$$\text{kaolinite} = 2\ \text{boehmite} + 2\ SiO_2(aq) + H_2O,$$

could not be fitted with the C_p^o of boehmite derived from either set of measurements but consistency could be achieved assuming the C_p^o of boehmite to be equal to that of diaspore. Berman et al. point out that the "boehmite" entropy of Shomate and Cook (1946) leads to the stability of boehmite over diaspore at higher temperatures, which is contrary to geologic evidence cited by Perkins et al. (1979).

5.2 *Calculation of* log K_f^o*(T)(boehmite),* $\Delta H_{f,298}^o$*(boehmite) and* S_{298}^o*(boehmite)*

Because of the difficulties encountered in attempting to fit the log K_{r1} values derived from solubility data using the currently accepted thermodynamic properties of the participating minerals, an alternative approach was taken by attempting to regress all values of the formation reaction constant:-

$$Al + O_2 + 0.5\ H_2 = \underset{\text{(boehmite)}}{AlOOH} \qquad K_f^o(\text{boehmite})$$

Log K_f^o(T)(boehmite) was calculated from reactions:

$$\text{gibbsite} = \text{boehmite} + \text{water} \qquad K_{r1}$$

$$\text{boehmite} = \text{diaspore} \qquad K_{r2}$$

Using assumed values of log K_f^o(water), log K_f^o(gibbsite), and log K_f^o(diaspore) and assuming only the correctness of the Maier-Kelley high temperature heat capacity function for boehmite by Mukaibo et al. (1969);

$$C_p^o(T) = 25.81 + 4.14 \times 10^{-2}T - 6.01 \times 10^{5}T^{-2}$$

In this calculation, it is tacitly assumed that the thermodynamic properties of water and gibbsite are correct. Thermodynamic parameters for the two respective formation reactions:-

$$0.5\ O_2 + H_2 = H_2O(l) \qquad K_f^o(H_2O(l))$$

and

TABLE 9

POSSIBLE ERRORS LEADING TO INCORRECT PREDICTIONS OF THE THERMODYNAMIC PROPERTIES OF DIASPORE

Argument	Response	Conclusions
(1) Errors in $C_p^o(T)$(corundum) S_{298}^o(corundum) ΔH_f^o(corundum)	In section 3.5 the published thermodynamic properties of corundum are reviewed. The chief uncertainty lies in $\Delta H_{f,298}^o$ (corundum), which may be in error, because of the formation of small amounts of χAl_2O_3 during ignition of aluminum metal in an oxygen atmosphere. This would lead to a less negative value of $\Delta H_{f,298}^o$(corundum) than its true value No significant errors are anticipated in $C_p^o(T)$ or S_{298}^o.	Consider the published $\Delta H_{f,298}^o$ (corundum) to be potentially the least negative value.
(2) Position of reaction 2 dsp = cor + H_2O in P,T space.	The study by Haas (1972) demonstrated reversibility and, is essentially in agreement with the work of Fyfe and Hollander (1964) and Wefers(1967a). Helgeson et al., (1978) evaluated the subject univariant reaction, and concluded that the work of Kennedy (1959) is in error. Systematic errors in P or T measurements in the work of Haas (1972) may be possible.	The findings of Haas (1972) and Helgeson et al., (1978) are tentatively accepted.

TABLE 9 (Continued)

POSSIBLE ERRORS LEADING TO INCORRECT PREDICTIONS OF THE THERMODYNAMIC PROPERTIES OF DIASPORE

	Argument	Response	Conclusions
(3)	Errors in $C_p^o(T)$(diaspore) S_{298}^o(diaspore)	In Section 3.4, the published heat capacity measurements and entropy determinations were found to be consistent	The published entropy and heat capacity of Perkins et al. (1979) are tentatively accepted.
(4)	Discrepancies in the solubility products, K_{s4}, of diaspore	The $\log K_{s4}$ data by Apps (1970), this work, Druzhinina (1955) and Wefers (1967b) are in reasonable agreement above 200°C. Those of Chang et al. (1979) between 250 and 325 differ significantly. There is, however, no valid reason for rejecting Chang et al.'s data *a priori*	Consider the options of accepting alternative data sets.

$Al + 1.5\ O_2 + 1.5\ H_2 \ = \ \underset{\text{gibbsite}}{Al(OH)_3}$ $\qquad$ K^o_f(gibbsite)

were calculated using SUPCRT, and are given in Appendix I of this report.

The calculation of log K^o_f(boehmite) from diaspore solubility measurements is also subject to a number of potential errors. Potential sources of error are reviewed in Table 9. From Table 9, two further tentative assumptions affecting the calculation of log K^o_f(boehmite) from diaspore solubility measurements are made:-

(1) The published values of C^o_p(T)(diaspore) and S^o_{298}(diaspore) should be tentatively accepted, but varying $\Delta H^o_{f,298}$(diaspore) by increments of $\pm$ 250 cal.gfw^{-1} should be considered.

(2) Two alternative data sets of log K_{s4}(diaspore):

   (a) Using the data from Apps (1970), this work, Druzhinina (1955), Taylor et al. (1927) and Wefers (1967b).

   (b) Using data from Chang et al. (1979) instead of the data sets specified in (a) should be considered to establish which set is more consistent with gibbsite and boehmite solubility data.

The procedure adopted for the refinement of the thermodynamic properties of boehmite is as follows:

1. Calculate log $K^o_{f,T}$(boehmite) from the reactions:

   gibbsite = boehmite + water $\qquad$ K_{r1}

   and

   boehmite = diaspore $\qquad$ K_{r2}

   using K^o_f(T)(water), K^o_f(T)(gibbsite) and K^o_f(T)(diaspore) with alternative data sets, which are based on the assumptions described above.

2. With the computed values for log K^o_fT(boehmite), conduct a regression analysis using the equation after Clarke and Glew (1966), and fixing Cp^o_{298}, $Cp^{o\prime}_{298}$ and $Cp^{o\prime\prime}_{298}$. The regressed values of $\Delta H^o_{f,298}$(boehmite) and $\Delta S^o_{f,298}$(boehmite) are then used to compute S^o_{298}(boehmite) and $\Delta G^o_{f,298}$ (boehmite).

3. Insert $\Delta G^o_{f,298}$, $\Delta H^o_{f,298}$ and S^o_{298} for boehmite in the SUPCRT database where the Maier-Kelley heat capacity function for boehmite from Mukaibo et al. (1969) is already incorporated. Calculate log K^o_f(T)(boehmite) along the saturation surface of water using SUPCRT.

4. Using the equation after Clarke and Glew (1966), conduct a regression analysis of log K^o_f(T) boehmite from step 3 at 25°C intervals between 0 and 350°C. Obtain $C^o_{p,298}$, $C^{o\prime}_{p,298}$, and $C^{o\prime\prime}_{p,298}$, and insert these in the regression analysis of the experimental data set, (step 2).

5. Continue steps 2 through 4 until convergence is obtained, and no further changes occur in $\Delta S^o_{f,298}$ and $\Delta H^o_{f,298}$ for boehmite.

6. Repeat steps 1 through 5 for another log K^o_f(T) (boehmite) data set with a different set of initial assumptions.

7. Compare the results obtained in step 6 to determine which set of initial assumptions yields results that are compatible with independent results from phase equilibrium studies, and which set of assumptions yields the minimum variance in log $K^o_{f,T}$(boehmite).

The number of alternative assumptions, which could be tested, is substantial, and probably unnecessary. To reduce the number of separate regression analyses, the following procedure was adopted;

1. The thermodynamic properties of diaspore were calculated from the accepted properties of corundum and the phase equilibrium data of Haas (1972) for the reaction:

   $2\ AlOOH = Al_2O_3 + H_2O$

   2 diaspore = corundum + water

and used to calculate log K_f°(boehmite) at 150, 200, 250 and 300°C from log K_{s4}(boehmite) and log K_{s4}(diaspore) determined from the data by Apps (1970), this work, Druzhinina (1955) Taylor et al. (1927), and Wefers (1967b). Log K_f°(boehmite) was also calculated from the average values of log K_{s4}(gibbsite) and the average values of log K_{s4}(boehmite) between 50 and 130°C, and used to calculate $\Delta S^\circ_{f,298}$(boehmite) and $\Delta H^\circ_{f,298}$(boehmite).

2. As for No. 2, but substituting log K_{s4}(diaspore) derived from the data of Chang et al. (1979) to calculate the results.

3–6. As for No. 1, but using $\Delta H^\circ_{f,298}$(diaspore) + 250, −250, −500 and −750 cal. respectively. Varying the enthalpy of formation, $\Delta H^\circ_{f,298}$, of diaspore by arbitrary 250 calorie steps from + 250 cal. to −750 cal permits consideration of the effect of aggregate errors in $\Delta H^\circ_{f,298}$(corundum) and the phase equilibrium data obtained by Haas (1972). Positive increments of more than 250 cal. were not tested, because it was expected that this would lead to unrealistically low entropies for boehmite.

7. As for No. 1, but using the minimum values of log K_{s4}(gibbsite) below 100°C. These data are essentially those derived from Russell et al. (1955), which are also concordant with the data by Kittrick (1966) at 25°C.

8. As for No. 7, but using $\Delta H^\circ_{f,298}$(diaspore) + 250 cal.

9. As for No. 7, but using $\Delta H^\circ_{f,298}$(diaspore) − 250 cal.

10. As for No. 7, but omitting log K_f°(boehmite) data at 130°, and adjusting log K_{s4}(gibbsite) at 120°C by + 0.05. This case is designed to take into account the underestimation of logK_{s4}(gibbsite) at elevated temperatures due to its breakdown to boehmite.

The results of all ten regression analyses are summarized in Table 10.

TABLE 10

CALCULATED ALTERNATIVE THERMODYNAMIC PROPERTIES OF BOEHMITE AT 25 °C AND 0.032 BAR, GIVEN THE HIGH TEMPERATURE HEAT CAPACITY DATA BY MUKAIBO ET AL. (1969)

Case[1]	$\Delta S^\circ_{f,298}$ cal.gfw^{-1}.K^{-1}	S°_{298} cal.gfw^{-1}.K^{-1}	$\Delta H^\circ_{f,298}$ kcal.gfw^{-1}	$\Delta G^\circ_{f,298}$ kcal.gfw^{-1}	log$K^\circ_{f,298}$ –
1	− 62.97 ± 0.23[2]	8.42	− 238.167 ± 0.090	− 219.393	160.81 ± 0.12
2	− 67.42 ± 0.32	3.96	− 239.733 ± 0.128	− 219.635	160.99 ± 0.17
3	− 64.38 ± 0.16	7.01	− 238.668 ± 0.062	− 219.473	160.87 ± 0.08
4	− 61.80 ± 0.31	9.59	− 237.752 ± 0.121	− 219.327	160.76 ± 0.16
5	− 60.51 ± 0.39	10.88	− 237.295 ± 0.154	− 219.254	160.71 ± 0.20
6	− 59.27 ± 0.46	12.12	− 236.855 ± 0.188	− 219.184	160.66 ± 0.26
7	− 62.40 ± 0.19	8.99	− 237.893 ± 0.075	− 219.289	160.74 ± 0.10
8	− 63.82 ± 0.13	7.57	− 238.396 ± 0.052	− 219.368	160.79 ± 0.07
9	− 61.24 ± 0.26	10.15	− 237.489 ± 0.104	− 219.230	160.69 ± 0.14
10	− 62.34 ± 0.13	9.05	− 237.896 ± 0.052	− 219.310	160.75 ± 0.07

[1] See text

[2] All error estimates are 2σ

Case 1 yields an S^{o}_{298}(boehmite) = 8.42 cal.gfw^{-1}.K^{-1}. This value is in reasonable accord with that of diaspore. Case 2, in which the diaspore solubilities obtained from the data of Chang et al. (1979) are used yields a poorer fit and an unrealistic entropy, S^{o}_{298} = 3.96 cal.gfw^{-1}.K^{-1} for boehmite.

Cases 3–6 shows the effect of varying $\Delta H^{o}_{f,298}$(diaspore). By making $\Delta H^{o}_{f,298}$(diaspore) less stable by 250 cal (equivalent to a change in $\Delta H^{o}_{f,298}$(corundum) by + 500 cal) the fit is improved significantly, where 2 σ is decreased by 30 percent. However, this leads to an S^{o}_{298}(boehmite) of 7.01 cal.gfw^{-1}.K^{-1}, which is 1.5 cal.K^{-1} *less* than that of the more stable diaspore.

By varying $\Delta H^{o}_{f,298}$(diaspore) by incremental –250 calorie steps, the fit to the data deteriorates progressively, and yields a continuously increasing S^{o}_{298}(boehmite). From Figure 11, and the results given in Table 10, the difference between $\Delta H^{o}_{f,298}$(boehmite) and $\Delta H^{o}_{f,298}$(diaspore) can be calculated when S^{o}_{298}(boehmite) is 11.58 cal.gfw^{-1}.K^{-1}, the commonly accepted value for this mineral. This is ≈2.4 kcal.gfw^{-1}, which is inconsistent with the phase equilibrium studies of Hemley et al. (1980), and would suggest, either significant errors Haas' 1972 phase equilibrium results or that $\Delta H^{o}_{f,298}$(corundum) should be >1.2 kcal.gfw^{-1} *more* negative than is commonly accepted. Neither alternative appears reasonable.

In Case 7, the log K_{s4}(gibbsite) values derived from Russell et al. (1955) between 50 and 90°C, which are consistent with the measurements of Kittrick (1966) at 25°C, generally yield a better fit than when the average log K_{s4}(gibbsite) values are used, as can be seen by comparison of cases 1 and 7. Additional variation of $\Delta H^{o}_{f,298}$(diaspore) by + 250 cal., (case 8) or –250 cal., (case 9), yield similar responses in the thermodynamic parameters of boehmite to those in cases 3 and 4, when compared with case 1 although S^{o}_{298}(boehmite) and $\Delta H^{o}_{f,298}$ (boehmite) are approximately 0.5 cal.gfw^{-1}.K^{-1} larger and 250 cal.gfw^{-1} less negative, respectively.

Close inspection of the calculated values of log K'_{s4}(gibbsite) at 100°C and above from Russell et al. (1955) and Ikkatai and Okada (1964) suggests that the presently projected values of log K_{s4}(gibbsite), at zero ionic strength may be too low. This is in conformity with regression of log K^{o}_{f}(boehmite) values, which indicates that log K'_{s4}(gibbsite) should be higher than projected in that temperature region. By omitting the value of log K^{o}_{f}(boehmite) at 130°C, which is derived from shaky projection of log K'_{s4}(gibbsite), and adjusting log K_{s4}(gibbsite) at 120°C, by +0.05, (and hence log K^{o}_{f}(boehmite) by the same amount) to reflect the above observations, a significantly improved fit is achieved, as may be noted from case 10, although the computed thermodynamic parameters for boehmite change little between case 7 and case 10.

The conclusion of the above sensitivity study is that the most plausible interpretation is either case 7 or case 10. The fit to the data is good, and internal consistency of the calorimetrically derived thermodynamic parameters for gibbsite and corundum is maintained. In both cases, the resulting S^{o}_{298}(boehmite) is reasonably close to that of diaspore, which would be expected for a polymorph. The entropy difference between the two AlOOH polymorphs, is about 0.5 cal.gfw^{-1}.K^{-1}. It is interesting to note that this difference is similar to that computed from the equation due to Helgeson et al. (1978) (eqn. 62, p. 45) for estimating mineral entropies. Their equation yields ΔS = 0.49 cal.gfw^{-1}.K^{-1} for S^{o}_{298}(boehmite) – S^{o}_{298}(diaspore)

The results of case 7 were selected as the basis for fixing the thermodynamic properties of boehmite in subsequent calculations. log K_{r1}(T) and log K_{r2}(T) were calculated from the derived thermodynamic parameters for boehmite, and those for gibbsite and diaspore used in this report. They are summarized in Appendix I, Tables I-10 and I-11 and plotted as continuous lines on Figure 9.

Comparison of the predicted and experimental log K_{r1} and log K_{r2} values, based on the results of case 7, shows that good agreement is obtained up to 100°C with log K_{r1} when the low values of log K_{s4}(gibbsite) are used. A good fit is also obtained above 200°C with log K_{r2}. The relatively small deviations are significant as has been demonstrated in the preceding discussion. Between 100 and 200°C, it would be advantageous to obtain additional data on the solubility of diaspore in alkaline media, but as noted in Appendix F, reaction rates are generally too slow to obtain equilibrium data below 200°C.

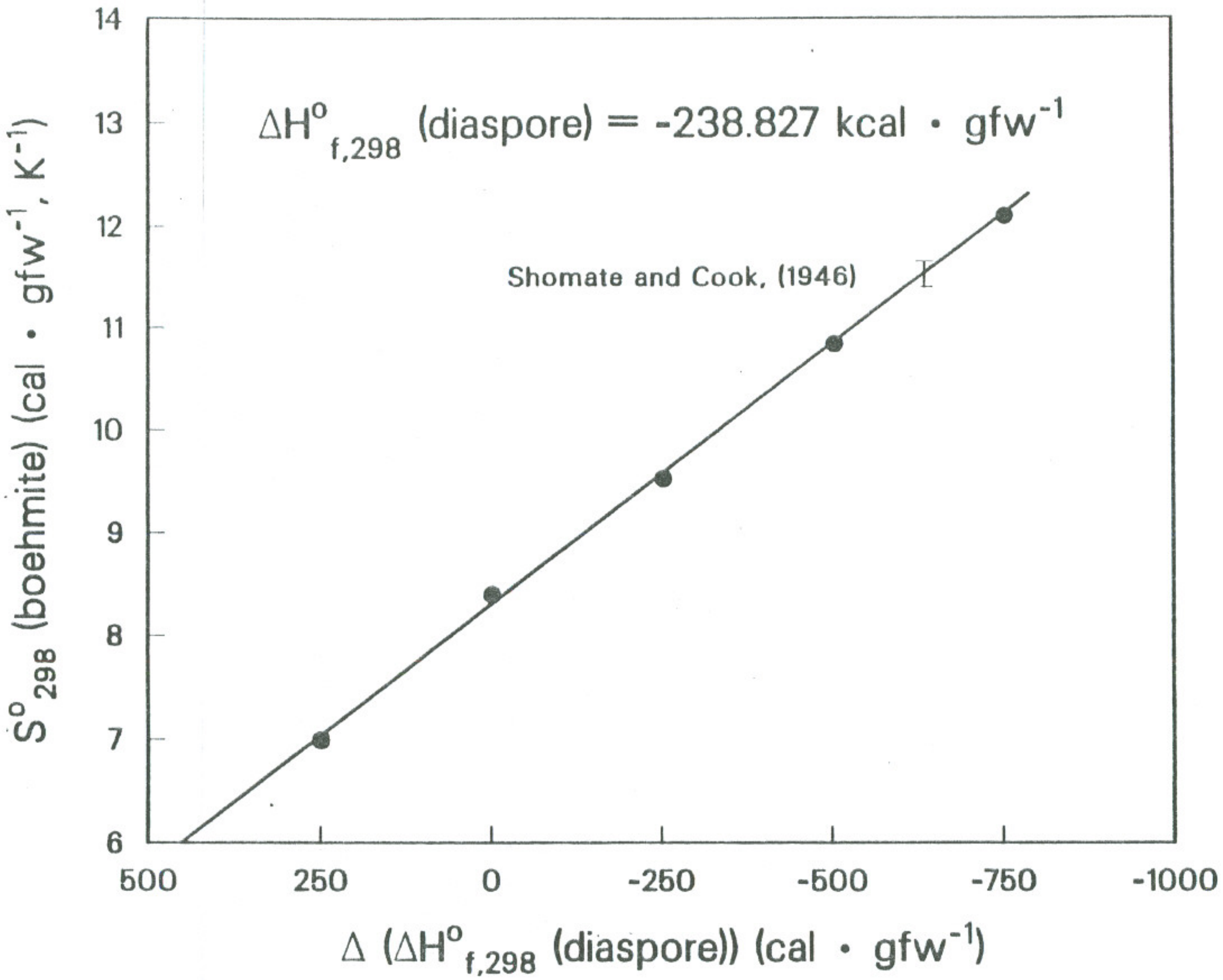

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Figure 11. Variation of S^o_{298}(boehmite) with $\Delta(\Delta H^o_{f,298}$(diaspore)) when fitted to ΔG^o_f(T)(boehmite), which is based, in turn, on solubility measurements of gibbsite, boehmite and diaspore.

6. CALCULATION OF THE THERMODYNAMIC PROPERTIES OF THE ALUMINATE ION, $Al(OH)_4^-$, AND LOG K_{s4}(T) (GIBBSITE, BOEHMITE, DIASPORE)

6.1 Derivation of log $\overline{K}^o_f$(T) and $\Delta\overline{G}^o_f$(T) from Solubility Measurements

The first attempt to derive the thermodynamic properties of the aluminate ion, $Al(OH)_4^-$, was made by calculating log $K^o_f(T)(Al(OH)_4^-)$ directly from log K_{s4} measurements of gibbsite, boehmite and diaspore. The equations used were:

$$\log \overline{K}^o_{f,T}(Al(OH)_4^-) = \log K_{s4,T}(\text{gibbsite}) + \log \overline{K}^o_{f,T}(OH^-) + \log K^o_{f,T}(\text{gibbsite})$$

and

$$\log \overline{K}^o_{f,T}(Al(OH)_4^-) = \log K_{s4,T}(\text{boehmite,diaspore}) + \log \overline{K}^o_{f,T}(OH^-)$$
$$+ \log K^o_{f,T}(H_2O) + \log K^o_{f,T}(\text{boehmite,diaspore})$$

where log $\overline{K}^o_{f,T}(OH^-)$ is obtained from the reaction:-

$$\frac{1}{2}O_2 + H_2 = OH^- + H^+ \qquad K^o_f(OH^-)$$

and where the thermodynamic properties for the hydroxyl ion are derived from the dissociation constant, Kw, for water:-

$$H_2O = OH^- + H^+ \qquad K_w$$

However, a regression of log $\overline{K}^o_f(Al(OH)_4^-)$ data as a function of $\frac{1}{T}$, K^{-1}, showed a poor fit above 300°C. The suspicion, subsequently substantiated by independent investigations by Tanger (personal communication, 1986), was that the perturbation in the data was due to errors in the computed thermodynamic properties of OH^- as a result of extrapolation errors in Kw above 300°C in Helgeson et al. (1981). To avoid introducing errors due to uncertainties in K_w, values of log $K^o_f(Al(OH)_4^-)$ were determined in two steps: (1) Regression of log K_{s4}(boehmite) as a function of temperature; (2) calculation of log $\overline{K}^o_f(Al(OH)_4^-)$ from log K_{s4}(boehmite).

6.1.1 Regression of LogK_{s4}(T)(boehmite) and Determination of LogK_{s4}(T)(gibbsite) and LogK_{s4}(T)(diaspore)

The log K_{s4}(boehmite) data were derived from calculation of the equivalent log K_{s4}(boehmite) from log K_{s4}(gibbsite) and log K_{s4}(diaspore) according to the equations:

$$\log K_{s4}(\text{boehmite}) = \log K_{s4}(\text{gibbsite}) - \log K_{r1}$$

where K_{r_1} is for the reaction;

$$\underset{\text{gibbsite}}{Al(OH)_3} = \underset{\text{boehmite}}{AlOOH} + \underset{\text{water}}{H_2O}$$

and

$$\log K_{s4}(\text{boehmite}) = \log K_{s4}(\text{diaspore}) + \log K_{r2}.$$

where K_{r2} is for the reaction

$$\underset{\text{boehmite}}{AlOOH} = \underset{\text{diaspore}}{AlOOH}$$

TABLE 11

SUMMARY OF LOG K_{s4}(BOEHMITE) DERIVED FROM EXPERIMENT AND FROM EXPERIMENTALLY MEASURED VALUES OF LOG K_{s4}(GIBBSITE) AND LOG K_{s4}(DIASPORE)

Source	T,°C	$\log K_{s4}$	$\log K_{r1,2}$	$\log K_{s4}$(boehmite)	
				Measured	Predicted
Gibbsite[1]					
Ikkatai and Okada (1962)	100.0	−0.14	+0.440	−0.580	−0.618
	100.0	−0.18	+0.440	−0.620	−0.618
	130.0	+0.14	+0.607	−0.467	−0.390
Kittrick (1966) (four measurements)	25.0	−1.31	−0.036	−1.274	−1.253
Russell et al. (1955)	40.0	−1.02	0.066	−1.086	−1.119
	50.0	−0.87	0.132	−1.002	−1.032
	60.0	−0.73	0.197	−0.927	−0.946
	70.0	−0.57	0.260	−0.830	0.861
	80.0	−0.43	0.321	−0.751	−0.778
	90.0	−0.32	0.381	−0.701	−0.697
	100.0	−0.16	0.440	−0.600	−0.618
	110.0	−0.06	0.497	−0.557	−0.540
	120.0	+0.03	0.553	−0.523	−0.464
	130.0	+0.11	0.607	−0.497	−0.390
Boehmite					
Apps (1970)	49.6	−1.04		−1.040	−1.035
	70.0	−0.87		−0.870	−0.861
	90.0	−0.76		−0.760	−0.697
	121.0	−0.48		−0.480	−0.457
	123.2	−0.45		−0.450	−0.440
	153.8	−0.22		−0.220	−0.223
	184.0	+0.02		−0.020	−0.026
	217.6	+0.28		+0.280	+0.171
	241.8	+0.35		+0.350	+0.298
	256.0	+0.40		+0.400	+0.367
	255.0	+0.35		+0.350	+0.362
Kuyunko et al. (1983)	200.0	+0.00		+0.000	+0.071
	250.0	+0.27		+0.270	+0.339
Magarshak (1938)	200.0	+0.03		+0.030	+0.071
Druzhinina (1955)	200.0	−0.06		−0.060	+0.071

[1] Results from Fulda and Gingsberg (1951) are coincident with those of Russell et al. (1955) and could have been incorporated in this summary, (Note added during proofing).

TABLE 11 (Continued)

Source	T,°C	$\log K_{s4}$	$\log K_{r1,2}$	$\log K_{s4}$(boehmite)	
				Measured	Predicted
Russell et al. (1955)	80.0	−0.73		−0.730	−0.778
	100.0	−0.55		−0.550	−0.618
	120.0	−0.45		−0.450	−0.464
	130.0	−0.38		−0.380	−0.390
	140.0	−0.32		−0.320	−0.319
	150.0	−0.25		−0.250	−0.249
	160.0	−0.18		−0.180	−0.181
	170.0	−0.11		−0.110	−0.115
Wefers (1967b)	95.0	−0.70		−0.70	−0.657
	105.0	−0.55		−0.55	−0.579
Diaspore					
Apps (1970)	226.5	−0.07	+0.251	+0.181	+0.219
	259.0	+0.23	+0.207	+0.437	+0.381
	260.0	+0.21	+0.205	+0.415	+0.386
This work	200	−0.25	+0.287	+0.037	+0.071
	225	−0.04	+0.253	+0.213	+0.211
	250	+0.05	+0.219	+0.269	+0.339
	275	+0.26	+0.185	+0.445	+0.453
	300	+0.30	+0.152	+0.452	+0.554
	325	+0.57	+0.119	+0.609	+0.642
	350	+0.60	+0.086	+0.686	+0.716
	350	+0.66	+0.086	+0.746	+0.716
	350	+0.68	+0.086	+0.766	+0.716
	325	+0.50	+0.119	+0.619	+0.642
	300	+0.43	+0.152	+0.582	+0.554
	275	+0.25	+0.185	+0.435	+0.453
	250	+0.18	+0.219	+0.399	+0.339
	225	+0.04	+0.253	+0.293	+0.211
	200	−0.14	+0.287	+0.147	+0.071
Druzhinina (1955)	200	−0.15	+0.287	+0.137	+0.071
	200	−0.15	+0.287	+0.137	+0.071
	220	−0.06	+0.260	+0.200	+0.184

These values were combined with those log K_{s4}(boehmite) values obtained by direct measurement. The data set and sources of the computed values of log K_{s4}(boehmite) are summarized in Table 11.

The regression of log K_{s4}(boehmite) data against $\frac{1}{T}$, K^{-1}, yields an equation;

$$\log K_{s4}(T)(\text{boehmite}) = -35.76 + 12.919 \log T + 787.00(T^{-1}) - 3.6707 \times 10^{-9}\, T^3$$

This, with the addition of log $K_{r1}(T)$ or subtraction of log $K_{r2}(T)$, yields log $K_{s4}(T)$(gibbsite) and log $K_{s4}(T)$(diaspore), respectively. Table 12 gives log K_{s4} for gibbsite, boehmite and diaspore at 25°C intervals between 0 and 350°C. The continuous lines drawn on Figures 4, 6 and 8 represent these calculated functions.

TABLE 12

CALCULATED VALUES OF LOG K_{s4}(GIBBSITE, BOEHMITE, DIASPORE) BETWEEN 0 AND 350°C ALONG THE SATURATION SURFACE OF WATER

T,°C	Gibbsite	Boehmite	Diaspore
0	−1.696	−1.480	−2.126
25	−1.289	−1.253	−1.834
50	−0.900	−1.032	−1.559
60	−0.749	−0.946	−1.453
75	−0.528	−0.819	−1.298
100	−0.178	−0.618	−1.054
125	+0.153	−0.427	−0.823
150	+0.464	−0.249	−0.608
175	+0.756	−0.083	−0.405
200		+0.071	−0.216
225		+0.211	−0.042
250		+0.339	+0.120
275		+0.453	+0.268
300		+0.554	+0.402
325		+0.642	+0.523
350		+0.716	+0.630

6.1.2 Calculation of log $\overline{K}^o_{f,T}(Al(OH)_4^-)$

Calculation of log $\overline{K}^o_{f,T}(Al(OH)_4^-)$ now follows from the reaction:

$$AlOOH + H_2O + OH^- = Al(OH)_4^- \qquad K_{s4}(\text{boehmite})$$

where

$$\log \overline{K}^o_{f,T}(Al(OH)_4^-) = \log K_{s4,T} + \log K^o_{f,T}(\text{boehmite}) + \log K^o_{f,T}(H_2O) + \log \overline{K}^o_{f,T}(OH^-)$$

Data used in this calculation is derived from this work for log K_{s4}(boehmite) and log K_f^o(boehmite), from Helgeson et al. (1978) for log $\overline{K}_f^o(H_2O)$, and from Tanger (personal communication 1986) for log $\overline{K}_f^o(OH^-)$, given in Appendix I, Table 6. The more recent work of Tanger is selected in this case, because he clearly demonstrates that the earlier thermodynamic parameters for OH^- and K_w derived from studies by Helgeson et al. (1981) deviate significantly above 300°C, due to an inadequate correction for the Born coefficient (see Tanger and Helgeson, 1988). This finding is consistent with difficulties experienced in refining log $K_f^o(Al(OH)_4^-)$ when the earlier values of log $K_f^o(OH^-)$, derived from Kirkham et al. (1978) were used.

The calculated values of log $\overline{K}_f^o(Al(OH)_4^-)$ and $\Delta\overline{G}_f^o(Al(OH)_4^-)$ are given in Table 13.

TABLE 13

Log $\overline{K_f^o}$ ($Al(OH)_4^-$) AND $\Delta\overline{G_f^o}$ ($Al(OH)_4^o$) BETWEEN 0 AND 350°C ALONG THE SATURATION SURFACE OF WATER

T°C	p, bars	log $\overline{K_f^o}$ ($Al(OH)_4^-$) —	$\Delta\overline{G_f^o}$ ($Al(OH)_4^-$) kcal.gfw^{-1}
0	0.006	252.556	−315.667
25	0.032	228.590	−311.862
50	0.123	208.307	−308.020
60	0.199	201.042	−306.476
75	0.386	190.925	−304.158
100	1.013	175.863	−300.281
125	2.320	162.679	−296.380
150	4.957	151.036	−292.446
175	8.918	140.672	−288.471
200	15.536	131.387	−284.460
225	25.478	123.001	−280.375
250	39.735	115.380	−276.202
275	59.425	108.403	−271.901
300	85.832	101.969	−267.428
325	120.447	95.971	−262.676
350	165.212	90.283	−257.436

6.2 Calculation of $\overline{C_p^o}$, $\overline{S_{298}^o}$ and $\Delta\overline{H_{f,298}^o}$

Calculation of the remaining thermodynamic parameters for $Al(OH)_4^-$ is difficult without the assistance of an appropriate electrolyte model, e.g. Tanger and Helgeson (1988), and an independent determination of the conventional partial molal heat capacity of the ion at 25°C. As a matter of interest, the remaining thermodynamic parameters are here calculated from the fitted log K_{s4}(gibbsite) between 20 and 70°C. The reader will recall that this is the range where solubility data for gibbsite is considered to be most reliable. Assuming $\Delta C_{p,s4}^o$ to be constant over this range, the following values are obtained, using the Clarke and Glew (1966) equation:-

$$\Delta\overline{S_{s4,\,298}^o} = +15.83 \text{ cal.K}^{-1}$$

$$\Delta\overline{H_{f,298}^o} = +6.480 \text{ kcal}$$

$$\Delta\overline{C_{p,\,s4,298}^o} = +31.62 \text{ cal.K}^{-1}$$

These parameters yield:

$$\overline{S_{298}^o}\,(Al(OH)_4^-) = +29.59 \text{ cal.K}^{-1}$$

$$\Delta\overline{H_{f,298}^o}\,(Al(OH)_4^-) = -357.56 \text{ kcal}$$

$$\overline{C_{p,\,298}^o}(Al(OH)_4^-) = +21.08 \text{ cal.K}^{-1}$$

The calculation of $\Delta\overline{G_{f,\,298}^o}(Al(OH)_4^-)$ from these values yields −311.88 kcal.gfw^{-1} in agreement with that in Table 13.

Hovey et al. (1988) have independently determined the conventional standard partial heat capacity to be:-

$$\overline{C^o_{p,\,298}}\,(Al(OH)_4^-) \;=\; +23.06\ \text{cal.K}^{-1}$$

Agreement with the corresponding value calculated above is very good, encouraging the belief that the computed thermodynamic properties of the aluminate ion have been determined satisfactorily.

6.3 Comparison of $\Delta\overline{G^o_f}(T)(Al(OH)_4^-)$, Predicted by the HKF Equation of State, with that Determined from Solubility Measurements

Helgeson and his students and coworkers have been developing an equation of state for molecular and ionic species in aqueous solutions with broad applicability, and covering a range of temperatures from 0–1000°C and 1 bar to 10 kbar. (Helgeson and Kirkham, 1974a,b; Helgeson et al., 1981; Shock and Helgeson, 1988; Tanger and Helgeson, 1988). It is designated the revised Helgeson-Kirkham-Flowers (HKF), equation of state after the principal developers. Recent significant modifications by Tanger and Helgeson (1988) have improved the HKF equation of state so that it is capable of very precise predictions of the standard state thermodynamic properties of ionic and molecular species to 450°C, and at pressures to 5 kb. Further research currently underway indicates that it may have predictive capabilities over a far wider range of pressures and temperatures. For precise predictions the standard state properties, $\overline{C^o_p}$, $\overline{S^o}$, $\Delta\overline{H^o_f}$, $\Delta\overline{G^o_f}$, and $\overline{V^o}$ should be known at 25° and 1 bar. Knowledge of other properties, e.g. $\overline{\kappa^o}$, the compressibility, while desirable, are not essential. From the $\overline{C^o_p}$, $\overline{S^o}$, and $\overline{V^o}$ for a particular species may be derived a series of parameters designated a_1, a_2, a_3, a_4, c_1, c_2 and the Born coefficient, $\omega_{Tr,Pr}$, necessary to calculate the standard state properties of that species at other temperatures and pressures. A detailed description of the HKF equations of state are given by Tanger and Helgeson (1988). Procedures for calculating the parameters characteristic of each species are presented by Shock and Helgeson (1988).

The HKF equation of state explicitly takes into account solvation effects about the ion. Therefore the incorporation of waters of solvation in the formula of the ionic or molecular species, e.g. $Al(OH)_4^-$ or $Si(OH)_4$ is in conflict with the premise of the equation of state. Application of the HKF equation of state therefore requires recasting the thermodynamic properties of $Al(OH)_4^-$ as AlO_2^- by subtracting twice the numerical value of the respective property of water. The properties of AlO_2^- are summarized in Table 14. The Born coefficient and a and c parameters for AlO_2^- were calculated according to the procedures recommended in Shock and Helgeson (1988) using $\overline{C^o_p}$ and $\overline{S^o_{298}}$ derived from this study, and $\overline{V^o}$ from Hovey and Hepler (1988). These coefficients are also given in Table 14.

Log $\overline{K^o_f}$ (T)($Al(OH)_4^-$) values at 25°C intervals are calculated using the HKF equation of state, along the water solution surface, and compared, in Table 15, with the corresponding values derived from solubility measurements in this report. Excellent agreement is obtained throughout the temperature range from 0 to 350°C. The maximum deviation occurs at 250°C, where $\Delta(\Delta\overline{G^o_{f,\,523}}) \leq 200$ cal. This is within the limits of error of $\Delta G^o_{f,298}$ for gibbsite, but slightly outside the limits for $\Delta G^o_{f,298}$ of corundum. The slightly better fit of the boehmite solubility data near 250°C (see Figure 6), and the slightly better fit of the log K^o_f(T)(boehmite) data, when $\Delta H^o_{f,298}$(diaspore) is increased by +250 cal.gfw^{-1} as noted in the discussion relating to the summary of regression analyses presented in Table 10, suggests that $\Delta H^o_{f,298}$ and $\Delta G^o_{f,298}$ for diaspore should be made more positive by about 0.1 kcal.gfw^{-1}. Similarly, $\Delta H^o_{f,298}$ and $\Delta G^o_{f,298}$ for corundum should be more positive by about 0.2 kcal.gfw^{-1}. Such minor corrections are scarcely justified at this time, but could be made, if more precise solubility data for diaspore or corundum becomes available. Furthermore, these arguments presume that the $\overline{C^o_p}$, $\overline{S^o_{298}}$ and $\overline{V^o}$ for AlO_2^- have been correctly determined, and that the HKF equation of state predicts precisely the standard state conditions of an aqueous species along the saturation surface of water. Neither assumption should be accepted without further corroborating evidence. In spite of these cautionary notes, the agreement between the experimentally derived $\Delta\overline{G^o_f}$ (T)($Al(OH)_4^-$) and that predicted by the HKF equation of state is remarkably good and lends confidence to the validity of the results obtained in this report.

TABLE 14

THERMODYNAMIC PROPERTIES OF THE ALUMINATE ION

Formula	$\overline{C}^{o}_{p,298}$ cal.gfw^{-1}.K^{-1}	$\overline{S}^{o}_{298}$ cal.gfw^{-1}.K^{-1}	$\Delta\overline{H}^{o}_{f,298}$ kcal.gfw^{-1}	$\Delta\overline{G}^{o}_{f,298}$ kcal.gfw^{-1}	log $\overline{K}^{o}_{f,298}$ –	$\overline{V}^{o}$ cm^{3}.gfw^{-1}
$Al(OH)_4^-$	+21.08	+29.59	−357.56	−311.88	+228.611	+46.22
AlO_2^-	−14.89	−3.81	−220.93	−198.506	+145.507	+10.08

HKF Equation of State Parameters

Formula	$a_1 \times 10^{1}$ cal.gfw^{-1}.bar^{-1}	$a_2 \times 10^{-2}$ cal.gfw^{-1}	a_3 cal.K.gfw^{-1}.bar^{-1}	$a_4 \times 10^{-4}$ cal.K.gfw^{-1}	c_1 cal.gfw^{-1}.K^{-1}	$c_2 \times 10^{-4}$ cal.K.gfw^{-1}	$\omega \times 10^{-5}$ cal.gfw^{-1}
AlO_2^-	0.31586	3.0566	−2.1559	−2.9054	13.331	−6.075	1.6866

Finally, it should be recognized that the calculations of the thermodynamic properties of $Al(OH)_4^-$ are also based on the assumed correctness of the thermodynamic properties of gibbsite. These also could be slightly in error, and may contribute to the minor discrepancy between predicted and measured values of log $\overline{K}^o(Al(OH)_4^-)$.

TABLE 15
COMPARISON OF LOG $\overline{K}_f^o$ ($Al(OH)_4^-$), DETERMINED IN THIS REPORT, WITH THAT PREDICTED BY THE HKF EQUATION OF STATE

	Log $\overline{K}_f^o$ ($Al(OH)_4^-$)		
T,°C	Apps et al. (This report)	SUPCRT'87 Tanger and Helgeson (1988)	Δ
0	252.56	252.580	−0.02
25	228.59	228.609	−0.02
50	208.31	208.322	−0.01
75	190.93	190.932	−0.00
100	175.86	175.858	−0.00
150	151.04	151.013	+0.03
200	131.39	131.333	+0.06
250	115.38	115.314	+0.07
300	101.97	101.910	+0.06
350	90.28	90.251	+0.03

7. THE THERMODYNAMIC PROPERTIES AND RELATIVE STABILITY OF BAYERITE IN RELATION TO OTHER $Al(OH)_3$ POLYMORPHS

7.1 Introduction

Three polymorphs of gibbsite have been identified; bayerite, doyleite and nordstrandite. Although all three have been found to occur naturally, only nordstrandite may be more than a mineralogical curiosity. No calorimetric, phase equilibria, or solubility studies of doyleite or nordstrandite have been made, so their thermochemical properties cannot be estimated with any degree of accuracy. In contrast, a number of solubility measurements of bayerite have been reported over a range of temperatures from 20 to 100°C. Several measurements have also been made of the enthalpy of dehydration of bayerite in relation to gibbsite dehydration. Finally, one paper describes results of several measurements of the heat of dissolution of both gibbsite and bayerite in hydrofluoric acid. This information is sufficient to derive an initial estimate of the thermodynamic properties of bayerite using gibbsite as a reference.

Evidence in the literature supports the contention that the precipitation of gibbsite on gibbsite seed crystals during the recovery step of the Bayer process, is not a simple reaction involving the direct growth of ordered gibbsite from the supersaturated solution. Instead, it involves the accretion of surface active material, which is, or initially reacts to form bayerite. The bayerite then recrystallizes to form gibbsite. The rate of transition of bayerite to gibbsite is sensitive to temperature, pH (or $p(OH)^-$), the aluminum concentration in solution, and the presence of other ionic and molecular species. These parameters have a direct bearing on the interpretation of experiments to measure gibbsite solubility when synthetic Bayer process gibbsite is used as a starting material. They also bear indirectly on the persistence of bayerite in nature, and may also allow estimates to be placed on the probability of its being observed in the natural environment.

In this section, the authors derive the thermodynamic properties of bayerite from solubility data in alkaline solutions and from available data on heats of decomposition. The observed spread in measured Bayer process gibbsite solubilities is then related to precipitation mechanisms during the Bayer process recovery stage. The implications of using Bayer process gibbsite for solubility measurements in dilute aqueous solution are considered. The natural occurrences of bayerite and nordstrandite are reviewed and a tentative estimate of log $K_{s4,298}$(nordstrandite) is made.

7.2 The Derivation of Bayerite Thermochemical Properties

Bayerite solubility measurements have been reported several times in the literature, e.g. Chistyakova (1964), Fricke (1928, 1929), Hem and Roberson (1967), Herrmann and Stipetić (1950) and Lyapunov et al. (1973). Russell et al. (1955) report on the solubility of the "β trihydrate", which is presumed also to be bayerite. The β trihydrate was never identified by its X-ray diffraction pattern either in Russell et al. (1955), or in the original Aluminum Company of America report by Taylor et al. (1927).

To test whether a consistent solubility product reflecting equilibrium with respect to a gibbsite polymorph might control the aluminum concentration in experiments involving the precipitation of aluminum hydroxide from solution and in natural systems, the experimental results of the above cited papers and others listed in Table 16 were reevaluated in a similar manner to those for gibbsite solubility data in Section 4.2 to obtain values of $\log K_{s4}(Al(OH)_3)$. Data involving the solubility of aluminum hydroxide in strong hydroxide solutions, and requiring empirical extrapolation to zero ionic strength include those by Chistyakova (1964), Fricke (1928, 1929), Herrmann and Stipetić (1950), Lyapunov et al. (1973), Russell et al., (1955), Sato (1954) and Taylor et al. (1927). $\log K_{s4}(Al(OH)_3)$ values were obtained by fairing lines through the $\log K'_{s4}(Al(OH)_3)$ versus ionic strength data so as to be consistent with the slopes of curves observed with

TABLE 16

SUMMARY OF SOLUBILITY PRODUCT CONSTANTS, K_{s4}, FOR $Al(OH)_3$

Source	Derivation	T,°C	Log K_{s4}	Comments
Chistyakova (1964)	Extrapolation	20.0	−1.05	Measurements after 8 mo–2 yr. duration. Bayerite precipitated
Fricke (1928)	Extrapolation	30.0	−0.94	Bayerite A after 3 days
	Extrapolation	30.0	−1.00	Bayerite B after 3 days
Fricke (1929)		30.0	−0.87	Equilibrium not attained after 36 days. Mixture of gibbsite and bayerite
Gayer et al. (1958)		25.0	−0.53	X-ray diffraction lines identified by Parks (1972) as bayerite.
Hem and Roberson (1967)		25.0	+0.034	Bayerite after aging 10 days.
Herrmann and Stipetić (1950)	Extrapolation	25.0	−1.15	Bayerite seed crystals.
		28.5	−1.07	
Lyapunov et al. (1973)	Extrapolation	40.0	−0.73	Bayerite
		50.0	−0.59	
		60.0	−0.51	
May et al. (1979)	from graph	25.0	−0.63	Synthetic gibbsite, 744 hrs.
	from graph	25.0	−0.13	Natural gibbsite, 384 hrs.
Raupach (1963)	from graph	20.0	−0.32	Arkansas bauxite, 356 hrs.
	from graph		−0.27	Precipitated gibbsite, 356 hrs.
Russell et al. (1955)	Extrapolation	40.0	−0.72	β trihydrate
		50.0	−0.60	
		60.0	−0.51	
		70.0	−0.39	
		80.0	−0.26	
		90.0	−0.15	
		100.0	−0.05	
Sanjuan and Michard (1987)	from graph	50.0	−0.03	Synthetic gibbsite Bayerite detected after run.
Sato (1954)		30.0	−0.78	Precipitation of gibbsite from sodium aluminate solution onto gibbsite seed crystals.
		40.0	−0.66	
		50	−0.57	
		60.0	−0.48	
		70.0	−0.38	
Taylor et al. (1927)	Extrapolation	150.0	≈ +0.08	Arkansas bauxite
			−0.17	Surinam bauxite
Thompson (1955)		25.0	−0.68	Described as "aluminum hydroxide", $Al(OH)_3$

respect to gibbsite, in the same temperature region, c.f. Figure 3. The calculations with respect to bayerite and other non specific aluminum hydroxides are summarized in Appendix J. Appendix K is a summary of bauxite solubility calculations given in Taylor et al. (1927). Results from Appendix J are presented graphically in Figure 12.

The data by Russell et al. (1955) for the β trihydrate may not reflect equilibrium. The observed trends of $\log K'_{s4}$ vs ionic strength shown in Figure 12 are inconsistent with those in Figure 3 for gibbsite at temperatures below 90°C. However, at 90° and 100°C, $\log K'_{s4}$ versus I is consistent with corresponding gibbsite data, suggesting that the data at these temperatures may be more reliable. In this evaluation, the relatively more stable measurements at an ionic strength, $I \approx 1$, were extrapolated to $I = 0$, in conformity with the data by Chistyakova (1964), and because these data are also consistent with those by Lyapunov et al. (1973).

The $\log K_{s4}(Al(OH)_3)$ data from the various studies are plotted in Figure 13 as a function of reciprocal temperature. Included on the figure are curves showing the calculated $\log K_{s4}$(gibbsite) as determined in section 6.1.2 of this report and $\log K_{s4}$(bayerite), determined below. $\mathrm{Log}K_{s4}$ for boehmite, diaspore and corundum are also included for comparison, where $\log K_{s4}$ for these two minerals reflects the reactions

$$AlOOH + OH^- + H_2O = Al(OH)_4^-$$

for boehmite and diaspore and diaspore, and:

$$\tfrac{1}{2}\, Al_2O_3 + OH^- + 1\tfrac{1}{2}\, H_2O = Al(OH)_4^-$$

for corundum. The measurements by Chistyakova (1964), Fricke (1928, 1929), Lyapunov et al. (1973) and Russell et al. (1955) display a fairly consistent trend and most probably reflect bayerite solubility. However, the solubility products of synthetic and natural gibbsite by May et al. (1979), of a bauxite by Raupach (1963), of "aluminum hydroxide" by Thompson (1955), and of freshly precipitated bayerite (Hem and Roberson, 1967) lie well above this trend. The data by Sato (1954) involving the precipitation of gibbsite on gibbsite seeds over 120 hours show a trend similar to those of Lyapunov et al. (1973) for bayerite and of Russell et al. (1955) for the β trihydrate. In contrast, the solubilities of Arkansas and Surinam bauxites at 150°C from Taylor et al. (1927) fall below the gibbsite solubility curve, suggesting a reaction of natural gibbsite converting to boehmite.

A regression analysis of the data by Chistyakova (1964), Fricke (1928, 1929), Lyapunov et al. (1973) and Russell et al. (1955) was made to calculate the thermodynamic properties of the bayerite dissolution reaction:

$$\underset{\text{bayerite}}{Al(OH)_3} + OH^- = Al(OH)_4^-$$

It is assumed that the data reflect bayerite solubility and that the heat capacity of bayerite is the same as for gibbsite. The derived thermodynamic properties of bayerite are summarized in Table 17.

These data were calculated using the revised thermodynamic properties of the OH^- ion computed from the electrolyte model described by Tanger and Helgeson (1988) and the thermodynamic properties of the aluminate ion, $Al(OH)_4^-$ derived in section 6 of this report. The heat capacity of the reaction:

$$\underset{\text{bayerite}}{Al(OH)_3} + OH^- = Al(OH)_4^-$$

is assumed constant over the range 0 – 100°C.

The calculated entropy is rather higher than expected for a polymorph of gibbsite, for which $S^{\circ}_{298} = 16.36$ $cal.gfw^{-1}.K^{-1}$, (Hemingway et al. 1977). However, alternative interpretations of the data, yield even less plausible values of S°_{298}, e.g. that using the relatively less stable ionic strength ≈ 0.5 measurements by Russell et al. (1955) as a basis for extrapolating $\log K'_{s4}$ to $I = 0$, gives $S^{\circ}_{298} = 23.0$ $cal.gfw^{-1}.K^{-1}$. Utilizing the "synthetic gibbsite" solubility product measured by May et al. (1979) at a 25°C, together with the sup-

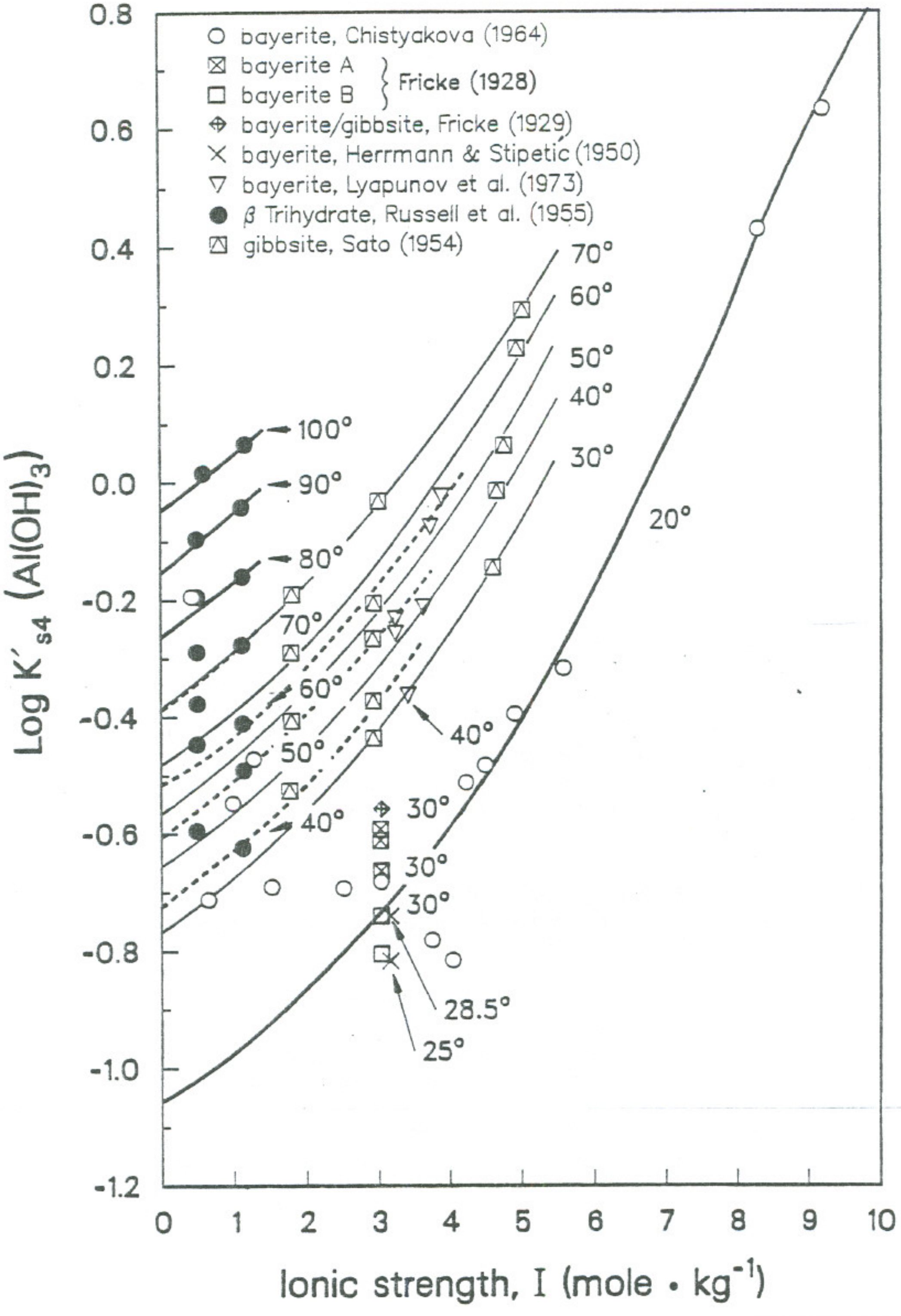

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Figure 12. Apparent solubility products, $K'_{s4}(Al(OH)_3)$ plotted against ionic strength.

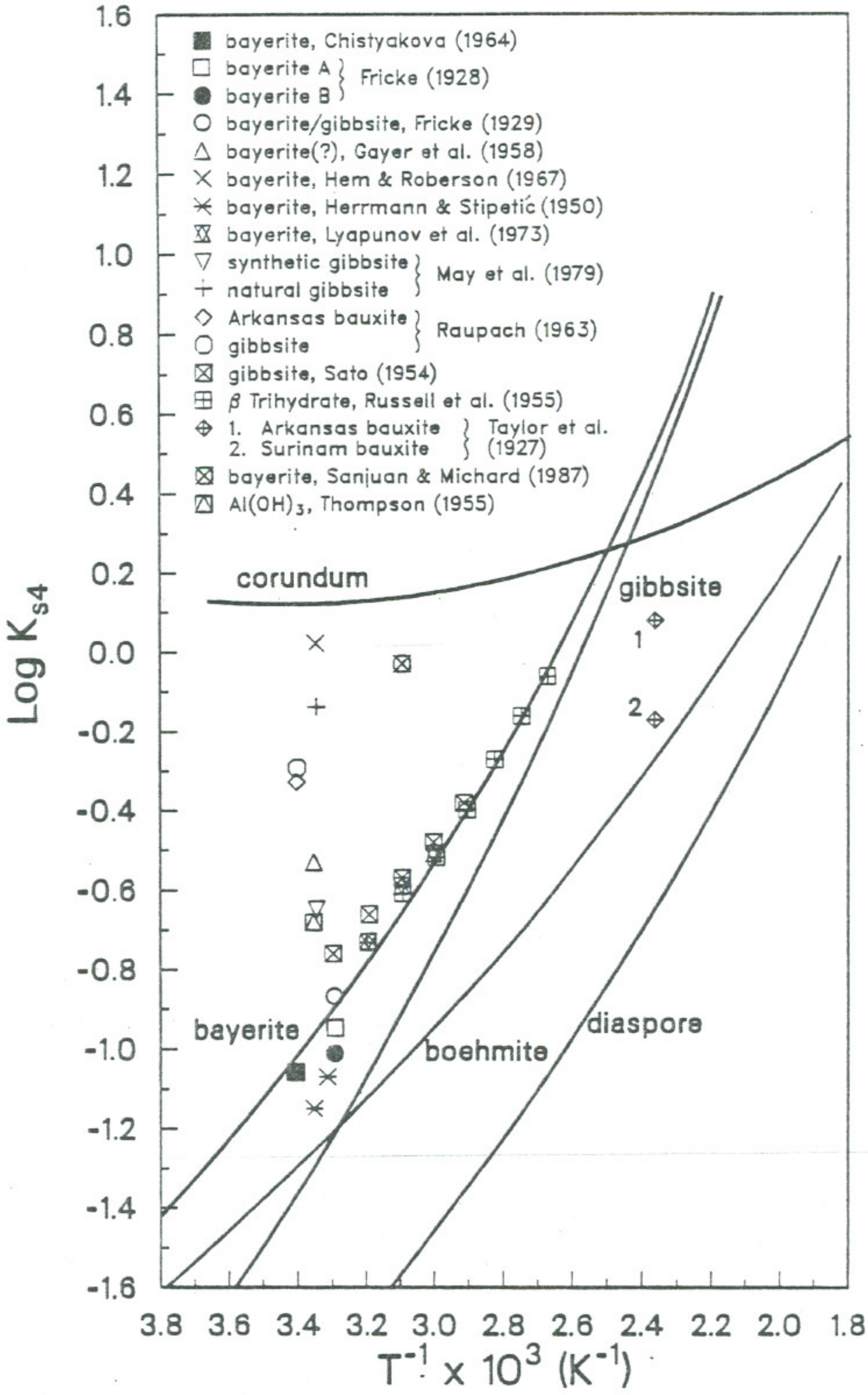

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Figure 13. The solubility products $K_{s4}(Al(OH)_3)$, as a function of reciprocal temperature.

TABLE 17

CALCULATED THERMODYNAMIC PROPERTIES OF BAYERITE

PARAMETER	UNIT	VALUE
$C^o_{p,298}$	$cal.gfw^{-1}.K^{-1}$	+23.005[1]
S^o_{298}	$cal.gfw^{-1}.K^{-1}$	+18.972
$\Delta H^o_{f,298}$	$kcal.gfw^{-1}$	−307.829
$\Delta G^o_{f,298}$	$kcal.gfw^{-1}$	−275.570
Log $K^o_{f,298}$	–	+201.995

[1] Using the Maier-Kelley heat capacity function for gibbsite reported by Helgeson et al. (1978)

posedly more reliable 90 and 100°C values of Russell et al. (1955) also yield a quite unrealistic value for the entropy. In all probability, the true value of S^o_{298}, for bayerite lies between the value accepted in this report and that of gibbsite. If so, bayerite probably has a somewhat larger heat capacity than is assumed here.

Several studies of the enthalpy of decomposition of both bayerite and gibbsite have been made, e.g. Fricke and Severin (1932), Eyraud et al. (1955), Michel (1959), Mukaibo et al. (1969) and Strobel and Henning (1972). Such studies permit rough estimates of the enthalpy of transition for the reaction: bayerite = gibbsite; and hence the enthalpy of formation, $\Delta H^o_{f,298}$(bayerite), given the corresponding value for $\Delta H^o_{f,298}$(gibbsite). Because the thermal decomposition of different bayerite and gibbsite samples rarely result in identical decomposition products, such an approach will produce questionable estimates of the heat of transition. Hence, the thermodynamic properties of bayerite derived from such data may be unreliable.

Of greater value are the data obtained from heat-of-solution determinations of bayerite and gibbsite in hydrofluoric acid. These measurements are summarized by Fricke and Wullhorst (1932) and probably permit the best estimate of $\Delta H^o_{f,298}$(bayerite). Unfortunately, the temperature at which the HF dissolution measurements were conducted, was not recorded. The most trustworthy data give −2.4 ± 0.52 kcal, normalized to gfw = $Al_2O_3.3H_2O$ or −1.2 ± 0.26 kcal for gfw = $Al(OH)_3$ for the reaction bayerite = gibbsite. This is in excellent agreement with the estimate of −1.24 kcal for the same reaction calculated from bayerite and gibbsite alkaline solubility measurements in this report, and with an earlier estimate of 1.38 kcal by Herrmann and Stipetić (1950) which was also based on solubility measurements. Relevant data from the calorimetric studies, along with decomposition and solubility data are summarized in Table 18. The average of value for $\Delta H^o_{r,T}$, from decomposition data normalized to the gfw for $Al_2O_3.3H_2O$, is −2.28 ± 1.05 kcal or 1.14 ± 0.52 kcal when normalized to gfw for $Al(OH)_3$. This estimate excludes the value of +1.7 kcal, derived from Mukaibo et al. (1969), which is in any case not cited in a subsequent publication from the same laboratory (Yamada et al., 1973).

While the limited solubility and calorimetric data appear to be in satisfactory accord, it should be emphasized that the available data are for most part incomplete, and the materials utilized in the experiments are often inadequately characterized. For example, the "β trihydrate" solubilities by Russell et al. (1955) may represent nothing more than steady state conversion of one polymorph to another, or even a non equilibrium trend produced as an artifice of systematic experimental procedures. The optical and X-ray diffraction evidence given respectively by Chistyakova (1964) and Fricke (1928, 1929), support the interpretation that the solubility data do reflect metastable equilibria with respect to bayerite. The higher

TABLE 18

DETERMINATION OF THE HEAT OF REACTION, $\Delta H^{o}_{r,T}$, for BAYERITE ($Al_2O_3 \cdot 3H_2O$) = GIBBSITE ($Al_2O_3 \cdot 3H_2O$)

Source	Method	Temperature °C	Starting material	Product	Enthalpy of decomposition, $\Delta H^{o}_{r,T}$, kcal.gfw.	Enthalpy of transition (bayerite = gibbsite), $\Delta H^{o}_{r,T}$, kcal.gfw.
Fricke and Wullhorst, (1932)	dissolution in HF	?	gibbsite	solution	−36.59 ± 0	
			bayerite a	solution	−37.84 ± 0	−2.4 ± 0.52
			bayerite b	solution	−37.53	–
Fricke and Severin (1932)	P_{H_2O} as f(T)	165	gibbsite	boehmite + steam	+36.3	−3.9
		120	bayerite	boehmite + steam	+32.4	
Herrmann and Stipetić (1950)	Solubility measurements		gibbsite bayerite	–	–	−2.76
Eyraud et al. (1955)	DSC		gibbsite	anhydrous alumina	+71.5	−2.0
			bayerite	anhydrous alumina	+69.5	
Michel (1957)	Calvet micro-calorimeter decomposition in vacuum	230	gibbsite	ρ,χ,η Al_20_3	+48.0	
		210	bayerite		+46.5	−1.5
Mukaiko et al. (1969)	adiabatic calorimetry	210	gibbsite	$\zeta' Al_2O_3$	+52.5	+1.7
		200	bayerite	ζAl_2O_3	+54.2	
Strobel and Henning (1972)	DSC	220–340	gibbsite	$Al_2O_3 \cdot 0.5H_2O$	+41.0 ± 1.8	−1.0
		210–305	bayerite	$Al_2O_30.4H_2O$	+40.0 ± 1.6	
	DTA	270–410	gibbsite	$Al_2O_3 \cdot 0.5H_2O$	+43.8 ± 4.0	−3.0
		210–370	bayerite	$Al_2O_3 \cdot 0.4H_2O$	+40.8 ± 4.0	

solubilities of precipitates also giving bayerite X-ray diffraction patterns, e.g. Hem and Roberson (1970), must reflect the effect of smaller particle sizes, as suggested by Parks (1972).

Because the reported bayerite solubility data are on poorly characterized material, and because of the tendency of bayerite to decompose to gibbsite in solution, the estimated solubility of bayerite cannot be determined as precisely as that of gibbsite. Yet in alkaline solutions, bayerite never has a solubility less than the minimum observed for gibbsite, supporting the belief that bayerite is the less stable polymorph over the range of temperatures and pressures studied.

7.3 A Comparison of Measured Bayerite and Gibbsite Solubilities in Alkaline Solutions

A comparison of the measured solubilities of bayerite and gibbsite in alkaline solutions provides some insight into the potential mechanisms involved in gibbsite formation and in the persistence of bayerite. This applies particularly to the precipitation of gibbsite from concentrated sodium aluminate solutions such as those used in the recovery of gibbsite in the Bayer process. In Figure 14 are plotted LogK_{s4} values derived from the precipitation or dissolution of gibbsite, bayerite, or unspecified aluminum hydroxides versus $1/T$ (K^{-1}). The data are divided into three categories; (a) those from experiments involving planned equilibration with gibbsite from undersaturation, designated with open symbols, (b) those from equilibration of gibbsite from oversaturation, designated with filled symbols, and (c) those from equilibration experiments from oversaturation or undersaturation where bayerite was identified as the participating phase, designated with partially filled symbols. The continuous lines in the figure represent, respectively, the calculated gibbsite solubility (see section 6.1.2), and the bayerite solubility, estimated in the preceding subsection.

The broad scatter in the solubility measurements of gibbsite may be attributed to the mechanism by which gibbsite is produced during the Bayer process for treating bauxitic aluminum ores. In this process, a concentrated sodium aluminate liquor (≤ 200 $g.^{-1}$ Na_2O) is cooled from as high as 250°C to approximately 50 – 60°C, diluted and seeded with gibbsite crystals. The solution, which is supersaturated with respect to gibbsite, precipitates aluminum hydroxide onto the seeds. According to Calvet et al. (1951), this process is not one of simple crystal growth, but instead it involves the accretion of pseudo-colloidal particles which have grown on "active centers", or nuclei. These "active centers" are introduced in trace amounts with poorly crystallized material associated with the well crystallized gibbsite seeds. This interpretation was made by Calvet et al. (1951) after concluding a lengthy series of calorimetric studies of the precipitation of gibbsite and bayerite from sodium aluminate solutions. It is supported by Bloom and Weaver (1982) who took SEM photographs of Bayer process gibbsite and found that "untreated samples contained abundant globular surface material". The identity of the surface active material remains in doubt. Van Straten (1984) also observed "an irregular layer with poor contrast on top of the [gibbsite] seed" when he studied the precipitation of $Al(OH)_3$ on gibbsite seeds in alkaline solutions between 25 and 90°C.

The tendency for bayerite to precipitate from alkaline solutions supersaturated with respect to gibbsite and then convert to gibbsite, is well known, (Geiling and Glocker, 1943; Brosset, 1952; Bye and Robinson, 1964; Ginsberg et al., 1962; Barnhisel and Rich, 1965; Wefers, 1967; Turner, 1972; Hemingway, 1982; Van Straten et al., 1964; Van Straten and de Bruyn, 1984). Also, Calvet et al. (1951) claim that a mixture of bayerite and gibbsite precipitates in synthetic solutions at 35°C, whereas Ginsberg et al. (1962) have shown that either a gel or bayerite forms initially from caustic aluminate solutions, but that in the presence of alkali metal ions, the bayerite transforms to gibbsite. At 20°C, this transition takes about 60 days to complete in sodium hydroxide solution at pH = 12.5. At 60°C, in the presence of potassium hydroxide, the reaction is complete in 48 hours. In a series of detailed precipitation experiments of aluminum hydroxide in alkaline solutions, Van Straten confirmed the observed precipitation sequence of hydroxides as a func-

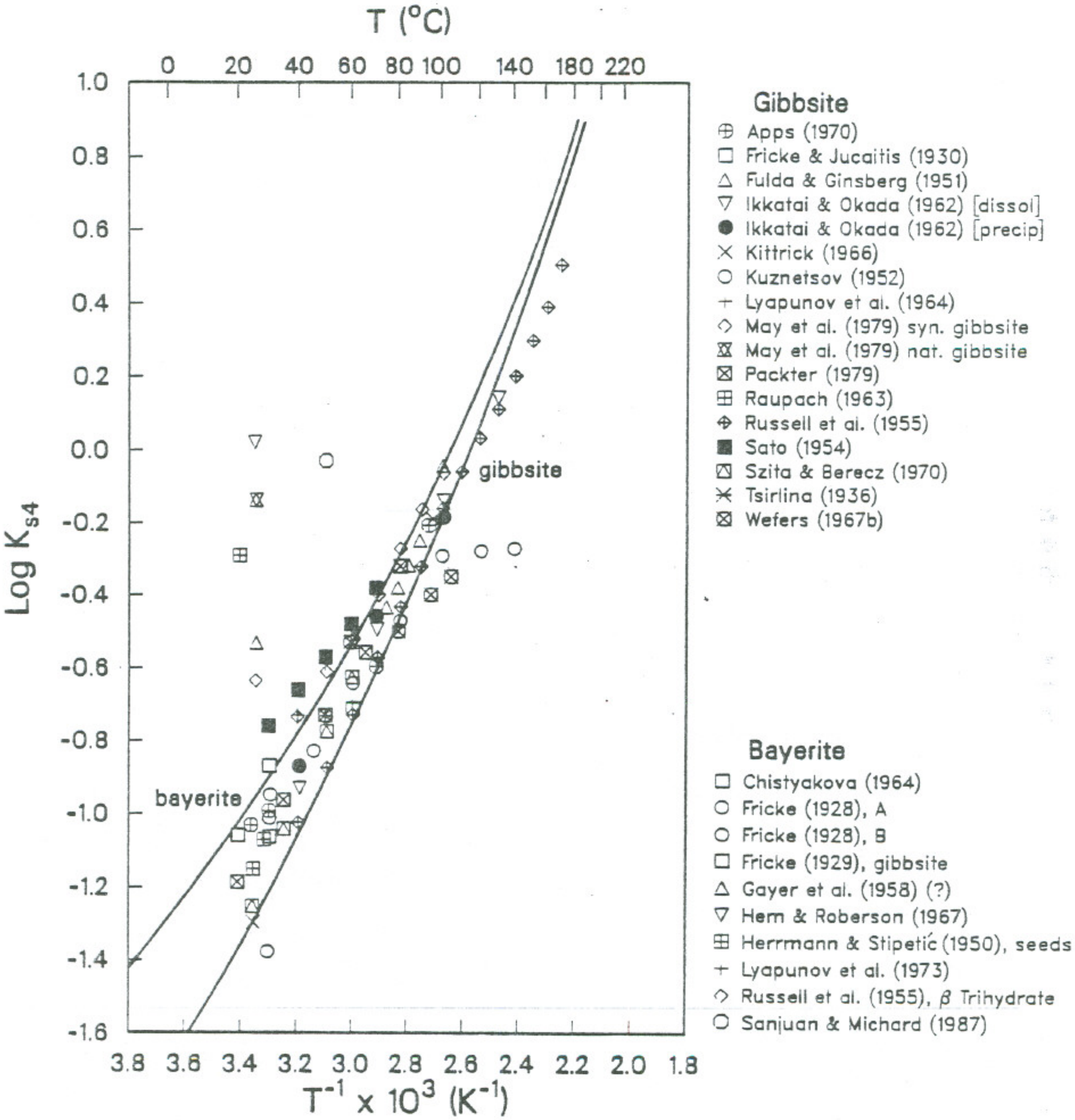

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Figure 14. A comparison of the solubility products, K_{s4} of gibbsite and bayerite, plotted as a function of reciprocal temperature.

tion of aluminum concentration and pH. (Van Straten, 1984; Van Straten et al., 1984; Van Straten and de Bruyn, 1984). This sequence:–

Amorphous $Al(OH)_3$–pseudoboehmite–bayerite–gibbsite

depends on a complex interplay of homogeneous and heterogeneous nucleation and growth reactions which are a function of the degree of supersaturation of the solution and of temperature. Van Straten and de Bruyn (1984) provide qualitative evidence that bayerite precipitation is favored over a wider range of $p(OH^-)$ at lower temperature, but as the temperature is raised, both gibbsite and pseudoboehmite precipitation fields increase at the expense of bayerite.

The short term secular equilibrium concentration of aluminum coexisting with aluminum hydroxide precipitate on gibbsite seed crystals in strong sodium aluminate solutions has also been studied by Sato (1954). The calculated solubility products, $\log K_{s4}$, after 120 hours, and at temperatures between 30 and 70°C are also plotted in Figure 14, where they bound the upper limits of all measurements of gibbsite solubility except for those on synthetic and natural gibbsite by May et al. (1979), and on gibbsite by Raupach (1963), in dilute alkaline solutions at 25°C and 20°C respectively. Commercial Bayer process gibbsite, recovered from the pregnant liquor, would presumably possesses a surface active layer of even higher solubility than that determined by Sato, because of the need to optimize precipitation rates from the pregnant liquor. This probably accounts for the enhanced solubility of synthetic gibbsite observed by Raupach (1963), May et al. (1979) and Sanjuan and Michard (1987).

According to Van Straten (1984) and Van Straten et al. (1984), the precipitation of both bayerite and gibbsite in alkaline solutions in the low supersaturation region is second order with respect to $[H^+]$ and $[Al(OH)_4^-]$, thus

$$-\frac{dc}{dt} = k_r O(t)[H^+]^2[Al(OH)_4^-]^2$$

where c refers to the concentration of the solute species, H^+ or $Al(OH)_4^-$, k_r is the rate constant and O(t) a surface area term. The activation energy for the growth rate of bayerite is estimated to be between 14 and 19 $kcal.mol.^{-1}$ (Van Straten and de Bruyn, 1984).

If, as is observed by Wefers (1967b), and predicted by Van Straten (1984), gibbsite forms in alkaline solutions through epitaxial growth on precursor bayerite somatoids; the recrystallization of a metastable layer of bayerite to gibbsite must take place through dissolution and reprecipitation. The rate at which this occurs is very temperature sensitive. Thus, for example, Kittrick (1966) estimated that it would take about several years to equilibrate Bayer process gibbsite in ~ 0.01 $\bar{N}$ sodium hydroxide solution at 25°C, but Russell et al. (1955) equilibrated gibbsite in only 264 hours in 0.5 – 8 $\bar{N}$ sodium hydroxide at 40°C; an increase in the rate by over 2 orders of magnitude. Finally, it should be noted that many ionic species will retard the rate of precipitation in natural systems.

We can now to examine the consequences of using untreated Bayer process gibbsite to measure its solubility dilute acid or alkaline solutions at relatively low temperatures, i.e. < 50°C. Because the surface active material on Bayer process gibbsite may be more soluble than bayerite, a solubility product exceeding that of bayerite may be obtained when measuring its solubility in dilute solution. Furthermore, the quantity of aluminum that must dissolve to attain equilibrium is very small, particularly if a high pulp density is used. Sometimes, less than a monolayer of surface material would have dissolved before attainment of secular equilibrium! Unless some mechanism accelerates the recrystallization of the surface layer, it would remain essentially intact. This is particularly true of short term experiments lasting only a few weeks at most where equilibration may occur with respect to the surface active layer rather than with respect to gibbsite. e.g. Raupach (1963), May et al. (1979) and Sanjuan and Michard (1987). Bloom and Weaver (1982) recognized the impact that this surface layer might have on the measurement of gibbsite solubility at 30°C in dilute acid solutions, and took steps to remove it before hand. In contrast, Kittrick (1966) reacted synthetic gibbsite in dilute alkaline solutions, over a period of years and estimated that even greater times would be required before the true solubility of gibbsite would have been attained.

Metastable equilibration with respect to a surface active layer may have occurred as an intermediate stage in Kittrick's experiments, because Kittrick's gibbsite solubilities after about 20 days, correspond roughly with those obtained by May et al. (1979) after the same time. Sanjuan and Michard (1987) suggest that the equilibrium solubility obtained by May et al. (1979) is due to bayerite. However, the $\log K_{s4}$ computed from their data is still 0.3 log units higher than that determined in this study.

7.4 Natural Occurrences of Nordstrandite and Bayerite

Until 1962, when two natural occurrences of nordstrandite were described (Hathaway and Schlanger, 1962; Wall et al. 1962), gibbsite was believed to be the only naturally occurring $Al(OH)_3$ polymorph. Shortly thereafter, bayerite was reported in nature for the first time (Bentor et al., 1963). Recently, yet another polymorph, given the mineralogical name of doyleite, has been described by Chao et al. (1985). Schoen and Roberson (1970) and Chao and Baker (1982) and Chao et al. (1985) describe differences in the polymorphs essentially as differences in the stacking of the octahedral layers. Thus bayerite is believed to have a brucite structure with the stacking sequence ABAB. Gibbsite has the sequence ABBA and nordstrandite is believed to have the sequence ABBCCA. Chao and Baker (1982) believe that polymorphism in $Al(OH)_3$ is much more complicated than previously believed, and there is evidence of yet more undescribed polymorphs, e.g. a triclinic gibbsite from the Urals has been reported by Saalfeld (1960). Inspection of the optical properties of nordstrandite tabulated by Chao and Baker (1982) also show, for example, that 2V varies from 0° to 40°, and the optical elongation is either negative or positive.

Most naturally occurring $Al(OH)_3$ polymorphs are very finely crystalline and are usually admixed with other minerals. Two or more $Al(OH)_3$ polymorphs may coexist. The nature of such material makes it difficult to characterize rigorously and as a consequence, many earlier descriptions of $Al(OH)_3$ natural occurrences are either incomplete or ambiguous. For example Davis and Hill (1974) and Davis et al. (1976) report the widespread occurrence of nordstrandite in terra-rossa bauxites prospected by the Aluminum Company of America in St. Ann parish, Jamaica, whereas only some fifteen miles to the east on Alcan Jamaica Company property, Porter and Jooste (1982) were able to find nordstrandite only in a black manganese rich zone at the contact between the bauxite and the underlying limestone. These apparent inconsistencies, when coupled with the evidence that as yet unidentified polymorphs may exist, makes speculation regarding their relative stabilities based on field observations alone, a risky enterprise at best.

In spite of these difficulties, it is possible to discern several consistent patterns of $Al(OH)_3$ polymorph occurrence that allow speculation as to what might be contributing to their persistence in nature. Although bayerite is the most readily synthesized gibbsite polymorph, it is nordstrandite that is most frequently observed to occur naturally after gibbsite. Milton et al. (1975), in reviewing the literature up to that time, classified three distinct types of nordstrandite occurrence. Chao and Baker (1982) expanded this classification to include a fourth type. Subsequent reports of nordstrandite all fall within these four types. However, some generalization and modification is justified in the light of subsequent observations. Nordstrandite is observed principally:–

1. In bauxitic and residual soils above limestones, usually immediately overlying the limestone interface.
2. In bauxitic soil profiles overlying weathered mafic igneous or metamorphic rocks.
3. In sedimentary formations that have undergone authigenesis by alkaline carbonate rich solutions. Usually, nordstrandite is an alteration product of dawsonite or aluminohydrocalcite.
4. As a late stage product of deuteric alteration in vugs and cavities in silica poor alkalic igneous rocks.

A summary of occurrences is given in Table 19.

TABLE 19

NATURAL OCCURRENCES OF NORDSTRANDITE

A. Bauxites and Residual Soils usually overlying Limestones

Source	Location	Host Rock	Paragenesis and Associated Minerals
Wall et al. (1962)	Gunong Kapor, No Bau, west Sarawak, Borneo	Residual soil in large sinkhole in limestone. Soil is a dark red clay loam, possibly a residue of dacite or shale.	Small quartz crystals and rounded pellets, some of limonite, others of nd. Associated minerals are goethite, kaolinite, minor euhedral diaspore. [Prismatic quartz, stibiconite, cinnabar and gold related are to gold mineralization]. Nd occurs as thick tabular crystals < 10-75 μm, occasionally up to 250 μm across.
Tertian (1966)	Vonji Do, Montenegro, Yugoslavia	White bauxite.	Very fine aggregate of amorphous (to electron diffraction) and crystalline material, identified by XRD as gibbsite and nd with smaller amounts of bayerite. Associated with "vitric" material identified by XRD as containing allophane.
Naray-Szabo and Peter (1967)	Hungary	"Ziegeltonen", i.e. brick clays.	1–5 μm fraction contained gibbsite, nordstrandite and bayerite, identified by XRD. Remainder consisted dominantly of chlorite, illite, quartz and calcite.
Maric (1968)	Mount Velebit, southwestern Dinarides, Croatia, Yugoslavia.	Terra rossa.	XRD shows the terra rossa to be nd and gibbsite with minor illite, goethite, quartz and hematite, and traces of boehmite. Samples appear to consist of ooides and aggregates of leaflets which under the election microscope have rhombohedral or hexagonal habit. The author claims that the pH is 8.5 in the terra rossa. He also notes Fe and SiO_2 migration with formation of black colored kaolinite, (halloysite), goethite and quartz with elevated concentrations of Ni, Co, Y, La, Pb, Ba and Mn.
Davis and Hill (1974)	Northern part of Jamaica	Bauxite	Nd was identified by XRD in association with gibbsite. The amount of nd seemed to bear a close relation to the amount of reactive silica (kaolinite) present. Authors note that studies by Lewis (1967) of insitu pH, showed that high silica bauxites were more alkaline than low silica bauxites.

TABLE 19

A. Continued

Source	Location	Host Rock	Paragenesis and Associated Minerals
Davis et al. (1976)	St. Ann parish, Jamaica. Alcoa Special Mining Lease (No. 71).	Bauxite overlying Walderston- Browns Town facies (limestone) and Troy limestone. Samples studied were from the top most interval of bauxite.	Bauxite dominated by nd and gibbsite as determined by XRD. Samples varied from predominantly gibbsite to predominately nd.
Porter and Jooste (1982)	Schwallenburgh area, St. Ann parish, Jamaica. Alcan orebody A-19, Ardock	Black manganese rich zone at contact with underlying limestone of either the Troy/ Claremont, Somerset, or Walderston-Browns Town formation.	Black and pink red grains. XRD showed the former to be largely lithiophorite, $(Al_{0.5}, Li_{0.5})Mn_2O_2(OH)_2$, and the latter to be largely nd, which occurs as platelets < 100 μm in diameter, and ≤ 10 μm thick.
Wilmot and Young (1985)	Castle Hill, Newhaven, Sussex, England.	Upper Chalk, Cretaceous. Solution pipes containing collapsed overlying Woolwich Beds.	Nd is found with allophane beneath an iron pan in a small hollow adjacent to the chalk. It occurs as impure nodules together with iron oxides and black manganiferous matter. Associated with basic aluminum sulfates, e.g. aluminite $(Al_2(SO_4)(OH)_4 \cdot 7H_2O)$, basaluminite, $(Al_4(SO_4)(OH)_{10} \cdot 5H_2O)$, aluminosilicate gel, gibbsite, bayerite (in a nodule with gibbsite and quartz), gypsum and jarosite. Alumino-silicate has features of IR spectrum in common with those of allophane and imogolite. Assemblage due to oxidation of pyrite in overlying sequence.

TABLE 19

B. Bauxitic Soil Profiles Overlying Mafic Igneous or Metamorphic Rocks

Source	Location	Host Rock	Paragenesis and Associated Minerals
Hathaway and Schlanger (1962, 1963)	Mount Alfon - Mount Lamlan ridge, South Guam.	In basal part of Miocene limestone overlying deeply weathered late Eocene and early Miocene basalt flows and conglomerates.	Nd occurs in secondary solution cavities concentrated in the basal parts of limestone near its contact with weathered basalt, as flamboyant aggregates filling spaces between previously deposited calcite. Aggregates appear to radiate from discrete parts or areas on the clay coated wall of the original void. Crystals are tabular and up to 0.4 mm in length.
Grubb (1971)	Boolarra-Mirboo area, Gibbsland, Victoria, Australia.	Bauxitized Thorpdale volcanics (basalts and pyroclastics), resting uncomfortably on Jurassic sediments, and overlain by Tertiary sands, clays and lignite horizons.	Nd observed in a grey aluminous clay at the base of a 3.5 m profile. The clay contains gibbsite as hard 3 mm modules with nd and a little scarbroite $(Al_5(OH)_{13}CO_3{\cdot}5H_2O)$.[1] Paragenetic sequence scarbroite-nordstrandite-gibbsite is suggested. Raggatt et al. (1945) noted the existence of significant amounts of pyrite, siderite and up to 0.03% free $Al_2(SO_4)_3$ in post bauxitization alteration of some deposits.
Kulikova et al. (1974)	Sokolovsko-Sarbay magnetite mines, USSR	Bauxitic rocks as lenses in solution cavities in fault zones near contacts with extrusive (andesite) and carbonate rocks of Valerianovskaya suite of early Carbonferous age. Overlain by sandy-clayey sediments of Turonian age.	Host rocks consist predominantly of hematite, gibbsite, geothite and magnetite with admixed alumina (corundum?) and kaolinite. Nd occurs as white aggregates filling pores in bauxite cement, as acicular crystals and flakes from fraction of mm to 0.3 cm, or is cryptocrystalline. Nd forming process may still be continuing due to redistribution of alumina by high alkalinity water percolating through bauxite that had contact with carbonate rocks. Nd occurs up to 10 m from the limestone contact.

[1] According to Brindley (1980).

TABLE 19

C. Sedimentary Formations

Source	Location	Host Rock	Paragenesis and Associated Minerals
Goldbery and Loughnan (1970)	Glen Davis, N.S.W., Australia	Permian Berry Formation of Sydney Basin consisting of blue grey siltstones. Lenticular and rounded masses of carbonate are prevalent near the top. The Berry Formation is overlain by coal measures.	Dawsonite ($NaAlCO_3(OH)_2$) invariably associated with nd. Around may dawsonite-rich rodules, nd forms a continuous rim. Calcite and kaolinite also present, but kaolinite is never in physical contact with nd. Dawsonite occurs as aggregates of fine needles arranged as sheaves, tufts and spherultic masses $\geq$ 1 mm diameter. Sometimes replaces "glendonites" up to 10 cm in length. Glendonites are pseudomorphs of glauberite ($Na_2SO_4 \cdot CaSO_4$). Calcite rims some nodules. In others, kaolinite is the dominant mineral. Nd is assumed to form as an alteration product of dawsonite: $NaAlCO_3(OH)_2 + H_2O = Al(OH)_3 + NaHCO_3$. Nd may react with $SiO_2(aq)$ to form kaolinite. Na, Mg, Ca, Al sulfates and K and Na jarosites are observed as superficial exudation products on recent exposures of siltstones. [Due to the oxidation of pyrite?]
Goldbery and Loughnan (1977)	Sydney Basin, New South Wales, Australia	Permian marine Shoalhaven Group of Sydney Basin. Siltstones, concretions and lenses of dolomite overlain by sandstones, siltstones, claystone, shale, carbonates and impure coal seams.	Nd associated with dawsonite in veins, solution cavity and nodular deposits (Glen Alice area), or as pseudomorphs after non fibrous dawsonite in horizontal veins in limestone. Nd occurs as vermicular or radiating crystals. In dawsonite nodules, individual fibers are continuous with dawsonite or alumohydrocalcite ($CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O$). Nd appears to be a breakdown product of both dawsonite and alumohydrocalcite: Commonly associated with small amounts of calcite, alumohydrocalcite forms as dendritic, hairline veinlets in massive nd. An isotropic phase is associated with dawsonite, alumohydrocalcite, nd and gorceixite ($BaAl_3(PO_4)_2(OH)_5$). Authors allude to allophane association with alumohydrocalcite, described by Kautz (1968) and Aikawa et al. (1972). Reactions assumed as follows:– $NaAlCO_3(OH)_2 + H_2O = Al(OH)_3 + Na^+ + HCO_3^-$ $CaAl_2(CO_3)_2(OH)_4 \cdot 3H_2O = 2Al(OH)_3 + Ca^{2+} + 2HCO_3^- + H_2O$.

TABLE 19

C. Continued

Source	Location	Host Rock	Paragenesis and Associated Minerals
Milton et al. (1975)	Rio Blanco County, Colorado	Green River Formation. Fine grained dolomitic siltstones and oil shale.	Nd occurs as thin layers of white platy or fibrous aggregates in fractures at high angles. Authigenic albite is present in cores. Also present: dawsonite, analcime, nahcolite. Suggested mechanism of formation:- $NaAlCO_3(OH)_2 + H_2O = Al(OH)_3 + NaHCO_3$. Dawsonite forms from analcime in equilibrium with nahcolite $NaAlSi_2O_6 \cdot H_2O + CO_2 = 2SiO_2 + NaAlCO_3(OH)_2$.
Wopfner and Hocker (1987)	Bozen and Meran, (northern Italy)	Permian Groeden Sandstone, a fluviatile red bed sequence with gypsum intercalations and halite casts. Underlain by trachy-andesite pyroclastics and lavas, and rhyo-dacitic ignimbrites.	Nd observed in underlying pyroclastics and sandstone. Associated with dawsonite. In sandstone, dawsonite constitutes up to 35% of the rock whereas nd attains only 20%. Average is 5% and 3% respectively. Nd replaces dawsonite as pseudo hexagnal platy crystals about 2 µm in diameter. Dawsonite-nd phase of diagenesis is connected with the formation of calcite and kaolinite. Calcite occurs as small rhombohedra on dawsonite needles and nd encrustrations, or it replaces dawsonite rosettes. Authigenic kaolinite fills voids in corroded dawsonite spherules. Isotropic alteration product of dawsonite may be allophane. Alumohydrocalcite observed filling vertical joints in dolomite nodules with dawsonite, nd, aragonite and kaolinite. Dawsonite and nd formation preceded by dolomitization and pyritization, with quartz and illite overgrowths on quartz and muscovite respectively. Nd formation assumed to be similar to that suggested by Goldbery and Loughnan (1970, 1977) and Milton et al. (1975).

TABLE 19

D. Late Stage Hydrothermal Alteration of Alkaline Igneous Rocks

Source	Location	Host Rock	Paragenesis and Associated Minerals
Petersen et al. (1976)	Narssârssuk, Greenland	Precambrian Igaliko nepheline syenite complex, contaminated by assimilated sandstone.	In spherical pegmatitic pockets several cm to approximately 1 m in diameter. Sequence of minerals observed: feldspar/aegirine → quartz → (quartz dissolution) → calcite/rhodochrosite/fluorite-tetranatrolite-gonnardite-nd. Last three minerals are closely associated.
Alker et al. (1981)	Stradner Kogel, southern Gleichenberg, Styria, Austria.	Hauyn-nephelinite	Phillipsite is overgrown by nd in cavities in the hauyn-nephelinite. Hydrotalcite ($Mg_4Al_2(OH)_{12}CO_3 \cdot 3H_2O$) is found on spherical aggregates of nd, also found with motukoreaite ($(Mg_{1.79}Al_{1.21})_3 (OH)_6 (SO_4)_{0.35} (CO_3)_{0.25} \cdot 2\text{–}3H_2O$) growing on phillipsite. The mineral assemblage appears to have formed during a low temperature cooling phase.
Chao and Baker (1982)	Mont St Hilaire, Quebec	Nepheline synenite	Nd occurs in pegmatites, miarolitic cavities and biotite-rich xenoliths. It is commonly associated with natrolite, tetranatrolite, sodalite, albite and microcline. Small amounts of either calcite, siderite, dolomite or dawsonite are present except in xenoliths were apatite substitutes for carbonate. Average crystal size is 0.2 mm. Order of crystallization is microcline → tetranatrolite → carbonates → nd → pyrite/serpentine.

As has been noted several times previously, (e.g. Hemingway, 1982), all nordstrandite occurrences are distinguished by alkaline environments where the groundwater pH during crystal growth was at least 7.0, and may have exceeded 10.0 in the fourth category. The temperature at which nordstrandite formed appears in all cases to be less than 100°C. On most occasions, nordstrandite is one of the last minerals to form. Unlike gibbsite, it does not seem to form in acid environments. Noteworthy is the recurring association of nordstrandite with either allophane or dawsonite. Also of interest is the fairly common association of lignitic or organic matter, and the recurrence of basic aluminum sulfates in nordstrandite occurrences. There appears to be some genetic association of these minerals with nordstrandite, but apart from the obvious association of dawsonite, it is not clear what the field relations are.

Bayerite, although easily synthesized, is rarely observed in nature. Table 20 summarizes reported natural occurrences of bayerite. It appears to form in a similar range of environments to that of nordstrandite. In one environment, i.e. in bauxite in Yugoslavia (Tertian, 1966), it coexists with nordstrandite. The bayerite occurrence in Israel is extremely alkaline as is evident from the host rock, which is composed of spurrite and calcite, and reports of ettringite and portlandite in the same "mottled" zone where bayerite is observed. (Bentor et al., 1963; Gross and Heller, 1964).

Of interest are DTA studies of bauxites by Gedeon (1956) and Yuan-Lung(1957). Both correlate an initial small endothermal peak with the presence of bayerite. The bauxites displaying this peak range in mineral composition from gibbsite to boehmite. Unfortunately, neither author presented independent evidence of the presence of bayerite. Given the subsequent discovery in nature of other polymorphs of gibbsite, it is possible that the observed peaks are not uniquely associated with bayerite. The DTA findings of Gedeon (1956) and Yuan-Lung (1957) suggest that bauxites have not been adequately characterized mineralogically, and that other polymorphs including bayerite may be quite commonly present in minor amounts.

In experimental studies at 25°C, Schoen and Roberson (1970) found that pure bayerite precipitated initially from a pH = 12 solution, but that after 90 days of aging, nordstrandite was detectable by XRD. At intermediate pH values between 9.46 and 12.0, both nordstrandite and bayerite precipitated, and their X-ray patterns both increased after 2 1/2 years of aging. However bayerite with nordstrandite aged at pH 9 for 2 years, showed a definite increase in the size of the nordstrandite crystals and corrosion of the bayerite crystals. Schoen and Roberson also noted that at pH between 8.5 and 9.5, initially precipitated microcrystalline gibbsite gradually disappeared in mixtures with bayerite.

According to Ross and Turner (1971), a precipitate obtained by 80% neutralization of $Al(ClO_4)_3$ solution at 25°C showed nordstrandite by XRD after 3 weeks. But after 13 months of aging a pattern resembling synthetic gibbsite was obtained from the precipitate. The evidence provided by experimental studies therefore suggests strongly that nordstrandite is more stable than bayerite, but that gibbsite is more stable than nordstrandite. The relative stability differences between all three polymorphs, expressed in terms of $\Delta G^\circ_{f,298}$, must be very small, certainly not exceeding the 500 calories between gibbsite and bayerite at 25°C. The free energy difference between nordstrandite and the gibbsite must be even less. This makes it likely that their formation will be controlled by subtle environmental conditions affecting nucleation, the rate of crystal growth, and even the relative growth rates of specific faces on the crystals.

Several possible conditions may affect the relative persistence the aluminum polymorphs in alkaline solutions, including variation in thermodynamic stability with temperature, particle size, competitive growth in a supersaturated solution involving the Ostwald rule of stages (Ostwald, 1987), and the relative persistence of a stable supersaturated solution compared with one that fluctuates with time (or season of the year). Each of these conditions will be discussed briefly.

7.5 Effect of Surface Area on the Stability of $Al(OH)_3$ *Polymorphs*

Because of the small Gibbs free energy difference separating the $Al(OH)_3$ polymorphs, it is quite possible that a faster growing polymorph could become more stable thermodynamically than another polymorph of smaller particle size, even though the latter would be more stable if surface free energy effects were eliminated. It is difficult to estimate the magnitude of the particle size effect, owing to the paucity of available

TABLE 20

NATURAL OCCURRENCES OF BAYERITE

Source	Location	Host Rock	Paragenesis and Associated Minerals
Gedeon (1956)	Twelve samples from five locations in Hungary.	Bauxite	Bayerite identified by DTA in bauxite containing gibbsite, boehmite, and kaolinite, with traces of chlorite (<7 wt %). Bayerite content estimated to range from 4.4 to 13.2 wt %.
	Fenyofo, Hungary	Bauxite	Sample with "white nodes" identified as relatively pure bayerite on the basis of the absence of TiO_2. It is claimed that it separated from a solution containing sulfate. Reference is also made to a fibrous travertine like formation believed to be bayerite from Portole (Istria?), also having precipitated from sulfurous springs. No direct crystallographic evidence is given to support the DTA interpretation.
Yuan-Lung (1957)	Fukien, China	Ferruginous gibbsitic bauxite	Bayerite identified on the basis of a DTA pattern. No crystallographic evidence is given that proves the existence of bayerite.
Bentor et al. (1963) and Gross and Heller (1964)	Hartrurim region, Israel	"Mottled" zone of the Ghareb and Tahiye formations of Campanian age. Comprises limestone, chalk, marl, shale, as well as gypseous, ferruginous and phosphatic rocks.	Mottled zone is composed mainly of calcite and spurrite ($2Ca_2SiO_4{\cdot}CaCO_3$). Bayerite occurs as fine white fibers, associated with calcite and gypsum. After heating to 230°C, its X-ray pattern was not affected.
Tertian (1966)	Vonj Do, Montenegro, Yugoslavia	White bauxite	Very fine aggregate of amorphous (to electron diffraction) and crystalline material identified by XRD as gibbsite, nordstrandite with smaller amounts of bayerite. Associated with vitric material, identified by XRD as containing allophane.

TABLE 20

Continued

Source	Location	Host Rock	Paragenesis and Associated Minerals
Khorosheva (1969)	Middle Dnepr region, USSR Vysokopolye region.	Bauxite representing the upper weathering crust of mafic and ultramafic rocks.	Bayerite is found in bauxites derived from amphibolite and serpentines, altered by epigenetic carbonatization. It occurs in cavities and as pisolites, independently or admixed with gibbsite, sometimes with diaspore. Traces of kaolinite are present. Usually the bayerite occurs as finely dispersed aggregates, less frequently as crystalline formations. Crystals are coarser in sideritized bauxite. Crystals are lamellar and tabular, 0.01 – 0.1 mm. Bayerite-diaspore mixtures are inseparable and occur as concretions. Khorosheva assumes that diaspore forms through dehydration of bayerite. In specific gravity fractions, traces of boehmite, diaspore, corundum, goethite-hydrogoethite, hematite, magnetite, sphene, leucoxene, ilimenite, siderite and pyrite are observed.
Naray-Szabo and Peter (1967)	Hungary	Ziegeltonen, i.e. brick clays	1–5 μm fraction contained gibbsite, nordstrandite and bayerite, identified by XRD. Remainder consisted of chlorite, illite, quartz and calcite.
Wilmot and Young (1985)	Castle Hill, Newhaven, Sussex, England	Upper Chalk, Cretaceous. Solution pipes containing collapsed overlying Woolwich Beds.	Detected by XRD in a nodule, which also contained gibbsite and quartz. The gibbsite is found throughout the pipe filling, but principally adjacent to the walls in proximity with basaluminite ($Al_4(SO_4)(OH)_{10}\cdot 5H_2O$) crusts and nodules.

data. However, Packter (1979) has measured the solubility of gibbsite in alkaline solutions as a function of particle size and temperature. Unfortunately, Packter did not report the BET surface areas of the samples he used, so these must be estimated from his reported particle size dimensions. Table 21 summarizes the surface area calculation based on Packer's reported data. Results are plotted in Figure 15 as log $K_{s4(s)}$ vs surface area in $m^2.gfw^{-1}$. Also noted on the figure are the values of log $K_{s4(s=0)}$(gibbsite) derived in this study. The variation of log K_{s4} with surface area shows a bimodal distribution of slopes possibly indicating that the mean free surface energy, $\overline{\gamma}$, is not constant. An estimate of the mean surface free energy, $\overline{\gamma}$, at 20°C for the steep portion of the slope yields ≈ 660 $erg.cm^{-2}$ and the shallow portion ≈ 140 $erg.cm^{-2}$. These values are consistent with range of surface free energies measured on other oxides surfaces e.g. see Stumm and Morgan (1970), Table 5.5, p. 214. They also agree well with estimates of edge and face surface free energies, respectively 140 ± 24 $erg.cm^{-2}$ and 483 ± 84 $erg.cm^{-2}$ derived by Smith and Hem (1972) on gibbsite in acid solutions by an entirely different line of measuring. Whether this is other than merely a coincidence must remain to be determined.

TABLE 21

SPECIFIC SURFACE AREA AS A FUNCTION OF LOG K_{s4}(GIBBSITE) FROM DATA BY PACKTER (1979)

Particle size,	Surface[1],	log $K_{s4,s}$(gibbsite) at T, °C				
nm	$(m^2.gfw^{-1}) \times 10^{-3}$	20	35	50	65	80
30[2]	26.7	−0.495		−0.071		0.248
60	13.3	−0.745		−0.268		0.057
130	6.16	−0.921		−0.450		0.108
260	3.08	−1.009		−0.553		0.201
450	1.78	−1.187	−0.959	−0.733	−0.553	0.319

[1] Calculations based on the assumption that the particles are hexagonal platelets with largest dimension, x, and thickness 0.1 x.

Total area of particle = $(\frac{3}{2} \text{Sin } 60° + 0.3)\, x^2 m^2$.

Volume of particle = $(\frac{0.3}{4} \text{Sin } 60°)\, x^3 m^3$; $\rho = 2.4 \times 10^6\ g.m^{-3}$; gfw = 78.0036.

[2] Sample contained 30% boehmite.

A possible explanation for the change in slope is that, while the gibbsite crystallites are small, growth occurs predominately on the prismatic faces to produce thin hexagonal platelets. However, as their size increases, growth on the basal pinacoid faces increases, in relation to the prismatic faces, leading to a shift in the relative surface free energy contributions of the faces. This appears to be consistent with the morphology of gibbsite crystals observed by Misra and White (1971). Another possibility is that recrystallization occurred during the solution equilibration period, which ranged from 1 hour in concentrated NaOH solutions at 80°C, up to 2 months in dilute NaOH solutions at 20°C. Therefore, the initial slope of ≈ 660 $erg.cm^{-2}$ may be more accurate.

In recollecting the observation of Schoen and Roberson (1970) regarding gibbsite dissolution in the presence of bayerite, it can be seen that the gibbsite platelets ≤ 0.1 μm in size, as illustrated in their Figure 4, would be more soluble than coarsely crystalline bayerite and would, on the basis of Figure 15 dissolve. Their observation and Packter's data are therefore consistent.

In contrast to laboratory synthesized material; naturally occurring bauxites do not have surface areas significantly exceeding 40 $m^2.g^{-1}$ (≈ 300 $m^2.gfw^{-1}$) Davis et al. (1976) noted that nordstrandite and gibbsite in

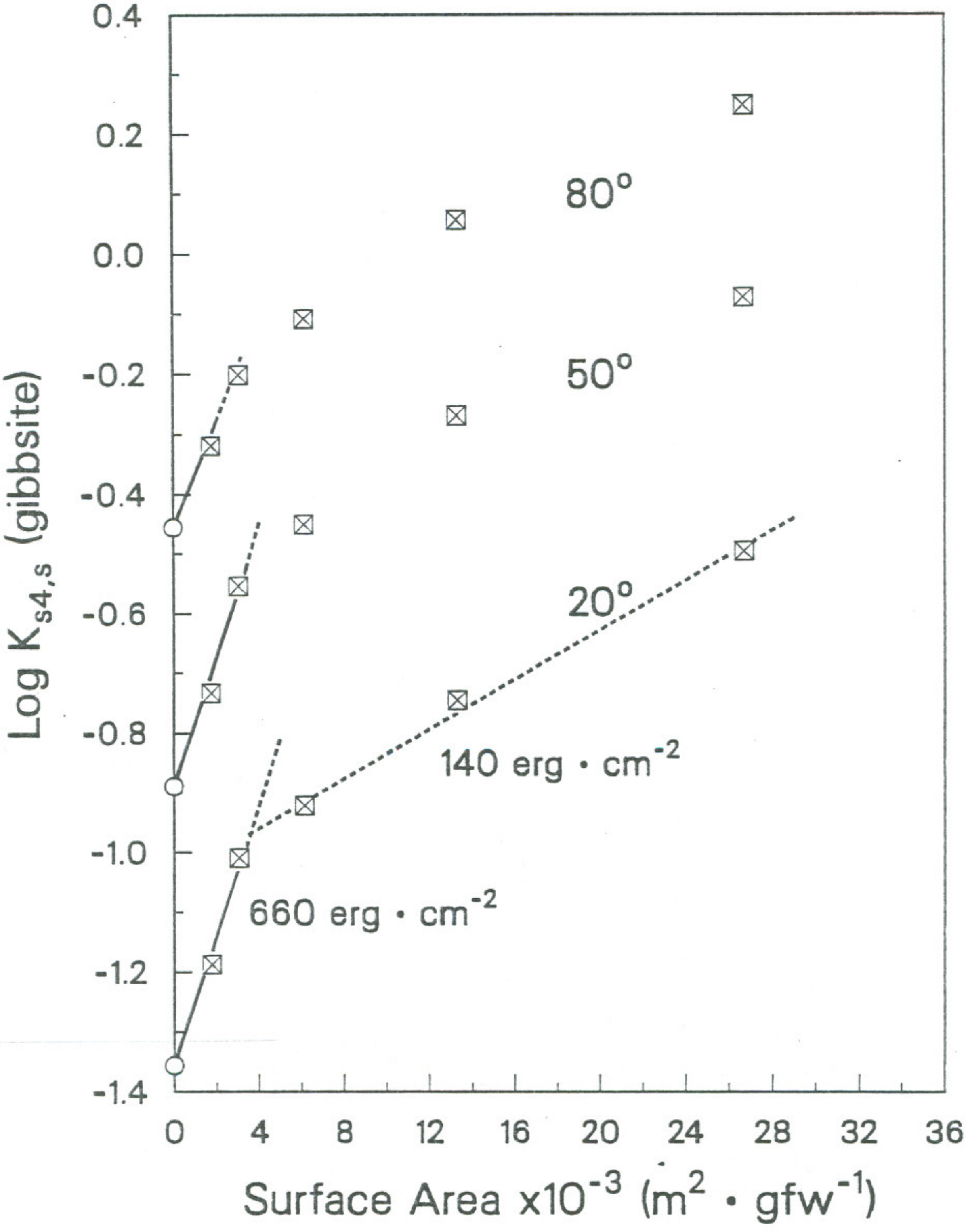

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Figure 15. Log $K_{s4,s}$(gibbsite) as a function of specific surface area, computed from data by Packter (1979).

Jamaican bauxites had different surface areas by BET measurements. Nordstrandite ranged from 18 – 20 $m^2.g^{-1}$, whereas gibbsite had values in excess of 30 $m^2.g^{-1}$. Bauxite from Haiti, containing 44% gibbsite, 18% boehmite and traces of nordstrandite, had a surface area in excess of 40 $m^2.g^{-1}$, (Bárdossy et al., 1977). Even if the assumption is made that the only significant contribution to surface area is due to the fractional quantity of gibbsite, the specific surface area of gibbsite would not appear to exceed 6000 $m^2.gfw^{-1}$, i.e. the particle size would be about 0.15 μ and $\log K_{s4,298}$ should be about –0.6 if $\bar{\gamma} \approx 660$ erg. cm^{-2}. This is close to the value $\log K_{s4}$ of –0.53 for Arkansas bauxite, given by Raupach (1963), and suggests that the higher solubilities observed on bauxites such as that by Raupach (1963), must be due either to the presence of finely crystalline gibbsite or to other less stable gibbsite polymorphs in the natural material.

Elsewhere, as noted in Table 19, nordstrandite tends to form crystals ranging from 1 µm to as large as 0.3 mm. In general, it is more coarsely crystalline than gibbsite. If it is assumed that the mean surface free energy for bayerite and nordstrandite are approximately equivalent, then an estimate of $\log K_{s4}$(nordstrandite) may be made by inspection of the electron microphotograph illustrated by Schoen and Roberson (1970) in their Figure 8. In this electron microphotograph, bayerite crystals 1.0×0.5 µm are dissolving in favor of prismatic crystals of nordstrandite, approximately 0.8×0.1 µm in size. This photograph was taken after the sample had aged for two years. Figure 16 is a schematic illustration of the possible free energy relations between gibbsite, nordstrandite and bayerite in which it is assumed that nordstrandite crystals with a specific surface area of 2000 $m^2.gfw^{-1}$ are growing at the expense of crystals of bayerite with a surface area of 1000 $m^2.gfw^{-1}$. The reaction rate must be quite slow, as Schoen and Roberson assumed from the interpretation of XRD patterns that growth of both bayerite and nordstrandite had occurred during 2 1/2 years of aging in samples precipitated at pH between 9.5 and 12.

Another means of estimating the relative stability of nordstrandite with respect to gibbsite and bayerite is to make use of the observation of Davis et al. (1976) that gibbsite and nordstrandite in Jamaican bauxites have differing BET surface areas. While there is no evidence to suggest that the two polymorphs are in equilibrium, it is interesting to speculate what might be the consequence of testing the hypothesis that they are in equilibrium, to see whether it is consistent with the schematic diagram presented in Figure 16. The specific surface area of nordstrandite is ≈ 1600 $m^2.gfw^{-1}$, whereas that of gibbsite is ≈ 2,300 $m^2.gfw^{-1}$. The coexistence plot in Figure 16 shows satisfactory agreement with laboratory studies. On this basis, we may tentatively assume that $\log K_{s4,298}$(nordstrandite) is -1.13 ± 0.07 and $\Delta G^{o}_{f,298} = -275.84$ $kcal.gfw^{-1}$.

The foregoing analysis is speculative and subject to many uncertainties. Although the interpretations are in satisfactory agreement with field and laboratory observations, it is clear that a more rigorous evaluation should be conducted. However, the implication is that the free energy differences between the three polymorphs must also be small. It is not clear why nordstrandite should form in alkaline environments in preference to gibbsite. The fact that it is generally observed to be more coarsely crystalline suggests that once it nucleates and grows, gibbsite nucleation and growth would be inhibited because of the significant free energy difference that would have to be overcome.

Laboratory experiments provide clear evidence that bayerite will dissolve in favor of nordstrandite in a few years at 25°C. In the field, bayerite would only persist provided the environment remains supersaturated with respect to bayerite, and the temperature remains low, i.e. less than 30°C. Conditions necessary to sustain continuous supersaturation with respect to either bayerite or nordstrandite are relatively difficult to achieve.

Possible processes include:

(1) Cooling of a silica poor solution associated with silica deficient igneous rocks.

(2) Partial neutralization of alkaline aluminum rich solutions.

(3) Neutralization of acid aluminum rich solutions.

All three processes would explain nordstrandite occurrences described in the literature.

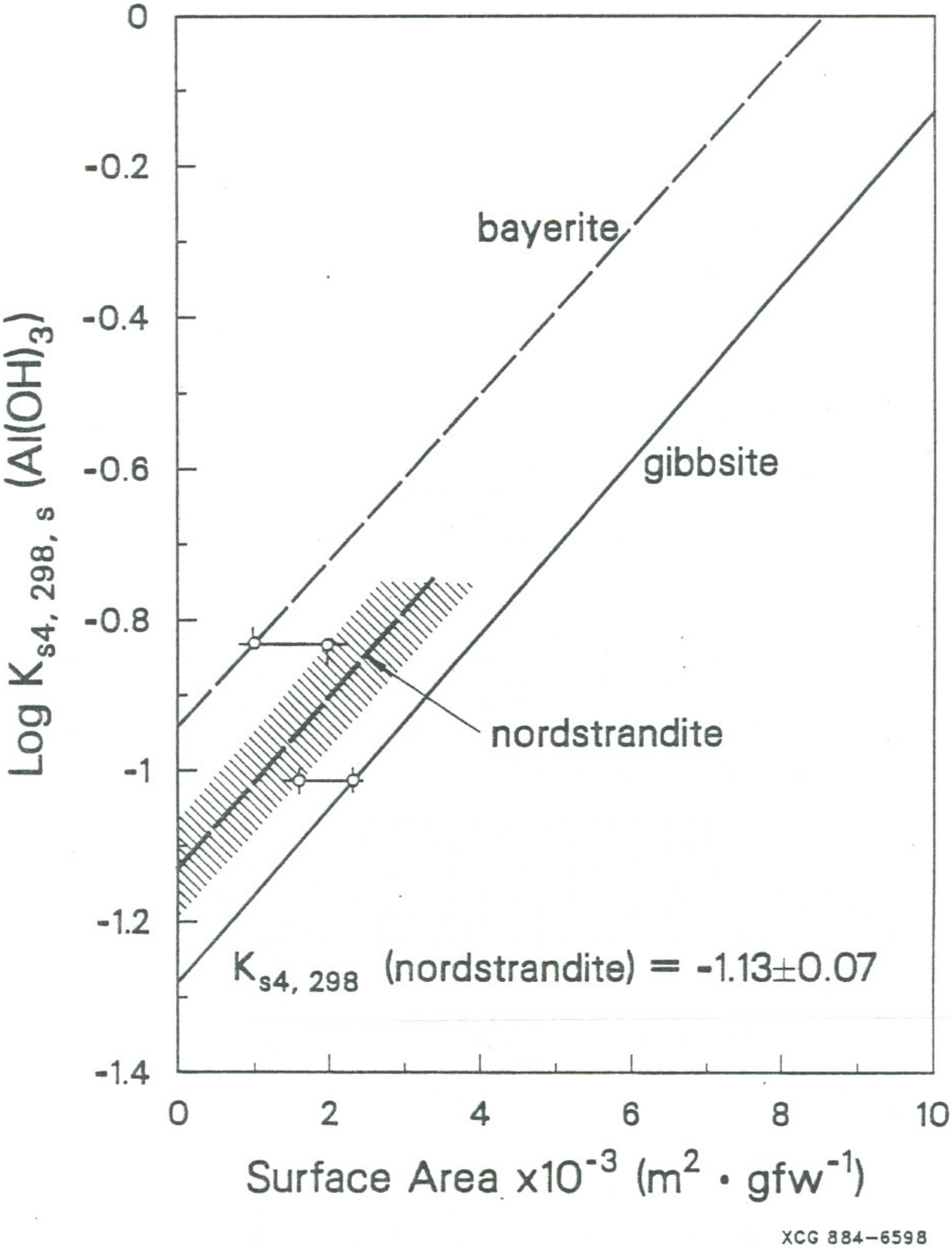

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Figure 16. Estimation of log K_{s4}(nordstrandite).

There remain other possible explanations for the occurrences of nordstrandite instead of gibbsite. One is that nordstrandite might become thermodynamically more stable than gibbsite at some temperature above 25°C. Figure 17 illustrates schematically, a possible situation where this might arise.

Seasonal fluctuations in rainfall, with alternate wetting and drying may cause fluctuating levels of aluminum in solution, leading at times to undersaturation with respect to nordstrandite, thereby facilitating the nucleation and growth of gibbsite at the expense of nordstrandite. Most nordstrandite crystallization and growth appears to have taken place in environments where water saturation was maintained, whereas many bauxites are subject to seasonal variations in rainfall and fluctuating water tables. However, it must be borne in mind that the latter may also be forming under acid instead of alkaline conditions.

7.6 Conclusions

From the evaluation of bayerite thermodynamic properties and the nature of gibbsite produced during the Bayer process, the following conclusions can be drawn:

(1) Bayerite is less stable thermodynamically than gibbsite at least below 100°C and one atmosphere pressure.

(2) Bayer process gibbsite is coated with a surface active layer of aluminum hydroxide. This surface active layer may be bayerite, or an even more soluble precipitate such as pseudoboehmite or amorphous aluminum hydroxide.

(3) In dilute alkaline solution ($pH < 11$) at 25°C, the surface active layer will slowly recrystallize to gibbsite, through a dissolution and precipitation mechanism, possibly retarded in the presence of foreign ions.

(4) Recrystallization identified in (3) above, may pass through an intermediate stage in which bayerite forms.

(5) Attempts to measure the solubility of gibbsite obtained from the Bayer process may result in equilibration with respect to an active surface layer, or bayerite unless precautions are taken to ensure that this layer is removed.

(6) Bayerite decomposition to gibbsite appears very sensitive to temperature.

An evaluation of field and laboratory conditions favorable for bayerite and nordstrandite nucleation and growth leads to the following tentative conclusions.

(1) Laboratory evidence of the kinetics of bayerite conversion to nordstrandite under alkaline conditions suggests that bayerite formation in the field must be governed by solutions in which supersaturation with respect to bayerite is sustained, and that the Ostwald rule of stages (Ostwald, 1897) must prevail.

(2) Variation in mean surface free energy, $\bar{\gamma}$, of gibbsite as a function of particle size is sufficient to explain higher increased solubilities of gibbsitic bauxites.

(3) Nordstrandite is intermediate in solubility between bayerite and gibbsite at 25°C. A preliminary value for $\log K_{s4,298}$ is -1.13 ± 0.07 and $\Delta G^{o}_{f,298} = -275.84$ kcal.gfw^{-1}.

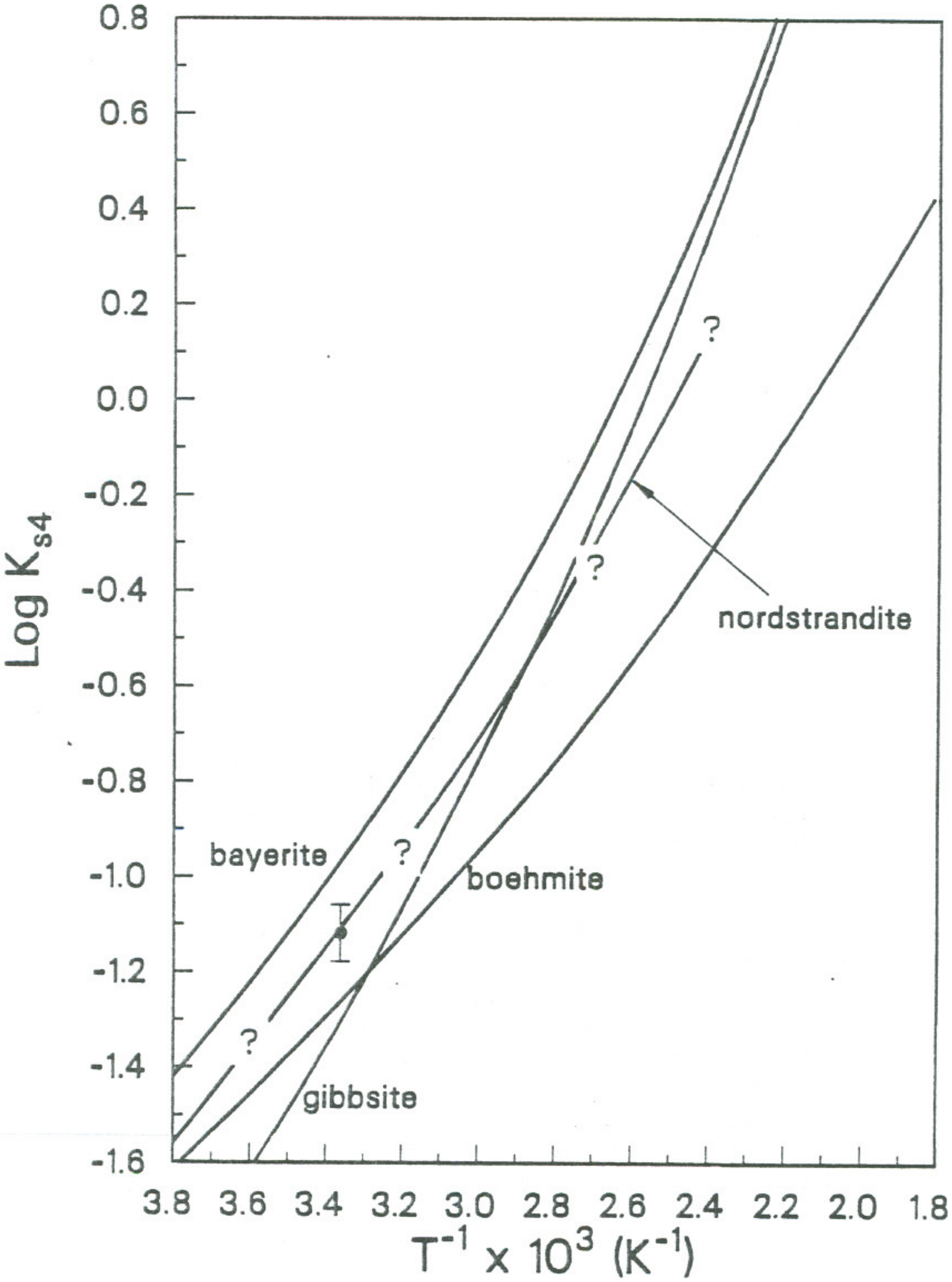

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Figure 17. Possible stability relationship of gibbsite and nordstrandite as a function of temperature.

8. SUMMARY, CONCLUSIONS, AND FINDINGS

8.1 Summary

1. Published and unpublished measurements of gibbsite, bayerite, boehmite, and diaspore solubilities in alkaline solutions, at temperatures ranging from 20 to 350°C, were collected and reviewed.
2. Evaluations were made by calculating the logarithms of the apparent dissolution constant, $\log K'_{s4}$ and the ionic strength of the solution using the simplified $\dot{B}$ expansion of the Debye-Huckel theory at the temperature at which the solubility measurement was made.
3. An empirical, but self consistent extrapolation of all $\log K'_{s4}$ to standard state conditions was made to recover $\log K_{s4}$ values at discrete temperatures.
4. Assuming that the calorimetrically derived thermodynamic properties of corundum are correct, the thermodynamic properties of diaspore were derived from phase equilibrium measurements by Haas (1972).
5. Assuming that the calorimetrically derived thermodynamic properties of gibbsite are correct, the thermodynamic properties of boehmite were evaluated, using the high temperature heat capacity measurements by Mukaibo et al. (1969), the thermodynamic properties for diaspore obtained in (2), above, and the solubility measurements evaluated in (1), (2) and (3), above.
6. Using the thermodynamic properties of gibbsite, boehmite, and diaspore, and selected solubility measurements of these phases in alkaline media, $\Delta\overline{G}_f^o$ and $\log \overline{K}_f^o$ of $Al(OH)_4^-$ were determined between 20 and 350°C.
7. Using gibbsite solubility data between 20 and 70°C, $\overline{C}_p^o$, $\overline{S}_{298}^o$, $\Delta\overline{H}_{f,298}^o$ and $\Delta\overline{G}_{f,298}^o$ were determined for $Al(OH)_4^-$.
8. $\overline{C}_p^o$ and $\overline{S}_{298}^o$ for $Al(OH)_4^-$ from this report, and $\overline{V}^o$ for $Al(OH)_4^-$, determined by Hovey and Hepler (1987), were used to calculate the Born coefficient and the a and c parameters of AlO_2^- for the HKF equation of state.
9. Using the HKF equation of state, $\Delta\overline{G}_f^o(T)$ and $\log \overline{K}_{f,T}^o$ for AlO_2^- were calculated and compared with corresponding results obtained from solubility measurements, of gibbsite, boehmite and diaspore.
10. Heat of decomposition and heat of solution data of gibbsite and bayerite were used in conjunction with bayerite solubility measurements in alkaline solutions to calculate S_{298}^o, $\Delta H_{f,298}^o$, $\Delta G_{f,298}^o$, for bayerite. C_p^o(bayerite) was assumed to be equal to that of gibbsite.
11. A comparison of gibbsite and bayerite solubilities in alkaline solutions was made, and reconciled with precipitation mechanisms operating during the recovery stage of the Bayer process.
12. During the evaluation of diaspore solubility data above 300°C, evidence was found for the existence of the aqueous species $Al(OH)_3^o$. Preliminary estimates were made for $\log K_4^{-1}$ of the reaction $Al(OH)_4^- = Al(OH)_3^o + OH^-$.

8.2 Conclusions

1. Gibbsite solubility measurements made in dilute alkaline solutions ($pH \leq 10$) at 25–50°C are prone to supersaturation. This appears to be due to contamination by bayerite or some surface active material when Bayer process synthetic gibbsite is used, and to unidentified surface active material when natural gibbsite is used.
2. The solubility measurements most closely approaching true saturation with respect to gibbsite are those by Russell et al. (1955) and Kittrick (1966).
3. Solubility measurements attempted on gibbsite above 120°C are likely to be undersaturated owing to the rapid decomposition of gibbsite to boehmite.

4. Boehmite solubilities are easily measured between 100 and 250°C. Below 100°C the rate of approach of boehmite saturation in dilute alkaline solutions is slow even with material of a high specific surface area. At temperatures below 50°C rates of dissolution become so slow that attainment of saturation in alkaline solutions is experimentally infeasible with well crystallized boehmite.

5. Reversible saturation with respect to diaspore in alkaline solutions, using –60 + 100 mesh cleavage fragments, is experimentally feasible between 200 and 350°C. Below 200°C, the rates of dissolution or precipitation become so slow that attainment of saturation is experimentally infeasible.

6. Bayerite tends to decompose eventually to produce gibbsite at all temperatures. However, above 60°C, the rate becomes so rapid in alkaline solutions, that measurement of its solubility is difficult. Below 30°C bayerite solubilities can be measured quite easily, because the decomposition times extend to periods of months or more.

7. Diaspore is the most stable of all four phases, (gibbsite, bayerite, boehmite, diaspore) at all temperatures between 0 and 350°C.

8. Below ≈ 30°C, gibbsite is more stable than boehmite in dilute solutions.

9. Bayerite is less stable than gibbsite, boehmite or diaspore below 100°C.

10. Because nordstrandite ($Al(OH)_3$) is observed to form from bayerite, and is known to decompose to gibbsite, it is presumably intermediate in stability between bayerite and gibbsite at 25°C. Its persistence in nature in slightly alkaline ($pH < 10$) low temperature environments (≈ 25°C) suggests that the free energy difference between the two phases is too small for gibbsite to overcome the nucleation activation energy and subsequent growth.

11. Although it has been claimed that the calorimetrically determined heats of formation, $\Delta H^{o}_{f,298}$ of gibbsite and corundum are inconsistent, no significant inconsistency has been found in this study. They appear to be consistent to within 200 $cal.(g.at.wt.Al)^{-1}$.

12. The value for S^{o}_{298}, of boehmite, normally attributed to be 11.58 $cal.gfw^{-1}.K^{-1}$ is incorrect. The value of 8.99 $cal.gfw^{-1}K^{-1}$ is very nearly correct. Hemingway, USGS, (personal communication), has found a provisional value of 8.89 $cal.gfw^{-1}.K^{-1}$ through low temperature heat capacity measurements.

13. The thermodynamic properties for the aluminate ion, presented in this report are more reliable than previously published values and may be used as a basis for calculating the solubilities of aluminosilicate minerals in aqueous solutions at elevated temperatures. Independent confirmation of $\overline{C}^{o}_{p,298}(Al(OH)_4^-)$ and the excellent agreement between the experimentally determined $\Delta G^{o}_{f}(T)(Al(OH)_4^-)$ and that predicted by the HKF equation of state, substantiates this conclusion.

8.3 Findings

Thermodynamic data used and derived in this report are summarized in Tables 22 and 23. Log $K_{s4}(T)$ for gibbsite, bayerite, boehmite and diaspore are summarized in Table 24. Log $K_4^{-1}(T)$ for the reaction $Al(OH)_4^- = Al(OH)_3^o + OH^-$ is given in Table 25.

TABLE 22

SUMMARY OF THERMODYNAMIC PROPERTIES OF ALUMINUM HYDROXIDES AND OXYHYDROXIDES, AND CORUNDUM

Mineral	Formula	$C^o_{p,298}$	Maier-Kelley Function parameters			S^o_{298}	$\Delta H^o_{f,298}$	$\Delta G^o_{f,298}$	$\log K^o_{f,298}$
		$cal.gfw^{-1}.K^{-1}$	a	$b \times 10^3$	$c \times 10^{-5}$	$cal.gfw^{-1}.K^{-1}$	$kcal.gfw^{-1}$	$kcal.gfw^{-1}$	–
Bayerite	$Al(OH)_3$	23.005	8.650	45.60	0.0	18.97	−307.829	−275.570	201.995
Gibbsite	$Al(OH)_3$	23.005	8.650	45.60	0.0	16.36 ± 0.08	−309.065 ± 1.284	−276.025	202.329
Nordstrandite	$Al(OH)_3$	–	–	–	–	–	–	−275.826	202.183
Boehmite	AlOOH		12.905	20.70	−3.005	8.99 ± 0.19	−237.893	−219.289	160.741 ± 0.26
Diaspore	AlOOH		14.430	0.780	0.120	8.446 ± 0.02	−238.827	−220.082	161.322
Corundum	Al_2O_3	18.889	27.490	2.820	−8.380	12.176 ± 0.03	−400.510 ± 0.300	−378.184	277.217

TABLE 23

SUMMARY OF THERMODYNAMIC PROPERTIES OF THE ALUMINATE ION

Formula	$\overline{C}^o_{p,298}$ $cal.gfw^{-1}.K^{-1}$	$\overline{S}^o_{298}$ $cal.gfw^{-1}.K^{-1}$	$\Delta\overline{H}^o_{f,298}$ $kcal.gfw^{-1}$	$\Delta\overline{G}^o_{f,298}$ $kcal.gfw^{-1}$	$\log\overline{K}^o_{f,298}$ –	$\overline{V}^o$ $cm^3.gfw^{-1}$
$Al(OH)_4^-$	+21.08	+29.59	−357.56	−311.88	+228.611	+46.22
AlO_2^-	−14.89	−3.81	−220.93	−198.506	+145.507	+10.08

HKF Equation of State Parameters

Formula	$a_1 \times 10^1$ $cal.gfw^{-1}.bar^{-1}$	$a_2 \times 10^{-2}$ $cal.gfw^{-1}$	a_3 $cal.K.gfw^{-1}.bar^{-1}$	$a_4 \times 10^{-4}$ $cal.K.gfw^{-1}$	c_1 $cal.gfw^{-1}.K^{-1}$	$c_2 \times 10^{-4}$ $cal.K.gfw^{-1}$	$\omega \times 10^{-5}$ $cal.gfw^{-1}$
AlO_2^-	0.31586	3.0566	−2.1559	−2.9054	13.331	−6.075	1.6866

TABLE 24
LOG K_{s4} FOR ALUMINUM HYDROXIDES AND OXYHYDROXIDES, AND CORUNDUM TAKEN ALONG THE WATER SATURATION SURFACE

T,°C	$\text{Log}K_{s4}$[1]				
	Gibbsite	Bayerite	Boehmite	Diaspore	0.5 Corundum
0	−1.679	−1.263	−1.462	−2.108	+0.127
25	−1.276	−0.943	−1.240	−1.821	+0.119
50	−0.889	−0.626	−1.022	−1.548	+0.138
60	−0.740	−0.502	−0.937	−1.445	+0.149
100	−0.184	−0.032	−0.623	−1.059	+0.210
150	+0.433	+0.499	−0.279	−0.638	+0.298
200			+0.018	−0.269	+0.391
250			+0.276	+0.257	+0.481
300			+0.500	+0.348	+0.568
350			+0.689	+0.604	+0.642

[1] Values are based on HKF Equation of state prediction of AlO_2^- thermodynamic properties, and differ slightly from those obtained from an empirical fit of gibbsite, bochmite and diaspore solubility data, given in Table 12.

TABLE 25
ESTIMATED VALUES OF LOG K_4^{-1} FOR THE REACTION $Al(OH)_4^- = Al(OH)_3^o + OH^-$

T,°C	$1/T$, $K^{-1} \times 10^3$	$\log K_4^{-1}$
0	3.661	−9.088
25	3.354	−8.517
50	3.095	−8.034
60	3.002	−7.861
100	2.680	−7.262
150	2.363	−6.673
200	2.133	−6.208
250	1.911	−5.832
300	1.745	−5.522
350	1.605	−5.261

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APPENDIX A

SUMMARY OF EXPERIMENTAL DATA FROM THE LITERATURE AND CALCULATIONS TO DETERMINE THE SOLUBILITY PRODUCTS OF GIBBSITE

TABLE A.1

GIBBSITE SOLUBILITIES REPORTED BY FRICKE AND JUCAITIS (1930) USED IN THIS STUDY

T,°C	Agitation Time, Weeks	Solution Composition		Solubility of the solid bodies
		Na_2O, %	Al_2O_3, %	
1. $Al(OH)_3$ XX with Sodium Hydroxide				
30	6	3.77	0.81	insoluble
		15.35	4.69	"
		17.78	6.99	"
		20.90	16.29	"
		21.55	24.34	"
		21.88	26.87	"
60	3	3.79	1.47	insoluble
		14.49	7.77	"
		16.80	11.02	"
		20.31	23.33	"
		20.09	24.48	partly soluble
2. $Al(OH)_3$ XXI with Sodium Hydroxide				
30	6	3.95	0.70	insoluble
		9.68	1.82	
		15.23	4.31	"
		17.98	6.63	"
		21.10	15.99	"
		21.80	20.56	"
		21.95	25.59	upper layer insoluble, lower insoluble
60	3	3.87	1.41	insoluble
		16.62	11.00	"
		19.94	24.45	"
		20.21	23.34	partly soluble

TABLE A.1, continued

GIBBSITE SOLUBILITIES REPORTED BY FRICKE AND JUCAITIS (1930)
USED IN THIS STUDY

T,°C	Agitation Time, weeks	Solution Composition		Solubility of the solid bodies
		Na_2O, %	Al_2O_3, %	
3. $Al(OH)_3$ XX with Potassium Hydroxide				
30	4	8.06	0.906	insoluble
		21.43	3.90	
		28.34	12.14	"
		28.86	16.23	"
60	1	8.06	1.54	insoluble
		26.03	16.43	"
		27.2	21.12	"
4. $Al(OH)_3$ XXI with Potassium Hydroxide				
30	3	7.77	0.95	insoluble
		21.00	2.62	"
		28.80	12.71	"
		29.10	16.70	"
60	1	7.92	1.90	insoluble
		21.60	10.24	"
		25.64	15.92	"
		27.81	19.42	"
		28.27	21.55	"

TABLE A.2

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF FRICKE AND JUCAITIS (1930)

T,°C	TDS mg.kg H_2O^{-1}	Na^+, m	Al^{+++}, m	log[H_2O]	Ionic Strength	log K'_{s4}
$Al(OH)_3$ XX with Sodium Hydroxide						
30	58592	1.288	0.1683	-0.0191	1.186	-0.763
	310136	6.489	1.205	-0.1326	4.577	-0.418
	402560	8.047	1.923	-0.1785	5.397	-0.226
	677454	11.313	5.360	-0.2783	7.658	+0.401
	917673	13.336	9.155	-0.3284	10.132	+1.007
	1014673	14.223	10.619	-0.3434	11.274	+1.246
60	64970	1.302	0.3067	-0.0194	1.205	-0.448
	335102	6.243	2.035	-0.1228	4.640	-0.077
	444188	7.829	3.122	-0.1641	5.629	+0.128
	832235	12.009	8.384	-0.2550	9.333	+0.983
	799833	11.668	7.937	-0.2502	8.989	+0.914
$Al(OH)_3$ XXI with Sodium Hydroxide						
30	58971	1.322	0.145	-0.0196	1.212	-0.848
	162701	3.632	0.415	-0.0619	2.918	-0.755
	302181	6.400	1.100	-0.1301	4.512	-0.462
	401810	8.133	1.822	-0.1812	5.401	-0.263
	677785	11.424	5.262	-0.2814	7.646	+0.377
	820334	12.806	7.341	-0.3171	8.971	+0.688
	976253	13.997	9.920	-0.3401	10.753	+1.112
60	65623	1.331	0.295	-0.0198	1.228	-0.480
	439019	7.717	3.105	-0.1612	5.581	+0.131
	847233	11.885	8.859	-0.2533	9.606	+1.111
	828210	11.923	8.369	-0.2538	9.306	+0.988

TABLE A.2, continued

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF FRICKE AND JUCAITIS (1930)

T,°C	TDS mg.kg H_2O^{-1}	K^+, m	Al^{+++}, m	log[H_2O]	Ionic Strength	log K'_{s4}
Al(OH)$_3$ XX with Potassium Hydroxide						
30	115404	1.908	0.1985	-0.0292	1.6904	-0.855
	403298	6.385	1.073	-0.1297	4.499	-0.475
	777902	10.698	4.233	0.2603	7.033	+0.212
	913665	11.727	6.093	0.2898	8.094	+0.517
60	121921	1.920	0.3388	-0.0295	1.7079	-0.584
	802997	9.965	5.811	-0.2174	7.420	+0.593
	991632	11.502	8.251	-0.2476	9.139	+1.005
Al(OH)$_3$ XXI with Potassium Hydroxide						
30	111583	1.834	0.2068	-0.0280	1.633	-0.818
	373142	6.123	0.7058	-0.1225	4.294	-0.678
	810970	11.076	4.516	-0.2715	7.248	+0.251
	938617	11.978	6.351	-0.2966	8.279	+0.552
60	123625	1.890	0.4191	-0.0290	1.693	-0.461
	518880	6.965	3.051	-0.1415	5.261	+0.172
	774704	9.662	5.542	-0.2104	7.205	+0.557
	965317	11.605	7.486	-0.2493	8.716	+0.820
	1058365	12.355	8.701	-0.2589	9.603	+1.021

TABLE A.3

GIBBSITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY FULDA AND GINSBERG (1951)

T,°C	Na_2O in starting solution, g.l^{-1}	Al_2O_3, g.l^{-1}	Precipitate
74	100	53.2	Al_2O_3+$3H_2O$
	130	80.4	
	140	89.7	
79	100	59.4	Al_2O_3+$3H_2O$
	130	85.2	
	140	93.5	
84	100	64.0	Al_2O_3+$3H_2O$
	130	92.6	
	140	106.8	
89	100	70.5	Al_2O_3+$3H_2O$
	130	98.6	
	140	110.6	
94	100	75.0	Al_2O_3+$3H_2O$
	130	105.2	
	140	117.0	
100	100	90.4	Al_2O_3+$3H_2O$
	130	120.0	
	140	132.2	
	190	206.0	

TABLE A.4

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE) FROM THE EXPERIMENTAL RESULTS REPORTED BY FULDA AND GINSBERG (1951)

T,°C	ρ, $g.cm^{-3}$	TDS, $mg.l^{-1}$	Na^+, m	Al^{+++}, m	$\log[H_2O]$	Ionic Strength	log K'_{s4}
74	1.1685	172867	3.2412	1.0481	-0.0540	2.759	-0.1855
	1.2206	233980	4.2522	1.5986	-0.0750	3.504	-0.0468
	1.2372	254544	4.5971	1.7904	-0.0827	3.747	-0.0086
79	1.1731	177971	3.2427	1.1709	-0.0540	2.780	-0.1103
	1.2239	239732	4.2551	1.6952	-0.0750	3.524	-0.0031
	1.2398	257672	4.5999	1.8674	-0.0826	3.763	-0.0237
84	1.1765	181758	3.2440	1.2620	-0.0540	2.793	-0.0560
	1.2289	244025	4.2596	1.8444	-0.0751	3.555	+0.0629
	1.2486	268622	4.6098	2.1376	-0.0827	3.830	+0.1322
89	1.1813	187110	3.2460	1.3911	-0.0540	2.813	-0.0188
	1.2330	248965	4.2634	1.9656	-0.0751	3.577	+0.1168
	1.2511	271751	4.6127	2.2151	-0.0827	3.841	+0.1654
94	1.1845	190815	3.2474	1.4805	-0.0541	2.824	+0.0710
	1.2373	254398	4.2678	2.0994	-0.0751	3.600	+0.1768
	1.2553	277020	4.6179	2.3459	-0.0827	3.864	+0.2205
100	1.1956	203494	3.2527	1.7874	-0.0542	2.880	+0.2430
	1.2471	266583	4.2781	2.4005	-0.0752	3.665	+0.3098
	1.2651	289530	4.6307	2.6580	-0.0828	3.937	-0.3500
	1.3567	414828	6.5098	4.2904	-0.1248	5.424	+0.6130

TABLE A.5

GIBBSITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY IKKATAI AND OKADA (1962)

1. Dissolution of Gibbsite

T,°C	NaOH, $g.l^{-1}$	Al_2O_3,$g.l^{-1}$
40	50.2	9.0
	98.0	17.6
	145.3	29.6
	186.1	45.2
70	49.4	17.9
	95.7	37.6
	142.6	59.2
	183.2	86.2
100	50.4	30.4
	96.4	60.1
	139.4	93.4
	177.7	128.1
130	51.2	42.6
	97.6	81.0
	142.2	122.6
	178.0	160.3[a]
2. Precipitation of Gibbsite		
40	49.8	8.1
	97.6	19.8
	142.7	32.0
	180.9	49.9
70	50.4	18.7
	97.1	38.0
	141.5	55.0
	180.3	86.8
100	50.6	29.3
	96.9	57.4
	139.4	89.9
	176.7	122.0

[a] Calculated from Na_2O/Al_2O_3 mole ratio given in text.

TABLE A.6

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF IKKATAI AND OKADA (1962)

1. Dissolution of Gibbsite

T,°C	ρ, $g.cm^{-3}$	TDS, $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	$\log[H_2O]$	Ionic Strength	$\log K'_{s4}$
40	1.0586	57608	28854	4763	-0.0186	1.156	-0.726
	1.1125	112489	56329	9315	-0.0388	2.108	-0.685
	1.1649	169669	83516	15666	-0.0623	2.944	-0.581
	1.2111	223314	106968	23922	-0.0860	3.614	-0.453
70	1.0656	63936	28279	9474	-0.0182	1.145	-0.336
	1.1266	126655	55007	19900	-0.0379	2.115	-0.247
	1.1845	191339	81964	31332	-0.0610	3.010	-0.169
	1.2369	254168	105301	45621	-0.0842	3.767	-0.046
100	1.0778	75428	28969	16089	-0.0187	1.185	+0.024
	1.1449	145882	55409	31808	-0.0383	2.176	+0.100
	1.2063	216298	80125	49432	-0.0595	3.068	+0.212
	1.2601	283164	102139	67797	-0.0810	3.866	+0.330
130	1.0891	86272	29429	22546	-0.0190	1.223	+0.353
	1.1619	164286	56099	42869	-0.0389	2.265	+0.403
	1.2287	243136	81734	64886	-0.0611	3.254	+0.510
	1.2808	310009	102312	84860	-0.0811	4.073	+0.625
2. Precipitation of Gibbsite							
40	1.0574	56469	28624	4287	-0.0184	1.146	-0.776
	1.1139	113902	56099	10479	-0.0386	2.107	-0.623
	1.1644	169047	82022	16936	-0.0609	2.912	-0.533
	1.2101	221983	103979	26410	-0.0829	3.562	-0.387
70	1.0675	65796	28969	9897	-0.0187	1.172	-0.323
	1.1282	128387	55812	20112	-0.0385	2.143	-0.248
	1.1805	186780	81332	29109	-0.0604	2.974	-0.213
	1.2350	251763	103634	45939	-0.0825	3.727	-0.032
100	1.0771	74721	29084	15507	-0.0187	1.187	+0.009
	1.1433	144158	55697	30379	-0.0385	2.176	+0.057
	1.2039	213415	80125	47580	-0.0594	3.050	+0.176
	1.2554	277147	101565	64569	-0.0803	3.812	+0.285

SOLUBILITY OF GIBBSITE REPORTED BY KITTRICK (1966)

Kittrick (1966) conducted experiments of solubility measurements on gibbsite samples in both acid and alkali solutions at 25°C. The average particle diameter of one was 0.05 micrometers with a surface area of 10 $m^2.g^{-1}$. The other contained particles up to 50 micrometers in diameter and had a surface area of 0.2 $m^2.g^{-1}$.

Equilibration in acid solutions took place over a period of up to four years. Equilibration constants were determined on the basis of the following equation:

$$Al(OH)_3 \text{ (gibbsite)} = Al^{3+} + 3(OH)^-$$

where

$$\log K_{S0} = \log[Al^{3+}]\,[OH^-]^3$$

Runs from undersaturation on two fractions each of each sample of gibbsite gave log K_{S0} = -34.02, -34.02, -33.99 and -33.97, respectively. One run from supersaturation gave -34.14, in close agreement.

Gibbsite added to dilute sodium hydroxide solution immediately supersaturated. The approach to equilibrium was monitored for up to 200 days and the solubility quotient, $^*Q_{s4}$, calculated assuming the reaction:

$$Al(OH)_3 \text{ (gibbsite)} + H_2O = Al(OH)_4^- + H^+ \qquad {}^*Q_{S4}$$

where

$$\log {}^*Q_{s4} \approx \log\,[Al(OH)_4^-]\,[H^+]$$

Kittrick plotted log $^*Q_{s4}$ versus the reciprocal of the square root of time and extrapolated log $^*Q_{s4}$ to $\frac{1}{\sqrt{t}}$ = 0. This procedure, which does not appear to have any theoretical basis, may lead to a log$^*K_{s4}$ that is more negative than the true value. Results of this experiment gave an average value of −15.30±0.05, or log K_{s4} = −1.31±0.05.

TABLE A.7

GIBBSITE SOLUBILITY PRODUCTS, K_{s4},
REPORTED BY KUZNETSOV (1952)

T, °C	K_{s4}
25	0.0114
30	0.043
45	0.147
60	0.23
80	0.34
100	0.51
120	0.53
140	0.54

SOLUBILITY OF GIBBSITE REPORTED BY LYAPUNOV ET AL. (1964)

Lyapunov et al., (1964) measured the solubility of gibbsite in sodium hydroxide solutions at both 60 and 95°C. However, only the measurements at 60°C are included here, as the data at 95°C were difficult to interpret.

TABLE A.8

GIBBSITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY LYAPUNOV ET AL. (1964)

T,°C	Na_2O, %	Al_2O_3, %	H_2O, %	Solid phase composition
60	7.31	2.78	89.91	gibbsite
	7.46	2.86	89.68	"
	9.75	3.80	86.45	"
	10.32	4.00	85.68	"
	10.58	4.30	85.12	"
	10.78	4.15	85.07	"
	12.39	5.68	81.93	"
	12.55	5.46	81.99	"

TABLE A.9

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4} (GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF LYAPUNOV ET AL. (1964)

T,°C,	TDS, mg.kg H_2O^{-1}	Na^+, M	Al^{+++}, M	$\log[H_2O]$	Ionic Strength	log K'_{s4}
60	132803	2.672	0.6174	-0.0430	2.301	-0.411
	136137	2.735	0.6374	-0.0441	2.348	-0.404
	186392	3.732	0.8839	-0.0640	3.044	-0.361
	199241	3.993	0.9414	-0.0695	3.212	-0.355
	207643	4.123	1.018	-0.0724	3.304	-0.324
	209607	4.207	0.9846	-0.0742	3.346	-0.352
	260517	5.040	1.404	-0.0932	3.894	-0.220
	260941	5.107	1.350	-0.0948	3.916	-0.249

SOLUBILITY OF GIBBSITE REPORTED BY MAY ET AL. (1979)

May et al. (1979) equilibrated synthetic and natural gibbsite samples in buffered acid and alkaline solutions at 25°C. The observed solubility produced for synthetic gibbsite, $^*K_{s4}$(gibbsite) under alkaline conditions was estimated by the authors to be 2.38×10^{-15}. However, they believed the solution to have equilibrated with respect to some unidentified mineral other than gibbsite. Their value for $^*K_{s4}$ is inconsistent with the results other investigations, and is believed by Hemingway (1982) to reflect the solubility of a the meta-stable $Al(OH)_3$ phase, nordstrandite.

SOLUBILITY OF GIBBSITE REPORTED BY PACKTER (1979)

In this study, Packter dissolved recrystallized gibbsite of different specific surface areas and particle sizes in sodium hydroxide solutions between 1 and 8 molar, and over a temperature range over a temperature range from 20 to 80°C. Packter generated the solubility product on the basis of the following reaction.

$$Al(OH)_3 + OH^- + 2H_2O = [Al(OH)_4(H_2O)_2]^-$$

The solubility products for the gibbsite with the largest particle size, 450 nm, are given in the table below.

TABLE A.10

SOLUBILITY PRODUCT FOR 450 nm GIBBSITE REPORTED BY PACKTER (1979)

Temperature, °C	log K'_{s4}
20	-1.187
35	-0.959
50	-0.733
65	-0.553
80	-0.319

TABLE A.11

GIBBSITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY RUSSELL ET AL. (1955)

T,°C	Equilibration Time, hr	ρ at 25°C, $g.ml^{-1}$	Na_2O, $g.l^{-1}$	Al_2O_3, $g.l^{-1}$
40	264	1.021	15.5	2.5
		1.053	38.5	6.0
		1.096	70.0	14.0
		1.107	78.0	16.3
		1.126	92.5	19.7
		1.163	122.	28.4
		1.199	149.	37.9
		1.292	217.	81.2
		1.371	268.	144.
50	168	1.021	15.5	3.3
		1.054	39.0	8.6
60	168	1.020	15.5	4.4
		1.055	38.5	11.2
		1.101	70.0	23.6
		1.113	78.5	27.1
		1.132	92.0	32.9
		1.172	120.	47.4
70	96	1.022	15.5	5.6
		1.058	39.0	15.2
		1.105	70.0	29.5
		1.117	78.0	33.5
		1.137	91.5	40.9
		1.178	120.	58.9
		1.220	149.	79.6
		1.320	206.	150.
		1.426	255.	232.
80	72	1.022	15.5	7.1
		1.059	38.5	18.9
		1.110	70.0	37.5
		1.123	78.0	42.8
		1.144	92.0	52.2
		1.186	118.	74.0
90	48	1.023	16.0	8.7
		1.061	38.0	22.2
		1.114	69.5	44.2
		1.127	77.5	51.0
		1.147	90.0	61.0
		1.192	117.	86.0

TABLE A.11, continued

GIBBSITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY RUSSELL ET AL. (1955)

T,°C	Equilibration Time, hr	ρ at 25°C, $g.ml^{-1}$	Na_2O, $g.l^{-1}$	Al_2O_3, $g.l^{-1}$
100	24	1.027	17.0	11.5
		1.064	38.5	27.1
		1.121	71.0	53.6
		1.135	79.0	60.8
		1.155	91.0	72.2
		1.202	117.	100.
		1.246	143.	128.
		1.347	198.	207.
		1.430	240.	284.
110	5	1.123	69.	60.
		1.137	79.	69.
		1.158	89.	78.
		1.158	90.	81.
		1.206	117.	111.
120	3	1.126	68.	63.
		1.150	82.	78.
		1.253	139.	149.
		1.347	192.	233.
130	1	1.130	68.	69.
		1.143	75.	79.
		1.154	81.	88.
		1.165	88.	92.
		1.189[a]	100.	112.
		1.214	113.	127.
		1.256	134.	161.
140	0.5	1.131	69.	73.
		1.155	81.	91.
		1.218[a]	112.	136.
150	0.5	1.131	66.	73.
		1.147	75.	84.
		1.158	81.	94.
		1.167	87.	101.
		1.203[a]	101.	126.
		1.222	111.	141.
		1.261	129.	168.
160	0.34	1.135	67.	75.
		1.160	80.	99.
170	0.34	1.134	64.	80.
		1.164	80.	106.
		1.181[a]	86.	111.
		1.210[a]	99.	124.
		1.222	109.	150.

[a] Density was calculated.

TABLE A.12

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF RUSSELL ET AL. (1955)

T,°C	TDS, $mg.l^{-1}$	Na^+, M	Al^{+++}, M	log[H_2O]	Ionic Strength	log K'_{s4}
40	22063	0.500	0.049	-0.0072	0.481	-0.933
	54630	1.242	0.1177	-0.0184	1.143	-0.921
	101873	2.259	0.2746	-0.0356	1.970	-0.765
	114095	2.517	0.3197	-0.0403	2.168	-0.734
	135605	2.985	0.3864	-0.0494	2.505	-0.709
	180841	3.937	0.5571	-0.0700	3.155	-0.632
	223512	4.808	0.7434	-0.0912	3.699	-0.558
	346924	7.002	1.593	-0.1572	5.037	-0.268
	464456	8.648	2.825	-0.2190	6.216	-0.034
50	22722	0.500	0.0647	-0.0072	0.482	-0.796
	58495	1.258	0.1687	-0.0189	1.172	-0.749
60	23626	0.500	0.0863	-0.0072	0.483	-0.648
	58911	1.242	0.2197	-0.0185	1.151	-0.606
	109777	2.259	0.4629	-0.0358	1.995	-0.491
	123628	2.533	0.5316	-0.0409	2.209	-0.468
	145826	2.969	0.6454	-0.0494	2.539	-0.434
	193904	3.872	0.9298	-0.0688	3.194	-0.345
70	24616	0.500	0.1098	-0.0072	0.483	-0.517
	62703	1.242	0.2982	-0.0185	1.157	-0.437
	114631	2.259	0.5787	-0.0358	2.010	-0.363
	128255	2.517	0.6571	-0.0406	2.216	-0.343
	151769	2.952	0.8023	-0.0492	2.555	-0.303
	203371	3.872	1.155	-0.0690	3.249	-0.212
	257842	4.808	1.561	-0.0919	3.926	-0.122
	389374	6.647	2.942	-0.1443	5.378	0.187
	520126	8.228	4.551	-0.1915	6.807	0.485
80	25848	0.5001	0.1393	-0.0072	0.485	-0.379
	65252	1.242	0.3707	-0.0186	1.164	-0.306
	121219	2.259	0.7356	-0.0359	2.032	-0.213
	135913	2.517	0.8395	-0.0407	2.243	-0.188
	161719	2.969	1.024	-0.0497	2.607	-0.149
	213227	3.808	1.451	-0.0677	3.272	-0.048
90	27812	0.5163	0.1707	-0.0075	0.501	-0.270
	67323	1.226	0.4355	-0.0183	1.154	-0.192
	126092	2.243	0.8670	-0.0357	2.034	-0.094
	142014	2.501	1.000	-0.0406	2.253	-0.059
	166384	2.904	1.196	-0.0485	2.587	-0.022
	221814	3.775	1.687	-0.0671	3.298	0.077

TABLE A.12, continued

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE)
FROM THE EXPERIMENTAL RESULTS OF RUSSELL ET AL. (1955)

T,°C	TDS, $mg.l^{-1}$	Na^+, M	Al^{+++}, M	log[H_2O]	Ionic Strength	log K'_{s4}
100	31407	0.458	0.2256	-0.0066	0.449	0.021
	72002	1.242	0.5316	-0.0186	1.175	-0.055
	135766	2.291	1.0514	-0.0367	2.093	0.043
	152031	2.549	1.193	-0.0416	2.312	0.070
	176893	2.936	1.416	-0.0493	2.641	0.113
	233337	3.775	1.962	-0.0672	3.342	0.217
	289946	4.614	2.511	-0.0871	4.033	0.304
	425978	6.389	4.060	-0.1343	5.649	0.586
	543579	7.744	5.571	-0.1711	7.179	0.884
110	138457	2.226	1.177	-0.0356	2.063	0.166
	158768	2.549	1.353	-0.0418	2.348	0.185
	179087	2.872	1.530	-0.0480	2.613	0.202
	182847	2.904	1.589	-0.0488	2.657	0.229
	242396	3.775	2.177	-0.0675	3.409	0.325
120	139633	2.194	1.236	-0.0349	2.042	0.228
	170051	2.646	1.530	-0.0436	2.446	0.276
	302076	4.485	2.923	-0.0842	4.098	0.511
	439636	6.195	4.570	-0.1290	5.866	0.821
130	144573	2.194	1.353	-0.0350	2.062	0.328
	176995	2.614	1.726	-0.0431	2.466	0.432
	189322	2.839	1.805	-0.0475	2.649	0.395
	221276	3.227	2.197	-0.0557	3.034	0.505
	250403	3.646	2.491	-0.0646	3.404	0.532
	305499	4.324	3.158	-0.0804	4.082	0.676
140	149160	2.226	1.432	-0.0357	2.105	0.383
	179467	2.614	1.785	-0.0432	2.479	0.481
	256526	3.614	2.668	-0.0640	3.438	0.656
150	145288	2.130	1.432	-0.0338	2.020	0.438
	165959	2.420	1.648	-0.0393	2.291	0.470
	181934	2.614	1.844	-0.0431	2.487	0.531
	195442	2.807	1.981	-0.0471	2.670	0.542
	234090	3.259	2.472	-0.0562	3.119	0.687
	259350	3.582	2.766	-0.0617	3.374	0.736
	304811	4.162	3.295	-0.0759	4.003	0.829
160	148220	2.162	1.471	-0.0343	2.047	0.459
	184762	2.581	1.942	-0.0426	2.485	0.638
170	148468	2.065	1.569	-0.0326	1.992	0.631
	190525	2.581	2.079	-0.0426	2.520	0.779
	202385	2.775	2.177	-0.0460	2.671	0.732
	229867	3.194	2.432	-0.0540	3.023	0.697
	264181	3.517	2.942	-0.0620	3.464	0.932

TABLE A.13

GIBBSITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY SATO (1954)

T,°C	Equilibration time, hr	ρ at 25°C $g.ml^{-1}$	Na_2O $g.l^{-1}$	Al_2O_3 $g.l^{-1}$
30	120	1.098	62.0	20±2
		1.167	108.5	38
		1.284	186.0	91
40	120	1.099	62.0	22
		1.170	108.5	42
		1.296	186.0	110
50	120	1.102	62.0	25
		1.176	108.5	50
		1.303	186.0	121
60	120	1.106	62.0	30
		1.180	108.5	55
		1.319	186.0	148
70	120	1.110	62.0	35
		1.191	108.5	71
		1.326	186.0	159

TABLE A.14

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF SATO (1954)

T,°C	ρ at 25°C $g.ml^{-1}$	TDS $mg.l^{-1}$	Na^+ m	Al^{+++} m	log $[H_2O]$ strength	Ionic strength	log K'_{s4}
30	1.098	96487	1.999	0.3919	-0.0308	1.783	-0.529
	1.167	171323	3.518	0.7489	-0.0596	2.906	-0.434
	1.285	314985	6.190	1.8410	-0.1243	4.605	-0.147
40	1.099	98134	1.999	0.4311	-0.0308	1.784	-0.475
	1.169	174616	3.519	0.8280	-0.0596	2.908	-0.374
	1.296	330628	6.215	2.234	-0.1241	4.689	-0.011
50	1.102	100604	1.999	0.490	-0.0309	1.789	-0.401
	1.176	181203	3.521	0.9863	-0.0596	2.934	-0.269
	1.303	339604	6.229	2.463	-0.1235	4.752	0.062
60	1.106	104721	1.998	0.5878	-0.0309	1.799	-0.291
	1.179	185319	3.523	1.085	-0.0597	2.953	-0.209
	1.319	361913	6.268	3.032	-0.1235	4.948	0.231
70	1.110	108837	1.998	0.6858	-0.0309	1.809	-0.191
	1.191	198492	3.528	1.403	-0.0597	3.017	-0.033
	1.326	370d976	6.285	3.266	-0.123	5.036	0.298

TABLE A.15

GIBBSITE SOLUBILITIES REPORTED BY SZITA AND BERECZ (1970)

T,°C	NaOH, m	$Al(OH)_3$, m
25	0.0520	0.0028
	0.0950	0.0052
	0.1440	0.0080
	0.3950	0.0234
	0.5480	0.0334
	1.1450	0.0759
	1.2935	0.0880
	2.8620	0.2400
	5.5590	0.6920
	6.3975	0.9080
	7.3640	1.2070
35	0.0545	0.0047
	0.0865	0.0076
	0.1555	0.0140
	0.2825	0.0260
	0.4550	0.0429
	0.8215	0.0820
	1.2265	0.1280
	2.6125	0.3240
	4.3630	0.6290
	6.0185	1.0780
	7.9920	1.8750
50	0.0485	0.0071
	0.0810	0.0120
	0.1325	0.0197
	0.3145	0.0478
	0.6215	0.0970
	0.9610	0.1540
	1.2955	0.2120
	2.5315	0.4540
	5.0110	1.2230
	7.5975	2.5790
60	0.0465	0.0090
	0.0620	0.0121
	0.1225	0.0300
	0.4105	0.0823
	0.7195	0.1470
	0.9030	0.1870
	1.3415	0.2870
	2.7475	0.6760
	5.3410	1.7620
	6.4185	2.3740
	7.4310	3.0550

TABLE A.16

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF SZITA AND BERECZ (1970)

T,°C	Na^+, m	Al^{+++}, m	log[H_2O]	Ionic Strength	log K'_{s4}
25	0.0520	0.0028	-0.0008	0.0517	-1.239
	0.0950	0.0052	-0.0014	0.0940	-1.228
	0.1440	0.0080	-0.0021	0.1419	-1.218
	0.3950	0.0234	-0.0057	0.3821	-1.175
	0.5480	0.0334	-0.0079	0.5249	-1.156
	1.1450	0.0759	-0.0169	1.0578	-1.096
	1.2935	0.0880	-0.0192	1.1847	-1.078
	2.8620	0.2400	-0.0464	2.3977	-0.930
	5.5590	0.6920	-0.1077	4.0564	-0.659
	6.3975	0.9080	-0.1306	4.5004	-0.568
	7.3640	1.2070	-0.1589	4.9865	-0.466
35	0.0545	0.0047	-0.0008	0.0541	-1.019
	0.0856	0.0076	-0.0013	0.0857	-1.008
	0.1555	0.0140	-0.0022	0.1531	-0.991
	0.2825	0.0260	-0.0041	0.2755	-0.974
	0.4550	0.0429	-0.0065	0.4387	-0.954
	0.8215	0.0820	-0.0119	0.7746	-0.911
	1.2256	0.1280	-0.0181	1.1293	-0.875
	2.6125	0.3240	-0.0418	2.2242	-0.745
	4.3630	0.6290	-0.0780	3.3770	-0.613
	6.0185	1.0780	-0.1192	4.3120	-0.448
	7.9920	1.8750	-0.1754	5.3298	-0.235
50	0.0485	0.0071	-0.0007	0.0482	-0.760
	0.0810	0.0120	-0.0012	0.0803	-0.751
	0.1325	0.0197	-0.0019	0.1308	-0.746
	0.3145	0.0478	-0.0045	0.3064	-0.724
	0.6215	0.0970	-0.0090	0.5942	-0.696
	0.9610	0.1540	-0.0141	0.9012	-0.669
	1.2955	0.2120	-0.0192	1.1924	-0.646
	2.5315	0.4540	-0.0403	2.1787	-0.556
	5.0110	1.2230	-0.0929	3.8364	-0.301
	7.5975	2.5790	-0.1603	5.3584	-0.001
60	0.0465	0.0090	-0.0007	0.0462	-0.614
	0.0620	0.0121	-0.0009	0.0616	-0.608
	0.1225	0.0300	-0.0018	0.1211	-0.477
	0.4105	0.0823	-0.0059	0.3979	-0.573
	0.7195	0.1470	-0.0104	0.6853	-0.549
	0.9030	0.1870	-0.0132	0.8516	-0.534
	1.3415	0.2870	-0.0200	1.2364	-0.500
	2.7475	0.6760	-0.0444	2.3629	-0.372
	5.3410	1.7620	-0.1004	4.1373	-0.100
	6.4185	2.3740	-0.1273	4.8156	+0.019
	7.4310	3.0550	-0.1536	5.4522	+0.138

TABLE A.17

GIBBSITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY TSIRLINA (1936)

T,°C	Equilibration Time, days	Na_2O, wt. %	Al_2O_3, wt. %	Character of Precipitate
95	15	1.14[a]	0.64	not soluble in water
		2.01	1.34	"
		2.84	1.91	"
		3.78	2.58	"
		5.59	4.13	"
		7.37	5.65	"
		8.26	6.42	"
		10.63	9.16	"
		12.98	11.50	"
		12.92	11.50	"
		13.77	12.56	"
		14.16	13.86	"
		14.21	14.57	"
		14.60	15.03	"
		15.65	16.08	"
		16.54	18.15	"
		17.98	21.01	"
		18.09	22.57	"
		18.36	23.19	"
		18.64	24.19	"
		19.59	27.3	"
		20.87	29.25	"

[a] Corrected value given by Magarshak (1938).

TABLE A.18

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF TSIRLINA (1936)

T,°C	TDS, mg.kg H_2O^{-1}	Na^+, m	Al^{+++}, m	log[H_2O],	Ionic Strength	log K'_{s4}
95	20390	0.3753	0.1281	-0.0054	0.3653	-0.256
	38393	0.6735	0.2729	-0.0097	0.6479	-0.122
	55274	0.9670	0.3954	-0.0141	0.9184	-0.103
	75300	1.312	0.5442	-0.0195	1.228	-0.078
	118754	2.018	0.9063	-0.0313	1.842	-0.011
	165008	2.771	1.292	-0.0449	2.460	+0.071
	189715	3.171	1.498	-0.0526	2.775	+0.098
	270018	4.356	2.282	-0.0770	3.696	+0.239
	355996	5.679	3.069	-0.1064	4.629	+0.327
	353970	5.645	3.054	-0.1056	4.607	+0.327
	391069	6.181	3.427	-0.1179	4.985	+0.376
	422203	6.498	3.867	-0.1252	5.285	+0.470
	435454	6.582	4.103	-0.1271	5.411	+0.531
	453863	6.849	4.286	-0.1332	5.598	+0.549
	502345	7.587	4.739	-0.1496	6.079	+0.584
	569620	8.377	5.588	-0.1662	6.749	+0.719
	680773	9.751	6.927	-0.1902	7.870	+0.904
	722057	10.052	7.624	-0.1943	8.357	+1.056
	747911	10.355	7.951	-0.1978	8.635	+1.104
	784872	10.735	8.469	-0.2015	9.058	+1.197
	914249	12.100	10.251	-0.2049	10.592	+1.519
	1041554	13.748	11.714	-0.1819	11.984	+1.677

APPENDIX B

GIBBSITE SOLUBILITY MEASUREMENTS BETWEEN 24 AND 90°C

This study, originally described by Apps in his Ph.D thesis in 1970, has remained unpublished. Accordingly, a more detailed description will be given.

Gibbsite solubility measurements were made between 24°C and 90°C in sodium hydroxide solutions of various concentrations between 0.0001 $\bar{\text{N}}$ and 0.1 $\bar{\text{N}}$. The gibbsite used was Baker's U.S.P. grade aluminum hydroxide (lot no. 37311, 97% pure). X-ray patterns from gibbsite of the type locality at Richmond, Berkshire County, Massachusetts, and of lot no. 37311, proved to be identical. Lot no 37311 consisted of aggregates of crystals that were readily observed under the microscope at 200X magnification. It was used without further treatment. Both optical and X-ray diffraction examinations revealed no additonal phases.

The alkali employed in the study was A.R. sodium hydroxide (Mallinkrodt, lot WMMC), which was dissolved in distilled deionized water and made up into concentrated solutions containing 40 and 400 g.l^{-1} sodium hydroxide, respectively.

Temperature was measured with standard mercury thermometers, the precision being ±0.2°C.

Aluminum was determined in solution using the "aluminon" method by Packham (1958). The method is rapid and convenient in use and the reagents will keep for several months. Aurintricarboxylic acid, triammonium salt (aluminon) is used as the color reagent. The color is measured at 532 mμ and is quite stable for at least twenty-four hours. It obeys Beer's Law over the range from 0.1 to 3.5 ppm (based upon a sample representing 50 per cent of the final volume).

Owing to the alkaline nature of the solutions investigated, only Beckman Type E2 and amber electrodes were used in this study. Fiber junction Ag-AgCl electrodes proved to be most satisfactory as reference electrodes.

The buffer chosen was a 0.01 $\underline{m}$ borax solution as recommended by the National Bureau of Standards. pH versus temperature correlations for this buffer are tabulated in Bates (1964, p. 76). The more precise data to 60°C differs from data extending the calibration to 90°C. Consequently, an empirical extrapolation based upon the virial equation of Bates was used. pH measurements were made directly in the reaction vessel at the operating temperature.

The experiment, conducted at approximately 24°C, employed 20 g of gibbsite in solutions of predetermined strength. The solutions were placed in sealed polyethylene bottles (capacity, six fluid ounces), shaken for a period of five days, and then analyzed.

The remaining solubility measurements were conducted in a one liter stainless steel beaker immersed in a constant temperature bath. The beaker was covered with a close fitting 1-inch thick slab of leucite plastic, held in position with three clamps. A Neoprene rubber seal minimized evaporation losses. Agitation was provided by a polypropylene propeller driven through a flexible shaft and gear reduction train by an AC/DC Bodine motor. Speed adjustment on the motor could be provided by a Variac transformer, allowing for agitation speeds between 0 and 328 r.min^{-1}.

Temperature control was maintained by a Precision Instruments temperature bath filled with water. The water was agitated by means of another motor and stirrer. The bath was covered with an aluminum lid through which a number of openings were cut to provide for insertion of the stirred reactor and additional vessels containing pH buffer solutions.

The following procedure was used to make Gibbsite solubility measurements in the stirred reactor. One liter of 0.0001$\overline{N}$ sodium hydroxide was employed as a starting solution. Once this solution had reached the desired temperature in the stirred reactor, 20 grams of gibbsite were added and the solution agitated at 300 $r.min^{-1}$ for twenty-four hours. The solution was then sampled and analyzed for aluminum, and the pH was measured using a Beckman amber electrode and fiber junction Ag/AgCl reference electrode. After an additional 10 to 20 hours, the solution was sampled and analyzed again to check for attainment of equilibrium. Subsequently, 10 ml of 40 g/l sodium hydroxide was added to increase the pH by one unit. Sampling and analysis was then repeated at the new pH after twenty-four hours and checked after a further 10 to 24 hours. The pH was then adjusted again by one unit with the addition of more NaOH solution and the process repeated.

After analyses had been made throughout a range of pH values from 8.0 to 12.0, the experiment was repeated at a different temperature. Investigations were made at 30, 50, 70, and 90°C.

The results of the solubility measurements are given in Table B.1 and plotted in Figure B.1. Computed values of log Q_{s4}(gibbsite) for each temperature are also summarized in Table B.1. These values were computed using the EQ3 code of Wolery (1983), in which electrical neutrality was achieved by adjusting the sodium concentration.

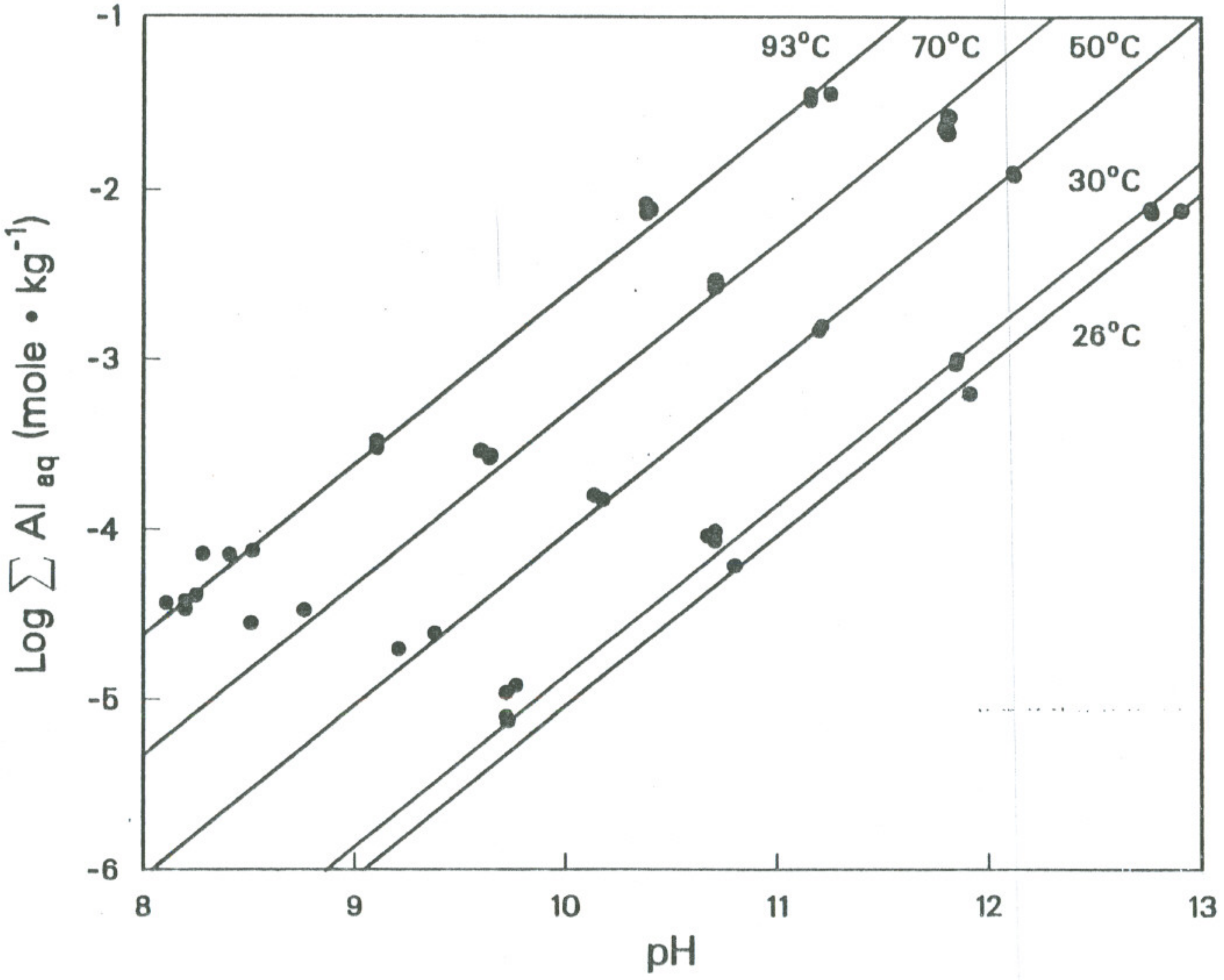

Figure B.1. The solubility of gibbsite at various temperatures expressed as log ΣAl(aq) versus pH.

TABLE B.1

GIBBSITE SOLUBILITY MEASUREMENTS BETWEEN 24°C AND 93°C

T,°C	ρ, at 25°C, g.cm^{-3} (calculated)	TDS, mg.l^{-1} (calculated)	pH	Na^+, M	Al^{+++}, M	log Q_{s4} (calculated)
24.0	0.997	2.84	9.73	0.0001	0.00000845	-0.79
	"	2.82	9.73	0.0001	0.00000823	-0.80
	"	31.24	10.81	0.001	0.0000660	-0.98
	"	365.16	11.89	0.01	0.000667	-1.09
	"	3836.91	12.89	0.10	0.00893	-1.03
29.70	"	4.59	9.77	0.0001	0.0000126	-0.83
	"	3.97	9.70	0.0001	0.0000115	-0.80
	"	39.03	10.72	0.001	0.0000886	-0.95
	"	39.41	10.71	0.001	0.000102	-0.87
	"	36.69	10.68	0.001	0.0000941	-0.88
	"	512.21	11.85	0.01	0.00102	-1.05
	"	513.85	11.85	0.01	0.00104	-1.04
	"	4121.72	12.75	0.10	0.00875	-1.08
	"	4157.78	12.75	0.10	0.00919	-1.06
	"	3994.48	12.75	0.10	0.00997	-0.99
49.70	"	7.18	9.37	0.0001	0.0000261	-0.69
	"	5.14	9.21	0.0001	0.0000203	-0.64
	"	44.64	10.17	0.001	0.000157	-0.72
	"	42.68	10.14	0.001	0.000159	-0.68
	"	467.13	11.19	0.01	0.00164	-0.75
	"	479.80	11.20	0.01	0.00170	-0.75
	"	4040.36	12.10	0.10	0.0163	-0.73
	"	4086.95	12.11	0.10	0.0161	-0.75
69.60	"	6.29	8.75	0.00001	0.0000352	-0.40
	"	4.61	8.57	0.00001	0.0000288	-0.30
	"	48.78	9.63	0.0001	0.000280	-0.39
	"	48.76	9.61	0.0001	0.000294	-0.35
	"	555.07	10.70	0.001	0.00307	-0.45
	"	547.39	10.71	0.001	0.00289	-0.49
	"	6126.47	11.79	0.01	0.0292	-0.65
	"	6675.68	11.79	0.01	0.0359	-0.56
	"	6134.67	11.79	0.01	0.0293	-0.65
	"	6951.49	11.86	0.01	0.0313	-0.71

TABLE B.1, continued

GIBBSITE SOLUBILITY MEASUREMENTS BETWEEN 24°C AND 93°C

T,°C	ρ, at 25°C, g.cm^{-3} (calculated)	TDS, mg.l^{-1} (calculated)	pH	Na^{+}, M	Al^{+++}, M	log Q_{s4} (calculated)
92.80	"	5.40	8.10	0.00001	0.0000396	-0.15
	"	5.80	8.18	0.00001	0.0000393	-0.23
	"	5.86	8.18	0.00001	0.0000400	-0.22
	"	6.30	8.22	0.00001	0.0000423	-0.24
	"	10.35	8.39	0.00001	0.0000752	-0.16
	"	9.34	8.27	0.00001	0.0000752	-0.04
	"	11.81	8.51	0.00001	0.0000767	-0.27
	"	47.96	9.10	0.0001	0.000323	-0.25
	"	47.71	9.10	0.0001	0.000320	-0.25
	"	48.51	9.10	0.0001	0.000330	-0.24
	"	1135.27	10.37	0.001	0.00897	-0.13
	"	1111.50	10.37	0.001	0.00868	-0.14
	"	1150.76	10.37	0.001	0.00915	-0.12
	"	6199.76	11.14	0.01	0.0469	-0.24
	"	6339.11	11.14	0.01	0.0486	-0.23
	"	6232.55	11.14	0.01	0.0473	-0.24
	"	7148.48	11.24	0.01	0.0514	-0.31

APPENDIX C

SUMMARY OF EXPERIMENTAL DATA FROM THE LITERATURE AND CALCULATIONS TO DETERMINE THE SOLUBILITY PRODUCTS OF BOEHMITE

TABLE C.1

BOEHMITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY BERNSHTEIN AND MATSENOK (1961)

T,°C	Na_2O, wt. %	Al_2O_3, wt. %
250	5.9	6.8
	10.7	13.1
	14.9	19.4
	18.1	24.4
	19.7	28.1
	24.3	36.3
300	6.0	7.9
	11.1	15.2
	13.9	19.8
	17.3	25.2
	19.7	28.9
	24.2	37.6

TABLE C.2

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BOEHMITE) FROM EXPERIMENTAL RESULTS OF BERNSHTEIN AND MATSENOK (1961)

T,°C	TDS mg.kg H_2O^{-1}	Na^+, m	Al^{+++}, m	log $[H_2O]$	Ionic Strength	log K'_{s4}
250	152,268	2.194	1.537	-0.0340	2.025	+0.574
	362,210	4.579	3.408	-0.0773	4.072	+0.838
	543,253	7.420	5.872	-0.1120	6.480	+1.154
	769,709	10.347	8.478	-0.0733	8.957	+1.381
	944,068	12.358	10.715	+0.0411	11.005	+1.590
	1564,400	20.028	18.186	*	*	*
300	165,589	2.250	1.801	-0.0342	2.116	0.844
	366,919	4.896	4.076	-0.0796	4.566	1.065
	520,699	6.820	5.906	-0.0989	6.402	1.246
	756,772	9.808	8.684	-0.0549	9.222	1.338
	969,304	12.519	11.164	+0.1399	11.755	1.215
	1644,851	20.654	19.506	*	*	*

*Calculation did not converge.

TABLE C.3

BOEHMITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY FULDA AND GINSBERG (1951)

T,°C	Na_2O starting solution, $g.l^{-1}$	Al_2O_3, $g.l^{-1}$	Precipitate
125	100	67.6	$Al_2O_3 \cdot 1\ H_2O$
	130	108.5	
	140	127.6	
	190	193.0	
150	130	114.0	$Al_2O_3 \cdot 1\ H_2O$
	140	135.2	
	190	203.	
160	100	83.9	$Al_2O_3 \cdot 1\ H_2O$
	130	122.4	
175	100	83.3	$Al_2O_3 \cdot 1\ H_2O$
	130	127.6	
	140	144.6	
	190	208.	
200	100	94.7	$Al_2O_3 \cdot 1\ H_2O$
	130	136.8	
	140	152.2	
	190	222.	

TABLE C.4

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BOEHMITE) FROM EXPERIMENTAL RESULTS REPORTED BY FULDA AND GINSBERG (1951)

T,°C	ρ g.cm^{-3}	TDS, mg.l^{-1}	Na^{+}, m	Al^{+++}, m	log [H_2O]	Ionic Strength	log K'_{s4}
125	1.1791	184722	3.2450	1.3334	-0.0540	2.759	+0.056
	1.2395	257115	4.2700	2.1633	-0.0747	3.575	+0.295
	1.2622	285747	4.6267	2.5633	-0.0821	3.885	+0.404
	1.3493	404125	6.4867	4.0053	-0.1214	5.276	+0.657
150	1.2432	261644	4.2739	2.2782	-0.0743	3.583	+0.352
	1.2670	292004	4.6333	2.7199	-0.0816	3.911	+0.477
	1.3550	412358	6.5044	4.2244	-0.1186	5.337	+0.738
160	1.1909	198142	3.2503	1.6577	-0.0539	2.809	+0.246
	1.2487	268559	4.2798	2.4495	-0.0742	3.627	+0.429
175	1.1905	197648	3.2501	1.6457	-0.0538	2.794	+0.246
	1.2521	272841	4.2836	2.5558	-0.0740	3.647	+0.482
	1.2730	299743	4.6417	2.9143	-0.0810	3.953	+0.568
	1.3578	416474	6.5135	4.3344	-0.1156	5.354	+0.787
200	1.1986	207034	3.2543	1.8733	-0.0538	2.835	+0.382
	1.2581	280415	4.2907	2.7446	-0.0736	3.690	+0.578
	1.2778	306001	4.6488	3.0721	-0.0804	3.990	+0.647
	1.3656	428001	6.5393	4.6445	-0.1128	5.485	+0.901

TABLE C.5

BOEHMITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY KUYUNKO ET AL. (1983)

T,°C	No. of Experiments	Run time, hr	OH^- at Equilibrium, m	Al, m
200	3	49,86,135	2.038	3.042
	3	62,90,135	1.013	1.397
	3	62,86,135	0.248	0.252
	3	68,86,135	0.0125	0.0125
250	3	60,85,110	1.032	3.778
	3	60,85,114	0.770	1.730
	3	60,85,114	0.168	0.332
	4	60,85,87,110	0.088	0.0162

TABLE C.6

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BOEHMITE) FROM EXPERIMENTAL RESULTS OF KUYUNKO ET AL. (1983)

T,°C	TDS, mg.kg H_2O^{-1}	Na^+, m	Al^{+++}, m	log $[H_2O]$	Ionic Strength	log K'_{s4}
200	330874	5.08	3.042	-0.08845	4.190	+0.555
	155032	2.41	1.397	-0.03814	2.169	+0.331
	30576	0.50	0.252	-0.00703	0.4818	+0.066
	1524.6	0.025	0.0125	-0.00036	0.02489	+0.007
250	350965	5.08	3.778	-0.08581	4.475	+0.872
	172609	2.55	1.730	-0.04031	2.317	+0.553
	33934	0.50	0.332	-0.00691	0.4830	+0.372
	1679.9	0.025	0.0162	-0.00036	0.02487	+0.275

TABLE C.7

BOEHMITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY MAGARSHAK (1938)

T,°C	Na_2O, wt. %	Al_2O_3, wt.%	Solid phase
150	3.35	4.82	Boehmite, AlOOH
	7.45	8.88	" "
	10.50	12.13	" "
	13.77	14.95	" "
	17.86	18.11	" "
	21.78	20.64	" "
	27.52	22.44	" "
200	5.44	5.03	AlOOH
	9.39	9.18	"
	13.28	14.61	"
	16.67	18.57	"
	17.59	19.85	"
	18.02	21.09	"
	20.46	25.54	"
	22.06	29.26	"
	22.74	31.85	"
	24.47	36.34	"

TABLE C.8

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BOEHMITE) FROM EXPERIMENTAL RESULTS OF MAGARSHAK (1938)

T,°C	TDS, mg.kg H_2O^{-1}	Na^+, m	Al^{+++}, m	log [H_2O]	Ionic Strength	log K'_{s4}
150	90403	1.179	1.030	-0.0174	1.161	0.939
	293759	2.894	2.097	-0.0472	2.687	0.631
	307825	4.431	3.111	-0.0775	3.930	0.694
	430229	6.354	4.195	-0.1158	5.263	0.749
	611854	9.289	5.725	-0.1543	6.978	0.856
	821641	12.802	7.376	-0.1007	8.676	0.898
	1173646	19.302	9.568	0.7491	10.919	0.147
200	125647	1.975	1.111	-0.0305	1.800	0.271
	244714	3.768	2.240	-0.0636	3.242	0.453
	411789	6.049	4.046	-0.1053	5.018	0.769
	584425	8.507	5.817	-0.1298	6.738	0.978
	640583	9.312	6.388	-0.1278	7.276	1.034
	684128	9.793	6.967	-0.1231	7.740	1.128
	902400	12.560	9.531	-0.0264	10.011	1.377
	1107360	14.988	12.100	0.2036	12.353	1.531
	1250920	16.517	14.063	0.4489	14.197	1.630
	1597483	20.510	18.515	*	*	*

*Calculation did not converge.

TABLE C.9

BOEHMITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS BY MAGARSHAK, REEVALUATED BY M.G. LAITAIZEN, AND REPORTED BY DRUZHININA (1955)*

T,°C	Na_2O, wt. %	Al_2O_3, wt. %
200	6.5	5.4
	6.9	5.7
	12.3	12.0
	12.9	12.6
	15.9	17.1
	16.2	17.4
	18.3	21.8

*Data obtained from a figure.

TABLE C.10

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BOEHMITE) FROM EXPERIMENTAL RESULTS BY MAGARSHAK, REEVALUATED BY M.G. LAITAIZEN, AND REPORTED BY DRUZHININA (1955)

T,°C	TDS, mg.kg H_2O^{-1}	Na^+, m	Al^{+++}, m	log $[H_2O]$	Ionic Strength	log K'_{s4}
200	147249	2.406	1.215	-0.0381	2.127	0.198
	157384	2.577	1.294	-0.0411	2.260	0.204
	346884	5.346	3.170	-0.0933	4.360	0.562
	370294	5.704	3.387	-0.0996	4.601	0.589
	529048	7.845	5.129	-0.1270	6.176	0.737
	544020	8.071	5.270	*	*	*
	711361	10.106	7.318	*	*	*

*Calculations did not converge.

TABLE C.11

BOEHMITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY RUSSELL ET AL. (1955)

T,°C	Equilibration Time, hr	ρ at 25°C, g.ml^{-1}	Na_2O, g.l^{-1}	Al_2O_3, g.l^{-1}
80	1008	1.103	70	19.6
		1.114	80	22.5
		1.131	93	26.5
		1.170	124	36.6
100	360	1.107	70	27.7
		1.119	79	31.6
		1.138	92	37.1
		1.176	122	51.5
120	230	1.105	70	32.6
		1.118	78	36.8
		1.136	92	44.6
		1.178	121	61.6
130	70	1.109[a]	69	36.9
		1.122[a]	78	41.3
		1.143	92	49.7
		1.144[a]	92	50.4
		1.191[a]	121	65.6
		1.255	160	108.6
		1.355	221	176.6
		1.448	274	260.1
		1.538	325	342.2
140	48	1.113	70	40.2
		1.124	77	44.1
		1.147	92	53.4
		1.192	120	71.4

[a] Density was calculated.

TABLE C.11, continued

BOEHMITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY RUSSELL ET AL. (1955)

T,°C	Equilibration Time, hr	ρ at 25°C, $g.ml^{-1}$	Na_2O, $g.l^{-1}$	Al_2O_3, $g.l^{-1}$
150	24	1.114	70	44.2
		1.128	78	49.5
		1.147	92	59.5
		1.148	91	59.6
		1.193	120	81.8
		1.261	159	123.6
		1.370	224	200.4
		1.464	274	286.7
		1.552	319	369.2
		1.631	366	460.3
160	24	1.117	70	48.5
		1.129	77	53.5
		1.152	92	63.0
		1.198	120	86.2
170	24	1.117	70	51.9
		1.133	78	58.2
		1.153	91	68.8
		1.154	91	70.2
		1.199	116	93.7
		1.262	153	143.0
		1.374	219	224.3
		1.470	271	308.2
		1.560	320	394.3
		1.641	365	477.7

TABLE C.12

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BOEHMITE)
FROM EXPERIMENTAL RESULTS BY RUSSELL ET AL. (1955)

T,°C	TDS, $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	log [H_2O]	Ionic Strength	log K'_{s4}
80	106484	51930	10373	-0.0356	1.967	-0.553
	121780	59349	11908	-0.0417	2.216	-0.533
	141850	68993	14025	-0.0499	2.524	-0.503
	190176	91991	19370	-0.0713	3.213	-0.430
100	113153	51930	14660	-0.0358	1.972	-0.355
	127980	58607	16724	-0.0412	2.196	-0.332
	149284	68251	19634	-0.0493	2.503	-0.303
	199860	90507	27255	-0.0700	3.187	-0.218
120	117187	51930	17253	-0.0360	1.987	-0.253
	130973	57865	19476	-0.0408	2.186	-0.230
	155462	68251	13604	-0.0498	2.533	-0.186
	206887	89765	32600	-0.0693	3.207	-0.097
130	119433	51188	19528	-0.0354	1.969	-0.165
	134675	57865	21857	-0.0408	2.194	-0.154
	159660	68251	26303	-0.0496	2.539	-0.114
	160234	68251	26673	-0.0496	2.541	-0.105
	210182	89765	34717	-0.0686	3.189	-0.054
	295916	118698	57474	-0.0979	4.157	+0.193
	430632	163951	93462	-0.1437	5.637	+0.479
	567784	203270	137652	-0.1695	7.263	+0.806
	701202	241105	181102	-0.1442	9.066	+1.072
140	123441	51930	21275	-0.0360	1.998	-0.114
	135687	57123	23339	-0.0401	2.174	-0.102
	162707	68251	28261	-0.0495	2.544	-0.063
	213666	89023	37787	-0.0681	3.193	+0.011

TABLE C.12, continued

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BOEHMITE) FROM EXPERIMENTAL RESULTS BY RUSSELL ET AL. (1955)

T,°C	TDS, mg.l^{-1}	Na^+, mg.l^{-1}	Al^{+++}, mg.l^{-1}	log $[H_2O]$	Ionic Strength	log K'_{s4}
150	126736	51930	23392	-0.0361	2.010	-0.045
	141428	57865	26197	-0.0408	2.213	-0.025
	167727	68251	31489	-0.0498	2.573	+0.018
	166518	67509	31542	-0.0490	2.547	+0.025
	222228	89023	43291	-0.0685	3.254	+0.271
	306976	117956	65412	-0.0967	4.222	+0.314
	454092	166177	106057	-0.1412	5.877	+0.614
	589685	203270	151729	-0.1551	7.569	+0.951
	715687	236654	195391	-0.1189	9.396	+1.123
	851349	271521	243603	-0.0557	11.960	+1.586
160	130278	51930	25668	-0.0361	2.021	+0.027
	143427	57123	28314	-0.0402	2.201	+0.043
	170610	68251	33341	-0.0496	2.575	+0.064
	225846	89023	45619	-0.0683	3.262	+0.162
170	133077	51930	27467	-0.0362	2.033	+0.083
	148589	57865	30801	-0.0409	2.238	+0.105
	174094	67509	36411	-0.0491	1.577	+0.144
	175244	67509	37152	-0.0491	2.584	+0.161
	226861	86056	49589	-0.0655	3.217	+0.256
	315207	113505	75679	-0.0924	4.257	+0.491
	467321	162467	118706	-0.1346	6.058	+0.782
	603513	201044	163108	*	*	*
	737646	237395	208674	*	*	*
	864382	270779	252812	+0.1254	12.343	+1.561

*Calculations did not converge

APPENDIX D

BOEHMITE SOLUBILITY MEASUREMENTS BETWEEN 50 AND 255°C

Apps conducted two studies on boehmite solubility, which have been described only in his Ph.D. thesis in 1970. The first involved measurement of the approach of boehmite saturation from undersaturation at 50, 70 and 90°C; the second was an autoclave study undertaken to measure the equilibrium solubility of boehmite in 0.1 $\bar{N}$ NaOH at a series of temperatures ranging from 125 to in excess of 250°C. Because these experiments have not previously been published, the experimental procedures and results will be described here in detail.

The boehmite was synthesized, as no naturally occurring material was sufficiently free of contaminating phases. An aluminum hydroxide gel was prepared according to the method of Milligan and McAtee (1956). The dried gel was compressed into pellets under 14,000 psi pressure, and then crushed into −10 mesh fragments, which were wrapped in silver foil and inserted into a 32 ml Morey bomb. The Morey bomb was closed with a copper seal and the boehmite synthesized in the presence of water at 375°C and 400 bars over a 4-day period. The product was dispersed in a Waring blender, washed in 15 percent hydrochloric acid, filtered and dried. Although individual crystals of boehmite could not be identified under the microscope, the product gave an x-ray diffraction pattern of well crystallized boehmite.

Temperature measurements below 100°C were made using a standard laboratory mercury thermometer accurate to ±0.2°C. Above 100°C, when an autoclave was used for solubility determinations, temperature was measured using a chromel-alumel thermocouple, which had an accuracy of ±1.0°C.

pH measurements below 100°C were made directly in the reaction vessel at the operating temperature as described in Appendix B. pH measurements on solution samples taken from the autoclave, were made after the samples had been quenched and equilibrated at 25°C.

Aluminum determinations were made using the same method as described in Appendix B.

Analyses of sodium in solution were performed by atomic absorption. Standards were made up from Baker's A.R. reagent sodium hydroxide, Lot No. 37646. Eighty grams of sodium hydroxide were rapidly weighed out and dissolved to make one liter of stock solution. This was then used to prepare two sets of standards ranging from 0 to 0.016 $\bar{N}$ and 0 to 0.10 $\bar{N}$ Na^+ respectively.

A Model 303 Perkin-Elmer atomic absorption spectrophotometer was used to measure the absorption of the 3302 Å resonance line. The light source was an arc discharge lamp, and the flame was produced with an acetylene-air mixture.

1.1 Solubility of Boehmite Between 50 and 90°C

Solubility measurements between 50 and 90°C were made using two jacketed one liter reaction vessels supplied by the Scientific Glass Apparatus Company (Catalog No. JR5130). These vessels were specially modified with flat bases and polypropylene liners. One contained a N.B.S. standard borax buffer, to calibrate the pH electrode and the other held the solution. The reaction vessels were covered with 1-inch thick polypropylene lids containing wells to allow the insertion and retention of electrodes. Stirring of the solutions was accomplished with stainless steel agitators, which were driven by Precision Scientific 20 watt AC/DC motors controlled through Variac transformers. Temperature was maintained to within 0.1°C up to 90°C by a Haake temperature controller, Model E2, which also pumped water through the jackets of the two reaction vessels.

Five grams of boehmite was introduced into the stirred reaction vessel together with one liter of approximately 0.01 $\bar{N}$ sodium hydroxide. Samples of the solution were taken at intervals ranging from one to two days and analyzed for aluminum and pH.

Solubility measurements were attempted at 30, 40, 50, 70 and 90°C. However, reaction rates were so low at 30 and 40°C that no satisfactory equilibrium value could be obtained. At 50°C, the experiment lasted for over 600 hours, but the equilibrium concentration had still not been attained (Figure D.1). Results at 70 and 90°C produced satisfactory and reproducible equilibrium values after 150 and 36 hours, respectively. The experimental results for these runs are given in Table D.1.

Individual measurements, given in Table D.1, were used to calculate log Q_{s4}, using the EQ3 code (Wolery, 1983) and plotted versus time as illustrated in Figure D.1. Log K'_{s4} for the respective temperatures are summarized in Table D.3.

Because the run at 50°C had not attained equilibrium by the time the experiment was terminated, an attempt was made to extrapolate the trend of the data to the final equilibrium concentration using absolute rate theory (Glasstone et al., 1941). It is assumed that the rate controlling reaction[1] is:

$$\mathrm{AlOOH + H_2O + OH^- = Al(OH)_4^-}$$

where the reaction involves the formation of an activated surface complex C*, thus:

$$\mathrm{AlOOH + H_2O + OH^-} \underset{k_b}{\overset{k_f}{\rightleftarrows}} \mathrm{C^*} \underset{k_b}{\overset{k_f}{\leftrightarrows}} \mathrm{Al(OH)_4^-}$$

in which two reactions participate in the formation and destruction of the activated complex, and where

$$\frac{k_f}{k_b} = K_f^*, K_b^*$$

K_f^* and K_b^* are equilibrium constraints relating the activated complex with the reactants and products respectively, and where

$$K_f^* = \frac{[C^*]}{[\mathrm{AlOOH}][\mathrm{H_2O}][\mathrm{OH^-}]} \; ; \; K_b^* = \frac{[C^*]}{[\mathrm{Al(OH)_4^-}]}$$

where [ ] denote activities.

From absolute rate theory, the rate of formation of the surface activated complex is;

$$\frac{dn(\mathrm{Al})_f}{dt} = \frac{\kappa kT}{h}[C^*]$$

$$= \frac{\kappa kT}{h} K_f^*[\mathrm{AlOOH}][\mathrm{H_2O}][\mathrm{OH^-}]$$

---

[1] Studies by Van Straten (1984) suggest that the pseudo boehmite precipitation rate is proportional to the relative supersaturation, $(\Pi-1)$. But Misra and White (1971), King (1973), and Van Straten (1984) found that gibbsite precipitation rates showed a second order dependence with respect to supersaturation. Furthermore, Scotford and Glastonbury (1972) found that the dissolution rate of boehmite exhibited a dependence on the term $[\mathrm{NaOH}][\mathrm{H_2O}]$, which was first order above 210 g.l^{-1} $\mathrm{Na_2O}$, but half order below that concentration. Clearly, the interpretation given above must be considered only as an exploratory exercise.

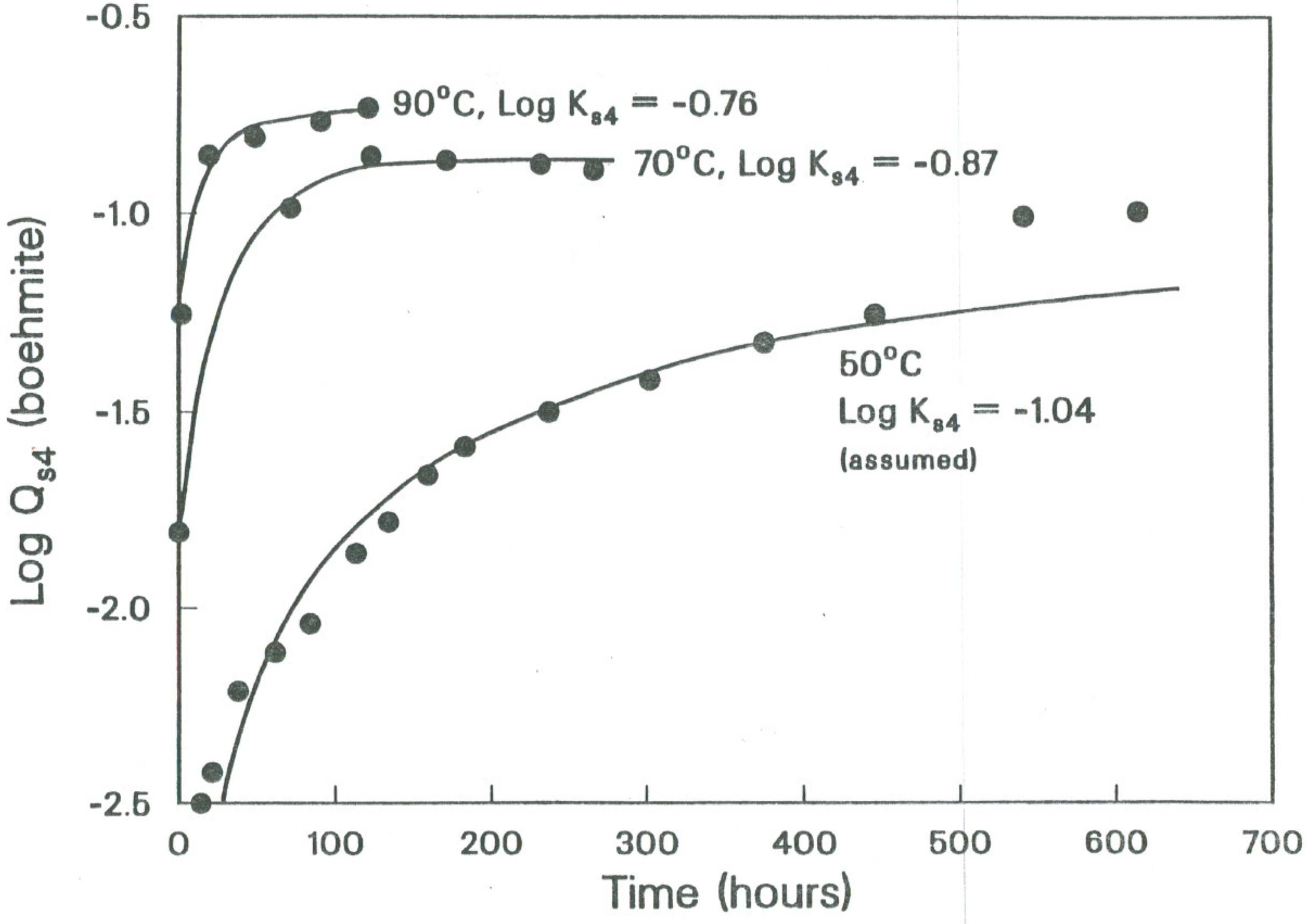

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Figure D.1. The approach to saturation of boehmite with time in a 0.01 $\bar{N}$ sodium hydroxide solution at 50, 70 and 90°C.

where κ = transmission coefficient
n = moles of Al going into solution
k = Boltzmann's constant
T = Absolute temperature
h = Planck's constant
t = time

Let

$$\frac{\kappa kT}{h} K_f^* = k_f'$$

where k_f' is the specific forward rate constant. Hence:

$$\frac{d[n(Al)]_f}{dt} = k_f'[AlOOH][H_2O][OH^-]$$

and similarly, for the corresponding back reaction:-

$$\frac{d[n(Al)]_b}{dt} = k_b'[Al(OH)_4^-]$$

These equations reflect the rate of aluminum transfer across the boehmite/aqueous phase interface in terms as mass.(unit surface area)$^{-1}$.(unit time)$^{-1}$, and are expressed as surface activity, rather than concentration to maintain consistency of units. However, what is actually measured is the change in concentration of alumina in solution represented as mass.(unit mass liquid)$^{-1}$.(unit time)$^{-1}$. Because the experiment was conducted in alkaline solution, the only alumina species present is the aluminate ion, $Al(OH)_4^-$.

By converting units, and letting

$$[n(Al)] \cdot \frac{A}{M} = [Al(OH)_4^-] \text{ mole}\cdot(\text{kg solvent})^{-1} \quad ,$$

where A = area of the boehmite and M = mass of solvent, the net change in aluminum activity with time can be written as

$$\frac{d[Al(OH)_4^-]}{dt} = k_f' \frac{A}{M}[AlOOH][H_2O][OH^-] - k_b' \frac{A}{M}[Al(OH)_4^-]$$

Assuming $[AlOOH][H_2O] \simeq 1$, integration yields

$$[Al(OH)_4^-]_{(t)} = [Al(OH)_4^-]_{t=0}\, e^{-k_b' \frac{A}{M} t} + \frac{k_f'[OH^-]}{k_b'}\left[1 - e^{-k_b' \frac{A}{M} t}\right]$$

Because the surface area of the boehmite was not measured, the parameters, $k_b'' = k_b' \frac{A}{M}$, and $k_f'' = k_f' \frac{A}{M}$ were determined.

Dividing throughout by $[OH^-]$ yields

$$Q_{s4}(t) = Q_{s4}(t{=}0)e^{-k_b' t} + \frac{k_f''}{k_b''}(1 - e^{-k_b'' t})$$

where

$$\frac{k_f''}{k_b''} = K_{s4} \, .$$

Regression of the expression against the data at 70 and 90°C yielded satisfactory fits where log $K_{s4} = -0.87$ and -0.76 respectively, as illustrated in Figure D.1. However, the data at 50°C proved to be insufficiently accurate to permit precise determination of K_{s4}. The problem was circumvented by calculating k_b'' from an assumed $\log K_{s4} = -1.04$, and regressing to obtain Q_{s4} (t=0) and k_f''. The less-than-perfect fit is illustrated in Figure D.1. The results at all three temperatures are not sufficiently precise to permit the assumption that the reaction proposed actually reflects the dissolution mechanism. Resolution of this issue will require more precise experimental results than those given here.

1.2 Solubility of Boehmite Between 121 and 255°C

Measurements of boehmite solubility between 121 and 255°C along the aqueous phase saturation surface were made using a one-gallon 316 stainless steel stirred autoclave fabricated by Autoclave Engineers. Ten grams of boehmite, prepared as described above was added to two liters of 0.01 $\bar{N}$ sodium hydroxide solution. The autoclave was sealed and raised to the appropriate temperature. After equilibration 24 hours later, 25 ml of solution was drawn off and rejected. An additional 25 ml was then sampled and quenched to 25°C, and the pH and concentrations of sodium and aluminum measured. The temperature was then raised 20°C and this process repeated.

The measurements of pH, Na(aq), and Al(aq) expressed as Na^+ and Al^{+++}, for each temperature are tabulated in Table D.2, together with calculated values of total dissolved solids and solution densities at 25°C.

Preliminary calculations indicated that a discrepancy arises between the measured pH (at 25°C) and that calculated from the sodium analysis when it is assumed that the only neutral salts in solution are NaOH and $NaAlO_2$ The discrepancy may be reconciled if it is assumed that another contaminating anion was present in solution, but not analyzed for, such as carbonate or chloride. Speciation in solution was therefore distributed at 25°C using the EQ3 code (Wolery, 1983) assuming that electrical neutrality could be achieved by the addition of chloride ion. Table D.2 shows the concentration of chloride ion required. The species in solution were then redistributed at the autoclave temperature and log K_{s4}'(boehmite) determined. These are summarized in Table D.3.

TABLE D.1

BOEHMITE SOLUBILITY MEASUREMENTS IN DILUTE SODIUM HYDROXIDE SOLUTION AS A FUNCTION OF TIME AT 50, 70, AND 90°C

T,°C	Time, hr	ρ, at 25 °C $g.cm^{-3}$ (calculated)	TDS, $mg.l^{-1}$ (calculated)	pH	Na^+, M	Al^{+++}, M	log Q_{s4} (calculated)
49.65	12.25	0.997	401.2	11.180	0.01	0.0000284	-2.50
	19.25	"	401.3	11.166	"	0.0000324	-2.42
	35.75	"	402.0	11.206	"	0.0000467	-2.21
	61.25	"	402.9	11.178	"	0.0000693	-2.11
	83.50	"	403.7	11.202	"	0.0000873	-2.04
	113.50	"	405.3	11.195	"	0.0001272	-1.86
	133.50	"	406.5	11.197	"	0.000155	-1.78
	158.50	"	409.3	11.233	"	0.000223	-1.66
	180.75	"	410.2	11.207	"	0.000244	-1.59
	235.25	"	413.0	11.218	"	0.000309	-1.50
	302.00	"	415.9	11.226	"	0.000379	-1.42
	374.00	"	420.1	11.226	"	0.000480	-1.32
	444.75	"	425.8	11.264	"	0.000614	-1.25
	540.75	"	434.4	11.151	"	0.000821	-1.01
	612.25	"	443.0	11.236	"	0.001025	-1.00
70.05	0.00	0.997	401.8	10.219	0.01	0.000043	-1.81
	70.75	"	412.7	10.245	"	0.000304	-0.99
	121.25	"	416.8	10.239	"	0.000401	-0.86
	169.25	"	418.5	10.287	"	0.000442	-0.87
	235.75	"	418.3	10.295	"	0.000437	-0.88
	264.75	"	419.5	10.325	"	0.000465	-0.89
90.05	0.00	0.997	413.6	10.125	0.01	0.000323	-1.25
	18.50	"	430.6	10.087	"	0.000729	-0.85
	23.50	"	432.2	10.098	"	0.000767	-0.84
	48.50	"	436.5	10.120	"	0.000869	-0.81
	89.75	"	440.8	10.123	"	0.000972	-0.77
	120.25	"	450.9	10.178	"	0.001213	-0.73

TABLE D.2

BOEHMITE SOLUBILITY MEASUREMENTS BETWEEN 121 AND 255°C IN DILUTE SODIUM HYDROXIDE SOLUTION

T,°C	ρ, at 25°C g.cm^{-3} (calculated)	TDS mg.l^{-1} (calculated)	pH at 25°C	Na^{+}, M	$^{+}$, M	Cl^{-} m (calculated)
121.05	0.997	537.0	(11.75)	0.0112	0.00212	0.00264
123.25	"	540.7	11.73	0.0112	0.00221	0.00284
			11.75	"	"	0.00255
153.85	"	575.2	11.66	0.0112	0.00303	0.00294
			11.68	"	"	0.00269
184.05	"	636.0	11.62	0.0014	0.00429	0.00234
			11.57	"	"	0.00285
217.65	"	720.3	11.44	0.0019	0.00582	0.00292
			11.42	"	"	0.00307
241.85	"	811.3	11.43	0.0130	0.00694	0.00296
			11.44	"	"	0.00289
256.05	"	1073.7	11.48	0.0170	0.00938	0.00410
			11.54	"	"	0.00357
255.05	"	1934.5	11.76	0.0317	0.01588	0.00885
			11.79	"	"	0.00834

(–) Estimated value

TABLE D.3

SUMMARY OF VALUES OF LOG K'_{s4}(BOEHMITE)

T,°C	$\frac{1}{T}\times10^3$, K^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}	Average, log K'_{s4}
49.65	3.098	-0.00017	0.0114	—	-1.04
70.05	2.914	-0.00006	0.0040	—	-0.87
90.05	2.753	-0.00012	0.0077	—	-0.76
121.05	2.537	-0.00017	0.0122	-0.481	-0.48
123.25	2.523	"	"	-0.443	-0.45
"	"	"	"	-0.463	
153.85	2.342	"	"	-0.235	-0.22
"	"	"	"	-0.215	
184.05	2.187	"	0.0114	-0.044	-0.02
"	"	"	"	-0.006	
217.65	2.037	"	"	+0.268	
"	"	-0.00018	0.0119	+0.353	+0.35
241.85	1.942	-0.00019	0.0130	+0.343	
256.05	1.890	-0.00025	0.0170	+0.430	+0.40
"	"	"	"	+0.370	
255.05	1.893	-0.00045	0.0316	+0.367	+0.35
"	"	"	"	+0.337	

APPENDIX E

SUMMARY OF EXPERIMENTAL DATA FROM THE LITERATURE AND CALCULATIONS TO DETERMINE THE SOLUBILITY PRODUCTS OF DIASPORE

TABLE E.1

DIASPORE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS
REPORTED BY BERNSHTEIN AND MATSENOK (1965)

T,°C	Na_2O, wt. %	Al_2O_3, wt. %
250	11.5	13.7
	15.5	19.7
	18.3	23.8
	20.7	28.2
	22.9	33.7
300	6.4	8.3
	10.8	14.4
	14.4	19.6
	17.6	24.9
	20.2	29.3

TABLE E.2

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4} (DIASPORE)
FROM EXPERIMENTAL RESULTS OF BERNSHTEIN AND MATSENOK (1965)

T,°C	TDS, mg.kg H_2O^{-1}	Na^+, m	Al^{+++}, m	log $[H_2O]$	Ionic Strength	log K'_{s4}
250	353573	5.023	3.637	-0.0849	4.389	+0.821
	567936	7.841	6.059	-0.1128	6.730	+1.125
	760952	10.399	8.220	-0.0715	8.795	+1.287
	997319	13.340	11.049	+0.1354	11.422	+1.399
	1341898	17.305	15.480	+0.8929	15.614	
300	177766	2.432	1.917	-0.0374	2.275	+0.821
	347657	4.697	3.807	-0.0765	4.345	+0.991
	531974	7.119	5.890	-0.0996	6.552	+1.120
	761020	10.001	8.601	-0.0470	9.271	+1.231
	1007779	13.087	11.539	+0.2088	12.203	+1.110

TABLE E.3

DIASPORE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY CHANG ET AL. (1979)

T,°C	Time, hr	Na_2O (initial), concentration, g.l^{-1}	AlO_2^-, M
250	116	6.8	0.08
	116	13.6	0.15
	95	22.3	0.22
	97	31.6	0.33
	94	63.6	0.51
	100	91.5	0.77
280	72	6.2	0.10
	72	13.6	0.23
	71	22.3	0.34
	71	31.6	0.48
	72	63.6	1.08
	70	119.0	2.29
300	82	4.9	0.09
	74	9.9	0.17
	74	22.3	0.39
	48	31.6	0.57
	70	45.6	0.83
	69	63.6	1.16
	7	91.1	1.81
	70	150.7	3.73
325	56	6.2	0.13
	65	13.6	0.21
	47	22.3	0.46
	48	32.5	0.71
	48	68.6	1.41
	45	119.0	2.80
	45	150.7	4.34

TABLE E.4

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4} (DIASPORE) FROM EXPERIMENTAL RESULTS OF CHANG ET AL. (1979)

T,°C	ρ, at 25 °C $mg.cm^{-3}$	TDS, $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{+++}, M	log [H_2O]	Ionic Strength	log K'_{s4}
250	1.011	12135	5045	0.08	-0.00301	0.2112	-0.197
	1.023	23849	10089	0.15	-0.00604	0.4125	-0.216
	1.039	38017	16543	0.22	-0.01006	0.6581	-0.263
	1.056	54636	23443	0.33	-0.01455	0.9146	-0.204
	1.104	103492	47182	0.51	-0.03148	1.700	-0.298
	1.148	150416	67880	0.77	-0.04774	2.335	-0.216
280	1.011	12199	4600	0.01	-0.00269	0.1923	+0.055
	1.027	27207	10089	0.23	-0.00592	0.4134	+0.128
	1.044	43053	16543	0.34	-0.00988	0.6602	+0.065
	1.063	61023	23443	0.48	-0.01432	0.9191	+0.086
	1.128	127419	47182	1.08	-0.03113	1.797	+0.253
	1.234	249711	88281	2.29	-0.06419	3.323	+0.487
300	1.008	10102	3635	0.09	-0.00210	0.1519	+0.182
	1.019	19913	7344	0.17	-0.00421	0.3001	+0.144
	1.047	45152	16543	0.39	-0.00971	0.6581	+0.205
	1.067	46710	23443	0.57	-0.01383	0.9068	+0.258
	1.096	93693	33829	0.83	-0.02110	1.468	+0.300
	1.131	130776	47182	1.16	-0.03077	1.803	+0.336
	1.187	193552	67583	1.81	-0.04666	2.592	-0.477
	1.311	351067	111798	3.73			
325	1.012	13459	4600	0.13	-0.00256	0.1895	+0.364
	1.026	26368	10089	0.21	-0.00564	0.3933	+0.095
	1.050	48091	16543	0.46	-0.00943	0.6580	+0.412
	1.075	71748	24110	0.71	-0.01415	0.9587	+0.511
	1.147	147723	47182	1.41	-0.03017	1.860	+0.586
	1.251	271117	88281	2.80	-0.06229	3.566	+0.739
	1.329	376670	111798	4.34	-0.08020	4.918	+1.255

TABLE E.5

DIASPORE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS BY DRUZHININA (1955)*

T,°C	Na_2O, wt. %	Al_2O_3, wt. %
200	11.4	9.5
	12.1	9.8
	11.9	10.2
	16.1	15.7
	16.6	16.2
	19.6	22.1
	20.0	22.5
	19.4	22.6
	19.9	22.8

*Data obtained from figure 1.

TABLE E.6

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(DIASPORE) FROM EXPERIMENTAL RESULTS BY DRUZHININA (1955)

T,°C	TDS, mg.kg H_2O^{-1}	Na^+, m	Al^{+++}, m	log $[H_2O]$	Ionic Strength	log K'_{s4}
200	290900	4.7486	2.4056	-0.0823	3.811	0.357
	310360	5.1161	2.5190	-0.0891	4.023	0.355
	311584	5.0363	2.6242	-0.0876	4.022	0.404
	505485	7.7725	4.6364	-0.1264	5.913	0.733
	532855	8.2106	4.8710	-0.1289	6.126	0.753
	769655	11.1921	7.6716	-0.0913	8.481	1.118
	796538	11.5940	7.9290	-0.0761	8.724	1.126
	774476	11.1080	7.8665	-0.0941	8.592	1.180
	800353	11.5605	8.0518	-0.0775	8.799	1.161

TABLE E.7

DIASPORE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS BY DRUZHININA (1955)[1]

T,°C	Na_2O, g.l^{-1}	Al_2O_3, g.l^{-1}
200	147	123
	217	215
	226	222
	281	322
	285	328
	289	336
	294	342
220	139	133
	144	136
	153	140
	141	143
	201	215
	233	271
	255	293
	265	310
	278	331
	291	348

[1] Data obtained from figure 2.

TABLE E.8

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4} (DIASPORE) FROM EXPERIMENTAL RESULTS BY DRUZHININA (1955)

T,°C	ρ, at 25°C, g.cm^{-3}	TDS, mg.l^{-1}	Na^+, M	Al^{+++}, M	log [H_2O]	Ionic Strength	log K'_{s4}
200	1.246	290335	4.743	2.413	-0.0863	3.954	0.376
	1.342	457086	7.002	4.217	-0.1274	6.019	0.754
	1.352	474465	7.293	4.355	-0.1293	6.238	0.767
	1.421	627782	9.068	6.316	-0.0826	8.717	1.157
	1.426	637885	9.197	6.434	-0.0729	8.894	1.172
	1.430	649634	9.326	6.591	-0.0600	9.136	1.197
	1.435	661027	9.487	6.708	-0.0441	9.348	1.179
220	1.243	288902	4.485	2.609	-0.0807	3.884	0.502
	1.249	297826	4.647	2.668	-0.0840	3.999	0.500
	1.259	312735	4.937	2.746	-0.0899	4.189	0.489
	1.249	299717	4.550	2.805	-0.0823	4.008	0.576
	1.329	436435	6.486	4.217	-0.1178	5.785	0.816
	1.372	523841	7.519	5.316	-0.1207	7.099	1.050
	1.395	570349	8.229	5.747	-0.1065	7.799	1.083
	1.407	597252	8.551	6.080	-0.0919	8.268	1.141
	1.421	631320	8.971	6.493	-0.0622	8.936	1.124
	1.435	662095	9.390	6.826	-0.0203	9.603	0.928

APPENDIX F

DIASPORE SOLUBILITY MEASUREMENTS BETWEEN 25 AND 350°C

1.0 Introduction

Diaspore is more thermodynamically stable below 500 bars pressure than either gibbsite or boehmite in the liquid aqueous phase over the temperature range between 0°C and 350°C. It would therefore appear to be an ideal mineral phase for calibrating the thermodynamic properties of aluminum species in solution. However, as shown below, diaspore is difficult to equilibrate with the aqueous phase in alkaline solutions below 200°C, apparently because the kinetics of dissolution and precipitation are very slow. In many experiments to measure diaspore solubility below this temperature, the senior author found that competing reactions involving the formation of boehmite (or surface phases) appear to dominate chemical equilibria with respect to aluminum in solution.

In the following sections, the results of six scoping experiments are reported, in which determination of the solubility of diaspore was attempted in alkaline solutions over the temperature range between 25°C and 350°C. Table F.1 summarizes these experiments.

2.0 Experimental

Temperature measurements below 100°C were made using a standard laboratory mercury thermometer accurate to +0.2°C. Above 100°C, when autoclaves were used for solubility determinations, the temperature was measured using chromel-alumel thermocouples, read from either a Speedomax, model S strip chart recorder of a Leeds and Northrup Series 60 D.A.T Control unit, and/or an Omega digital thermocouple.

pH measurements on runs below 100° were made directly in the reaction vessel at the operating temperature as described in Appendix B. Samples drawn from autoclaves above 100°C were rapidly quenched and the pH measured at 25°C. For experiment 2, the electrodes and calibration methods used were as described in Appendix D. For experiments 3, 4 and 5, either Vanlab or Radiometer combination glass pH electrodes were used, standardized immediately before and after use against Mallinkrodt Buffar standard buffer solutions at pH = 7.0 and 10.0, or against corresponding Radiometer buffers. For experiment 6, an Orion 91-05 combination electrodes were used. A 2–3 ml aliquot of the solution sample was agitated under a nitrogen atmosphere, the nitrogen having been passed over Ascarite to remove traces of CO_2. The electrode system potential was measured by a Copenhagen Radiometer, model PHM84 pH meter and recorded continuously by a Precision Digital Model 1045 recorder, thereby facilitating observation of transient changes in pH.

Aluminum in solution was determined using the method of Packham (1958), except for experiment 4, when a lumogallion method (Nishikawa et al., 1967; Shigematsu et al., 1970) was used, and experiment 6, when aluminum was determined using an ARL model 3510 PC inductively coupled plasma spectrophotometer. Sodium measurements for experiment 2 were conducted as described in Appendix D. For experiments 3, 4 and 5, both specific ion potentiometry using Orion Research sodium electrodes 94-11 and 96-11, and Perkin Elmer atomic absorption spectrophotometers models 560 and 3030 were employed. For experiment 6, Na^+ was analysed using the ARL model 3510 PC I.C.P. spectrophotometer. Sample solutions required dilution in all cases, which was carried out using Gilson and Eppendorff micro-pipettes. Standard solutions ranging from 2.00 to 50.00 ppm. that were used for calibration purposes.

Chloride analyses were made using a chloride ion specific electrode (Orion Research models 94-17, 94-35 and 94-53). For convenience, most analyses were made by direct comparison of the potentials of the

TABLE F.1

EXPERIMENTS TO MEASURE DIASPORE SOLUBILITY

No.	Investigator(s)	Diaspore Source Range, °C	Temperature M	NaOH, electrolyte	Supporting measured	Parameters
1	Apps	Chester, Mass.	25–99	0.01	—	pH, Al^{+++}
2	"	Chester, Mass.	125–260	0.010	—	pH*, Na^{+}, Al^{+++}
3	Apps and Neil	Nev.	175, 250, 325	0.0001	0.01 $\bar{N}$ NaCl	pH*,'other'†
4	"	S.W. Anatolia, Turkey	100–350	0.0	0.01 $\bar{N}$ NaCl	pH*,'other'†
5	"	S.W. Anatolia, Turkey	100–350	0.001	0.01 $\bar{N}$ NaCl	pH*,'other'†
6	Apps and Landers	S.W. Anatolia, Turkey	197	0.01	—	pH*, Na^{+}, Al^{+++}

*pH measured at 25°C on quenched solution sample drawn from the autoclave at operating temperature.

†'other' = Na^{+}, K^{+}, Ca^{++}, Al^{+++}, SiO_2 aq, Cl^{-}, MoO_4^{--}

samples against the potential of standards. However, some analyses were conducted using the chloride ion specific electrode as an end point indicator during silver nitrate titrations.

Because of concern that contaminants could be present in natural diaspore samples, and because of the discovery that the Hastelloy C autoclave alloy, used for experiments 3, 4 and 5 was contributing molybdenum to the solution, additional supplementary analyses on the sample solutions were made. These included silica, analysed colorimetrically by the molybdenum yellow method (American Public Health Association, 1975), potassium, by atomic absorption, using standards made up in sodium chloride solutions of equivalent ionic strength to those used in the experiments, calcium by atomic absorption, using the method of additions for most samples, and molybdenum by atomic absorption, which was independently checked using a Dionex 2020i liquid ion chromatography system. In experiment 6, the autoclave was chromium plated to minimize molybdenum contamination.

In all supplementary atomic absorption measurements, a Perkin Elmer model 303 atomic absorption spectrophotometer was used.

2.1 Solubility of Diaspore in 0.10 $\bar{N}$ NaOH Between 25 and 99°C

The equipment used for experiment 1, between 25 and 90°C was as described for the measurement of boehmite solubilities over a similar temperature range (Appendix D). The diaspore came from Chester, Massachusetts, and was part of the same collection of samples at Harvard University used by King and Weller (1961) in their calorimetric investigation of diaspore.

Coarsely crystalline aggregates of the Chester material were crushed to -35 mesh in a manganese steel pestle and mortar. They were then ground to –300 mesh in a Fisher motor-driven mortar grinder. Both X-ray and optical studies revealed the existence of no additional phases.

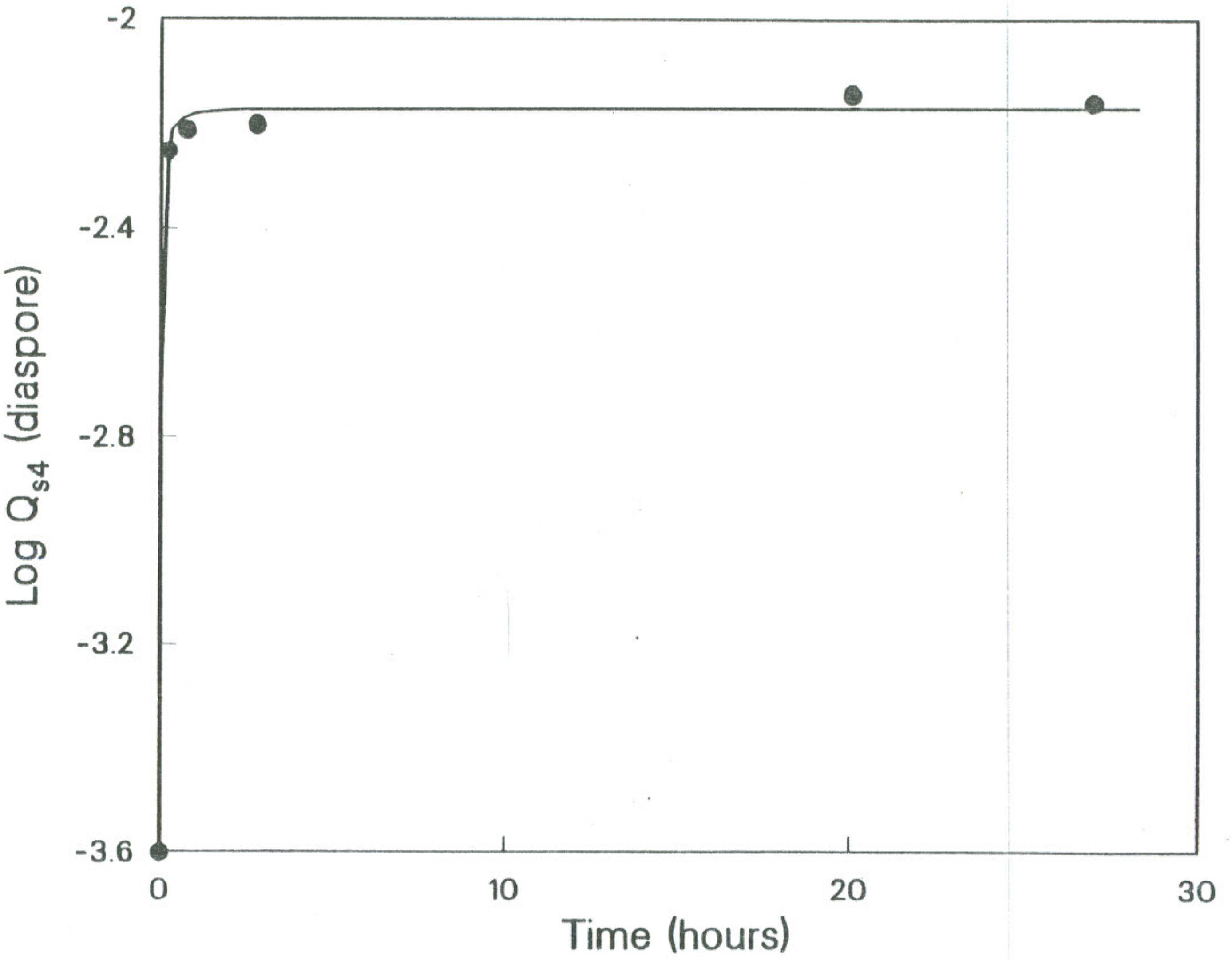
An initial study in which 10 grams of diaspore were agitated with one liter of 0.074 N sodium hydroxide at 25°C, (Table F.2 and Figure F.1), suggested that diaspore tends to reach an ''equilibrium'' state very rapidly in an alkaline solution, 90 percent ''equilibration'' having been achieved within the first half hour. Over time, a slight upward drift in pH, accompanied by a corresponding increase in aluminum concentration was noted. However, the computed solubility products remained unchanged to within experimental error. The data were fitted to an analogous expression used to model the kinetics of boehmite dissolution, using absolute rate theory (Appendix D), represented by the continuous line on Figure F.1. The fit does not give any indication that the model is an accurate representation of the dissolution mechanism.

Based on this finding, a similar experiment was set up in which 10 grams of diaspore were agitated with 0.1 $\bar{N}$ sodium hydroxide at various temperatures between 30 and 99°C. The solutions were allowed to equilibrate for 24 hours, after the solution was sampled the pH and aluminum concentration was measured. Sampling was repeated 8 to 10 hours later to check for equilibration. The temperature was then raised approximately 10°C and the process repeated.

The experimental results are given in Table F.3. These were used to calculate log Q_{s4}(diaspore) using the EQ3 code of Wolery (1983). Estimated values of log K_{s4}(diaspore) are summarized in Table F.5.

2.2 Solubility of Diaspore in 0.01 $\bar{N}$ NaOH Between 124 and 260°C

Solubility measurements between 124 and 260°C along the aqueous phase saturation surface were made using a one-gallon, 316 stainless steel, mechanically agitated autoclave as used for similar boehmite solubility measurements. Five grams of diaspore from Chester, Massachusetts, ground to –200 mesh were added to 3 liters of 0.01 $\bar{N}$ sodium hydroxide. The sampling and analysis procedure was the same as adopted for boehmite solubility measurements, (Appendix D).



XCG 865-7248

Figure F.1. The dissolution of 10 g of minus 300 mesh diaspore in 0.764 $\bar{N}$ sodium hydroxide at 25°C.

TABLE F.2

DIASPORE SOLUBILITY MEASUREMENTS IN DILUTE SODIUM HYDROXIDE SOLUTION AS A FUNCTION OF TIME AT 25°C

Time, hours	ρ at 25°C, g.cm^{-3} (calculated)	TDS, mg.l^{-1} (calculated)	pH	Na$^+$, M	Al^{+++}, mg.l^{-1}
0	1.0	2960	(12.75)	0.074	0.5
0.25			(12.75)		11.0
0.75			(12.75)		12.0
2.75			(12.75)		12.4
20.0			12.75		13.9
27.0			12.77		14.2

Time, hours	log [H_2O]	Ionic Strength	log Q_{s4}
0	-0.00108	0.0731	-3.59
0.25	-0.00109	0.0735	-2.25
0.75			-2.21
2.75			-2.20
20.0		0.0736	-2.15
27.0	-0.00115	0.0774	-2.16

( ) Estimated value.

TABLE F.3

DIASPORE SOLUBILITY MEASUREMENTS IN DILUTE SODIUM HYDROXIDE SOLUTION BETWEEN 30 AND 99°C

T,°C	ρ at 25°C, $g.cm^{-3}$ (calculated	TDS, $mg.l^{-1}$ (calculated)	pH	Na^+, M	Al^{+++}, M	log Q_{s4} (calculated)
28.90	1.001	3220	12.75	0.10	0.000517	-2.28
	"	3371	12.77		0.000533	-2.29
40.70	"	3297	12.40		0.000560	-2.25
	"	3453	12.42		0.000592	-2.25
51.30	"	3158	12.12		0.000651	-2.19
	"	3308	12.14		0.000687	-2.19
	"	3462	12.16		0.000705	-2.20
60.70	"	3971	12.00		0.000755	-2.24
	"	2588	11.81		0.000779	-2.02
	"	2708	11.83		0.000797	-2.03
	"	2709	11.83		0.000811	-2.03
	"	2771	11.84		0.000820	-2.03
	"	2836	11.85		0.000843	-2.03
	"	2837	11.85		0.000854	-2.03
80.50	"	2722	11.41		0.000967	-1.95
	"	2785	11.42		0.000994	-1.95
	"	2788	11.42		0.00102	-1.94
93.50	"	2248	11.08		0.00122	-1.83
99.10	"	2405	11.01		0.00126	-1.77
	"	2412	11.01		0.00134	-1.79

The experimental results are given in Table F.4, and were processed using the EQ3 code by Wolery (1983) to obtain log K_{s4}(diaspore). These values are summarized in Table F.5.

2.3 Solubility of Nevada Diaspore in 0.01 N NaCl Solution at 175, 250 and 325°C: Initial pH adjusted to 9.5

Solubility experiments were conducted in a one liter magnetically stirred autoclave fabricated by Autoclave Engineers from Hastelloy C-276. The experiment was carried out in a similar manner to that described for measurement of boehmite solubility at elevated temperature (Appendix D).

Owing to the unavailability of diaspore from Chester, Massachussetts, material from Nevada, was used instead. This material, purchased from Ward's Scientific Establishment consisted of coarse pinkish-hued crystals of diaspore intergrown with pyrophyllite and possibly kaolinite. The samples were crushed to –1/2 inch in a "Chipmunk" jaw crusher, then reduced further with a ceramic jaw crusher. The material was screened and the –65 + 100 mesh fraction subjected to a heavy liquid separation using methylene iodide, CH_2I_2. The heavy fraction, consisting principally of diaspore, with very small traces of pyrophyllite, as tentatively determined by X-ray diffraction, was passed through a Frantz magnetic separator to remove iron bearing minerals and again separated by methylene iodide.

A 60 g sample was sonicated eight times in ethyl alcohol and four times in acetone. Fifty grams of the cleaned –65 + 100 mesh material was added to 810 ml of 0.01 $\bar{N}$ NaCl solution previously sparged with nitrogen gas for 30 minutes and the pH adjusted to 9.5 with sodium hydroxide. The nitrogen had been passed through a bed of Ascarite to remove carbon dioxide.

The autoclave was brought up to operating temperature (175°C) and agitation commenced. Solution samples were taken at periodic intervals for six hours, then left overnight and another sample taken approximately 22 hours after starting the experiment. The temperature was then raised to 250°C and the sampling process repeated. Finally, the temperature was raised to 325°C and a final set of samples taken before terminating the run. Sampling involved drawing an initial 6 ml of sample, which was rejected, followed by a further 30 ml upon which analyses were conducted. One aliquot of 2–3 ml was used for pH measurements. Twenty milliliters were treated with 2–3 ml of 0.01 $\bar{N}$ KOH to prevent precipitation of silica and aluminum.

pH measurements were made under CO_2 free nitrogen atmosphere at 25°C and within 5–10 minutes of sampling. pH measurements on the solutions were recorded every five minutes until apparent equilibrium had been attained. Interpretation of the pH measurements is not easy. Figure F.2a, b and c show the actual measurements taken at 175, 250 and 325°C. It is not known whether the solution at 25°C attains internal equilibrium with respect to pH within the first few minutes of sampling, or whether equilibrium is achieved slowly, as manifested by the drift in pH. The pH of a typical solution at elevated temperature is significantly lower than that of the same solution at 25°C. Therefore if the solution was slow to attain equilibrium, this should be reflected by a long term rise rather than fall in pH. The decision was therefore made to accept the highest pH value measured as closest to the true pH of the quenched solution.

Aluminum and silica were determined colorimetrically. Sodium and chloride were determined using specific ion electrodes. The species K^+, Ca^{++} and MoO_4^{--} were measured by atomic absorption using an aliquot untreated with 0.01 $\bar{N}$ KOH. The experimental results are reported in Table F.6.

Upon opening the autoclave after completion of the run, an irregular piece of scale approximately 2 mm thick was found attached to the bottom of the autoclave. Subsequent XRD analyses indicated that the material was dominantly diaspore with traces of pyrophyllite. Quantitative determination of the composition of the cementing material was not made. However, by X-ray mapping with a scanning electron microscope, the scale appeared to be predominantly silica with very little alumina present.

TABLE F.4

DIASPORE SOLUBILITY MEASUREMENTS BETWEEN 121 AND 260°C IN DILUTE SODIUM HYDROXIDE SOLUTION

T,°C	ρ at 25°C, g.cm^{-3} (calculated)	TDS mg.l^{-1} (calculated)	pH	Na^{+}, M	Al^{+++}, M	Cl^{-} M (calculated)
124.0	0.997	417.3	11.77	0.00993	0.000475	0.00275
"	"	"	11.83	"	"	0.00175
160.0	"	507.3	11.73	0.01190	0.000743	0.00500
"	"	"	11.72	"	"	0.00514
"	"	"	11.83	"	"	0.00340
184.5	"	536.9	11.78	0.0124	0.000972	0.00450
"	"	"	11.80	"	"	0.00417
208.5	"	568.9	11.49	0.0125	0.001614	0.00735
"	"	"	11.47	"	"	0.00751
226.5	"	606.6	11.39	0.0127	0.00235	0.00755
"	"	"	11.38	"	"	0.00761
259.0	"	680.3	11.29	0.0128	0.00401	0.00656
"	"	"	11.34	"	"	0.00629
260.0	"	687.4	11.34	0.0128	0.00418	0.00612
"	"	"	11.35	"	"	0.00606

TABLE F.5

SUMMARY OF VALUES OF LOG K_{s4}(DIASPORE) FROM EXPERIMENTS 1 AND 2

T,°C	1/T, $K^{-1} \times 10^3$	log [H_2O]	Ionic Strength	log K_{s4}	Average log K_{s4}
29.8	3.311	-0.0015	0.1063	—	-2.28
40.7	3.186	-0.0016	0.1073	—	-2.25
51.3	3.082	-0.0016	0.1083	—	-2.19
60.7	2.995	-0.0014	0.0927	—	-2.03
80.5	2.828	-0.0013	0.0903	—	-1.94
93.5	2.727	-0.0010	0.0708	—	-1.83
99.1	2.686	-0.0011	0.0761	—	-1.78
124.0	2.518	-0.00015	0.00994	-1.15	-1.18
"	"	"	"	-1.21	
160.0	2.309	-0.00018	0.0119	-0.92	-0.95
"	"	"	"	-0.91	
"	"	"	"	-1.02	
184.5	2.185	"	0.0124	-0.85	-0.86
"	"	"	"	-0.87	
208.5	2.076	-0.00019	0.0125	-0.34	-0.33
"	"	"	"	-0.32	
226.5	2.001	"	0.0127	-0.08	-0.07
"	"	"	"	-0.07	
259.0	1.879	"	0.0128	+0.26	+0.23
"	"	"	0.0127	+0.21	
260.0	1.876	"	0.0127	+0.21	+0.21
"	"	"	0.0128	+0.21	

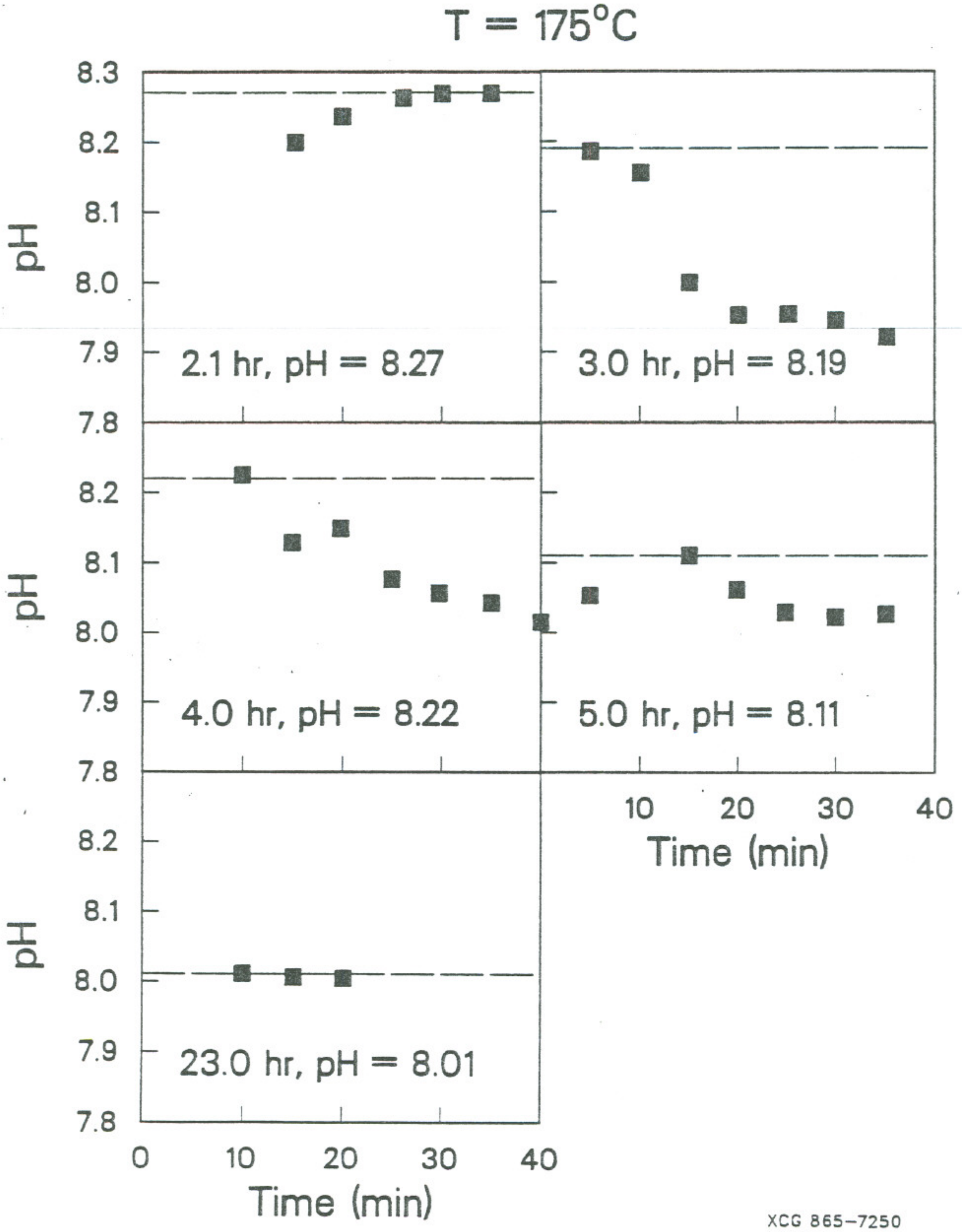


Figure F.2a. Variation of pH with time in solution aliquots quenched to 25°C, drawn from an autoclave at 175, 250 and 325°C. (a) 175°C.

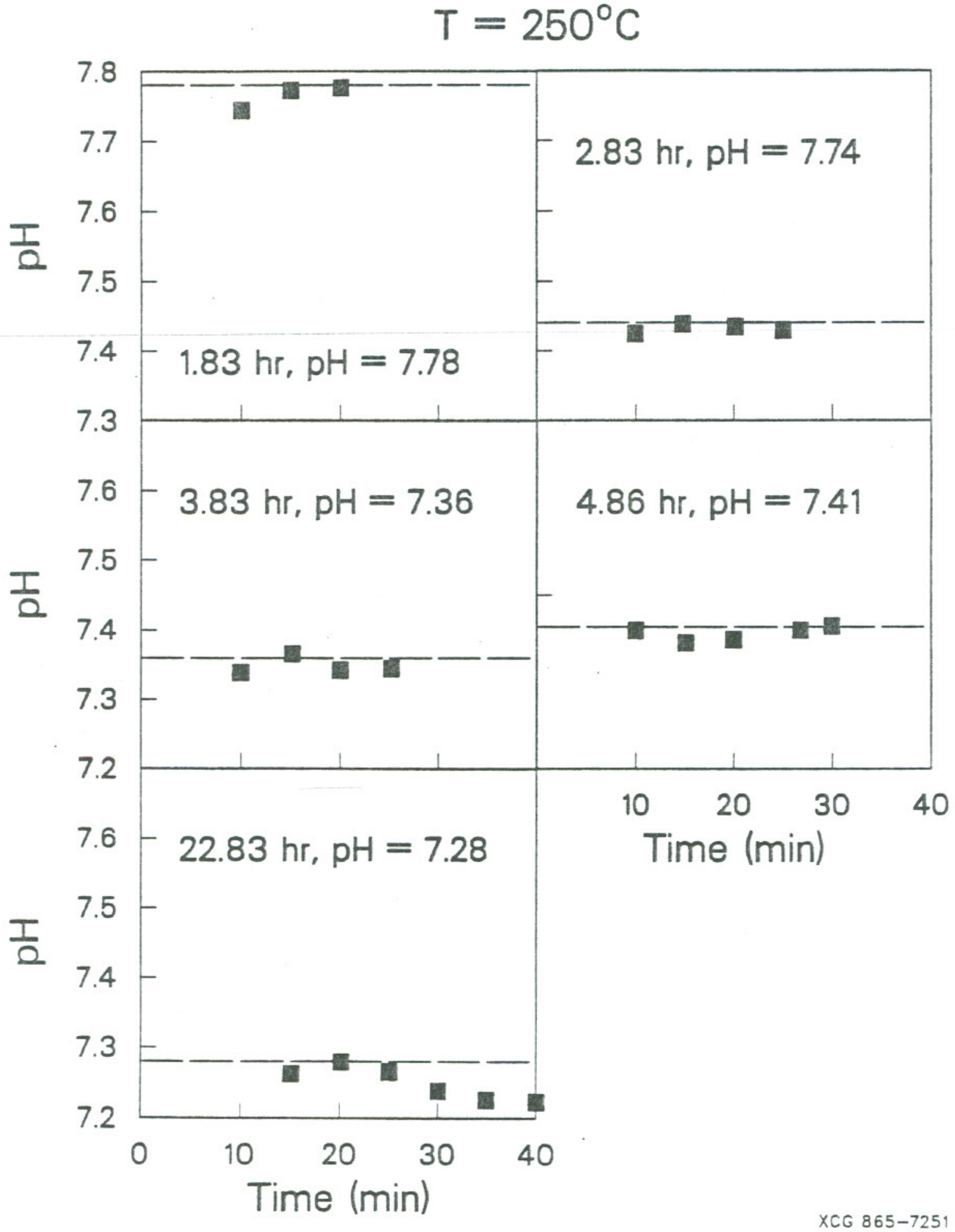


Figure F.2b. Variation of pH with time in solution aliquots quenched to 25°C, drawn from an autoclave at 175, 250 and 325°C. (b) 250°C.

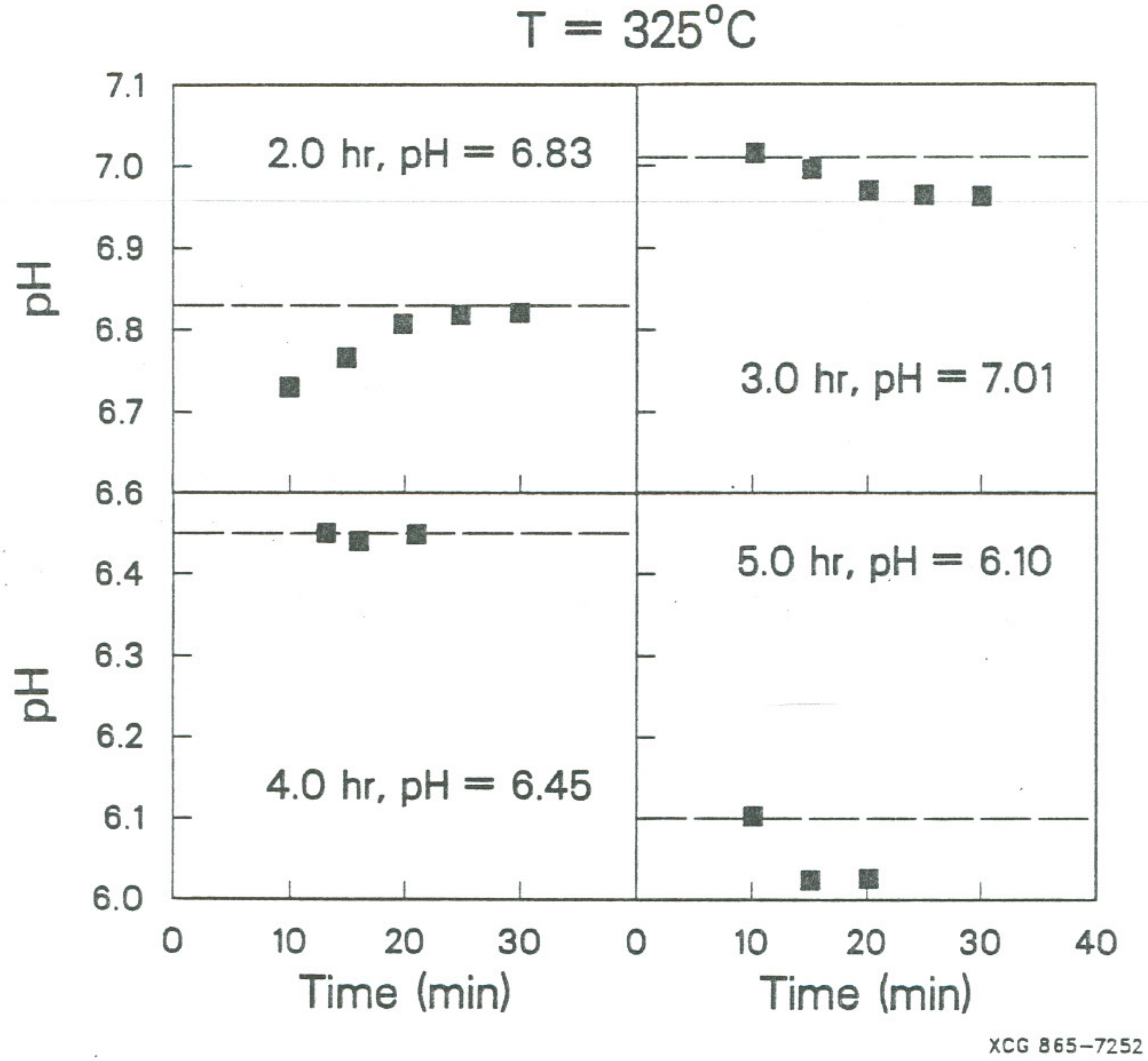


Figure F.2c. Variation of pH with time in solution aliquots quenched to 25°C, drawn from an autoclave at 175, 250 and 325°C. (c) 325°C.

TABLE F.6

DIASPORE SOLUBILITY MEASUREMENTS IN 0.01 $\bar{N}$ NaCl SOLUTION AT 175, 250 AND 325°C
INITIAL pH ADJUSTED TO 9.5 AT 25°C

T, °C	Time, hour	ρ at 25°C, $g.cm^{-3}$ (calculated)	TDS, $mg.l^{-1}$ (calculated)	pH	Na^+, $mg.l^{-1}$	K^+, $mg.l^{-1}$	Ca^{++}, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	SiO_2 aq, $mg.l^{-1}$	Cl^{-1}, $mg.l^{-1}$
175	0	0.997	627	~9.5	275	(0.4)	(1.32)	0.025	n.d.	350
"	2.12	"	627	8.27	224	0.41	(1.32)	1.27	25.6	374
"	3.00	"	623	8.19	225	0.60	1.32	1.11	15.4	380
"	4.00	"	634	8.22	227	0.47	1.43	1.04	15.2	389
"	4.03	"	638	8.22	227	0.47	(1.43)	0.99	15.9	392
"	5.00	"	647	8.11	234	0.50	1.34	1.07	16.4	394
"	23.0	"	655	8.01	232	0.55	1.63	0.90	22.8	397
250	1.83	"	642	7.78	221	0.66	1.41	1.11	33.0	385
"	2.83	"	633	7.44	212	0.55	1.57	1.13	36.9	380
"	3.83	"	636	7.36	210	0.55	1.46	1.00	40.6	382
"	3.88	"	638	(7.38)	212	0.55	(1.46)	0.67	40.8	382
"	4.86	"	652	7.41	217	0.49	1.59	0.88	45.3	387
"	22.83	"	689	7.28	222	0.64	1.41	0.50	64.1	400
325	2.00	"	339	6.83	90.2	0.35	0.47	0.29	64.4	185
"	3.00	"	281	7.01	68.6	0.31	0.44	0.18	64.9	147
"	4.00	"	324	6.45	94.6	0.42	0.51	0.14	64.4	164
"	4.03	"	310	6.45	79.9	0.42	0.51	0.12	66.0	163
"	5.00	"	372	6.10	103	0.65	0.65	0.09	64.5	202

( ) Estimated Value

2.4 Solubility of Turkish Diaspore in 0.01 N NaCl Solution Between 100 and 350°C

The purpose of this study was to measure the minimum solubility of diaspore at several discrete temperatures between 100 and 350°C. The solubility measurements were made in neutral solution near the presumed isoelectric point. Because of the difficulties in separating diaspore from the matrix of material from Nevada, it was resolved to start with a pure material for subsequent solubility measurements. Accordingly, a large single crystal of "gem quality" diaspore was purchased from Wards Scientific Establishment. The crystal originated from Muglu, in southwestern Anatolia, Turkey. A description of the deposit, from which this sample was obtained, is given by Onay (1949). Inspection under the optical microscope revealed traces of an accessory mineral that was identified by X-ray diffraction as being chloritoid.

The crystal was broken up and approximately 10 grams, which appeared to be free of iron stains and inclusions, was crushed in a mortar and pestle to pass through a 120 mesh screen. 9.80 g of this material was added to 950 ml of 0.01 $\bar{N}$ NaCl solution in the one-liter autoclave, as used in the preceding experiment. The solution was sparged with CO_2 free nitrogen for 20 minutes, after which agitation was started, and the autoclave brought up to the initial operating temperature of 100°C. Three solution samples were taken over 16 hours, after which the temperature was raised to 125°C. After twelve hours, one sample was taken and the temperature raised a further 25°C. After twelve hours at 125°C, a single sample was taken again. This process was repeated at twelve hour intervals thereafter until 350°C was reached, at which point the temperature was lowered through successive 25°C intervals to 100°C.

pH measurements and chemical analyses were conducted as for the previous experiment with the exception of aluminum. The aluminum concentration was expected to be relatively low in concentration, because no alkali had been added to the solution, and was therefore analysed using the lumogallion method. The experimental results are given in Table F.7. Similar difficulties in interpreting pH measurements to those of the previous experiment were encountered. The maximum recorded pH was selected as most closely approximating the true pH.

2.5 Solubility of Turkish Diaspore in 0.01 $\bar{N}$ NaCl Solution Between 100 and 350°C: Initial pH adjusted to 10.7

The purpose of the experiment was to establish a preliminary fix on the solubility of diaspore with respect to the aluminate ion, $Al(OH)_4^-$ or AlO_2^-. Hence, sufficient sodium hydroxide was added to the starting solution to raise the initial pH to 10.7 to ensure that the diaspore would equilibrate well away from the isoelectric region where uncertainties arising from the possible formation of other aluminum species in solution, or to transient supersaturation or the precipitation of adsorbed phases would be avoided.

Fragments of Turkish diaspore taken from the same source material as used in the previous experiment, were hand picked to be free from iron stains and inclusions, crushed by hand with an agate mortar and pestle and screened through −65 mesh. The −65 + 400 mesh function was sonicated in ethyl alcohol until the ethyl alcohol remained clear. It was then dried at 130°C for one hour.

One liter of 0.01 $\bar{N}$ NaCl solution was made up with water previously sparged with CO_2 free nitrogen and adjusted to pH = 10.7. 960 ml of this solution and 10.05 g of diaspore was sealed in the autoclave and sparged with CO_2 free nitrogen for a further 20 minutes. The autoclave was then brought to 100°C and the first sample taken. The experiment then proceeded in the same manner as for the preceding experiment.

pH measurements and chemical analyses were conducted, as previously, with the exception that the aluminon colorimetric method was used for aluminum instead of the lumogallion fluorometric method, as sufficient aluminum was present in solution to permit the use of a less sensitive method. To prevent the precipitation of aluminum from solution prior to analysis, 0.05 ml of saturated KOH solution was added to each

TABLE F.7

DIASPORE SOLUBILITY MEASUREMENTS IN 0.01 $\bar{N}$ NaCl SOLUTION BETWEEN 100 AND 350°C

T,°C	ρ at 25°C, $g.cm^{-3}$ (calculated)	TDS, $mg.l^{-1}$ (calculated)	pH	Na^+, $mg.l^{-1}$	K^+, $mg.l^{-1}$	Ca^{++}, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	SiO_2aq, $mg.l^{-1}$	Cl^-, $mg.l^{-1}$
100	0.997	540	7.90	214	0.25	1.06	0.0953	0.34	324
"	"	570	7.30	229	0.26	(0.73)	0.0765	0.39	346
"	"	530	7.62	205	0.39	0.40	0.0642	0.44	322
125	"	530	8.00	201	0.77	0.97	0.222	0.51	328
150	"	530	8.62	206	(0.91)	1.17	0.563	0.80	328
175	"	540	8.82	208	1.04	0.82	0.644	1.01	328
200	"	540	8.67	210	1.22	0.91	0.658	1.24	333
225	"	540	8.54	212	1.45	1.16	0.717	1.30	330
250	"	540	8.76	215	1.72	0.74	0.922	1.24	330
275	"	540	8.67	207	2.13	0.74	1.050	0.99	330
300	"	560	8.54	219	2.78	0.49	1.250	0.38	336
325	"	550	8.30	217	3.07	0.25	1.180	0.19	333
350	"	530	8.03	208	2.76	0.09	0.718	0.19	324
"		530	8.11	205	3.06	0.07	0.715	0.19	329
325	"	530	8.32	223	3.39	0.13	1.210	0.19	346
300	"	570	8.49	225	3.52	0.69	1.270	0.19	350
275	"	570	8.69	220	3.39	0.84	1.180	0.19	347
250	"	560	8.93	216	3.48	0.54	1.060	0.19	345
225	"	550	9.06	213	4.45	0.93	0.884	0.19	342
200	"	570	9.05	237	(4.48)	1.60	0.718	0.19	337
175	"	550	9.30	223	4.52	1.31	0.621	0.19	330
150	"	530	8.60	212	3.41	1.40	0.351	0.19	317
125	"	500	9.26	192	3.62	1.38	0.223	0.19	308
100	"	500	8.07	189	3.76	1.56	0.0656	0.19	308

sample immediately after collection instead of the usual 5 ml of 0.01 $\bar{N}$ KOH solution.

The experimental results are reported in Table F.8.

2.6 Solubility of Turkish Diaspore in 0.01 $\bar{N}$ NaOH at 197°C

This exploratory experiment was conducted to obtain some idea of the rate of equilibration of diaspore in solution at 200°C, prior to planning further equilibrium experiments at lower temperatures.

0.01 $\bar{N}$ sodium hydroxide solution was prepared with distilled deionized water. This water had been flushed for 20 minutes with 99.999% N_2 which had been stripped of CO_2 by passing it through Ascarite CO_2 absorbant. 700 ml of the solution was placed in a one-liter Hastelloy C autoclave and the head torqued down. The solution was then flushed again with CO_2 free, high purity, nitrogen for 15 minutes, and the temperature raised to 50°C. At this point, 9.5 g of –65 mesh Turkish diaspore, the same charge previously used for experiment 5, was inserted in the autoclave, and the solution purged yet again with CO_2 free, high purity, nitrogen. The temperature was then raised to about 197°C and agitation started. At periodic intervals the autoclave agitation was turned off, followed, after 10 minutes by the withdrawal of 12 ml of solution from the autoclave, which was rejected. This was followed by a second 35 ml sample which was filtered through a Gelman 0.45 μm micropore disposable filter. 5.0 ml of the aliquot was submitted for pH measurement. pH measurements proved to be difficult, as the Orion 91-05 combination electrode used was several years old, but it was the only one available at the time. This electrode equilibrated very slowly in the alkali solution, and, as it subsequently proved, fell short of the true pH measurement by approximately 0.1 unit. The electrodes were calibrated before measurement with Mallinkrodt pH = 7.00±0.01 and pH = 10.00±0.01 buffers at 25°C. 20 ml of the filtered sample was immediately acidified with 200 γ of concentrated nitric acid and submitted for analysis for Na^+ and Al^{+++} respectively using an ARL Model 3510 PC inductively coupled plasma unit. The total sodium was also calculated based on an assumed initial concentration of 0.0102 $\bar{N}$, which took into account the concentration effect caused by partial vaporization of the initial volume of solution and the solution remaining after successive withdrawals of 50 ml samples. The results of this experiment are given in Table F.9.

3.0 Interpretation of the Results of Experiments 3, 4 and 5

3.1 Summary of Observations

Initial evaluations, not given here, showed that several uncertainties made it difficult to reconcile the results of experiments 3, 4 and 5. In order to place into context the arguments developed in the following sections, some of the potential problems are summarized here.

(1) The relatively close approach of experiments 3 and 4 to the isoelectric region, introduces the possibility that aqueous species other than $Al(OH)_4^-$, such as $Al(OH)_3^\circ$ might be participating in the equilibrium process. Little is known of the thermodynamic properties of this species.

(2) The very slow dissolution and precipitation rates of diaspore under the conditions of the three experiments, suggest that equilibration was not attained below 200°C.

(3) In experiment 3, it is possible that the solution became supersaturated with respect to both diaspore and boehmite due to the dissolution of traces of pyrophyllite or other contaminants.

(4) The solutions in experiments 3 and 4 may have equilibrated with respect to a disordered surface layer of aluminum hydroxide, rather than with respect to any crystalline phase.

(5) The pH measurements on quenched solution samples are of questionable accuracy.

(6) The sudden increase in the calculated value of K_{s4}(diaspore) above 325°C in experiment 5, may be due to formation of neutral complexes, to transient supersaturation, or to incorrect calculation of species distribution near the critical point (see (7) below).

TABLE F.8

DIASPORE SOLUBILITY MEASUREMENTS IN 0.01 $\bar{N}$ NaCl SOLUTION BETWEEN 100 AND 350°C
INITIAL pH ADJUSTED TO 10.7 WITH NaOH AT 25°C

T,°C	ρ at 25°C, $g.cm^{-3}$ (calculated)	TDS, $mg.l^{-1}$ (calculated)	pH at 25°C	Na^+, $mg.l^{-1}$	K^+, $mg.l^{-1}$	Ca^{++}, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	SiO_2aq, $mg.l^{-1}$	Cl^-, $mg.l^{-1}$	MoO_4^{--}, $mg.l^{-1}$
100	0.997	718	10.45	275	16.01	0.14	0.182	2.97	424	1.68
"	"	703	10.46	272	9.83	0.11	0.331	2.34	419	1.78
125	"	765	10.45	296	8.08	0.07	0.730	3.74	456	2.22
150	"	736	10.36	284	6.84	0.10	1.62	4.97	438	2.07
175	"	825	10.42	318	7.01	0.15	3.82	5.90	490	(2.60)
200		731	10.38	281	7.20	0.14	5.15	4.59	433	3.12
225	"	767	10.36	295	7.38	0.16	7.43	2.88	455	2.33
250	"	761	10.37	292	7.25	0.11	9.16	2.37	450	2.38
275	"	754	10.18	288	8.12	0.10	10.51	2.64	444	2.45
300	"	781	10.20	298	8.74	0.08	11.89	2.43	460	3.65
325	"	758	9.88	289	9.04	0.07	12.34	2.06	446	5.02
350	"	716	8.70	275	10.78	0.11	3.60	2.03	424	8.70
"		793	8.82	305	10.88	0.09	(4.73)	1.77	470	12.80
"	"	751	8.96	287	12.62	0.07	5.87	2.19	443	14.05
325	"	786	9.61	301	13.71	0.06	6.28	1.49	464	(15.26)
300	"	794	9.83	303	15.65	0.07	7.42	1.35	467	16.47
275	"	827	10.12	316	16.62	0.10	7.46	0.13	487	16.57
250	"	805	10.28	307	16.06	0.13	9.10	0.13	473	17.14
225	"	795	10.37	303	16.84	0.17	8.04	0.13	467	18.32
200	"	817	10.36	313	16.40	0.24	5.17	0.13	483	18.87
175	"	756	9.54	289	15.43	0.23	5.69	0.13	446	16.50
150	"	756	10.18	289	16.36	0.35	4.74	0.18	446	19.16
125	"	722	9.78	276	16.16	0.33	3.60	0.13	446	16.44
100	"	733	9.23	281	17.13	0.47	1.72	0.13	433	18.44

(-) Estimated Value

TABLE F.9

DIASPORE SOLUBILITY MEASUREMENTS IN 0.01 $\bar{N}$ NaOH SOLUTION AT 197°C

Time, hour	T, °C	ρ at 25 °C, $g.cm^3$ (calculated)	TDS, $mg.l^{-1}$ (calculated)	pH at 25°C	Na^+, $mg.l^{-1}$	Al^{+++} $mg.l^{-1}$	log Q_{s4} measured	log Q_{s4} calculated
0	197.4	0.997	408.0	11.80	34.6	0.001		
3	198.0		491.0	11.623	35.8	51.8	-0.635	-0.619
6	197.7		519.0	11.658	36.0	69.9	-0.468	-0.485
24	197.4		552.0	11.649	36.3	90.4	-0.312	-0.301
52	197.6		559.0	11.595	36.5	96.0	-0.279	-0.280
74	197.6		562.0	11.592	36.8	96.2	-0.273	-0.279
96	197.4		559.0	11.450	37.1	94.0	-0.289	-0.279
144	197.6		564.0	11.655	37.5	97.4	-0.267	-0.279

(7) Solution equilibria in dilute solutions become difficult to predict as the critical point of water is approached, i.e. above 300°C, when conducting experiments on the aqueous saturation surface.

Because of these uncertainties, a number of hypotheses were tested using the data from experiments 3, 4 and 5 in an attempt to reconcile the calculated values of $\log K_{s4}$(diaspore) from these experiments.

The following cases are considered.

(1) All relevent species in solution are adequately taken into account. No $Al(OH)_3^o$ is present.

(2) The species $Al(OH)_3^o$ is present and must be considered.

(3) The species $NaAlO_2^o$ is present and must be considered.

(4) Polynuclear complexes, such as $Al_{13}(OH)_{34}^{5+}$ may be present in the neutral pH region.

(5) Errors may have been introduced from incorrect values being assigned to the dissociation constants of participating aqueous species.

(6) Phases other than diaspore, such as boehmite or even disordered surface phases may be present.

Each of these possibilities is explored in turn.

3.2 Initial Analysis of Experiments 3, 4 and 5 Assuming No $Al(OH)_3^o$ is Present

There is a considerable divergence of opinion regarding the presence of the neutral species, $Al(OH)_3^o$, in solution. Russian investigators, notably Khodakovskiy and his coworkers (e.g. Kuyunko et al., 1983) believe that $Al(OH)_3^o$ is the dominant aluminum species in solution over a substantial range of pH at elevated temperatures. However, recent studies reported in the western literature, do not indicate a significant stability field for $Al(OH)_3^o$ below 70°C (May et al., 1979; Couturier et al., 1984). Lafon (personal communication, 1984), who conducted solubility studies on diaspore at 200°C, has also failed to detect the presence of $Al(OH)_3^o$ in solution. The $Al(OH)_3^o$ species was omitted from the data base used with the EQ3/EQ6 code (Wolery, 1983). The two experiments conducted near the neutral pH region, i.e., experiments 3 and 4, afford an opportunity of testing for the existence of $Al(OH)_3^o$ between 100 and 350°C.

As a preliminary step, we will assume that $Al(OH)_3^o$ does not exist, and analyze the data accordingly using EQ3. A distribution of aqueous species was initially made at 25°C, electrical neutrality being achieved by adjusting the concentration of Na^+. The solution species were then redistributed at the operating temperature using the newly calculated Na^+ concentration and adjusting pH to achieve electrical neutrality. Calculated values of log K_{s4} are given for the respective experiments in Tables F.10 to F.12. Log $[Al(OH)_4^-]$ values from Experiments 3, 4 and 5 are plotted against pH in Figures F.3a, b and c at 175, 250 and 325°C. These results lead to the following observations.

(1) In comparing the results of experiments 3, and 4, only fair agreement is obtained at the temperatures where comparison can be made.

(2) In Experiments 4 and 5, reversible equilibrium was achieved between 200 and 350°C. In experiment 5, solutions below 200°C were either undersaturated or supersaturated, depending on whether the preceding sample temperature was lower or higher.

(3) Although the equilibration measurements in experiment 5 are in reasonable accord with independent measurements of diaspore solubility discussed elsewhere in this report, a sharp deviation to higher values is observed at 325 and 350°C.

(4) The results of experiments 3 and 4 appear to bear little relation to those of experiment 5.

Although these initial results raise more questions than they answer, some preliminary conclusions can be reached. It is clear that rates of dissolution or precipitation of diaspore below 200°C for the condition of experiment 5 are so slow, that the time allowed between sampling, 12 hours, was quite insufficient to allow equilibrium to be achieved. This would also apply to experiment 2, whose results are consistent with the

TABLE F.10

DETERMINATION OF LOG K_{s4}(DIASPORE) FROM SOLUBILITY MEASUREMENTS IN 0.01 $\bar{N}$ NaCl SOLUTION AT 175, 250, AND 325°C

				Log K_{s4}		
T,°C	Time, hour	Log $[H_2O]$	Ionic Strength	No additional complexes	with $Al(OH)_3^o$	with $NaAlO_2^o$
175	2.12	-0.00016	0.0107	0.309	0.291	0.309
	3.00	-0.00016	0.0108	0.504	0.463	0.504
	4.00	-0.00016	0.0111	0.453	0.416	0.453
	4.03	-0.00017	0.0112	0.416	0.382	0.416
	5.08	-0.00017	0.0112	0.540	0.491	0.540
	23.0	-0.00017	0.0113	0.016	0.007	0.016
250	1.83	-0.00016	0.0109	0.592	0.447	0.592
	2.83	-0.00016	0.0108	0.893	0.609	0.893
	3.83	-0.00016	0.0108	0.893	0.595	0.893
	3.88	-0.00016	0.0108	0.655	0.433	0.655
	4.86	-0.00016	0.0109	0.736	0.505	0.736
	22.83	-0.00017	0.0113	0.481	0.305	0.481
325	2.00	-0.0008	0.0051	1.146	0.229	1.120
	3.00	-0.0006	0.0041	0.519	-0.057	0.479
	4.00	-0.0007	0.0046	0.998	0.019	0.983
	4.03	-0.0007	0.0045	0.880	-0.052	0.864
	5.00	-0.0008	0.0056	0.802	-0.159	0.776

TABLE F.11

DETERMINATION OF LOG K_{s4}(DIASPORE) FROM SOLUBILITY MEASUREMENTS IN 0.01 $\bar{N}$ NaCl SOLUTION BETWEEN 100 AND 350°C

T, °C	1/T, $K^{-1} \times 10^3$	Log [H_2O]	Ionic Strength	Log Ks4		
				No additional complexes	with $Al(OH)_3^o$	with $NaAlO_2^o$
100	2.680	-0.00014	0.0092	0.371	+0.336	0.371
100	2.680	-0.00015	0.0098	0.319	+0.285	0.319
100	2.680	-0.00014	0.0091	0.315	+0.277	0.315
125	2.512	-0.00014	0.0093	0.584	+0.515	0.584
150	2.363	-0.00014	0.0093	0.498	+0.452	0.498
175	2.231	-0.00014	0.0093	0.350	+0.310	0.350
200	2.113	-0.00014	0.0095	0.450	+0.371	0.450
225	2.007	-0.00014	0.0094	0.564	+0.428	0.564
250	1.911	-0.00014	0.0093	0.518	+0.382	0.518
275	1.824	-0.00014	0.0093	0.684	+0.440	0.684
300	1.745	-0.00014	0.0094	0.954	+0.489	0.937
325	1.672	-0.00013	0.0091	1.192	+0.458	1.101
350	1.605	-0.00013	0.0086	1.257	+0.262	0.949
350	1.605	-0.00013	0.0088	1.194	+0.249	0.851
325	1.672	-0.00014	0.0095	1.138	+0.440	1.045
300	1.745	-0.00014	0.0098	1.022	+0.517	1.004
275	1.824	-0.00014	0.0098	0.797	+0.507	0.797
250	1.911	-0.00014	0.0098	0.548	+0.413	0.548
225	2.007	-0.00014	0.0097	0.359	+0.293	0.359
200	2.113	-0.00014	0.0096	0.281	+0.238	0.281
175	2.231	-0.00014	0.0094	-0.016	-0.028	-0.016
150	2.363	-0.00013	0.0090	0.381	0.335	0.381
125	2.512	-0.00013	0.0088	0.279	0.252	0.279
100	2.680	-0.00013	0.0088	0.126	0.103	0.126

TABLE F.12

DETERMINATION OF LOG K_{s4}(DIASPORE) FROM SOLUBILITY MEASUREMENTS IN 0.01 $\bar{N}$ NaCl SOLUTION BETWEEN 100 AND 350°C. INITIAL pH AT 25°C ADJUSTED TO 10.7

T, °C	1/T, $K^{-1} \times 10^3$	Log $[H_2O]$	Ionic Strength	Log K_{s4} No additional complexes	Log K_{s4} with $Al(OH)_3^o$	Log K_{s4} with $NaAlO_2^o$
100	2.680	-0.00018	0.0124	-1.781	-1.713	-1.713
100	2.680	-0.00018	0.0122	-1.456	-1.456	-1.456
	2.512	-0.00019	0.0132	-1.131	-1.132	-0.132
150	2.363	-0.00019	0.0126	-0.736	-0.736	-0.736
175	2.231	-0.00021	0.0141	-0.433	-0.434	-0.434
200	2.113	-0.00018	0.0125	-0.249	-0.251	-0.250
225	2.007	-0.00019	0.0131	-0.041	-0.044	-0.041
250	1.911	-0.00019	0.0129	+0.053	+0.049	+0.052
275	1.824	-0.00018	0.0127	+0.277	+0.265	+0.275
300	1.745	-0.00019	0.0130	+0.323	+0.305	+0.301
325	1.672	-0.00018	0.0124	+0.638	+0.566	+0.506
350	1.605	-0.00017	0.0115	+1.243	+0.603	+0.747
350	1.605	-0.00019	0.0128	+1.243	+0.658	-0.719
350	1.605	-0.00018	0.0121	+1.143	+0.679	+0.625
325	1.672	-0.00019	0.0131	+0.610	+0.499	+0.477
300	1.745	-0.00019	0.0136	+0.485	+0.435	+0.463
275	1.824	-0.00020	0.0143	+0.262	+0.248	+0.261
250	1.911	-0.00020	0.0140	+0.187	+0.181	+0.187
225	2.007	-0.00020	0.0139	+0.043	+0.039	+0.042
200	2.113	-0.00021	0.0144	-0.141	-0.143	-0.141
175	2.231	-0.00019	0.0133	+0.712	+0.690	+0.712
150	2.363	-0.00019	0.0134	-0.001	-0.002	-0.001
125	2.512	-0.00018	0.0128	+0.278	+0.276	+0.278
100	2.680	-0.00019	0.0131	+0.500	+0.496	+0.500

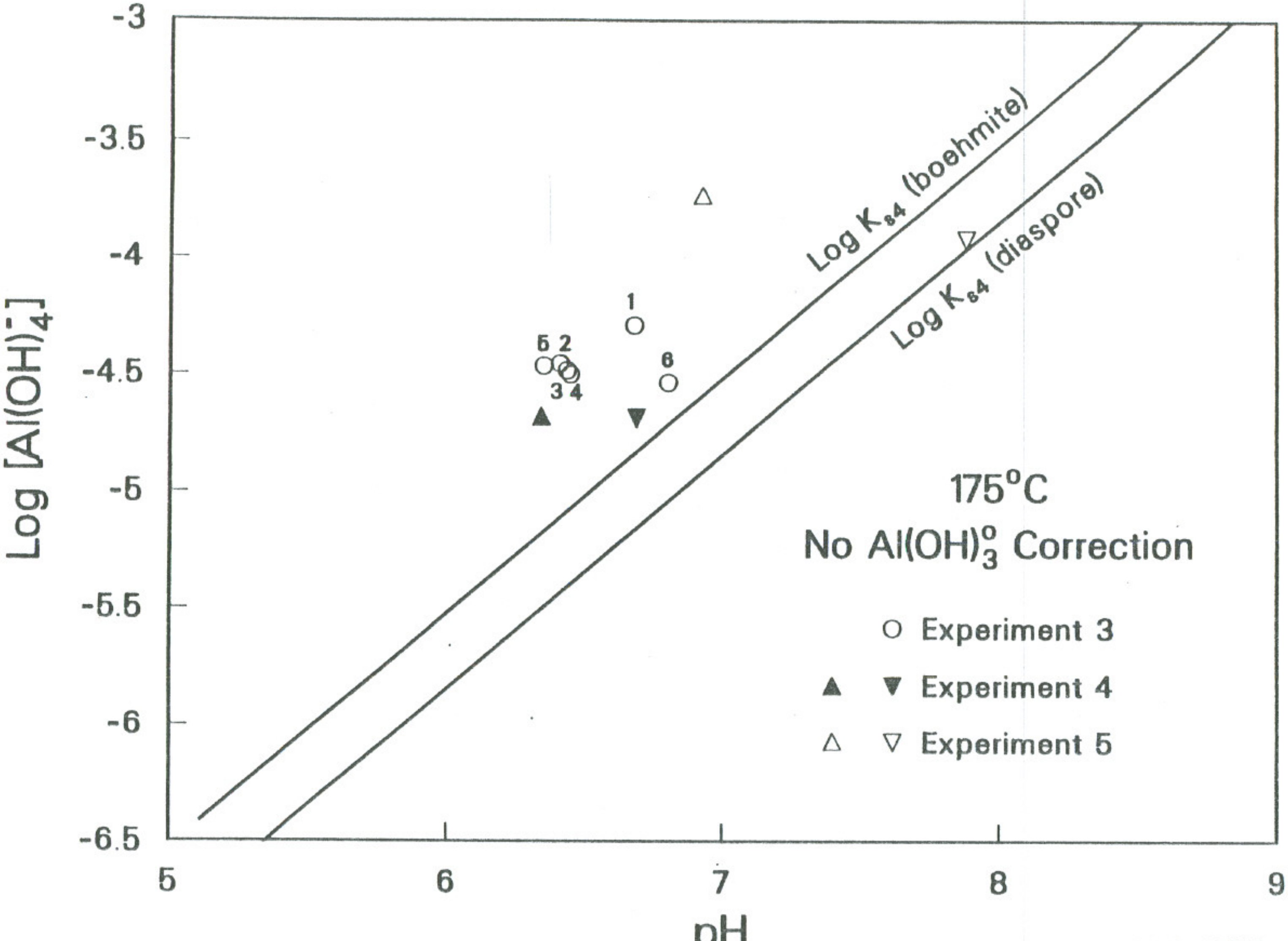


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Figure F.3a. Comparison of diaspore solubilities from three experiments at 175, 250 and 325°C, plotted as log[AlOH)$_4^-$] vs pH: No correction for Al(OH)$_3^o$. (a) 175°C.

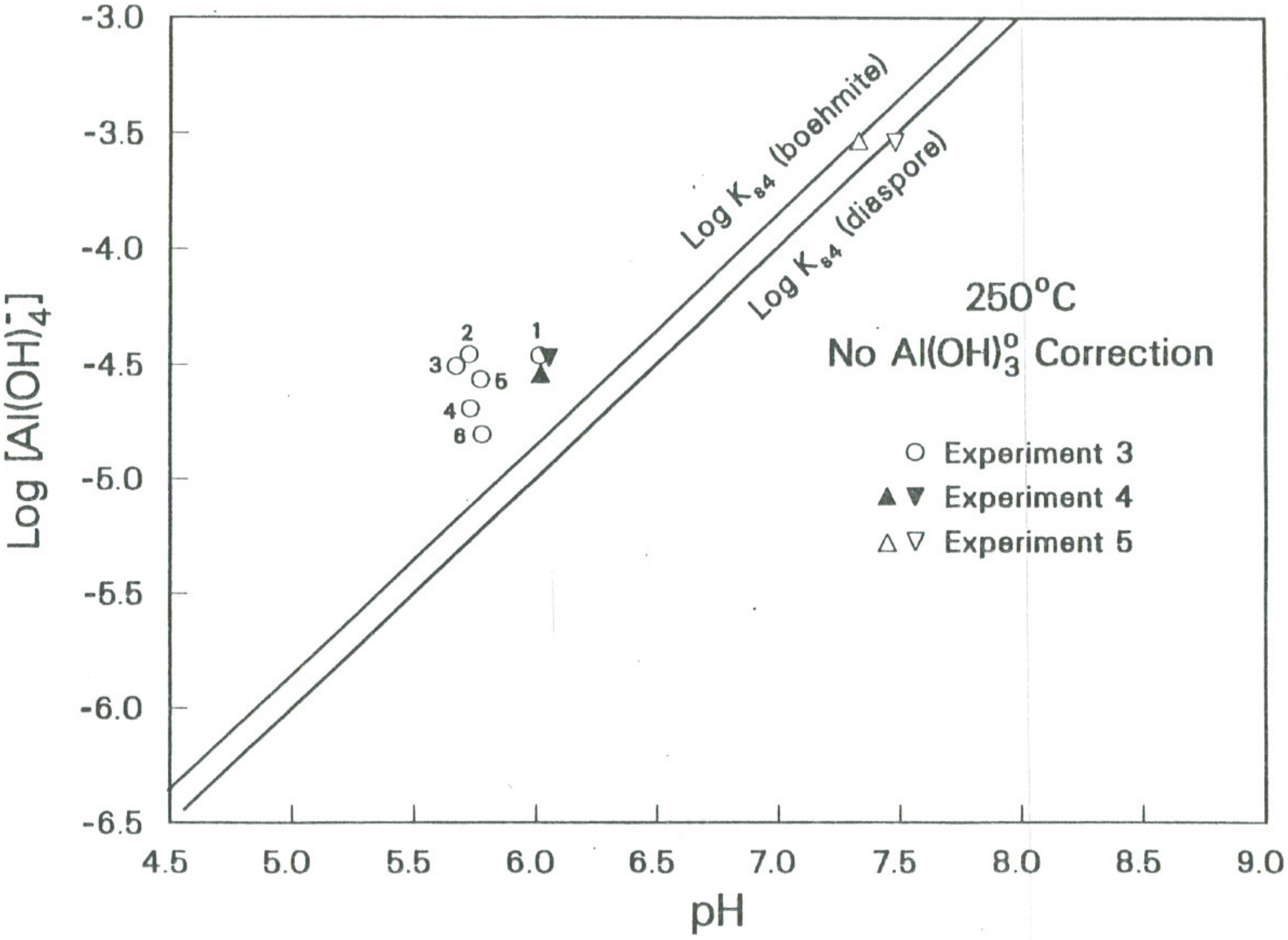

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Figure F.3b. Comparison of diaspore solubilities from three experiments at 175, 250 and 325°C, plotted as log[AlOH)$_4^-$] vs pH: No correction for Al(OH)$_3^o$. (b) 250°C.

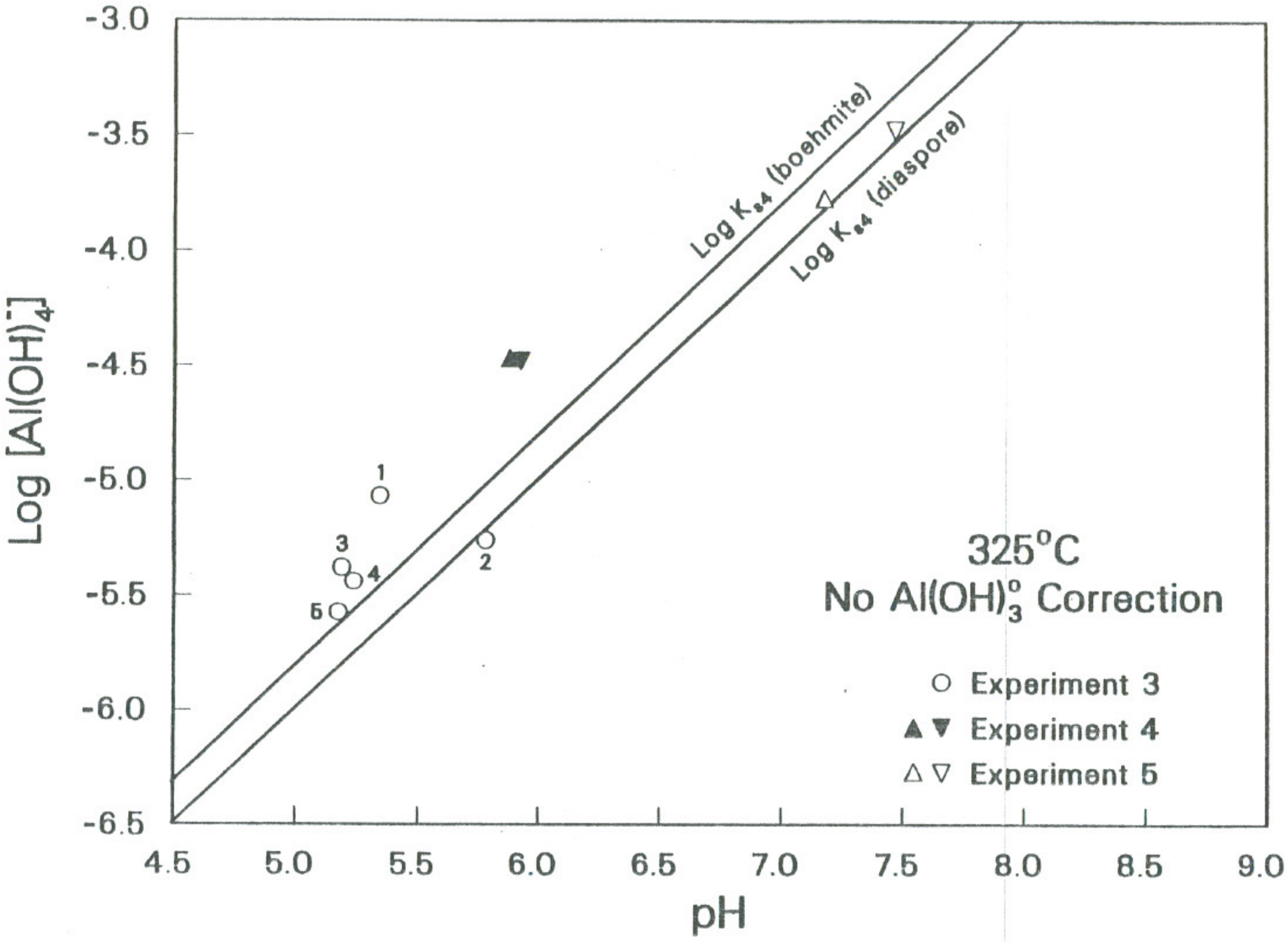

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Figure F.3c. Comparison of diaspore solubilities from three experiments at 175, 250 and 325°C, plotted as log[AlOH)$_4^-$] vs pH: No correction for Al(OH)$_3^o$. (c) 325°C.

results of experiment 5, and throws into question the validity of results from experiment 1. The results from experiment 1, illustrated in Figure F.1, suggested that equilibrium had been achieved at 25°C, but this may well be an experimental artifice caused by dissolution of diaspore dust or accelerated dissolution from structural defects. Although the log K_{s4}(diaspore) determined at 25°C is in approximate concordance with log K_{s4}(diaspore) based on extrapolation from higher temperature results, values between 25°C and 200°C from experiments 1 and 2 fall below the trend.

3.3 Analysis of Experiments 3, 4 and 5 Taking into Account the Presence of $Al(OH)_3^o$

The addition of $Al(OH)_3^o$ to the aqueous species could have the desired effect of reconciling the results from experiments 3, 4 and 5. In particular, the positive deviation of log K'_{s4}(diaspore) observed in experiment 5 above 300°C may be due to the formation of $Al(OH)_3^o$, because it is well known that neutral species tend to stabilize with increasing temperature and decreasing density of the aqueous phase. In order to conduct such an analysis, the stability constant, β_3^{-1}, must be determined between 25 and 350°C.

As pointed out above, there is some dispute regarding the presence of $Al(OH)_3^o$ in aqueous solution at or around 25°C. May et al. (1979), in a meticulous evaluation of natural and synthetic solubility gibbsite in buffered solutions, derived on upper limit to the stability constant, $^*K_{s3}$, as defined by the reaction:

$$\underset{\text{gibbsite}}{Al(OH)_3} = Al(OH)_3^o \qquad {}^*K_{s3}$$

where $\log {}^*K_{s3} \leq -8.652$

This result contrasts with the earlier work of Dezelic et al. (1971) who calculated a value where $\log {}^*K_{s3} = -3.92$. Dezelic et al. obtained their value from equilibrium concentrations of aluminum hydroxide gels, precipitated from solution. The findings of May et al. (1979) also differ from those of Baes and Mesmer (1976) on aluminum hydroxy species in solution. The latter investigators give a dissolution constant for the reaction:

$$Al^{+++} + 3H_3O = Al(OH)_3^o + 3H^+ \qquad {}^*\beta_3$$

where $\log {}^*\beta_3 = -15.0$, and where $\log {}^*\beta4 = -23.0$ for the reaction:

$$Al^{+++} + 4H_2O = Al(OH)_4^- + 4H^+ . \qquad {}^*\beta_4$$

The authors tentatively accept the findings of May et al. (1979) as being the most accurate estimate $Al(OH)_3^o$ stability at 25°C.

Kuyunko et al. (1983) in their study on boehmite solubility at 200 and 250°C estimated $^*K_{s3}$(boehmite) for the reaction:

$$AlOOH + H_2O = Al(OH)_3^o \qquad {}^*K_{s3}$$

to be 1.0×10^{-6} at 200°C, and 2.48×10^{-6} at 250°C. This study was repeated by Bourcier et al. (1987) with similar results. Their data are incorporated in Table F.14.

Finally, we have measurements of diaspore solubility at 300, 325 and 350°C from experiment 5 that may reflect the presence of $Al(OH)_3^o$ in solution. These measurements may be analysed by assuming that the reversible solubility measurements between 200 and 300°C may be extrapolated linearly to 350°C, on a log K_{s4} vs $1/T(K^{-1})$ plot and then computing the deviation as being due to the presence of $Al(OH)_3^o$. The deviations are summarized in Table F.13:

TABLE F.13

CORRECTED VALUES OF LOG K'_{s4}(DIASPORE) FROM EXPERIMENT 5

T,°C	log K'_{s4}(diaspore)	
	Measured	Corrected
300	+0.323	0.46
	+0.485	
325	+0.638	0.51
	+0.610	
350	+1.243	0.68
	+1.243	
	+1.143	

Direct comparison of the data from different sources is preferably made after elimination of the solid phases, because the relation between the thermodynamic properties of the gibbsite, boehmite, and diaspore are the subject of this investigation. This may be done by relating the formation of $Al(OH)_3^o$ to $Al(OH)_4^-$ by the reaction:

$$Al(OH)_4^- = Al(OH)_3^o + OH^- \qquad K_4^{-1}$$

Using the appropriate dissociation constants of the required conversion equations, whenever possible from the original data sources, values of the log K_4^{-1} were computed at the respective temperatures. These are given in Table F.14 and plotted in Figure F.4.

TABLE F.14

VALUES OF LOG K_4^{-1} AT VARIOUS TEMPERATURES, ESTIMATED FROM EXPERIMENTAL STUDIES

T,°C	1/T, $K^{-1} \times 10^3$	log K_4^{-1}	Source
25	3.354	≤8.64	May et al. (1979)
		-5.29	Dezelic et al. (1971)
		-5.99	Baes and Mesmer (1976)
150	2.363	-6.64	Bourcier et al. (1987)
200	2.113	-5.80	
		-6.00	Kuyunko et al. (1983)
250	1.9115	-6.09	Bourcier et al. (1987)
		-5.89	Kuyunko et al. (1983)
300	1.745	-5.84	This work
325	1.672	-5.05	
		-5.44	
350	1.605	-5.41	
		-5.30	
		-5.25	

Because of the low precision of the data and the absence of information permitting calculation of the heat capacity change during the reaction, $\Delta\overline{C}^o_{p,r}$, is assumed to be zero and a linear regression of log K_4^{-1} made of the data as a function of reciprocal temperature. The computed values of log K_4^{-1} as a function of

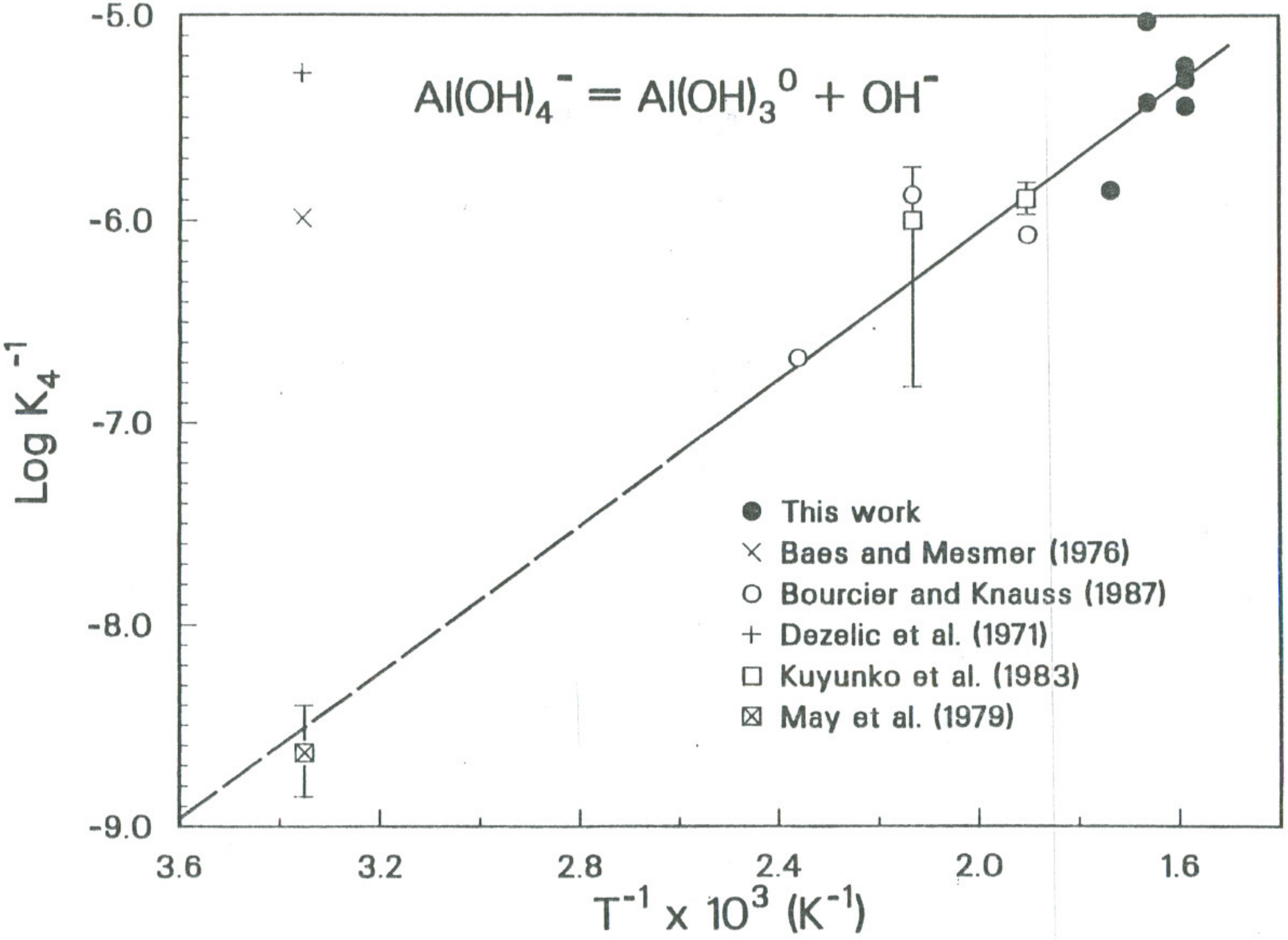

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Figure F.4. Log K_4^{-1} as a function of reciprocal temperature.

temperature are given in Table F.15. These are based on the equation:-

$$\log K_4^{-1} = -1898.24\ T^{-1} - 2.2239$$

TABLE F.15

CALCULATED VALUES OF LOG K_4^{-1}

T,°C	$1/T, K^{-1} \times 10^3$	$\log K_4^{-1}$
0	3.661	-9.088
25	3.354	-8.517
50	3.095	-8.034
60	3.002	-7.861
75	2.872	-7.620
100	2.680	-7.262
125	2.512	-6.949
150	2.363	-6.673
175	2.231	-6.428
200	2.133	-6.208
225	2.007	-6.011
250	1.911	-5.832
275	1.824	-5.670
300	1.745	-5.522
325	1.672	-5.386
350	1.605	-5.261

The assumption that $\Delta\overline{C}^{o}_{p,r} = 0$ is reasonable, as it has been found that reactions involving balanced like charges have small heat capacities of reaction (Lindsay, 1980; Cobble et al., 1982; Phillips and Silvester, 1984)*. Using the calculated values of log K_4^{-1}, the appropriate values of the reaction:-

$$Al^{+++} + 3(OH)^- = Al(OH)_3^o \qquad \beta_3$$

were evaluated for incorporation in the database of the EQ3 computer code (Wolery, 1983).

The apparent solubility products of diaspore, K'_{s4}(diaspore), were then recomputed for all runs. A comparison of the revised solubility products of diaspore in experiments 3, 4 and 5 shows that no significant improvement in correlation between all three experiments was obtained. [Compare Figures F.3a,b,c with Figures F.5a,b,c.] The results of experiment 5 are illustrated in Figure F.6, where it is evident that reversible equilibrium was attained only between 200 and 350°C.

The computed values of log K_4^{-1} appear to be consistent with Lafon's observation (Lafon, personal communication, 1984), that the presence of $Al(OH)_3^o$ is not detected when measuring the solubility of diaspore at 200°C. Log K_{s3}(diaspore) is calculated to be -6.45, which would put the concentration of aluminum in solution due to $Al(OH)_3^o$ at 0.01 ppm. The ability to detect this small contribution to the total aluminum concentration would be very unlikely.

A final test for consistency of the 325°C data, is to calculate the equilibrium constant for the reaction:

$$AlOOH(diaspore) + H_2O = Al(OH)_3^o \qquad K_{s3}$$

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*Perhaps it should be noted that the approach described above is very approximate. Further refinements using the latest HKF equation of state (Tanger and Helgeson, 1988) will be attempted after completion of this report.

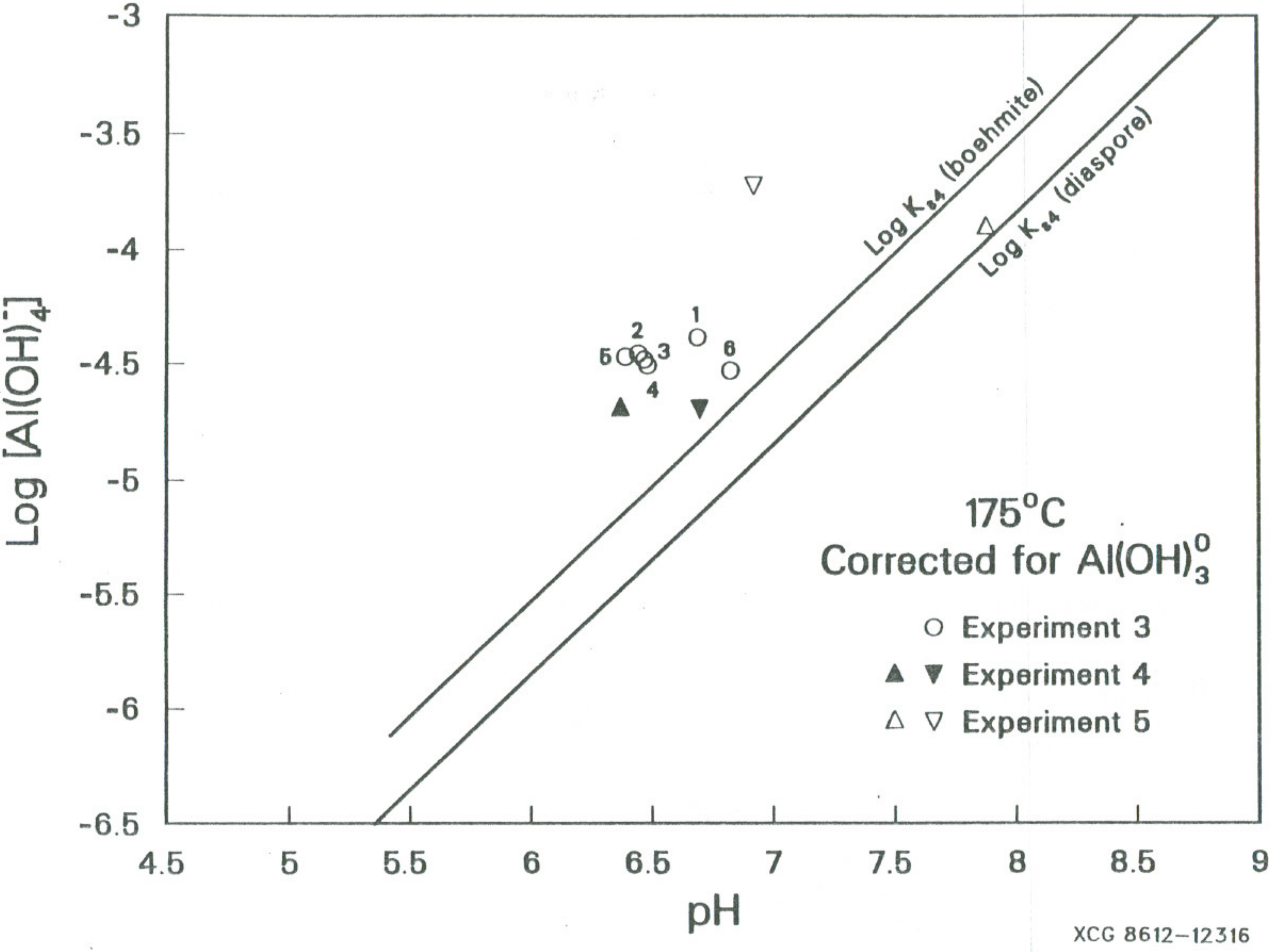

Figure F.5a. Comparison of diaspore solubilities from three experiments at 175, 250 and 325°C, plotted as log[Al(OH)$_4^-$] vs pH: Corrected for Al(OH)$_3^0$. (a) 175°C.

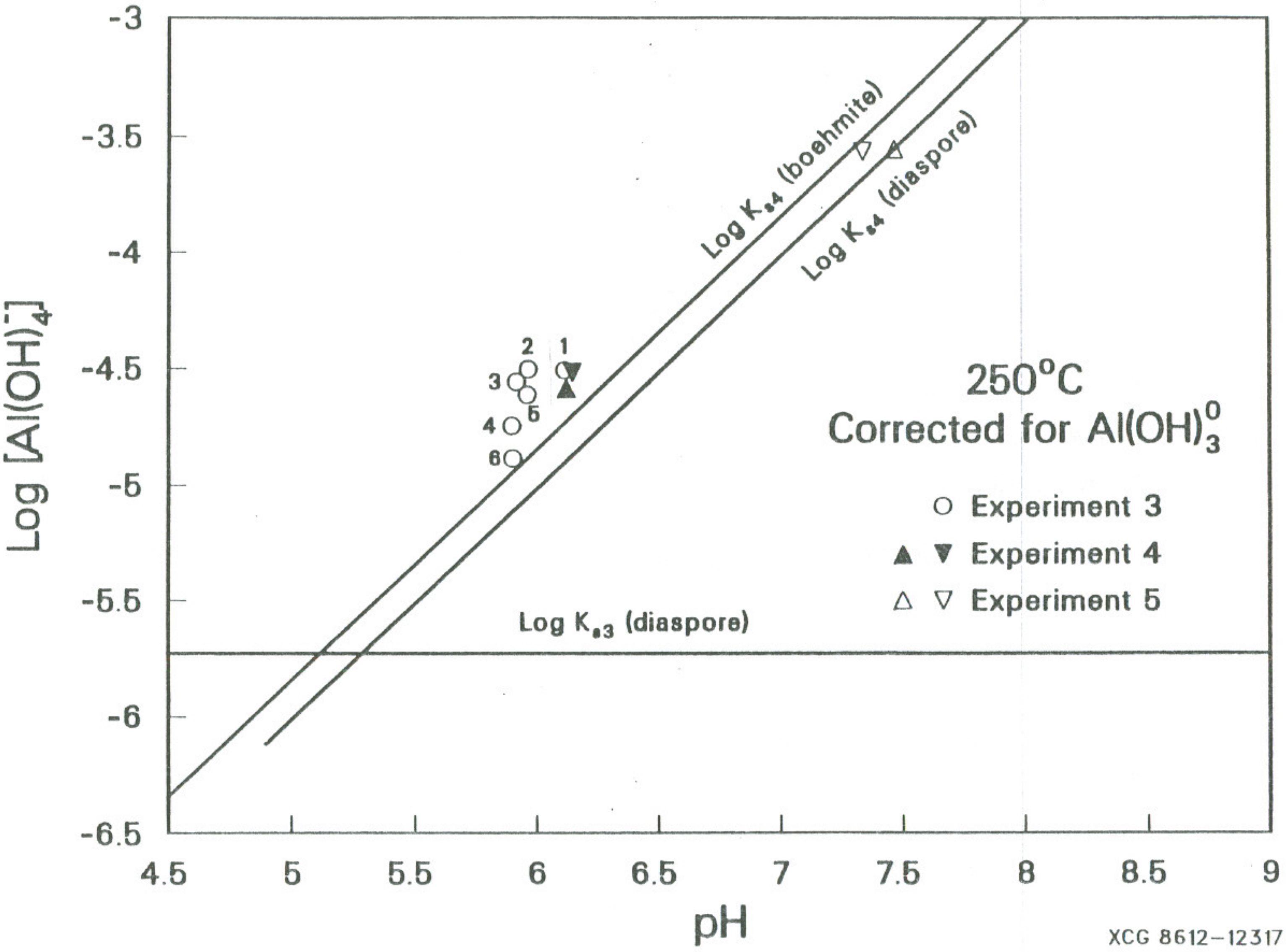

Figure F.5b. Comparison of diaspore solubilities from three experiments at 175, 250 and 325°C, plotted as log[Al(OH)$_4^-$] vs pH: Corrected for Al(OH)$_3^0$. (b) 250°C.

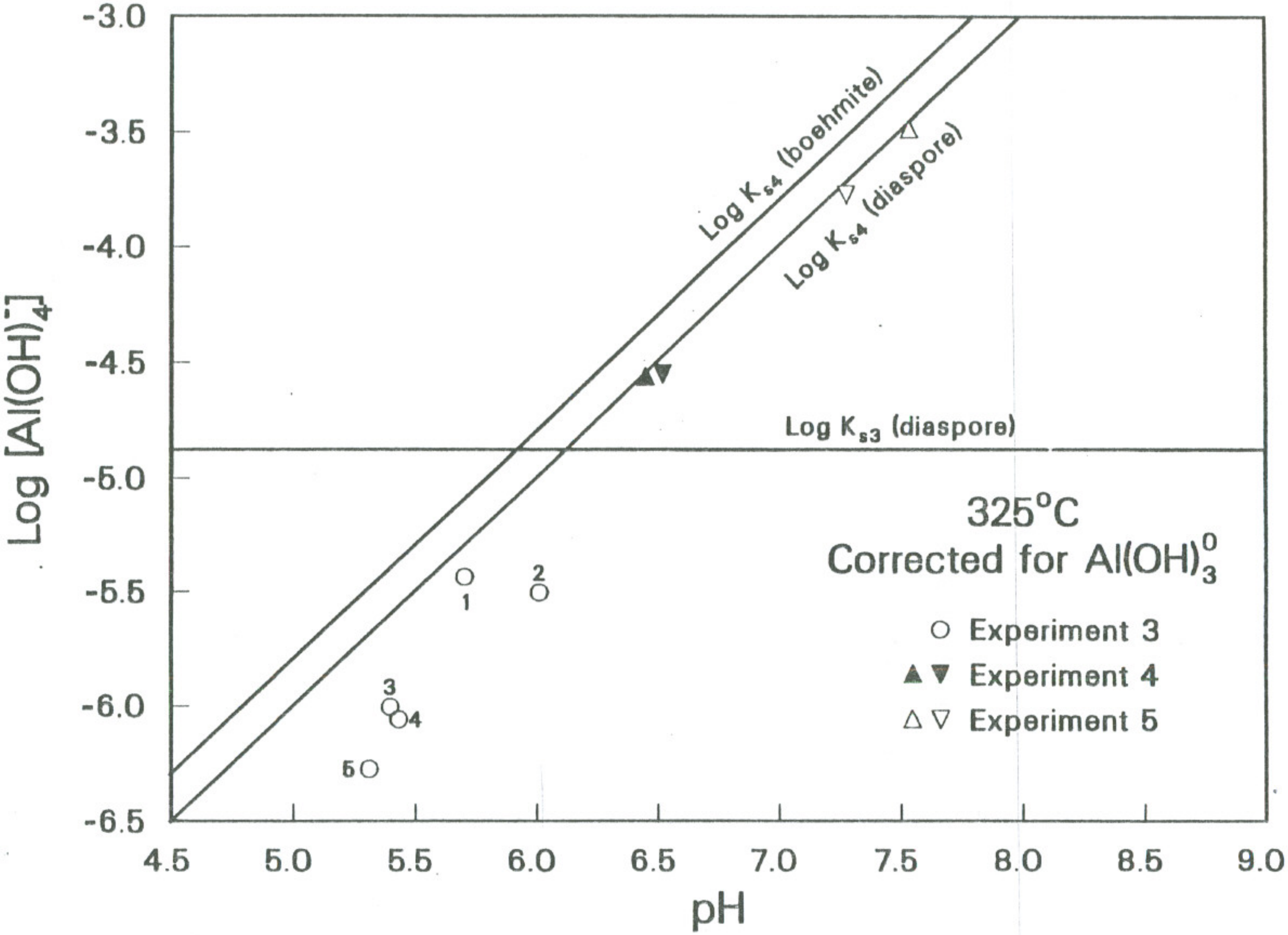

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Figure F.5c. Comparison of diaspore solubilities from three experiments at 175, 250 and 325°C, plotted as log[Al(OH)$_4^-$] vs pH: Corrected for Al(OH)$_3^o$. (c) 325°C.

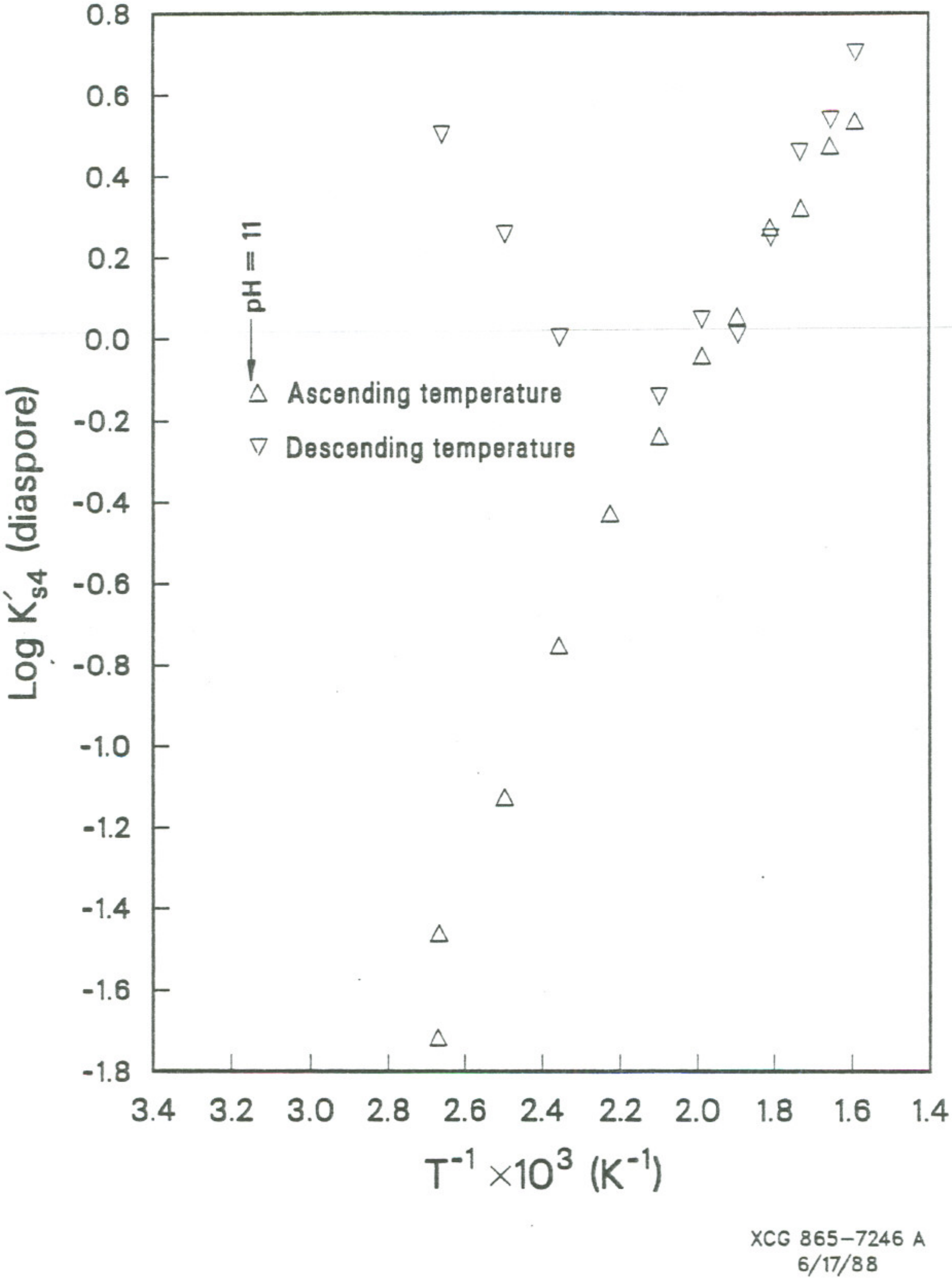


Figure F.6. Variation of K_{s4}(diaspore) versus the reciprocal of temperature calculated from the results of Experiment 5.

log K_{s3}(diaspore) = −5.02, which exceeds solubilities based on the results of experiment 3 at 325°C. (See Figure F.5c). This may be due to the precipitation of a phase other than diaspore, or it may be that the presence of $Al(OH)_3^o$ at this temperature is still questionable.

Incorporation of $Al(OH)_3^o$ as a species, and analysis of the data from experiments 3, 4 and 5, leads to the following conclusions.

1. Results of experiments reported by May et al. (1979), Kuyunko et al. (1983) and Bourcier et al. (1987) concerning the stabilities of $Al(OH)_3^o$ are consistent with observations from the experiments reported here at temperatures above 300°C. However, the evidence is too tenuous to draw definitive conclusions regarding the existence of $Al(OH)_3^o$ as a significant species in solution over the range of temperatures studied.
2. The data for experiments 3 and 4 do not correlate with the results from experiment 5 and suggest that some explanation other than the presence of $Al(OH)_3^o$ must be found.

An alternative explanation is that very rapid precipitation occurs with respect to some surface or disordered phase, which is relatively stable in near neutral solutions and persists for the duration of the experiment without recrystallizing to a more ordered phase. This interpretation may also be invoked to explain the boehmite solubility behavior observed by Kuyunko et al. (1983) and Bourcier et al. (1987). The possible persistence of a highly reactive precipitate in the vicinity of the isoelectric region would lead to higher observed aluminum solubilities in that region than would be obtained with a reversible equilibrium with respect to diaspore or even boehmite. This could easily be interpreted as evidence for the existence of $Al(OH)_3^o$, whereas, in fact, it is an experimental artifice.

3.4 The Possible Existence of the Species $NaAlO_2^o$

Another possible explanation for the inconsistency between experiments 3, 4 and 5 could be the presence of unaccounted for additional species, or the effect of species that are recognized, but whose thermodynamic properties are inappropriately defined. For example, if we consider the reaction:-

$$AlOOH + OH^- + H_2O = Al(OH)_4^-$$

where

$$K_{s4} = \frac{[Al(OH)_4^-]}{[OH^-]\,[AlOOH]\,[H_2O]}$$

K_{s4} may be varied by adjusting either $Al(OH)_4^-$ or OH^- activities. Variation in $Al(OH)_4^-$ due to the formation of $Al(OH)_3^o$ is one such possibility. Another may be the formation of $NaAlO_2^o$. The existence of this species has been suggested elsewhere (Eremin et al., 1974). We can consider the reaction:-

$$NaAlO_2^o + 4H^+ = Na^+ + Al^{+++} + 2H_2O \qquad {}^*\beta_4^{-1}$$

and can calculate appropriate values of ${}^*\beta_4^{-1}$ to account for the deviation observed at 350°C in Experiment 5. These values are given in Table F.16.

TABLE F.16

ESTIMATED VALUES OF LOG ${}^*\beta_4^{-1}$ AT 300, 325 AND 350°C

T,°C	1/T, $K^{-1} \times 10^3$	Log ${}^*\beta_4^{-1}$
300	1.745	8.69
325	1.672	6.90
		7.02
350	1.605	5.04
		5.09
		5.23

A linear regression through the data at 325 and 350°C yields the equation:

$$\log {}^*\beta_4^{-1} = +25864.9\ T^{-1} - 36.3604$$

which was used to calculate appropriate values for insertion into the EQ3 database, as given below in Table F.17.

TABLE F.17

CALCULATED VALUES OF LOG $^*\beta_4^{-1}$

T,°C	1/T, $K^{-1} \times 10^3$	Log $^*\beta_4^{-1}$
0	3.661	58.331
25	3.354	50.390
60	3.002	41.278
100	2.680	32.958
150	2.363	24.758
200	2.113	18.292
250	1.911	13.067
300	1.745	8.774
325	1.672	6.886
350	1.605	5.153

Calculated values of log K_{s4}(diaspore) in the presence of $NaAlO_2^o$ and in the absence of $Al(OH)_3^o$ are summarized in Tables F.10 to F.12. At temperatures below 250°C no significant deviation from the base case with either $NaAlO_2^o$ or $Al(OH)_3^o$ is observed. At 325°C, correlation between the experimental results of experiments 3, 4 and 5 is worse than that for the base case illustrated in Figure F.3c. This suggests that $NaAlO_2^o$ is not a significant species under the conditions of the three experiments, at least below 350°C.

3.5 The Possible Presence of the Species $Al_{13}(OH)_{34}^{5+}$

The possibility that large polynuclear complexes of aluminum, such as $Al_{13}(OH)_{34}^{5+}$, might be present in solution near the isoelectric point, and give higher than predicted aluminum concentrations in solution, was also investigated.

Data pertaining to the reaction:-

$$13Al^{+++} + 34H_2O = Al_{13}(OH)_{34}^{5+} + 34H^+ \qquad {}^*K_{34}^{-1}$$

determined by Baes and Mesmer (1971) on a 1 molal KCl solution and summarized here in Table F.18, were regressed using a three parameter Clarke and Glew equation to obtain $\overline{S^o_{298}}$, $\Delta\overline{H^o_{f,298}}$ and $\overline{C^o_{p,298}}$, and extrapolated values to 300°C. The regressed values are also given Table XVII together with $\log\beta'^{-1}_{34}$ values of the corresponding equation:

$$Al_{13}(OH)_{34}^{5+} = 13Al^{+++} + 34(OH)^- \qquad \beta_{34}^{-1}$$

It should be noted that this extrapolation is purely empirical and subject to large errors above 200°C. Furthermore, no attempt was made to correct log $^*K'^{-1}_{34}$ to standard state conditions owing to the difficulties of making such a correction. An estimate of the magnitude of the correction, using the Davies equation:

$$-\log\gamma_i = \frac{A|z|^2\sqrt{I}}{1+\sqrt{I}} - 0.3I$$

suggests that $\Delta(\log {}^*K'^{-1}_{34})$, ≈ +10.0. The uncorrected data were incorporated in EQ3 and the solution analyses from experiment 4 were distributed using EQ3. Results showed that under the conditions of the experiment, the species $Al_{13}(OH)_{34}^{5+}$ was an insignificant contributor to the total aluminum concentration

TABLE F.18

CALCULATION OF LOG $*K'^{-1}_{34}$ and LOG β'^{-1}_{34} OF THE COMPLEX $Al_{13}(OH)^{5+}_{34}$

T,°C	$\log *K'^{-1}_{34}$		$\log\beta'^{-1}_{34}$
	measured[1]	calculated	calculated
0		-129.075	+378.65
25	-110.350	-110.374	+365.25
60		-88.263	+354.52
99.6	-67.840		
100		-67.329	+349.34
124.8	55.600		
149.9	-46.120		
150		-45.853	+349.94
200		-28.144	+356.23
250		-13.196	+367.40
300		-0.340	+384.81

[1] Mesmer and Baes (1971) in 1m KCl solution.

over the whole range of temperatures investigated, and that corrections to standard state conditions for log $*K'^{-1}_{34}$ would not alter this finding. The discrepancy in log K_{s4}(diaspore) values between experiments 3 and 4, and experiment 5 cannot therefore be attributed to omission of this polynuclear species. It is possible that other polynuclear complexes may have contributed. As yet, no published data allow further speculation regarding the nature of such species, if they exist.

3.6 The Effect of Homogeneous Hydrolysis Reactions

The third possible explanation for the variation in log K_{s4}(diaspore) between experiments 3, 4 and 5 is that an incorrect estimation of $[OH^-]$ was made due to an incorrect evaluation of the effect of competing reactions with other species in solution. These include:-

$$H_2O = H^+ + OH^- \qquad K_w$$

$$NaOH = Na^+ + OH^- \qquad \beta^{-1}$$

$$Ca(OH)^+ = Ca^{++} + OH^- \qquad \beta^{-1}$$

$$SiO(OH)_3^- + H_2O = Si(OH)_4^\circ + OH^- \qquad \beta^{-1}$$

If any of these species is unaccounted for or incorrectly measured, or if the corresponding dissociation constants are incorrect, they may have a marked effect on the calculated value of K_{s4}(diaspore). A case in point is the effect of varying SiO_2(aq) concentration. Comparison may be made between the samples taken after 5.08 and 23.0 hours for experiment 3 at 175°C, whose respective silica concentrations were measured at 16.4 and 22.8 mg.l^{-1}. Although the measured pH differed by 0.1 unit, the calculated values of log K_{s4} differ by 0.524. This is due to an initial contribution of $SiO(OH)_3^-$ to the ionic species at 25°C that is all but eliminated at 175°C, due to a shift in species equilibrium. Table F.19 shows the effect of changing the SiO_2(aq) concentration from 22.8 to 16.0 mg.l^{-1}.

TABLE F.19

EFFECT OF VARYING $SiO_2(aq)$ CONCENTRATION ON 23 HR SAMPLE OF EXPERIMENT 3 AT 175°C

	Total $SiO_2(aq)$, $mg.l^{-1}$	
Aqueous Species	22.8	16.0
pH @ 25°C	8.01	8.01
pH @ 175°C	6.82	6.27
log $[OH^-]$	-4.56	-5.11
log $[SiO_2aq]$	-3.42	-3.57
log $[SiO(OH)_3^-]$	-5.83	-6.53
log $[Ca^{++}]$	-4.65	-4.65
log $[Ca(OH)^-]$	-6.82	-7.36
log $[Al(OH)_4^-]$	-4.54	-4.54
log K_{s4}	+0.02	+0.57

This result suggests that the presence of other species in solution must be taken into account if accurate values of log K_{s4}(diaspore) are to be computed in the near neutral region from measurements made on quenched solution samples.

A sensitivity study was conducted on the 350°C data of experiment 5, to test for an alternative explanation for the sharp deviation of K_{s4}(diaspore), other than ascribing it to the presence of $Al(OH)_3^o$. Uncertainties in Kw, and in β^{-1} for NaOH and $Ca(OH)^+$, cannot account for the deviation observed. The concentration of $SiO_2(aq)$ is also too low to affect the results. The precipitation of some phase other than diaspore, appears to be the only remaining explanation. This is considered in Section 3.7.

3.7 The Possibility of Phases other than Diaspore Controlling the Solution Composition

In the preceding sections, 3.2-3.6, factors affecting the interpretation of the solubility measurements of diaspore in experiments 3.4 and 5 are examined. The following conclusions may be drawn:-

(1) The $Al(OH)_3^o$ species may become an increasingly important species in the neutral pH region, with increasing temperature.

(2) The species $NaAlO_2^o$ and the polynuclear cationic complex, $Al_{13}(OH)_{34}^{5+}$, are not significant species under the conditions of the experiments.

(3) Solubility determinations of slightly soluble hydroxides in the neutral pH region are subject to interference by hydrolyzable ionic and molecular species, particularly if pH corrections must be applied at elevated temperature. Failure to take these species into account, or to measure their concentrations accurately, can lead to serious errors.

(4) The equilibria measured in experiment 5 above 200°C represent the reversible solubility of diaspore in alkaline solution.

It remains to explain why the solubility products calculated from the solution analyses of experiments 3 and 4 cannot be reconciled with those of diaspore. In the analysis which follows, the refined thermodynamic properties of boehmite, diaspore and $Al(OH)_4^-$ derived in the body of this report together with updated thermodynamic data for several of the participating minerals, e.g. kaolinite, margarite and paragonite, from carefully evaluated sources, e.g. Robinson et al. (1982) and Robie and Hemingway (1984) were incorporated in the EQ3 database. The solution analyses of experiments 3 and 4 were then reevaluated. The following paragraphs describe the results thus obtained.

As has been noted above, the diaspore from Nevada, and used in experiment 3 contained traces of contaminants, one of which was identified as pyrophyllite. At 175°C, the solution supersaturated with respect to both boehmite and diaspore within the first two hours. Calculations indicate that the solution also supersaturated with respect to kaolinite and the calcium and sodium micas, margarite and paragonite. After 22 hours the solution had almost achieved saturation with respect to imogolite, whose thermodynamic properties were computed from the solubility measurements conducted by Farmer et al. (1979). Figure F.7a illustrates the results. Data at 175°C might be explained by postulating that pyrophyllite or other finely divided or reactive aluminosilicates dissolved rapidly until saturation was attained with respect to imogolite or an analogous phase. Precipitation of this phase then occurred, which stabilized the solution composition, over the brief period that measurements were made.

By raising the temperature to 250°C, and reequilibrating for 23 hours, boehmite and diaspore and margarite remained supersaturated. Although the scatter in the data is less than desirable, there appears to be a general trend indicating that boehmite and diaspore were slowly approaching equilibrium during the 23 hour period, (Figure F7.b). Upon raising the temperature to 325°C, all minerals, including diaspore became undersaturated. Calculation of $\log \frac{Q}{K}$ indicated that the degree of undersaturation increased continuously during the five hour period that measurements were made as is shown in Figure F.7c. The calculated distribution of aluminum species indicates that the species $Al(OH)_3^o$ would have predominated, although significant concentrations of $Al(OH)_4^-$ were also present.

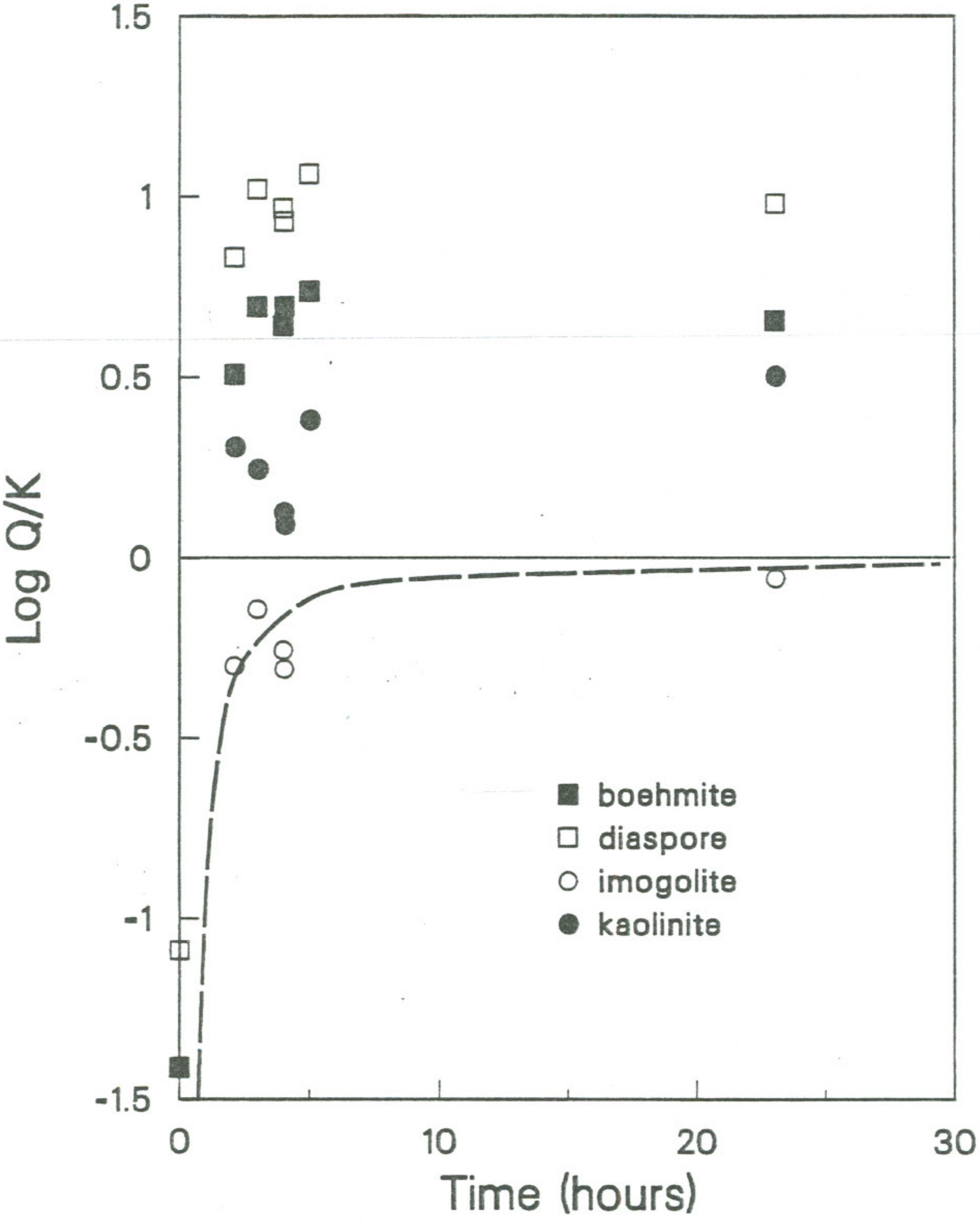
The observed decrease in the solubility quotient, Q_{s4}, below the limits of saturation of diaspore is puzzling. Even, if all aluminum in solution is assigned to $Al(OH)_3^o$, the solution remains undersaturated with respect to diaspore. A possible explanation is that some of the aluminum was escaping into the vapor phase, but calculations based on the Martynova ray diagram (Lindsay, 1979) lead to the conclusion that little over 5 wt percent of the total dissolved aluminum, would have escaped into the vapor phase in the autoclave at 325°C. And this presupposes that diaspore was not dissolving sufficiently fast to offset aluminum losses to the vapor. One could speculate that an aluminum chloride or oxychloride may be contributing to the volatilization of aluminum. It is clear that further experimental study would be required to resolve the question.

The data from experiment 4, when plotted as $\log K_{s4}$(AlOOH) versus reciprocal temperature and compared with the predicted values of $\log K_{s4}$(boehmite) and $\log K_{s4}$(diaspore), as illustrated in Figure F.8, suggest that reversible equilibrium was achieved between 250° and 350°C with respect to boehmite. Below 250°C, the data become erratic with a significant divergence, in some cases, between the measurements made during ascending temperature, when compared with those made during descending temperature. The erratic behavior can be traced in part to fluctuating pH values measured during the descending temperature phase. The observed precipitation of aluminum from alkaline solution, should cause a corresponding increase in pH. It is therefore suspected that the low pH readings at 100 and 150°C, taken during the descending temperature phase, may be in error. This may have been due to CO_2 in the aqueous sample, due to uptake from the atmosphere, although precautions were taken to prevent this.

There appears to be no ambiguity regarding the ascending temperature phase. Here it is quite clear that the diaspore initially supersaturated in solution, finally precipitating and equilibrating at 250°C with respect to metastable boehmite. We may conclude that experiment 4 represents equilibrium with respect to boehmite from supersaturation, and that the aluminum concentration in solution was controlled above 250°C by saturation with respect to boehmite.

4.0 Interpretation of the Results of the Diaspore Solubility Study at 197°C (Experiment 6)

Initial calculation of $\log Q_{s4}$(diaspore) from the data summarized in Table F.9, and using the pH measured at 25°C to compute electrical balance and the distribution of species at 25°C, showed that the measured pH



XCG 886-6717
6/20/88

Figure F.7a. Plots of $\log\frac{Q}{K}$ for various minerals as a function of time, calculated from the results of Experiment 3. (a) 175°C.

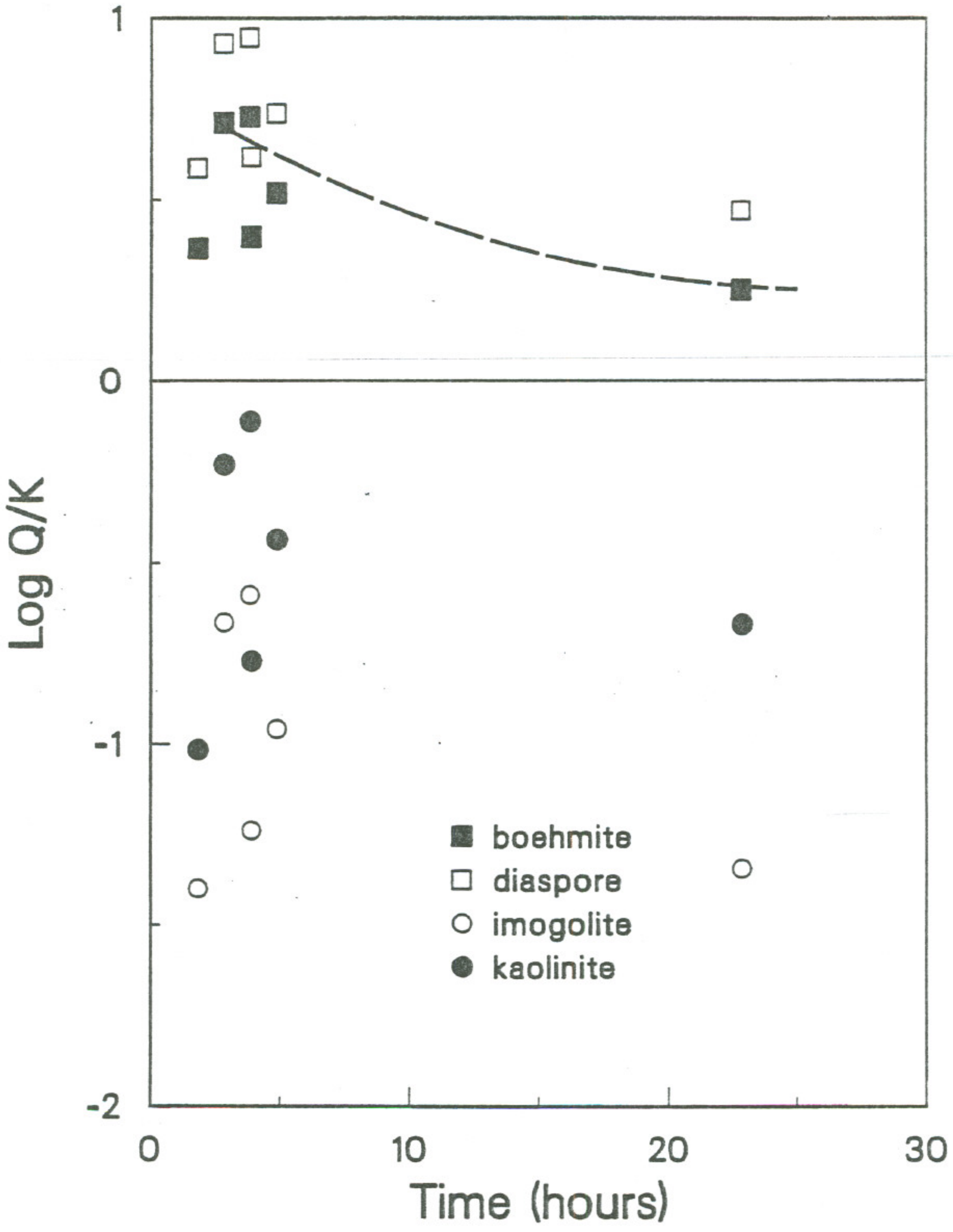


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Figure F.7b. Plots of $\log\frac{Q}{K}$ for various minerals as a function of time, calculated from the results of Experiment 3. (b) 250°C.

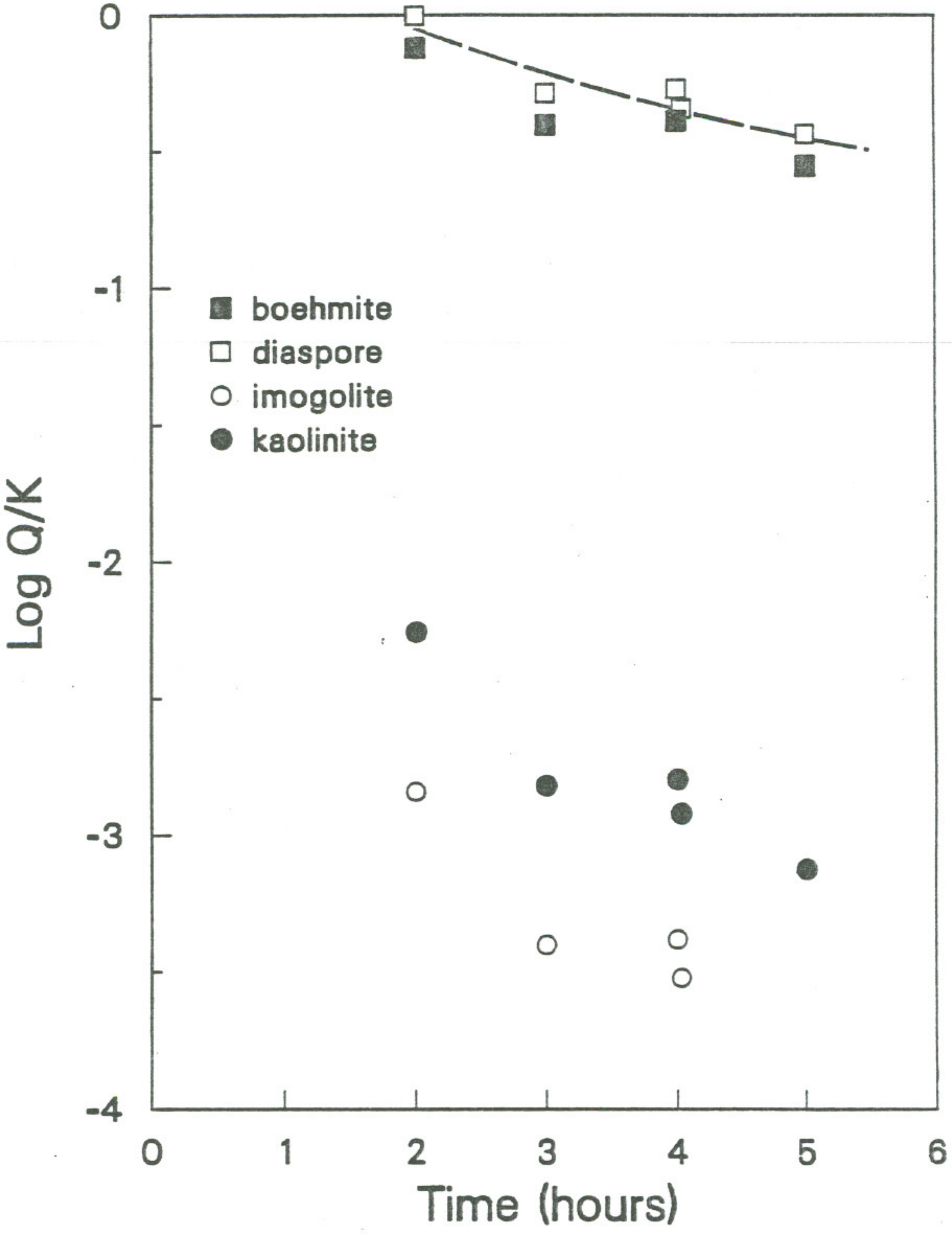

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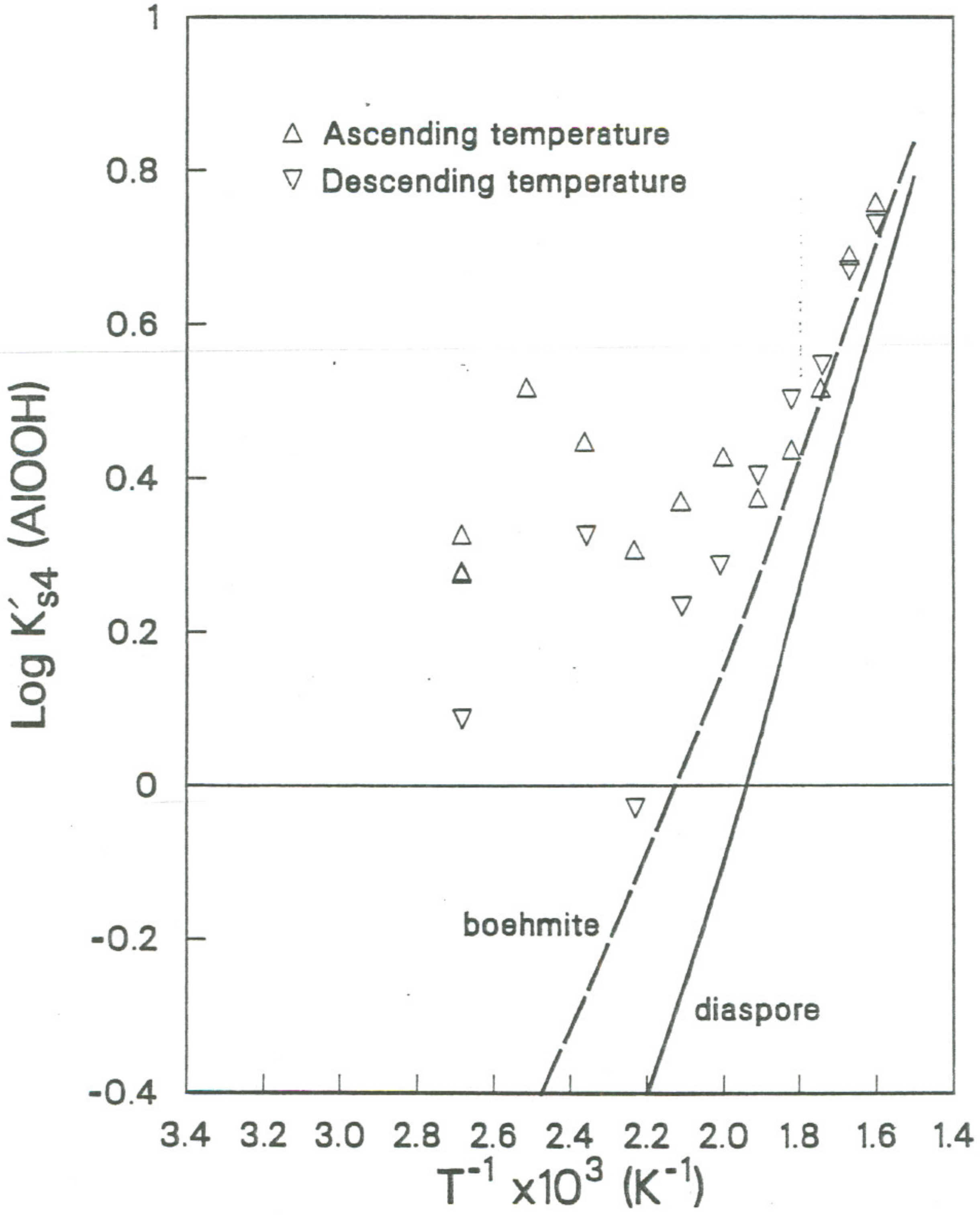
Figure F.7c. Plots of $\log\frac{Q}{K}$ for various minerals as a function of time, calculated from the results of Experiment 3. (c) 325°C.



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6/21/88

Figure F.8. Variation of log K_{s4}(AlOOH) versus the reciprocal of temperature, calculated from the results of Experiment 4.

was less than the true pH by approximately 0.1 unit. Because considerable care had been taked to avoid contamination by CO_2, we decided instead to assume that all Na^+ was initially balanced with OH^- and that dissolution of diaspore led to neutralization of the NaOH, thus

$$AlOOH + NaOH = NaAlO_2 + H_2O$$

On this basis, the elevated temperature species distributions were calculated using the EQ3 code, and log Q_{s4} determined. Using absolute rate theory, the equation was fitted to the data as illustrated in Figure F.9. Log K_{s4}(diaspore) at 197°C is –0.28.

5.0 Conclusions

Interpretation of the results of the six attempts to measure the solubility of diaspore over the temperature range between 25 and 350°C leads to the following preliminary conclusions.

1. Diaspore attains equilibrium with respect to alkali solutions (0.001–0.01 $\bar{N}$ NaOH) only very slowly below 200°C. For example, a 10 g charge of –60 + 400 mesh diaspore in 700 ml of 0.01 $\bar{N}$ NaOH solution does not attain equilibrum in less than 50 hours at 200°C.
2. The true solubility of diaspore in solutions near the isoelectric point is very difficult to measure: transient supersaturation may lead to precipitation of a metastable solid or disordered surface phase that will persist for several days at least at temperatures below 300°C. The metastable phase may show reversible equilibrium with respect to the aqueous phase.
3. Minor contaminants in solution, such as SiO_2(aq), if not accounted for, may seriously perturb the calculated value of K_{s4}(diaspore) in the isoelectric region, thereby making estimation of K_{s4}(diaspore) potentially unreliable.
4. Evidence is presented both by Kuyunko et al. (1983) and by Bourcier et al. (1987) for the presence of the aqueous species, $Al(OH)_3^\circ$, under near neutral pH conditions at 200 and 250°C. Preliminary indications in this study suggest also that it may be a significant species above 300°C. However, all evidence so far presented is tenuous and subject to review.
5. As the critical point of water is approached, homogeneous solution equilibria and heterogeneous equilibrium with respect to liquid and vapor phases can change rapidly, leading to the formation of species not considered at lower temperatures. These could include $NaAlO_2^\circ$. However, the evidence for this species in dilute NaOH solution, i.e., less than 0.1 $\bar{N}$ Na^+ is negative.
6. The utilization of pH measurements of quenched solutions can lead to meaningful results. However, interpretation of the measurements is difficult, and the results are less precise than is possible with accurate measurements on unquenched solutions at lower temperatures.
7. When dilute alkaline solutions are used for diaspore solubility measurements, dissolution of minor contaminants or fines, or any crystallographically disturbed material, can lead to supersaturation of the solutions with respect to diaspore and equilibration with respect to metastable phases. Diaspore samples of the utmost purity are required for solubility studies.

6.0 Recommendations

1. Reliable measurements of diaspore solubility in alkaline solutions should be made with a minimum initial NaOH concentration of 0.001 $\bar{N}$. Preliminary experiments should be made to determine the kinetics of dissolution before embarking on experiments to measure diaspore solubility below 200°C.
2. For precise work, an accurate method of continuously monitoring the course of reaction without perturbing the system, is required. An electrochemical cell of the type utilized by Berecz and Szita (1970), modified for operation at elevated temperatures would be particularly valuable.
3. Measurement of pH on quenched solution samples is fraught with so many difficulties, that development of high temperature pH sensors is merited for solubility investigations.

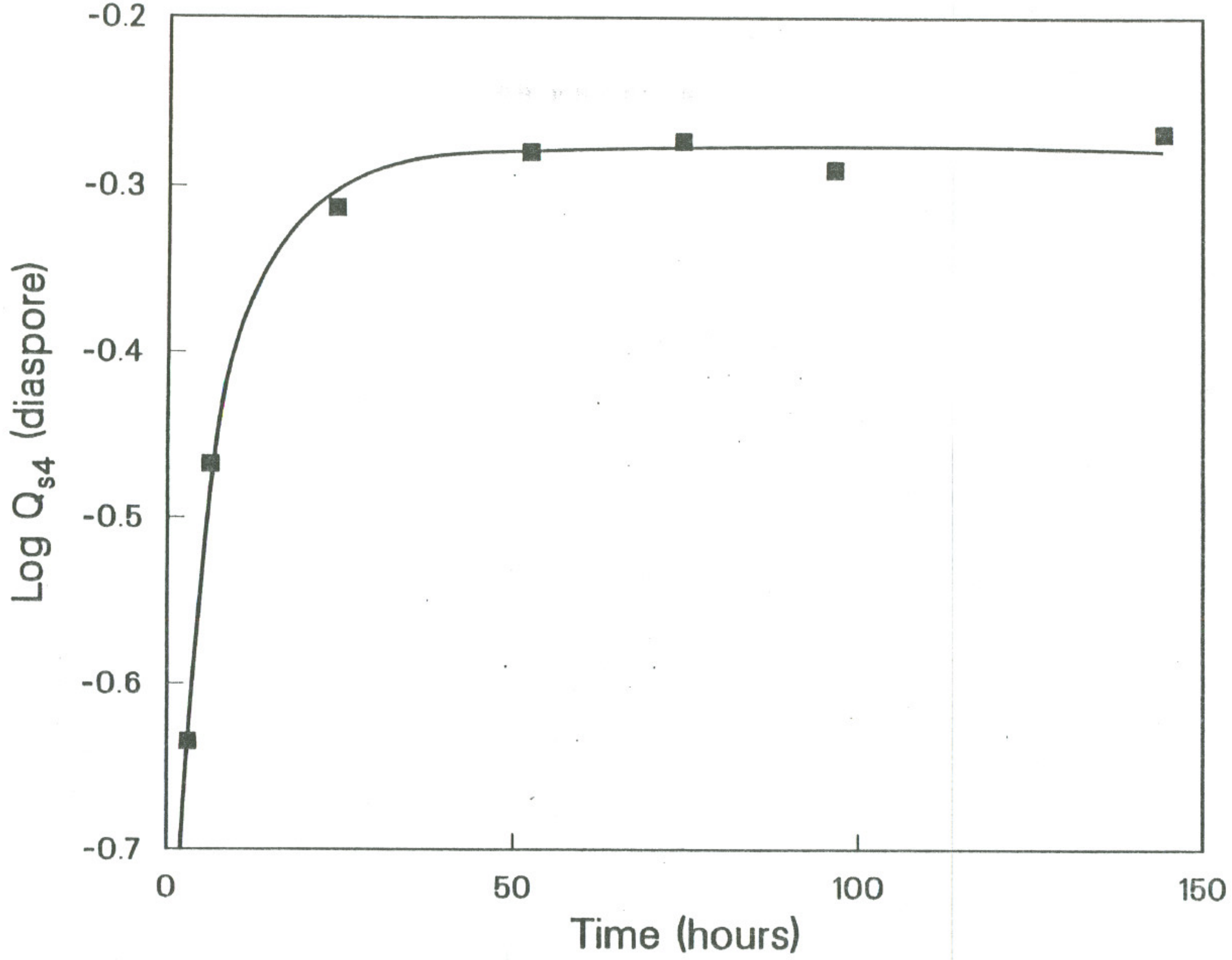


Figure F.9. Dissolution of diaspore in 0.01 $\bar{N}$ NaOH at 197°C.

4. The difficulties encountered in attempting to measure true diaspore solubility in the isoelectric region suggest that equilibrium solubility measurements as a means of interpreting aqueous aluminum hydroxide speciation may not be appropriate in any but the most meticulous investigations. Speciation studies avoiding the use of a coexisting solid phase in ''equilibrium'' with the solution are recommended.

APPENDIX G

EXPERIMENTAL RESULTS BY WEFERS (1967b) ON SOLUBILITIES OF PHASES IN THE SYSTEM Al_2O_3–Na_2O–H_2O BETWEEN 60 AND 350°C, AND CALCULATED SOLUBILITY PRODUCTS, K_{s4}, FOR GIBBSITE, BOEHMITE AND DIASPORE

Dr. Karl Wefers, of the Aluminum Company of America conducted, as part of his Ph.D. thesis, an extensive series of autoclave runs between 60 and 350°C to examine phase relations in the system $Na_2O - Al_2O_3 - H_2O$. His interpretation of the resulting data is presented in graphical form in Wefers (1967b). Dr. Wefers kindly sent the authors the original data from his thesis, which are reproduced here as Tables G.1–G.10.

The data in Tables G.1 through G.10 were used to calculate M_{Na^+}, $M_{Al^{+++}}$ and total dissolved solids, given in Tables G.11 through G.20. These data were input to the EQ3 code and log K'_{s4} for gibbsite, boehmite or diaspore were calculated as appropriate. The log K'_{s4} values are also summarized in Tables G.11 through G.20 together with calculated values of the activity of water and the ionic strength.

Log K'_{s4} values are plotted against ionic strength in Figures G.1 through G.3. As may be observed, there is considerable scatter in the plotted values. The scatter may be attributed to experimental difficulties associated with the sluggish kinetics of reactions between the seed phases, the highly concentrated viscous sodium aluminate solutions and difficulties encountered in separating the final solution from the solids after quenching the autoclave. Significant back reaction may also have occurred in some of the autoclave runs during quenching.

Extrapolation of calculated log K'_{s4} values to zero ionic strength was achieved by an internally consistent empirical correlation of log K'_{s4} versus ionic strength, established through evaluation of the work of other investigators, as illustrated in Figures 3 and 5 of the text of this report. The results are summarized in Table G.21.

As may be noted, the K'_{s4} values are consistent with the mineral solubilities assumed by Wefers to be controlling the solution concentration at the lowest temperature, 60°C, and at temperatures of 250° and above. However, between 80°C and 150°C, the present authors believe that the relatively short duration of the experiments resulted in metastable equilibrium being achieved with respect to gibbsite below 150°C and boehmite above 150°C, even though only diaspore apparently remained in the products at 135 and 150°C. This interpretation is consistent with the observations regarding the slow rates of diaspore equilibration in alkaline solutions below 200°C, as discussed in Appendix F, and observations regarding the kinetics of gibbsite to boehmite conversion in strong sodium aluminate solutions as reported by Taylor et al. (1927).

A consequence of the present authors' interpretation of Wefers' data is that they believe that the reaction:

gibbsite = diaspore + water (l)

will occur only below 0°C in the metastable liquid region, instead of circa 100°C as proposed by Wefers (1967b). The present authors also believe that thermodynamic equilibrium between the aqueous phase and diaspore above 250°C, and at ionic strengths greater than two, may also have been subject to either kinetic constraints or to precipitation during cooling. Therefore, only those log K'_{s4} values at $I \leq 2$ are used to estimate log K'_{s4}(diaspore). This interpretation is supported by analysis of the data which suggests that the flattening of the log K'_{s4} versus I slope with increasing ionic strength is not due to the effect of saturation with respect to corundum, because corundum remains substantially undersaturated, even at 350°C. If diaspore did alter to corundum at high ionic strength between 330 and 350°C as Wefers claims, then the apparent undersaturation must be due to precipitation of secondary aluminum phases during the cooling process.

This is in agreement with observations by Wefers (1967b) regarding the secondary precipitation of $Al(OH)_3$ and $2NaAlO_2{\cdot}2.5H_2O$, which were found in the residues after filtering solutions quenched from 250–350°C to near room temperatures.

TABLE G.1

60°C ISOTHERM

Sample 1: Gibbsite + 5% Diaspore in Standard Solution (H), 310 hr.
Sample 2: Diaspore in Standard Solution (D), 500 hr.

Expt. No.	Na_2O $g.l^{-1}$	Al_2O_3 $g.l^{-1}$	Molar ratio[1]	Density $g.ml^{-1}$	Na_2O wt%	Al_2O_3 wt%	Solids remaining
631(H)	40.8	20.2	3.33	1.065	3.83	1.90	gibbsite
585(H)	84.5	31.8	4.37	1.115	7.58	2.85	gibbsite
632(H)	81.5	42.4	3.17	1.128	7.23	3.76	gibbsite
587(H)	125.0	86.4	2.37	1.199	10.43	7.21	gibbsite
588(H)	165.0	163.0	1.67	1.289	12.80	12.65	gibbsite
634(H)	253.0	215.0	1.93	1.415	17.88	15.19	gibbsite
635(H)	306.0	225.0	2.24	1.485	20.61	15.15	NAH[1]
589(D)	43.5	20.2	3.52	1.073	4.05	1.88	gibbsite, ≈ 10% diaspore
590(D)	81.5	35.3	3.79	1.121	7.27	3.15	gibbsite, ≈ 10% diaspore
591(D)	112.0	62.0	2.97	1.169	9.58	5.30	gibbsite, < 10% diaspore
592(D)	165.0	146.0	1.85	1.281	12.88	11.40	gibbsite, < 10% diaspore

[1] NAH = $2NaAlO_2.2.5H_2O$

TABLE G.2

80°C ISOTHERM

Sample 1: Gibbsite; Diaspore = 1:1 In Standard Solution (H), 310 hr.
Sample 2: $2NaAlO_2.2.5\ H_2O$ + 2% Gibbsite + 2% Diaspore In Standard Solution (N), 310 hr.

Expt. No.	Na_2O $g.l^{-1}$	Al_2O_3 $g.l^{-1}$	Molar ratio	Density $g.ml^{-1}$	Na_2O wt.%	Al_2O_3 wt.%	Solids remaining
638(H)	52.4	9.2	9.4	1.079	4.86	0.85	gibbsite, ≈ 20% diaspore
639(H)	102.0	86.2	1.95	1.177	8.67	7.32	gibbsite, ≈ 20% diaspore
640(H)	222.0	205.0	1.78	1.375	16.15	14.91	diaspore
641(H)	264.0	236.0	1.83	1.440	18.33	16.39	diaspore
642(H)	318.0	271.0	1.93	1.520	20.92	17.83	diaspore
653(H)	322.0	254.0	2.09	1.516	21.24	16.75	NAH, ≈ 5% diaspore
654(H)	535.0	11.0	78.00	1.458	36.70	0.75	NAH
648(N)	265.0	306.0	1.42	1.465	18.09	20.89	diaspore, ≈ 10% gibbsite
649(N)	291.0	321.0	1.49	1.502	19.37	21.37	NAH
652(N)	333.0	390.0	1.40	1.576	21.13	24.75	NAH
646(N)	450.0	66.8	11.10	1.467	30.67	4.55	NAH

TABLE G.3

95°C ISOTHERM

Sample 1: 2g Diaspore + 2g $NaAlO_2.2.5\ H_2O$ In 100 ml Total Concentration Held "IT" (H), 150 hr.

Sample 2: $2NaAlO_2.2.5\ H_2O$ + 2% Diaspore + 2% Gibbsite In Solution (N), 150 hr.

Expt. No.	Na_2O $g.l^{-1}$	Al_2O_3 $g{\cdot}l^{-1}$	Molar ratio	Density $g.ml^{-1}$	Na_2O wt%	Al_2O_3 wt%	Solids remaining
656(H)	225.0	222.0	1.67	1.387	16.22	16.01	diaspore, ≈ 5% boehmite
657(H)	321.0	413.0	1.28	1.567	20.49	26.36	NAH, ≈ 5% diaspore
658(H)	307.0	303.0	1.67	1.518	20.22	19.96	NAH, < 5% diaspore
671(N)	62.8	25.4	4.07	1.098	5.72	2.31	gibbsite, < 10% diaspore
661(N)	82.2	49.8	2.74	1.128	7.29	4.41	gibbsite, < 10% diaspore
672(N)	146.0	93.5	2.55	1.230	11.87	7.60	gibbsite, < 10% diaspore
662(N)	141.0	110.0	2.10	1.233	11.44	8.92	gibbsite, < 10% diaspore
663(N)	295.0	305.0	1.60	1.502	19.64	20.31	diaspore, ≈ 5% boehmite
664(N)	314.0	373.0	1.38	1.548	20.28	24.10	diaspore, ≈ 5% boehmite
675(N)	314.0	294.0	1.76	1.523	20.62	19.30	NAH, ≈ 5% diaspore
666(N)	317.0	325.0	1.60	1.538	20.61	21.13	NAH, < 5% diaspore
665(N)	329.0	400.0	1.35	1.575	20.89	25.40	NAH, < 5% diaspore
677(N)	350.0	206.0	2.80	1.530	22.88	13.46	NAH
678(N)	353.0	195.0	2.99	1.516	23.28	12.86	NAH
668(N)	381.0	148.0	4.25	1.505	25.32	9.80	NAH
647(N)	452.0	88.0	8.45	1.482	30.50	5.94	NAH
669(N)	462.0	48.8	15.60	1.447	31.93	3.37	NAH
670(N)	583.0	25.7	37.30	1.506	38.71	1.71	NAH

TABLE G.4

105°C ISOTHERM

Sample 1: Gibbsite: Diaspore = 1:1 In Standard Solution (H), 310 hr.

Sample 2: Diaspore In Standard Solution (D), 310 hr.

Expt. No.	Na_2O $g.l^{-1}$	Al_2O_3 $g.l^{-1}$	Molar ratio	Density $g.ml^{-1}$	Na_2O wt%	Al_2O_3 wt%	Solids remaining
601(H)	30.0	18.7	2.63	1.052	2.85	1.78	diaspore, gibbsite, ≈ 1:1
602(H)	119.0	75.7	2.58	1.186	10.03	6.38	diaspore
603(H)	177.0	166.0	1.76	1.305	13.56	12.72	diaspore
604(H)	255.0	277.0	1.52	1.445	17.65	16.17	diaspore
605(H)	416.0	524.0	1.30	1.721	24.17	30.45	NAH, ≈ 10% diaspore
606(D)	47.7	28.9	2.71	1.079	4.42	2.68	diaspore
607(D)	103.0	58.0	2.91	1.156	8.91	5.02	diaspore
608(D)	211.0	180.0	1.93	1.344	15.70	13.39	diaspore
609(D)	293.0	312.0	1.54	1.503	19.49	20.76	diaspore
610(D)	373.0	400.0	1.53	1.632	22.86	24.51	NAH, diaspore, ≈ 1:1

TABLE G.5

135°C ISOTHERM

Sample: Gibbsite: Diaspore = 1:1 In Standard Solution, 460 hr.

Expt. No.	Na_2O g.l^{-1}	Al_2O_3 g.l^{-1}	Molar ratio	Density g.ml^{-1}	Na_2O wt%	Al_2O_3 wt%	Solids remaining
580	38.6	20.8	3.04	1.062	3.63	1.96	diaspore
575	48.6	29.1	2.75	1.082	4.49	2.69	diaspore
581	87.0	57.0	2.52	1.137	7.65	5.01	diaspore
576	86.0	60.0	2.37	1.139	7.55	5.27	diaspore
582	179.0	140.0	2.11	1.292	13.85	10.84	diaspore
583	221.0	218.0	1.67	1.379	16.03	15.81	diaspore
578	261.0	272.0	1.57	1.450	18.00	18.76	diaspore
579	408.0	460.0	1.46	1.695	24.07	27.14	diaspore
679	550.0	141.0	6.70	1.570	35.03	8.98	NAH

TABLE G.6

150°C ISOTHERM

Sample: Diaspore In Standard Solution, 260 hr.

Expt. No.	Na_2O g.l^{-1}	Al_2O_3 g.l^{-1}	Molar ratio	Density g.ml^{-1}	Na_2O wt%	Al_2O_3 wt%	Solids remaining
533	86.4	70.0	2.03	1.149	7.52	6.09	diaspore
534	110.0	97.0	1.87	1.192	9.23	8.14	diaspore
535	131.0	112.0	1.83	1.228	10.67	9.12	diaspore
536	149.0	138.0	1.77	1.259	11.83	10.96	diaspore
537	190.0	166.0	1.88	1.319	14.40	12.59	diaspore
538	199.0	195.0	1.67	1.343	14.82	14.52	diaspore
539	206.0	208.0	1.62	1.358	15.17	15.32	diaspore
540	223.0	248.0	1.48	1.392	16.02	17.82	diaspore
562	255.0	284.0	1.47	1.450	17.59	19.59	diaspore
541	259.0	285.0	1.50	1.450	17.86	19.66	diaspore
564	315.0	371.0	1.40	1.548	20.35	23.97	diaspore
563	321.0	389.0	1.36	1.561	20.56	24.92	diaspore
565	462.0	537.0	1.41	1.786	25.87	30.07	$NaAlO_2 \approx 20\%$, diaspore

TABLE G.7

250°C ISOTHERM

Sample: Diaspore In Standard Solution, 290 hr.

Expt. No.	Na_2O $g.l^{-1}$	Al_2O_3 $g.l^{-1}$	Molar ratio	Density $g.ml^{-1}$	Na_2O wt%	Al_2O_3 wt%	Solids remaining
542	44.0	52.4	1.38	1.107	3.97	4.73	diaspore
543	88.6	108.0	1.34	1.183	7.49	9.13	diaspore
517	103.0	125.0	1.38	1.205	8.55	10.37	diaspore
544	118.0	142.0	1.36	1.231	9.59	11.54	diaspore
545	143.0	175.0	1.34	1.271	11.25	13.77	diaspore
546	154.0	187.0	1.36	1.289	11.95	14.51	diaspore
521	189.0	213.0	1.46	1.342	14.08	15.87	diaspore
547	187.0	222.0	1.39	1.341	13.94	16.55	diaspore
548	217.0	268.0	1.33	1.394	15.57	19.23	diaspore
549	233.0	298.0	1.29	1.422	16.39	20.96	diaspore
550	233.0	317.0	1.21	1.428	16.32	22.20	diaspore
551	247.0	361.0	1.13	1.457	16.95	24.78	diaspore
560	422.0	520.0	1.33	1.728	24.42	30.01	diaspore

TABLE G.8

300°C ISOTHERM

Sample: Diaspore In Standard Solution, 300 hr.

Expt. No.	Na_2O $g.l^{-1}$	Al_2O_3 $g.l^{-1}$	Molar ratio	Density $g.ml^{-1}$	Na_2O wt%	Al_2O_3 wt%	Solids remaining
508	34.4	32.5	1.75	1.078	3.19	3.01	diaspore
509	39.2	31.4	2.05	1.078	3.64	2.91	diaspore
510	57.6	45.8	2.06	1.109	5.19	4.13	diaspore
512	57.2	73.5	1.28	1.135	5.04	6.48	diaspore
518	53.0	76.3	1.14	1.135	4.67	6.72	diaspore
519	96.0	136.0	1.16	1.207	7.95	11.27	diaspore
511	108.0	147.0	1.21	1.223	8.83	12.02	diaspore
516	152.0	207.0	1.20	1.295	11.74	15.98	diaspore
520	190.0	252.0	1.25	1.335	14.23	18.88	diaspore
611	204.0	282.0	1.19	1.381	14.77	20.42	diaspore
612	256.0	358.0	1.18	1.467	17.45	24.40	diaspore
613	283.0	392.0	1.19	1.512	18.72	25.93	diaspore
614	320.0	445.0	1.18	1.573	20.34	28.29	diaspore

TABLE G.9

330°C ISOTHERM

Sample: Diaspore : Corundum = 1:1 In Standard Solution, 240 hr.

Expt. No.	Na_2O g.l^{-1}	Al_2O_3 g.l^{-1}	Molar ratio	Density g.ml^{-1}	Na_2O wt%	Al_2O_3 wt%	Solids remaining
597	58.5	72.6	1.32	1.133	5.16	6.41	diaspore
507	91.0	118.0	1.23	1.190	7.65	9.92	diaspore, < 5% corundum
593	110.0	137.0	1.33	1.220	9.02	11.23	diaspore, < 5% corundum
598	164.0	212.0	1.27	1.310	12.52	16.18	diaspore, < 5% corundum
594	210.0	278.0	1.24	1.388	15.13	20.03	diaspore, < 5% corundum
599	250.0	335.0	1.23	1.452	17.22	23.07	diaspore, < 10% corundum
595	285.0	393.0	1.19	1.516	18.80	25.92	diaspore, < 10%, corundum 1:1
600	347.0	486.0	1.17	1.617	21.46	30.06	corundum
596	445.0	652.0	1.13	1.785	24.93	36.53	corundum

TABLE G.10

350°C ISOTHERM

Sample: Diaspore : Corundum = 1:1 In Standard Solution, 200 hr.

Expt. No.	Na_2O g.l^{-1}	Al_2O_3 g.l^{-1}	Molar ratio	Density g.ml^{-1}	Na_2O wt%	Al_2O_3 wt%	Solids remaining
552	48.0	63.1	1.25	1.122	4.28	5.62	diaspore, < 10% corundum
505	94.8	126.0	1.25	1.194	7.94	10.55	diaspore, < 10% corundum
553	95.4	123.0	1.27	1.199	7.96	10.26	diaspore, < 10% corundum
554	146.0	192.0	1.25	1.283	11.38	14.96	diaspore, ≈ 10% corundum
555	182.0	241.0	1.24	1.342	13.56	17.96	diaspore, corundum ≈ 1:1
556	256.0	364.0	1.16	1.470	17.41	24.76	diaspore, corundum ≈ 1:1
557	271.0	404.0	1.11	1.499	18.08	26.95	corundum
558	385.0	525.0	1.19	1.680	22.92	31.25	corundum
559	427.0	594.0	1.18	1.750	24.40	33.94	corundum

TABLE G.11

60°C ISOTHERM

CALCULATION OF LOG K'_{s4}(GIBBSITE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(gib)
631(H)	69373	30268	10691	-0.0197	1.231	-0.301
585(H)	135431	62687	16830	-0.0451	2.382	-0.413
632(H)	140259	60461	22440	-0.0428	2.329	-0.269
587(H)	232677	92732	45727	-0.0735	3.496	+0.032
588(H)	350566	122406	86268	-0.1382	5.576	+0.479
634(H)	503904	187690	113789	-0.1932	6.587	+0.407
635(H)	580678	227008	119081	-0.2374	7.282	+0.343
589(D)	72865	32271	10691	-0.0210	1.299	-0.338
590(D)	134426	60461	18683	-0.0428	2.310	-0.335
591(D)	195815	83088	32814	-0.0636	3.105	-0.144
592(D)	333384	122406	77271	-0.1072	4.632	+0.304

TABLE G.12

80°C ISOTHERM

CALCULATION OF LOG K'_{s4}(GIBBSITE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]]	Ionic Strength	log K'_{s4}(gib)
638(H)	75341	38873	4869	-0.0256	1.499	-0.843
639(H)	202761	75669	45621	-0.0567	2.983	+0.199
640(H)	455589	164692	108496	-0.1579	6.071	+0.446
641(H)	535386	195850	124903	-0.1934	6.953	+0.481
642(H)	633993	235911	143427	-0.2242	7.972	+0.520
653(H)	625200	238878	134430	-0.2247	7.807	+0.439
654(H)	701089	396894	5822	—	—	—[1]
648(N)	594189	196592	161951	-0.2010	7.935	+0.857
649(N)	640145	215881	169889	—	—	—[1]
652(N)	751161	247039	206408	—	—	—[1]
646(N)	636980	333836	35354	—	—	—[1]

[1] Equilibrated with respect to NAH.

TABLE G.13

95°C ISOTHERM

CALCULATION OF LOG K'_{s4}(GIBBSITE) AND LOG K'_{s4}(BOEHMITE/DIASPORE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(gib)	log K'_{s4}(boe) log K'_{s4}(dia)
656(H)	473436	166918	117494	-0.1573	6.225	+0.5501	+0.7074
657(H)	754535	238136	218580	-0.1999	10.494	+1.3201	+1.520
658(H)	652566	227750	160363	-0.2053	8.274	+0.7269	+0.9322
671(N)	101460	46589	13443	-0.0315	1.796	-0.3891	-0.3576
661(N)	147244	60981	26357	-0.0436	2.361	-0.1096	-0.0660
672(N)	265675	108311	49485	-0.0885	3.885	+0.0135	+0.1020
662(N)	272763	104602	58218	-0.0853	3.900	+0.1652	+0.2505
663(N)	632174	218848	161421	-0.2030	8.158	+0.7685	+0.9715
664(N)	712617	232943	197410	-0.2047	9.545	+1.0860	+1.2907
675(N)	647714	232943	155600	-0.2055	8.158	+0.6611	+0.8666
666(N)	677063	235169	172006	-0.2055	8.669	+0.8601	+1.0116
665(N)	754203	244071	211700	-0.1975	10.234	+1.1912	+1.3887
677(N)	621985	259650	109026	—	—	—	—[1]
678(N)	616829	261876	103204	—	—	—	—[1]
668(N)	614435	282648	78329	—	—	—	—[1]
647(N)	656984	335320	46574	—	—	—	—[1]
669(N)	637715	342738	25827	—	—	—	—[1]
670(N)	775257	432503	13602	—	—	—	—[1]

[1] Equilibrated with respect to NAH.

TABLE G.14

105°C ISOTHERM

CALCULATION OF LOG K'_{s4}(GIBBSITE) AND LOG K'_{s4}(BOEHMITE/DIASPORE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(gib)	log K'_{s4}(boe) log K'_{s4}(dia)
601(H)	54170	22256	9897	-0.0142	0.917	-0.155	-0.141
602(H)	216125	88281	40064	-0.0685	3.254	-0.021	+0.048
603(H)	365338	131309	87855	-0.1147	4.916	+0.413	+0.527
604(H)	557428	189174	146602	-0.1775	7.252	+0.772	+0.949
605(H)	968615	308613	277327	+0.1486	13.967	+1.692	+1.544
606(D)	85446	35387	15295	-0.0234	1.422	-0.151	-0.128
607(D)	180887	76411	30697	-0.0572	2.842	-0.128	-0.070
608(D)	420821	156532	95265	-0.1429	5.583	+0.373	+0.516
609(D)	635338	217364	165126	-0.1930	8.184	+0.834	+1.027
610(D)	811119	276713	211700	-0.1221	10.449	+1.071	+1.193

TABLE G.15

135°C ISOTHERM

CALCULATION OF LOG K'_{s4}(GIBBSITE) AND LOG K'_{s4}(BOEHMITE/DIASPORE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(gib)	log K'_{s4}(boe) log K'_{s4}(dia)
580	67020	28636	11008	-0.0186	1.1541	-0.2358	-0.2172
575	86774	36054	15401	-0.0238	1.4351	-0.1517	-0.1279
581	159368	64542	30167	-0.0468	2.4700	-0.0339	+0.0129
576	160539	63800	31755	-0.0461	2.4583	+0.0118	+0.0579
582	346564	132792	74095	-0.1126	4.6941	+0.2471	+0.3597
583	464975	163951	115377	-0.1439	6.0455	+0.5734	+0.7173
578	561082	193625	143956	-0.1635	7.2039	+0.7391	+0.9026
579	905687	302678	243455	+0.1648	12.0167	+1.3358	+1.1710
579	827295	408022	74624	—	—	—	—[1]

[1] Equilibrated with respect to NAH.

TABLE G.16

150°C ISOTHERM

CALCULATION OF LOG K'_{s4}(GIBBSITE) AND LOG K'_{s4}(BOEHMITE/DIASPORE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(gib)	log K'_{s4}(boe) log K'_{s4}(dia)
533	169272	64096	37048	-0.0463	2.4960	+0.1392	+0.1855
534	221982	81604	51337	-0.0620	3.1437	+0.2542	+0.3162
535	261470	97183	59276	-0.0763	3.6360	+0.2578	+0.3341
536	306115	110537	73037	-0.0900	4.1601	+0.3702	+0.4602
537	382154	140953	87856	-0.1194	5.0529	+0.3821	+0.5015
538	417621	147630	103204	-0.1264	5.4694	+0.5302	+0.6566
539	437356	152823	110084	-0.1311	5.7020	+0.5828	+0.7139
540	492209	165434	131254	-0.1426	6.4280	+0.7649	+0.9075
562	563179	189174	150307	-0.1543	7.2703	+0.8455	+0.9998
541	569175	192141	150836	-0.1551	7.3623	+0.8384	+0.9935
564	712268	233685	196352	-0.1234	9.404	+1.1416	+1.265
563	734817	238136	205878	-0.1110	9.835	+1.2330	+1.244
565	1038799	342738	284208	*	*	*	*

*Computer simulation gave unreasonable results.

TABLE G.17
250°C ISOTHERM
CALCULATION OF LOG K'_{s4}(BOEHMITE/DIASPORE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(boe) log K'_{s4}(dia)
542	99966	32642	27733	-0.0207	1.3349	0.5678
543	203337	65729	57159	-0.0470	2.6796	0.7133
517	235931	76411	66156	-0.0564	3.1120	0.7416
544	269301	87539	75154	-0.0662	3.5451	0.7647
545	328751	106086	92619	-0.0828	4.3290	0.8594
546	352839	114246	98970	-0.0895	4.6442	0.8739
521	419474	140211	112730	-0.1065	5.4864	0.8357
547	424281	138727	117494	-0.1062	5.5805	0.9183
548	500879	160983	141839	-0.1128	6.6339	1.0654
549	546223	172853	157717	-0.1098	7.3580	1.1783
550	561832	172853	167772	-0.1090	7.6621	1.3392
551	616090	183239	191059	-0.0973	8.7043	1.6297
560	973090	313064	275210	+1.1191	13.9664	1.6350

TABLE G.18
300°C ISOTHERM
CALCULATION OF LOG K'_{s4}(BOEHMITE/DIASPORE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(boe) log K'_{s4}(dia)
508	71199	25520	17201			
509	76504	29081	16618	-0.0179	1.1149	0.1499
510	112136	42731	24240	-0.0276	1.6085	0.1810
512	134376	42434	38900	-0.0273	1.7340	0.7682
518	131243	39318	40382	-0.0249	1.6467	1.0546
519	235913	71218	71978	-0.0508	3.0378	1.0849
511	260473	80121	77800	-0.0584	3.3962	0.9928
516	366683	112762	109555	-0.0851	4.9066	1.0658
520	452808	140953	133371	-0.0993	6.3358	1.0531
611	495564	151339	149249	-0.0993	6.8768	1.1674
612	625268	189916	189472	-0.0546	9.0527	1.1999
613	688127	209946	207466	+0.0125	10.1427	1.1260
614	779531	237394	235517	+0.1993	11.8746	0.9796

TABLE G.19

330°C ISOTHERM

CALCULATION OF LOG K'_{s4}(BOEHMITE/DIASPORE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(boe) log K'_{s4}(dia)
597	135318	43399	38424	-0.0273	1.7519	0.7297
507	214657	67509	62452	-0.0464	2.8065	0.8531
593	254844	81604	72507	-0.0579	3.3882	0.7934
598	386313	121665	112201	-0.0866	5.3383	0.8978
594	500040	155790	147132	-0.0892	7.1850	0.9440
599	598611	185464	177299	-0.0479	8.9713	0.9190
595	691535	211429	207955	+0.0522	10.7070	0.8776
600	848141	257425	257216	—	—	—[1]
596	1111288	330127	345071	—	—	—[1]

[1] Equilibrated with respect to corundum.

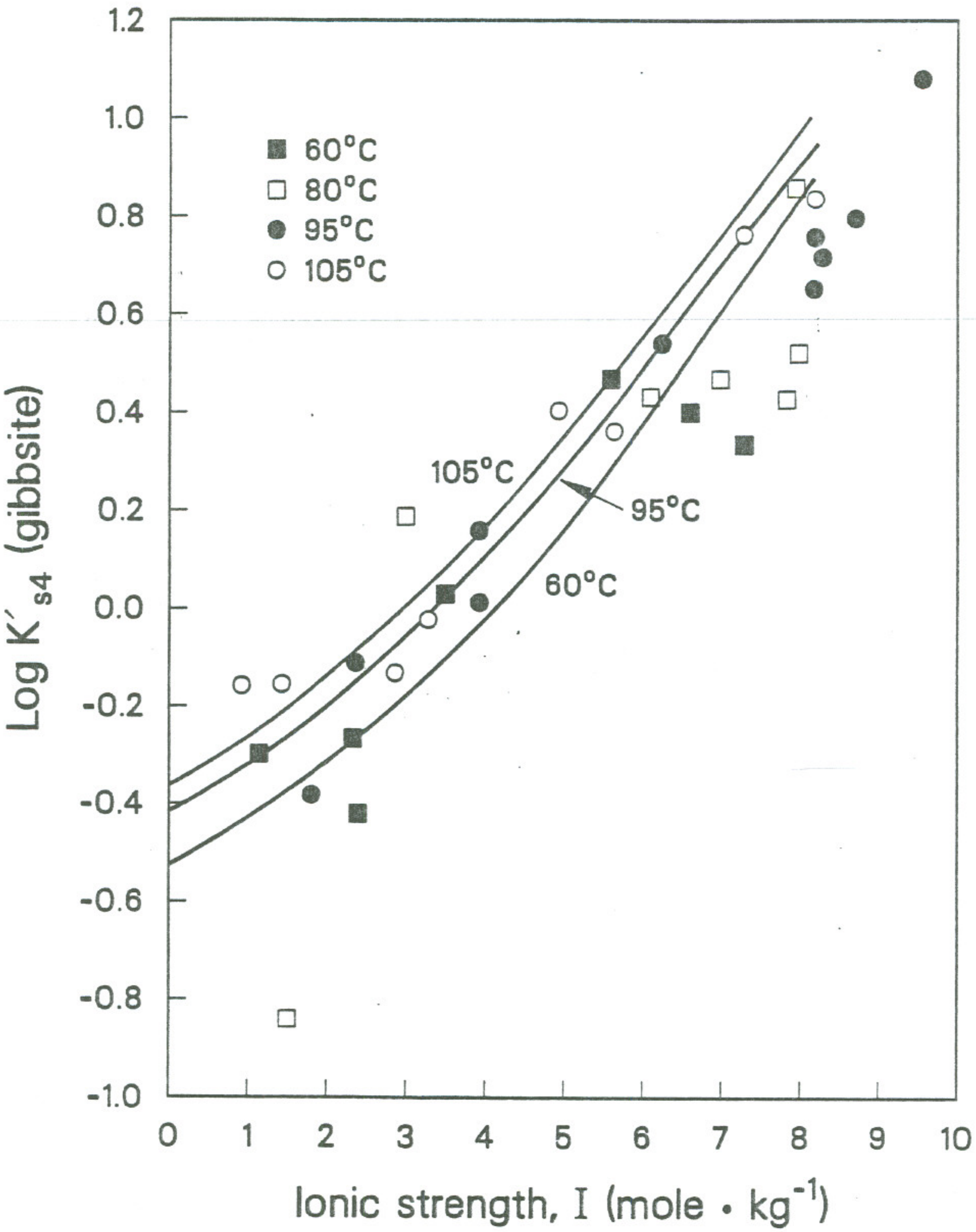
TABLE G.20

350°C ISOTHERM

CALCULATION OF LOG K'_{s4}(BOEHMITE/DIASPORE)

Expt. No.	TDS mg.l^{-1}	Na^+ mg.l^{-1}	Al^{+++} mg.l^{-1}	log [H_2O]	Ionic Strength	log K'_{s4}(boe) log K'_{s4}(dia)
552	113931	35609	33396	-0.0210	1.4382	0.8502
505	226145	70328	66686	-0.0479	2.9783	0.9058
553	224457	70773	65098	-0.0479	2.9532	0.8413
554	346598	108311	101616	-0.0764	4.7767	0.8916
555	433422	135018	127549	-0.0873	6.1987	0.8991
556	630197	189916	192647	-0.0158	9.6769	0.9771
557	682463	201043	213817	—	—	—[1]
558	929337	285615	277857	—	—	—[1]
559	1040353	316773	314375	—	—	—[1]

[1] Equilibrated with respect to corundum.



XCG 877–11334

Figure G.1. The apparent solubility products, K'_{s4} (gibbsite), plotted against ionic strength at 60, 80, 95 and 105°C, from Wefers (1967b).

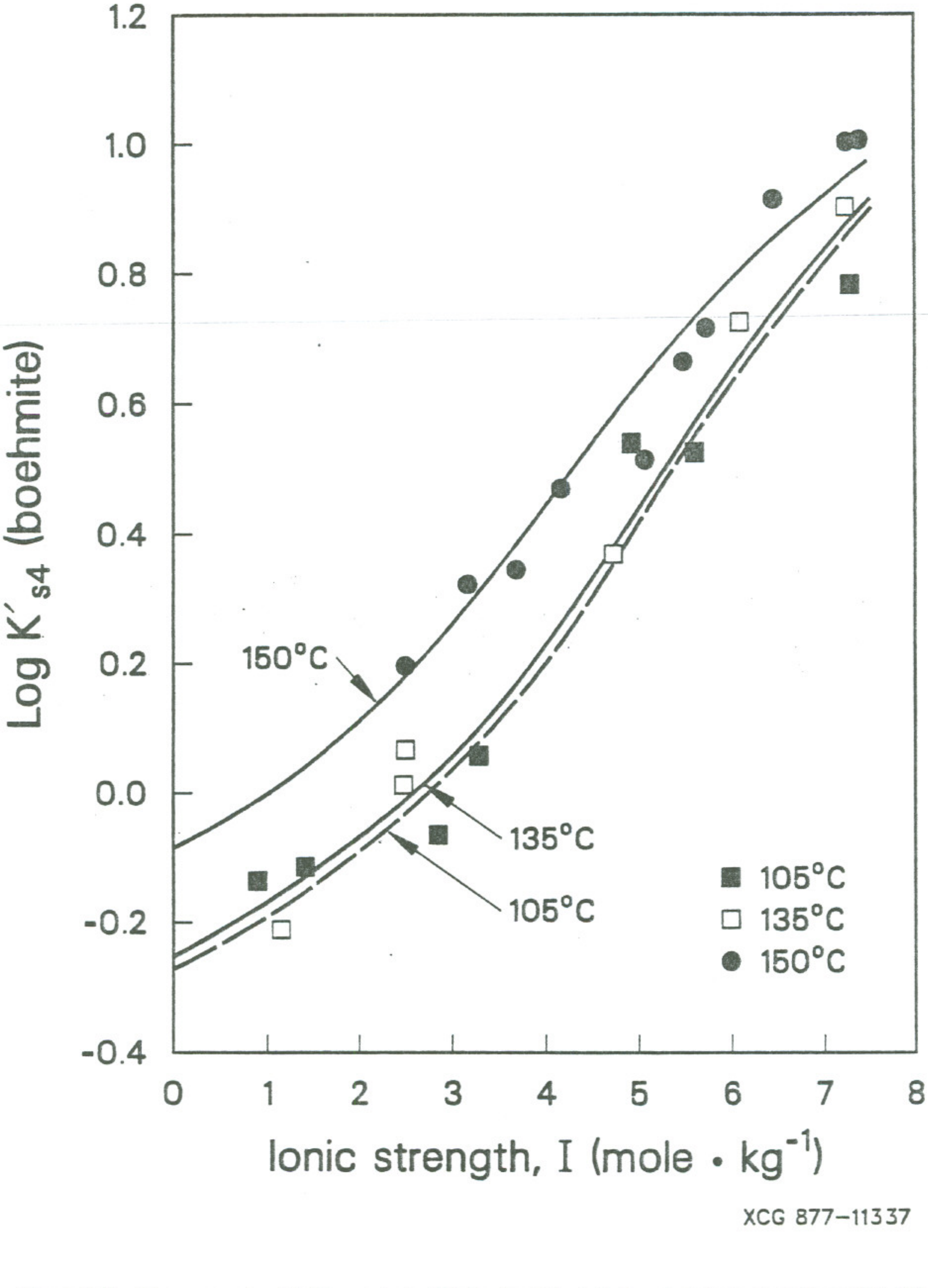


Figure G.2. The apparent solubility products, K'_{s4}(boehmite), plotted against ionic strength at 105, 135, and 150°C, from Wefers (1967b).

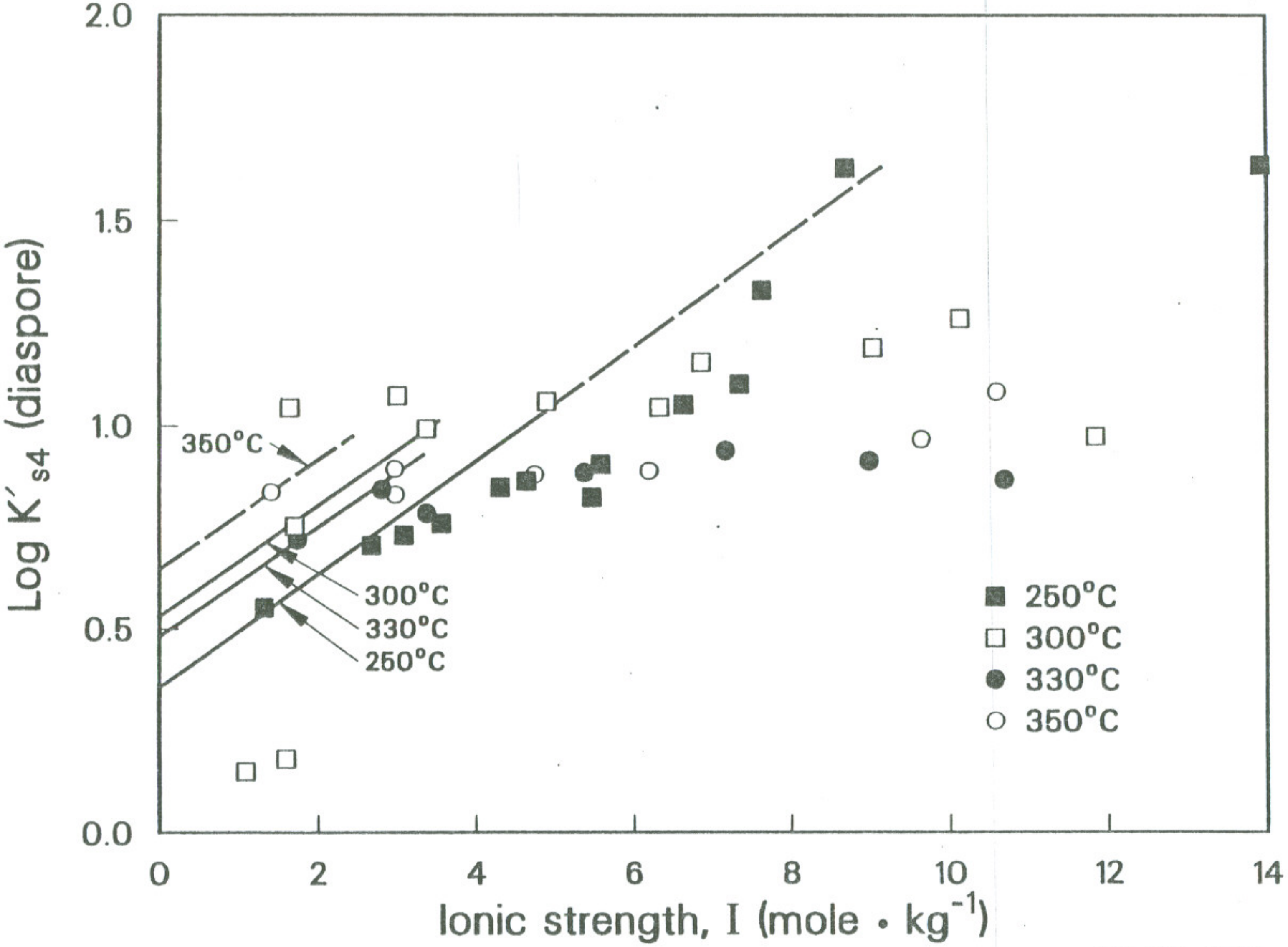


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Figure G.3. The apparent solubility products, K'_{s4}(diaspore), plotted against ionic strength at 250, 300, 330 and 350°C, from Wefers (1967b).

TABLE G.21

SUMMARY OF SOLUBILITY PRODUCT CONSTANTS, K_{s4}, FROM THE DATA BY WEFERS (1967b)

T, °C	log K_{s4}	Aluminum hydroxide/oxide remaining	Apparent equilibrium with respect to:-
60	-0.53	primarily gibbsite	gibbsite
80	≈ -0.5	gibbsite, diaspore	gibbsite
95	-0.4	diaspore, boehmite, gibbsite	gibbsite
105	-0.35/-0.30	diaspore, gibbsite in one sample	gibbsite/boehmite
135	-0.25	diaspore	boehmite
150	-0.10	diaspore	boehmite
250	+0.36	diaspore	diaspore
300	+0.54	diaspore	diaspore
330	+0.48	diaspore, corundum	diaspore
350	+0.66	diaspore, corundum	diaspore

APPENDIX H

REDUCTION OF LITERATURE DATA

Solubility data of the aluminum hydroxides, reported in the literature, are given in terms of a variety of parameters. In most cases two concentrations are given describing respectively the sodium and aluminum components of the solution. Sodium may be reported as Na_2O or as initial NaOH, and aluminum as Al_2O_3, $NaAlO_2$ or Al. The units used include wt. %, $g.kg^{-1}$, $mole.kg^{-1}$, $g.l^{-1}$, or $mole.l^{-1}$. Solution densities are occasionally reported as $g.cm^{-3}$. All data must be converted to total Na^+ and total Al^{+++}, expressed in terms of molalities ($mole.kgH_2O^{-1}$).

The EQ3 code (Wolery, 1983) has provision for automatic conversion of some data to standardized units. However, the total dissolved solids per liter of solution, or per kg of H_2O is required, and if the conversion is from volume units, the density of the solution is also required. The procedures used for calculating total dissolved solids and solution densities are given below.

1.1 Calculation of Total Dissolved Solids

Total dissolved solids (TDS) may be computed in units of mg.kg H_2O^{-1} or $mg.l^{-1}$ as appropriate. When calculating TDS from data presented in weight percent, it is assumed that the salts dissolved in water are NaOH and $NaAlO_2$. This arbitrary choice of salts is preferred over alternatives, such as the hydrated form of sodium aluminate, $NaAlO_2.2H_2O$, in the absence of definitive information regarding the degree of solvation of the aluminate ion or the amount of "free" water that may be present.

In calculating TDS (mg.kg H_2O^{-1}) from data expressed in weight percent Na_2O and Al_2O_3, the following procedure was used:

1. Calculate concentrations of water
   $100 - (Na_2O + Al_2O_3) = H_2O$
2. Divide Na_2O by 30.991 = A
3. Divide Al_2O_3 by 50.980 = B
4. Divide H_2O by 18.016 = C
5. Calculate H_2O corr $= C - \frac{A-B}{2} = D$
6. Mulitply D by 18.016 = E
7. Evaluate $\frac{A}{E} \times 1000 = F$
   $= Na^+$, mole.kg H_2O^{-1}
8. Evaluate $\frac{B}{E} \times 1000 = G$
   $= Al^{+++}$, mole.kg H_2O^{-1}

To calculate TDS (mg.kg H_2O^{-1})

$$TDS = ((39.997 \times (F-G)) + (81.9710 \times G)) \times 1000$$

To calculate TDS ($mg.l^{-1}$) from data expressed as Na_2O and Al_2O_3 in $g.l^{-1}$, the following expression was used:

$$1000 \times \left[\left[\left[\frac{Na_2O\ exp}{30.9895} - \frac{Al_2O_3\ exp}{50.9810}\right] \times 39.9971\right] + \left[\left[\frac{Al_2O_3\ exp}{50.981}\right] \times 81.9701\right]\right].$$

1.2 Calculation of Solution Densities

Whenever a source of solubility data included solution densities at 25°C, these were used to recompute solubilities from a volumetric to a mass basis. However, when density data was not included, use was made of an equation fitting the densities of sodium aluminate solutions. The density data is given by Dibrov et al. (1964b), and the equation used to fit the data is

$$\rho\ (g{\cdot}cm^{-3}) = b_1\ (\frac{1}{T}) + b_2\ (Na_2O) + b_3(Al_2O_3) + b_4$$

where: N_2O and Al_2O_3 are expressed in weight percent

T is in K

$b_1 = +114.46$

$b_2 = +0.14302 \times 10^{-1}$

$b_3 = +0.10178 \times 10^{-1}$

$b_4 = +0.62005$

This simple equation has a percentage standard error of 0.81 but a few individual values vary by as much as 3.0 percent at 250°C. Because its use was confined to calculations at 25°C, no further effort was expended to refine the equation to improve the fit of elevated temperature data.

In practice, a simplified expression was used where

$$\rho = b_1\ T + b_2\ (Na_2O) + b_3\ (Al_2O_3) + b_4$$

where: Na_2O and Al_2O_3 are expressed in weight percent

T = 25°C

$b_1 = -0.77104 \times 10^{-3}$

$b_2 = +0.14302 \times 10^{-1}$

$b_3 = +0.10178 \times 10^{-1}$

$b_4 = +0.10161 \times 10^{-1}$

To compute densities, an iterative procedure was used, thus:-

1. Read initial concentration of Na_2O (experimental), $g.l^{-1}$
   Read initial concentration of Al_2O_3 (experimental), $g.l^{-1}$
2. Compute molarities and TDS ($mg.l^{-1}$)
   let:

$$M_{Na^{+}} = \left[\frac{Na_2O(experimental) \times 2}{61.9789}\right]$$

$$M_{Al^{+++}} = \left[\frac{Al_2O_3(experimental) \times 2}{101.961}\right]$$

3. Calculate initial weight percent

$$Na_2O\ (wt\%) \approx \frac{Na_2O\ (experimental)}{10}$$

$$Al_2O_3\ (wt\%) \approx \frac{Al_2O_3(experimental)}{10}$$

4. Compute the initial density, g.cm^{-3}, using the equation:-

$$\rho = b_1\ (T) + b_2(Na_2O\ wt\%) + b_3\ (Al_2O_3\ wt\%) + b_4$$

where T 25°C

5. Compute molalities.

The molality, $m_i = \dfrac{\text{weight of solute} \times 1000}{\text{formula weight solute} \times \text{weight of water}}$

hence:

$$m_{Na^+} = \frac{M_{Na^+} \times 1000}{1000 \times \rho - TDS/1000}$$

$$m_{Al^{+++}} = \frac{M_{Al^{+++}} \times 1000}{1000 \times \rho - TDS/1000}$$

where TDS is in mg.l^{-1}

6. Compute new weight percents

$$Na_2O\ (wt\%) = \frac{m_{Na^+} \times 61.9789 \times 100}{2\left[1000 + \frac{1}{2}\ [m_{Na^+} \times 61.9789) + (m_{Al^{+++}} \times 101.961]\right]}$$

$$Al_2O_3\ (wt\%) = \frac{m_{Al^{+++}} \times 101.961 \times 100}{2\left[1000 + \frac{1}{2}\ [m_{Na^+} \times 61.9789) + (m_{Al^{+++}} \times 101.961]\right]}$$

7. Go to step 4 and repeat until converged.

TDS given in this procedure is expressed in mg.l^{-1} and is the same expression as presented in the preceding section.

The procedure for the calculation of density was used with appropriate modifications wherever solution densities were required.

APPENDIX I
TABULATIONS OF THE THERMODYNAMIC PROPERTIES OF PARTICIPATING MINERALS AND AQUEOUS SPECIES

The following tables are mainly SUPCRT printouts of reactions involving the minerals gibbsite, boehmite, and diaspore and water, computed along the aqueous saturation surface. A tabulation of the thermodynamic properties of OH^- and log K_W, based on the latest version of the HKF equation of State by Tanger and Helgeson (1988), is given. All these tables were either used in this study or represent calculations of the thermodynamic properties of minerals investigated in this report.

The following is a list of tables included in this appendix.

I.1 $0.5\,O_2 + H_2 = H_2O$

I.2 $Al + 1.5O_2 + 1.5H_2 = Al(OH)_3$ (gibbsite)

I.3 $Al + 1.5O_2 + 1.5H_2 = Al(OH)_3$ (bayerite)

I.4 $Al + O_2 + 0.5H_2 = AlOOH$ (boehmite)

I.5 $Al + O_2 + 0.5H_2 = AlOOH$ (diaspore)

I.6 $2Al + 1.5O_2 = Al_2O_3$ (corundum)

I.7 $0.5O_2 + H_2 = OH^- + H^+$

I.8 Estimates of Log K_w Between 0 and 350°C Along the Saturation Surface of Water (from the Literature)

I.9 $H_2O = OH^- + H^+$

I.10 Gibbsite = Boehmite + H_2O

I.11 Boehmite = Diaspore

I.12 Gibbsite + $OH^- = AlO_2^- + 2H_2O$

I.13 Bayerite + $OH^- = AlO_2^- + 2H_2O$

I.14 Boehmite + $OH^- = AlO_2^- + H_2O$

I.15 Diaspore + $OH^- = AlO_2^- + H_2O$

I.16 0.5 Corundum + $OH^- = AlO_2^- + 0.5H_2O$

TABLE I.1

```
                                                                                   07/ 5/88
                                                                                   page  1

          --------------------------------------------------------------------
                    0.50oxygen + 1.00hydrogen =  1.00h2o
          --------------------------------------------------------------------

      ----------------------------------------------------------------------------
              species properties in their standard state of 25 degrees c and 1 bar
      ----------------------------------------------------------------------------

                                 .....minerals.....


                                   .....ions.....


                                   .....gases.....

                                                                                   maier-kelley power fun. coef.
   name          coef.   enthalpy (cal)  entropy (cal)  free energy(cal)  volume (cc/mol)   a       bx10**3      cx10**-5
   ----          -----   --------------  -------------  ----------------  ---------------  -----    -------      --------
 oxygen         -0.500        0.0          49.029             0.0            0.00000       7.160    1.0000        -0.400
 hydrogen       -1.000        0.0          31.234             0.0            0.00000       6.520    0.7800         0.120

                                    .....h2o.....

   name          coef.   enthalpy (cal)  entropy (cal)  free energy (cal)  volume (cc/mol)
   ----          -----   --------------  -------------  -----------------  ---------------
 water           1.000      -68315.7         16.7           -56686.8          18.0692


      ----------------------------------------------------------------------------
                        reaction properties at 25 degrees c and 1 bar
      ----------------------------------------------------------------------------

   enthalpy (cal)    entropy (cal)    free energy (cal)  delta vol (cc/mol)  heat capacity      log k

  -0.683157E+05     -0.390361E+02     -0.566868E+05      0.180692E+02       0.762251E+01     0.415518E+02

                         fugacity coefficents are listed in this order

                                 gas number  1 = oxygen

                                 gas number  2 = hydrogen
```

```
        ----------------------------------------------------------------------------------------------------------------
                                    0.50oxygen + 1.00hydrogen =  1.00h2o
        ----------------------------------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp     delta h(t,p)   delta s(t,p)   delta g(t,p)    log k(t,p)    delta v(t,p)  fug coef
-----------  ------------ ------------   ------------   ------------   ------------    ----------    ------------  --------
   0.006         0.0      0.786822E+01  -0.685078E+05  -0.397091E+02  -0.576708E+05   0.461421E+02   0.180193E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.009         5.0      0.773443E+01  -0.684688E+05  -0.395677E+02  -0.574726E+05   0.451570E+02   0.180163E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.012        10.0      0.767275E+01  -0.684303E+05  -0.394306E+02  -0.572752E+05   0.442072E+02   0.180208E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.017        15.0      0.764534E+01  -0.683921E+05  -0.392965E+02  -0.570784E+05   0.432908E+02   0.180317E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.023        20.0      0.763192E+01  -0.683539E+05  -0.391651E+02  -0.568823E+05   0.424062E+02   0.180480E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.032        25.0      0.762251E+01  -0.683157E+05  -0.390361E+02  -0.566868E+05   0.415518E+02   0.180692E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.042        30.0      0.761293E+01  -0.682776E+05  -0.389094E+02  -0.564920E+05   0.407260E+02   0.180947E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.056        35.0      0.760213E+01  -0.682396E+05  -0.387850E+02  -0.562977E+05   0.399274E+02   0.181243E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.074        40.0      0.759057E+01  -0.682016E+05  -0.386627E+02  -0.561041E+05   0.391548E+02   0.181575E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.096        45.0      0.757925E+01  -0.681637E+05  -0.385426E+02  -0.559112E+05   0.384069E+02   0.181942E+02 0.1000E+01
                                                                                                                 0.1000E+01

   0.123        50.0      0.756926E+01  -0.681258E+05  -0.384245E+02  -0.557188E+05   0.376825E+02   0.182343E+02 0.1000E+01
                                                                                                                 0.1000E+01
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 0.158      55.0    0.756154E+01  -0.680880E+05  -0.383083E+02  -0.555269E+05    0.369806E+02    0.182775E+02 0.1000E+01
                                                                                                              0.1000E+01

 0.199      60.0    0.755676E+01  -0.680501E+05  -0.381940E+02  -0.553357E+05    0.363001E+02    0.183238E+02 0.1000E+01
                                                                                                              0.1000E+01

 0.250      65.0    0.755532E+01  -0.680123E+05  -0.380815E+02  -0.551450E+05    0.356402E+02    0.183731E+02 0.1000E+01
                                                                                                              0.1000E+01

 0.312      70.0    0.755740E+01  -0.679745E+05  -0.379706E+02  -0.549549E+05    0.349998E+02    0.184253E+02 0.1000E+01
                                                                                                              0.1000E+01

 0.386      75.0    0.756302E+01  -0.679367E+05  -0.378613E+02  -0.547653E+05    0.343781E+02    0.184803E+02 0.1000E+01
                                                                                                              0.1000E+01

 0.474      80.0    0.757204E+01  -0.678989E+05  -0.377534E+02  -0.545763E+05    0.337744E+02    0.185382E+02 0.1000E+01
                                                                                                              0.1000E+01

 0.578      85.0    0.758427E+01  -0.678609E+05  -0.376469E+02  -0.543877E+05    0.331878E+02    0.185989E+02 0.1000E+01
                                                                                                              0.1000E+01

 0.701      90.0    0.759949E+01  -0.678229E+05  -0.375417E+02  -0.541997E+05    0.326177E+02    0.186623E+02 0.1000E+01
                                                                                                              0.1000E+01

 0.845      95.0    0.761746E+01  -0.677848E+05  -0.374377E+02  -0.540123E+05    0.320635E+02    0.187285E+02 0.1000E+01
                                                                                                              0.1000E+01

 1.013     100.0    0.763796E+01  -0.677466E+05  -0.373348E+02  -0.538253E+05    0.315243E+02    0.187974E+02 0.1000E+01
                                                                                                              0.1000E+01

 1.208     105.0    0.766083E+01  -0.677083E+05  -0.372331E+02  -0.536388E+05    0.309997E+02    0.188691E+02 0.1000E+01
                                                                                                              0.1000E+01

 1.432     110.0    0.768594E+01  -0.676699E+05  -0.371324E+02  -0.534528E+05    0.304891E+02    0.189436E+02 0.1000E+01
                                                                                                              0.1000E+01

 1.690     115.0    0.771321E+01  -0.676313E+05  -0.370326E+02  -0.532673E+05    0.299919E+02    0.190209E+02 0.1000E+01
                                                                                                              0.1000E+01
```

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  1.985    120.0    0.774263E+01   -0.675926E+05   -0.369338E+02   -0.530823E+05    0.295076E+02    0.191011E+02 0.1000E+01
                                                                                                                 0.1000E+01

  2.320    125.0    0.777422E+01   -0.675537E+05   -0.368359E+02   -0.528978E+05    0.290358E+02    0.191841E+02 0.1000E+01
                                                                                                                 0.1000E+01

  2.700    130.0    0.780808E+01   -0.675146E+05   -0.367389E+02   -0.527137E+05    0.285759E+02    0.192701E+02 0.1000E+01
                                                                                                                 0.1000E+01

  3.129    135.0    0.784433E+01   -0.674754E+05   -0.366426E+02   -0.525300E+05    0.281275E+02    0.193591E+02 0.1000E+01
                                                                                                                 0.1000E+01

  3.612    140.0    0.788315E+01   -0.674359E+05   -0.365470E+02   -0.523469E+05    0.276902E+02    0.194511E+02 0.1000E+01
                                                                                                                 0.1000E+01

  4.153    145.0    0.792476E+01   -0.673963E+05   -0.364522E+02   -0.521642E+05    0.272636E+02    0.195463E+02 0.1000E+01
                                                                                                                 0.1000E+01

  4.757    150.0    0.796940E+01   -0.673564E+05   -0.363580E+02   -0.519819E+05    0.268473E+02    0.196447E+02 0.1000E+01
                                                                                                                 0.1000E+01

  5.430    155.0    0.801736E+01   -0.673162E+05   -0.362645E+02   -0.518000E+05    0.264409E+02    0.197464E+02 0.1000E+01
                                                                                                                 0.1000E+01

  6.177    160.0    0.806894E+01   -0.672758E+05   -0.361715E+02   -0.516186E+05    0.260442E+02    0.198515E+02 0.1000E+01
                                                                                                                 0.1000E+01

  7.003    165.0    0.812450E+01   -0.672351E+05   -0.360790E+02   -0.514376E+05    0.256567E+02    0.199602E+02 0.1000E+01
                                                                                                                 0.1000E+01

  7.915    170.0    0.818439E+01   -0.671941E+05   -0.359870E+02   -0.512571E+05    0.252782E+02    0.200726E+02 0.1000E+01
                                                                                                                 0.1000E+01

  8.918    175.0    0.824900E+01   -0.671528E+05   -0.358953E+02   -0.510769E+05    0.249083E+02    0.201888E+02 0.1000E+01
                                                                                                                 0.1000E+01

 10.019    180.0    0.831876E+01   -0.671112E+05   -0.358041E+02   -0.508972E+05    0.245468E+02    0.203089E+02 0.1000E+01
                                                                                                                 0.1000E+01
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11.225        185.0       0.839411E+01  -0.670691E+05  -0.357131E+02  -0.507178E+05    0.241933E+02    0.204333E+02 0.1000E+01
                                                                                                                   0.1000E+01

12.542        190.0       0.847554E+01  -0.670267E+05  -0.356224E+02  -0.505388E+05    0.238477E+02    0.205619E+02 0.1000E+01
                                                                                                                   0.1000E+01

13.976        195.0       0.856355E+01  -0.669838E+05  -0.355318E+02  -0.503603E+05    0.235096E+02    0.206951E+02 0.1000E+01
                                                                                                                   0.1000E+01

15.536        200.0       0.865870E+01  -0.669405E+05  -0.354414E+02  -0.501821E+05    0.231789E+02    0.208331E+02 0.1000E+01
                                                                                                                   0.1000E+01

17.229        205.0       0.876160E+01  -0.668967E+05  -0.353510E+02  -0.500043E+05    0.228553E+02    0.209761E+02 0.1000E+01
                                                                                                                   0.1000E+01

19.062        210.0       0.887289E+01  -0.668523E+05  -0.352607E+02  -0.498269E+05    0.225385E+02    0.211245E+02 0.1000E+01
                                                                                                                   0.1000E+01

21.042        215.0       0.899330E+01  -0.668074E+05  -0.351702E+02  -0.496498E+05    0.222284E+02    0.212784E+02 0.1000E+01
                                                                                                                   0.1000E+01

23.178        220.0       0.912361E+01  -0.667618E+05  -0.350796E+02  -0.494732E+05    0.219247E+02    0.214382E+02 0.1000E+01
                                                                                                                   0.1000E+01

25.478        225.0       0.926471E+01  -0.667156E+05  -0.349887E+02  -0.492968E+05    0.216273E+02    0.216044E+02 0.1000E+01
                                                                                                                   0.1000E+01

27.950        230.0       0.941758E+01  -0.666687E+05  -0.348976E+02  -0.491209E+05    0.213359E+02    0.217772E+02 0.1000E+01
                                                                                                                   0.1000E+01

30.603        235.0       0.958334E+01  -0.666210E+05  -0.348060E+02  -0.489452E+05    0.210504E+02    0.219572E+02 0.1000E+01
                                                                                                                   0.1000E+01

33.446        240.0       0.976326E+01  -0.665725E+05  -0.347140E+02  -0.487700E+05    0.207707E+02    0.221448E+02 0.1000E+01
                                                                                                                   0.1000E+01

36.487        245.0       0.995878E+01  -0.665231E+05  -0.346213E+02  -0.485950E+05    0.204965E+02    0.223407E+02 0.1000E+01
                                                                                                                   0.1000E+01
```

```
 39.735     250.0    0.101716E+02  -0.664728E+05  -0.345280E+02  -0.484205E+05   0.202276E+02   0.225453E+02 0.1000E+01
                                                                                                              0.1000E+01

 43.201     255.0    0.104036E+02  -0.664215E+05  -0.344339E+02  -0.482462E+05   0.199640E+02   0.227594E+02 0.1000E+01
                                                                                                              0.1000E+01

 46.893     260.0    0.106571E+02  -0.663690E+05  -0.343389E+02  -0.480723E+05   0.197055E+02   0.229838E+02 0.1000E+01
                                                                                                              0.1000E+01

 50.821     265.0    0.109347E+02  -0.663154E+05  -0.342429E+02  -0.478987E+05   0.194519E+02   0.232194E+02 0.1000E+01
                                                                                                              0.1000E+01

 54.996     270.0    0.112397E+02  -0.662605E+05  -0.341457E+02  -0.477254E+05   0.192032E+02   0.234671E+02 0.1000E+01
                                                                                                              0.1000E+01

 59.429     275.0    0.115759E+02  -0.662043E+05  -0.340472E+02  -0.475525E+05   0.189590E+02   0.237282E+02 0.1000E+01
                                                                                                              0.1000E+01

 64.128     280.0    0.119478E+02  -0.661465E+05  -0.339471E+02  -0.473798E+05   0.187195E+02   0.240039E+02 0.1000E+01
                                                                                                              0.1000E+01

 69.107     285.0    0.123612E+02  -0.660871E+05  -0.338454E+02  -0.472075E+05   0.184843E+02   0.242957E+02 0.1000E+01
                                                                                                              0.1000E+01

 74.376     290.0    0.128231E+02  -0.660259E+05  -0.337418E+02  -0.470355E+05   0.182534E+02   0.246056E+02 0.1000E+01
                                                                                                              0.1000E+01

 79.946     295.0    0.133422E+02  -0.659628E+05  -0.336360E+02  -0.468638E+05   0.180267E+02   0.249355E+02 0.1000E+01
                                                                                                              0.1000E+01

 85.832     300.0    0.139297E+02  -0.658975E+05  -0.335278E+02  -0.466924E+05   0.178041E+02   0.252879E+02 0.1000E+01
                                                                                                              0.1000E+01

 92.044     305.0    0.146000E+02  -0.658298E+05  -0.334168E+02  -0.465212E+05   0.175855E+02   0.256660E+02 0.1000E+01
                                                                                                              0.1000E+01

 98.597     310.0    0.153721E+02  -0.657595E+05  -0.333026E+02  -0.463504E+05   0.173707E+02   0.260733E+02 0.1000E+01
                                                                                                              0.1000E+01
```

```
105.505      315.0      0.162711E+02   -0.656861E+05   -0.331847E+02   -0.461799E+05    0.171596E+02    0.265143E+02 0.1018E+01
                                                                                                                     0.1036E+01

112.783      320.0      0.173320E+02   -0.656093E+05   -0.330626E+02   -0.460096E+05    0.169522E+02    0.269949E+02 0.1020E+01
                                                                                                                     0.1039E+01

120.447      325.0      0.186037E+02   -0.655286E+05   -0.329355E+02   -0.458397E+05    0.167484E+02    0.275221E+02 0.1021E+01
                                                                                                                     0.1041E+01

128.514      330.0      0.201576E+02   -0.654434E+05   -0.328025E+02   -0.456700E+05    0.165481E+02    0.281054E+02 0.1023E+01
                                                                                                                     0.1043E+01

137.003      335.0      0.221020E+02   -0.653527E+05   -0.326623E+02   -0.455006E+05    0.163512E+02    0.287576E+02 0.1025E+01
                                                                                                                     0.1046E+01

145.933      340.0      0.246090E+02   -0.652555E+05   -0.325133E+02   -0.453315E+05    0.161576E+02    0.294962E+02 0.1027E+01
                                                                                                                     0.1049E+01

155.328      345.0      0.279702E+02   -0.651501E+05   -0.323531E+02   -0.451626E+05    0.159672E+02    0.303467E+02 0.1030E+01
                                                                                                                     0.1051E+01

165.212      350.0      0.327210E+02   -0.650343E+05   -0.321783E+02   -0.449940E+05    0.157799E+02    0.313480E+02 0.1032E+01
                                                                                                                     0.1054E+01

175.614      355.0      0.399592E+02   -0.649043E+05   -0.319832E+02   -0.448257E+05    0.155958E+02    0.325640E+02 0.1034E+01
                                                                                                                     0.1057E+01

186.568      360.0      0.523352E+02   -0.647535E+05   -0.317579E+02   -0.446576E+05    0.154146E+02    0.341114E+02 0.1037E+01
                                                                                                                     0.1060E+01

198.118      365.0      0.781850E+02   -0.645684E+05   -0.314820E+02   -0.444898E+05    0.152363E+02    0.362421E+02 0.1040E+01
                                                                                                                     0.1064E+01

210.327      370.0      0.162302E+03   -0.643110E+05   -0.310975E+02   -0.443223E+05    0.150610E+02    0.397025E+02 0.1043E+01
                                                                                                                     0.1067E+01
```

TABLE I.2

```
                                                                                     07/ 5/88
                                                                                     page  1

        ------------------------------------------------------------------------------------
                    1.00aluminum + 1.50oxygen + 1.50hydrogen =  1.00gibbsite
        ------------------------------------------------------------------------------------

     -----------------------------------------------------------------------------------------------
                  species properties in their standard state of 25 degrees c and 1 bar
     -----------------------------------------------------------------------------------------------

                                      .....minerals.....

                                                                                        maier-kelley power fun. coef.
   name           coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a      bx10**3       cx10**-5
   ----           -----    --------------   -------------   ----------------   ---------------  -----    -------       --------
  gibbsite        1.000      -309065.0         16.358          -276025.0          31.95600       8.650   45.6000         0.000
  aluminum       -1.000            0.0          6.780                0.0           9.99900       4.940    2.9600         0.000
     --first tran--               0.00          0.00         temp=2726.8           0.00000      0.000    0.0000         0.000


                                        .....ions.....


                                        .....gases.....

                                                                                        maier-kelley power fun. coef.
   name           coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a      bx10**3       cx10**-5
   ----           -----    --------------   -------------   ----------------   ---------------  -----    -------       --------
  oxygen         -1.500            0.0         49.029                0.0           0.00000       7.160    1.0000        -0.400
  hydrogen       -1.500            0.0         31.234                0.0           0.00000       6.520    0.7800         0.120

                                         .....h2o.....


     -----------------------------------------------------------------------------------------------
                            reaction properties at 25 degrees c and 1 bar
     -----------------------------------------------------------------------------------------------

     enthalpy (cal)     entropy (cal)      free energy (cal)   delta vol (cc/mol)   heat capacity        log k

    -0.309065E+06      -0.110817E+03      -0.276025E+06        0.219570E+02       -0.442047E+01      0.202328E+03

                        fugacity coefficents are listed in this order

                               gas number  1 = oxygen

                               gas number  2 = hydrogen
```

```
           ------------------------------------------------------------------------------------------
                          1.00aluminum + 1.50oxygen + 1.50hydrogen =  1.00gibbsite
           ------------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp      delta h(t,p)   delta s(t,p)   delta g(t,p)    log k(t,p)    delta v(t,p)  fug coef
-----------  ------------  ------------   ------------   ------------   ------------   -----------   ------------  --------

   0.006         0.0      -0.532927E+01  -0.308944E+06  -0.110389E+03  -0.278791E+06  0.223059E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.009         5.0      -0.514948E+01  -0.308970E+06  -0.110484E+03  -0.278239E+06  0.218616E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.012        10.0      -0.496863E+01  -0.308995E+06  -0.110574E+03  -0.277686E+06  0.214329E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.017        15.0      -0.478681E+01  -0.309019E+06  -0.110659E+03  -0.277133E+06  0.210190E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.023        20.0      -0.460406E+01  -0.309043E+06  -0.110740E+03  -0.276579E+06  0.206192E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.032        25.0      -0.442047E+01  -0.309066E+06  -0.110817E+03  -0.276026E+06  0.202329E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.042        30.0      -0.423608E+01  -0.309087E+06  -0.110888E+03  -0.275471E+06  0.198592E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.056        35.0      -0.405094E+01  -0.309108E+06  -0.110956E+03  -0.274917E+06  0.194976E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.074        40.0      -0.386510E+01  -0.309128E+06  -0.111020E+03  -0.274362E+06  0.191476E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.096        45.0      -0.367860E+01  -0.309146E+06  -0.111080E+03  -0.273806E+06  0.188085E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

   0.123        50.0      -0.349150E+01  -0.309164E+06  -0.111136E+03  -0.273251E+06  0.184799E+03  0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01
```

```
0.158       55.0   -0.330381E+01  -0.309181E+06  -0.111188E+03  -0.272695E+06   0.181613E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

0.199       60.0   -0.311558E+01  -0.309197E+06  -0.111236E+03  -0.272139E+06   0.178523E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

0.250       65.0   -0.292684E+01  -0.309212E+06  -0.111281E+03  -0.271583E+06   0.175524E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

0.312       70.0   -0.273761E+01  -0.309227E+06  -0.111323E+03  -0.271026E+06   0.172612E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

0.386       75.0   -0.254793E+01  -0.309240E+06  -0.111361E+03  -0.270469E+06   0.169783E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

0.474       80.0   -0.235783E+01  -0.309252E+06  -0.111396E+03  -0.269912E+06   0.167035E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

0.578       85.0   -0.216731E+01  -0.309263E+06  -0.111428E+03  -0.269355E+06   0.164363E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

0.701       90.0   -0.197642E+01  -0.309274E+06  -0.111457E+03  -0.268798E+06   0.161764E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

0.845       95.0   -0.178516E+01  -0.309283E+06  -0.111482E+03  -0.268241E+06   0.159236E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

1.013      100.0   -0.159356E+01  -0.309291E+06  -0.111505E+03  -0.267683E+06   0.156776E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

1.208      105.0   -0.140163E+01  -0.309299E+06  -0.111525E+03  -0.267125E+06   0.154381E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

1.432      110.0   -0.120940E+01  -0.309305E+06  -0.111542E+03  -0.266568E+06   0.152048E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01

1.690      115.0   -0.101687E+01  -0.309310E+06  -0.111557E+03  -0.266010E+06   0.149775E+03   0.219570E+02 0.1000E+01
                                                                                                           0.1000E+01
```

```
   1.985        120.0     -0.824068E+00  -0.309315E+06  -0.111569E+03  -0.265452E+06    0.147560E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   2.320        125.0     -0.630999E+00  -0.309318E+06  -0.111578E+03  -0.264894E+06    0.145401E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   2.700        130.0     -0.437681E+00  -0.309321E+06  -0.111584E+03  -0.264336E+06    0.143295E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   3.129        135.0     -0.244123E+00  -0.309322E+06  -0.111589E+03  -0.263777E+06    0.141241E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   3.612        140.0     -0.503386E-01  -0.309323E+06  -0.111590E+03  -0.263219E+06    0.139236E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   4.153        145.0      0.143662E+00  -0.309322E+06  -0.111590E+03  -0.262661E+06    0.137280E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   4.757        150.0      0.337869E+00  -0.309321E+06  -0.111587E+03  -0.262103E+06    0.135369E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   5.430        155.0      0.532273E+00  -0.309318E+06  -0.111582E+03  -0.261544E+06    0.133503E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   6.177        160.0      0.726864E+00  -0.309315E+06  -0.111575E+03  -0.260986E+06    0.131681E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   7.003        165.0      0.921634E+00  -0.309310E+06  -0.111565E+03  -0.260428E+06    0.129899E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   7.915        170.0      0.111657E+01  -0.309305E+06  -0.111554E+03  -0.259870E+06    0.128158E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

   8.918        175.0      0.131168E+01  -0.309298E+06  -0.111540E+03  -0.259311E+06    0.126456E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01

  10.019        180.0      0.150694E+01  -0.309290E+06  -0.111524E+03  -0.258753E+06    0.124792E+03    0.219570E+02 0.1000E+01
                                                                                                                    0.1000E+01
```

```
 11.225      185.0      0.170235E+01  -0.309282E+06  -0.111507E+03  -0.258195E+06    0.123164E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 12.542      190.0      0.189790E+01  -0.309272E+06  -0.111487E+03  -0.257637E+06    0.121571E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 13.976      195.0      0.209359E+01  -0.309261E+06  -0.111466E+03  -0.257079E+06    0.120012E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 15.536      200.0      0.228941E+01  -0.309249E+06  -0.111442E+03  -0.256520E+06    0.118486E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 17.229      205.0      0.248536E+01  -0.309237E+06  -0.111417E+03  -0.255962E+06    0.116992E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 19.062      210.0      0.268143E+01  -0.309223E+06  -0.111390E+03  -0.255404E+06    0.115529E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 21.042      215.0      0.287761E+01  -0.309208E+06  -0.111362E+03  -0.254847E+06    0.114095E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 23.178      220.0      0.307391E+01  -0.309192E+06  -0.111332E+03  -0.254289E+06    0.112691E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 25.478      225.0      0.327031E+01  -0.309175E+06  -0.111300E+03  -0.253731E+06    0.111316E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 27.950      230.0      0.346681E+01  -0.309157E+06  -0.111266E+03  -0.253173E+06    0.109967E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 30.603      235.0      0.366341E+01  -0.309137E+06  -0.111231E+03  -0.252616E+06    0.108645E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 33.446      240.0      0.386011E+01  -0.309117E+06  -0.111194E+03  -0.252058E+06    0.107349E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01

 36.487      245.0      0.405689E+01  -0.309096E+06  -0.111155E+03  -0.251500E+06    0.106078E+03    0.219570E+02 0.1000E+01
                                                                                                                  0.1000E+01
```

```
39.735        250.0      0.425377E+01  -0.309073E+06  -0.111116E+03  -0.250943E+06   0.104831E+03   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

43.201        255.0      0.445072E+01  -0.309050E+06  -0.111074E+03  -0.250386E+06   0.103608E+03   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

46.893        260.0      0.464776E+01  -0.309025E+06  -0.111031E+03  -0.249829E+06   0.102408E+03   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

50.821        265.0      0.484488E+01  -0.308999E+06  -0.110987E+03  -0.249272E+06   0.101231E+03   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

54.996        270.0      0.504207E+01  -0.308972E+06  -0.110941E+03  -0.248714E+06   0.100075E+03   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

59.429        275.0      0.523934E+01  -0.308944E+06  -0.110894E+03  -0.248158E+06   0.989398E+02   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

64.128        280.0      0.543667E+01  -0.308915E+06  -0.110846E+03  -0.247601E+06   0.978254E+02   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

69.107        285.0      0.563407E+01  -0.308885E+06  -0.110796E+03  -0.247044E+06   0.967311E+02   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

74.376        290.0      0.583154E+01  -0.308853E+06  -0.110745E+03  -0.246487E+06   0.956563E+02   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

79.946        295.0      0.602907E+01  -0.308821E+06  -0.110692E+03  -0.245931E+06   0.946004E+02   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

85.832        300.0      0.622666E+01  -0.308787E+06  -0.110639E+03  -0.245374E+06   0.935629E+02   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

92.044        305.0      0.642431E+01  -0.308752E+06  -0.110584E+03  -0.244818E+06   0.925435E+02   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

98.597        310.0      0.662201E+01  -0.308716E+06  -0.110528E+03  -0.244262E+06   0.915416E+02   0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01
```

```
105.605       315.0       0.681977E+01   -0.308679E+06   -0.110470E+03   -0.243706E+06    0.905567E+02    0.219570E+02 0.1018E+01
                                                                                                                       0.1036E+01

112.783       320.0       0.701758E+01   -0.308640E+06   -0.110412E+03   -0.243150E+06    0.895885E+02    0.219570E+02 0.1020E+01
                                                                                                                       0.1039E+01

120.447       325.0       0.721544E+01   -0.308601E+06   -0.110352E+03   -0.242594E+06    0.886365E+02    0.219570E+02 0.1021E+01
                                                                                                                       0.1041E+01

128.514       330.0       0.741336E+01   -0.308560E+06   -0.110291E+03   -0.242038E+06    0.877003E+02    0.219570E+02 0.1023E+01
                                                                                                                       0.1043E+01

137.003       335.0       0.761132E+01   -0.308518E+06   -0.110229E+03   -0.241482E+06    0.867795E+02    0.219570E+02 0.1025E+01
                                                                                                                       0.1046E+01

145.933       340.0       0.780932E+01   -0.308475E+06   -0.110166E+03   -0.240927E+06    0.858738E+02    0.219570E+02 0.1027E+01
                                                                                                                       0.1049E+01

155.328       345.0       0.800737E+01   -0.308430E+06   -0.110102E+03   -0.240371E+06    0.849828E+02    0.219570E+02 0.1030E+01
                                                                                                                       0.1051E+01

165.212       350.0       0.820546E+01   -0.308385E+06   -0.110036E+03   -0.239815E+06    0.841061E+02    0.219570E+02 0.1032E+01
                                                                                                                       0.1054E+01

175.614       355.0       0.840360E+01   -0.308338E+06   -0.109970E+03   -0.239260E+06    0.832433E+02    0.219570E+02 0.1034E+01
                                                                                                                       0.1057E+01

186.568       360.0       0.860178E+01   -0.308289E+06   -0.109902E+03   -0.238705E+06    0.823942E+02    0.219570E+02 0.1037E+01
                                                                                                                       0.1060E+01

198.118       365.0       0.879999E+01   -0.308240E+06   -0.109834E+03   -0.238149E+06    0.815585E+02    0.219570E+02 0.1040E+01
                                                                                                                       0.1064E+01

210.327       370.0       0.899824E+01   -0.308189E+06   -0.109765E+03   -0.237594E+06    0.807357E+02    0.219570E+02 0.1043E+01
                                                                                                                       0.1067E+01
```

TABLE I.3

```
                                                                                                   07/ 5/88
                                                                                                   page  1


            -----------------------------------------------------------------------------
                        1.00aluminum + 1.50oxygen + 1.50hydrogen =  1.00bayerite
            -----------------------------------------------------------------------------

        -------------------------------------------------------------------------------------
                  species properties in their standard state of 25 degrees c and 1 bar
        -------------------------------------------------------------------------------------

                                         .....minerals.....

                                                                                     maier-kelley power fun. coef.
  name            coef.    enthalpy (cal)    entropy (cal)    free energy(cal)    volume (cc/mol)     a        bx10**3        cx10**-5
  ----            -----    --------------    -------------    ----------------    ---------------   -----      -------        --------
 bayerite         1.000      -307829.0          18.972           -275570.0          31.95600        8.650     45.6000          0.000
 aluminum        -1.000            0.0           6.780                 0.0           9.99900        4.940      2.9600          0.000
    --first tran--                0.00           0.00          temp=2726.8           0.00000        0.000      0.0000          0.000


                                          .....ions.....


                                          .....gases.....

                                                                                     maier-kelley power fun. coef.
  name            coef.    enthalpy (cal)    entropy (cal)    free energy(cal)    volume (cc/mol)     a        bx10**3        cx10**-5
  ----            -----    --------------    -------------    ----------------    ---------------   -----      -------        --------
 oxygen          -1.500            0.0          49.029                 0.0           0.00000        7.160      1.0000         -0.400
 hydrogen        -1.500            0.0          31.234                 0.0           0.00000        6.520      0.7800          0.120

                                          .....h2o.....


        -------------------------------------------------------------------------------------
                             reaction properties at 25 degrees c and 1 bar
        -------------------------------------------------------------------------------------

   enthalpy (cal)     entropy (cal)      free energy (cal)   delta vol (cc/mol)    heat capacity        log k

  -0.307829E+06      -0.108203E+03      -0.275570E+06        0.219570E+02       -0.442047E+01     0.201995E+03

                           fugacity coefficents are listed in this order

                                   gas number   1 = oxygen

                                   gas number   2 = hydrogen
```

```
 ---------------------------------------------------------------------------------------------------
                 1.00aluminum + 1.50oxygen + 1.50hydrogen =  1.00bayerite
 ---------------------------------------------------------------------------------------------------

pres (bars)   temp (deg c)    delta cp       delta h(t,p)    delta s(t,p)    delta g(t,p)     log k(t,p)      delta v(t,p)   fug coef
-----------   ------------   ------------    ------------    ------------    ------------     -----------     ------------   --------

   0.006          0.0       -0.532927E+01   -0.307708E+06   -0.107775E+03   -0.278270E+06   0.222643E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.009          5.0       -0.514948E+01   -0.307734E+06   -0.107870E+03   -0.277731E+06   0.218217E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.012         10.0       -0.496863E+01   -0.307759E+06   -0.107960E+03   -0.277192E+06   0.213947E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.017         15.0       -0.478681E+01   -0.307783E+06   -0.108045E+03   -0.276652E+06   0.209825E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.023         20.0       -0.460406E+01   -0.307807E+06   -0.108126E+03   -0.276111E+06   0.205843E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.032         25.0       -0.442047E+01   -0.307830E+06   -0.108203E+03   -0.275571E+06   0.201995E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.042         30.0       -0.423608E+01   -0.307851E+06   -0.108274E+03   -0.275029E+06   0.198273E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.056         35.0       -0.405094E+01   -0.307872E+06   -0.108342E+03   -0.274488E+06   0.194672E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.074         40.0       -0.386510E+01   -0.307892E+06   -0.108406E+03   -0.273946E+06   0.191186E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.096         45.0       -0.367860E+01   -0.307910E+06   -0.108466E+03   -0.273404E+06   0.187808E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01

   0.123         50.0       -0.349150E+01   -0.307928E+06   -0.108522E+03   -0.272861E+06   0.184536E+03    0.219570E+02  0.1000E+01
                                                                                                                           0.1000E+01
```

```
0.158        55.0    -0.330381E+01   -0.307945E+06   -0.108574E+03   -0.272318E+06     0.181362E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

0.199        60.0    -0.311558E+01   -0.307961E+06   -0.108622E+03   -0.271775E+06     0.178284E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

0.250        65.0    -0.292684E+01   -0.307976E+06   -0.108667E+03   -0.271232E+06     0.175297E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

0.312        70.0    -0.273761E+01   -0.307991E+06   -0.108709E+03   -0.270689E+06     0.172397E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

0.386        75.0    -0.254793E+01   -0.308004E+06   -0.108747E+03   -0.270145E+06     0.169579E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

0.474        80.0    -0.235783E+01   -0.308016E+06   -0.108782E+03   -0.269601E+06     0.166842E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

0.578        85.0    -0.216731E+01   -0.308027E+06   -0.108814E+03   -0.269057E+06     0.164181E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

0.701        90.0    -0.197642E+01   -0.308038E+06   -0.108843E+03   -0.268513E+06     0.161593E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

0.845        95.0    -0.178516E+01   -0.308047E+06   -0.108868E+03   -0.267969E+06     0.159075E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

1.013       100.0    -0.159356E+01   -0.308055E+06   -0.108891E+03   -0.267424E+06     0.156625E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

1.208       105.0    -0.140163E+01   -0.308063E+06   -0.108911E+03   -0.266879E+06     0.154239E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

1.432       110.0    -0.120940E+01   -0.308069E+06   -0.108928E+03   -0.266335E+06     0.151915E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01

1.690       115.0    -0.101687E+01   -0.308074E+06   -0.108943E+03   -0.265790E+06     0.149652E+03     0.219570E+02 0.1000E+01
                                                                                                                     0.1000E+01
```

```
  1.985      120.0    -0.824068E+00   -0.308079E+06   -0.108955E+03   -0.265245E+06    0.147446E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  2.320      125.0    -0.630999E+00   -0.308082E+06   -0.108964E+03   -0.264700E+08    0.145295E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  2.700      130.0    -0.437681E+00   -0.308085E+06   -0.108970E+03   -0.264155E+06    0.143197E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  3.129      135.0    -0.244123E+00   -0.308086E+06   -0.108975E+03   -0.263610E+06    0.141151E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  3.612      140.0    -0.503386E-01   -0.308087E+06   -0.108976E+03   -0.263065E+06    0.139155E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  4.153      145.0     0.143662E+00   -0.308086E+06   -0.108976E+03   -0.262520E+06    0.137206E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  4.757      150.0     0.337869E+00   -0.308085E+06   -0.108973E+03   -0.261974E+06    0.135303E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  5.430      155.0     0.532273E+00   -0.308082E+06   -0.108968E+03   -0.261429E+06    0.133445E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  6.177      160.0     0.726864E+00   -0.308079E+06   -0.108961E+03   -0.260884E+06    0.131629E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  7.003      165.0     0.921634E+00   -0.308074E+06   -0.108951E+03   -0.260339E+06    0.129855E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  7.915      170.0     0.111657E+01   -0.308069E+06   -0.108940E+03   -0.259794E+06    0.128121E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

  8.918      175.0     0.131168E+01   -0.308062E+06   -0.108926E+03   -0.259248E+06    0.126426E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01

 10.019      180.0     0.150694E+01   -0.308054E+06   -0.108910E+03   -0.258703E+06    0.124768E+03    0.219570E+02 0.1000E+01
                                                                                                                   0.1000E+01
```

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 11.225      185.0     0.170235E+01  -0.308046E+06  -0.108893E+03  -0.258158E+06    0.123146E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 12.542      190.0     0.189790E+01  -0.308036E+06  -0.108873E+03  -0.257613E+06    0.121559E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 13.976      195.0     0.209359E+01  -0.308025E+06  -0.108852E+03  -0.257068E+06    0.120007E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 15.536      200.0     0.228941E+01  -0.308013E+06  -0.108828E+03  -0.256523E+06    0.118487E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 17.229      205.0     0.248536E+01  -0.308001E+06  -0.108803E+03  -0.255978E+06    0.116999E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 19.062      210.0     0.268143E+01  -0.307987E+06  -0.108776E+03  -0.255433E+06    0.115541E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 21.042      215.0     0.287761E+01  -0.307972E+06  -0.108748E+03  -0.254888E+06    0.114114E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 23.178      220.0     0.307391E+01  -0.307956E+06  -0.108718E+03  -0.254343E+06    0.112716E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 25.478      225.0     0.327031E+01  -0.307939E+06  -0.108686E+03  -0.253799E+06    0.111345E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 27.950      230.0     0.346681E+01  -0.307921E+06  -0.108652E+03  -0.253254E+06    0.110002E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 30.603      235.0     0.366341E+01  -0.307901E+06  -0.108617E+03  -0.252709E+06    0.108686E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 33.446      240.0     0.386011E+01  -0.307881E+06  -0.108580E+03  -0.252165E+06    0.107395E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01

 36.487      245.0     0.405689E+01  -0.307860E+06  -0.108541E+03  -0.251621E+06    0.106129E+03    0.219570E+02 0.1000E+01
                                                                                                                 0.1000E+01
```

```
39.735        250.0      0.425377E+01   -0.307837E+06   -0.108502E+03   -0.251076E+06    0.104887E+03    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

43.201        255.0      0.445072E+01   -0.307814E+06   -0.108460E+03   -0.250532E+06    0.103669E+03    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

46.893        260.0      0.464776E+01   -0.307789E+06   -0.108417E+03   -0.249988E+06    0.102474E+03    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

50.821        265.0      0.484488E+01   -0.307763E+06   -0.108373E+03   -0.249444E+06    0.101301E+03    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

54.996        270.0      0.504207E+01   -0.307736E+06   -0.108327E+03   -0.248900E+06    0.100149E+03    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

59.429        275.0      0.523934E+01   -0.307708E+06   -0.108280E+03   -0.248356E+06    0.990189E+02    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

64.128        280.0      0.543667E+01   -0.307679E+06   -0.108232E+03   -0.247812E+06    0.979090E+02    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

69.107        285.0      0.563407E+01   -0.307649E+06   -0.108182E+03   -0.247269E+06    0.968191E+02    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

74.376        290.0      0.583154E+01   -0.307617E+06   -0.108131E+03   -0.246725E+06    0.957485E+02    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

79.946        295.0      0.602907E+01   -0.307585E+06   -0.108078E+03   -0.246182E+06    0.946968E+02    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

85.832        300.0      0.622666E+01   -0.307551E+06   -0.108025E+03   -0.245638E+06    0.936635E+02    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

92.044        305.0      0.642431E+01   -0.307516E+06   -0.107970E+03   -0.245095E+06    0.926482E+02    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01

98.597        310.0      0.662201E+01   -0.307480E+06   -0.107914E+03   -0.244552E+06    0.916502E+02    0.219570E+02 0.1000E+01
                                                                                                                      0.1000E+01
```

```
105.505       315.0      0.681977E+01   -0.307443E+06   -0.107856E+03   -0.244009E+06     0.906693E+02     0.219570E+02 0.1018E+01
                                                                                                                        0.1036E+01

112.783       320.0      0.701758E+01   -0.307404E+06   -0.107798E+03   -0.243466E+06     0.897050E+02     0.219570E+02 0.1020E+01
                                                                                                                        0.1039E+01

120.447       325.0      0.721544E+01   -0.307365E+06   -0.107738E+03   -0.242923E+06     0.887568E+02     0.219570E+02 0.1021E+01
                                                                                                                        0.1041E+01

128.514       330.0      0.741336E+01   -0.307324E+06   -0.107677E+03   -0.242380E+06     0.878243E+02     0.219570E+02 0.1023E+01
                                                                                                                        0.1043E+01

137.003       335.0      0.761132E+01   -0.307282E+06   -0.107615E+03   -0.241838E+06     0.869072E+02     0.219570E+02 0.1025E+01
                                                                                                                        0.1046E+01

145.933       340.0      0.780932E+01   -0.307239E+06   -0.107552E+03   -0.241295E+06     0.860051E+02     0.219570E+02 0.1027E+01
                                                                                                                        0.1049E+01

155.328       345.0      0.800737E+01   -0.307194E+06   -0.107488E+03   -0.240752E+06     0.851177E+02     0.219570E+02 0.1030E+01
                                                                                                                        0.1051E+01

165.212       350.0      0.820546E+01   -0.307149E+06   -0.107422E+03   -0.240210E+06     0.842444E+02     0.219570E+02 0.1032E+01
                                                                                                                        0.1054E+01

175.614       355.0      0.840360E+01   -0.307102E+06   -0.107356E+03   -0.239668E+06     0.833852E+02     0.219570E+02 0.1034E+01
                                                                                                                        0.1057E+01

186.568       360.0      0.860178E+01   -0.307053E+06   -0.107288E+03   -0.239125E+06     0.825395E+02     0.219570E+02 0.1037E+01
                                                                                                                        0.1060E+01

198.118       365.0      0.879999E+01   -0.307004E+06   -0.107220E+03   -0.238583E+06     0.817070E+02     0.219570E+02 0.1040E+01
                                                                                                                        0.1064E+01

210.327       370.0      0.899824E+01   -0.306953E+06   -0.107151E+03   -0.238041E+06     0.808875E+02     0.219570E+02 0.1043E+01
                                                                                                                        0.1067E+01
```

TABLE I.4

```
                                                                                      07/ 5/88
                                                                                      page  1

          ------------------------------------------------------------------------
                    1.00aluminum + 1.00oxygen + 0.50hydrogen =  1.00boehmite
          ------------------------------------------------------------------------

      --------------------------------------------------------------------------------
               species properties in their standard state of 25 degrees c and 1 bar
      --------------------------------------------------------------------------------

                                    .....minerals.....

                                                                                        maier-kelley power fun. coef.
  name            coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a         bx10**3      cx10**-5
  ----            -----    --------------   -------------   ----------------   ---------------   -----     -------      --------
 boehmite         1.000      -237893.0          8.988          -219289.0          19.53500       12.905    20.7000       -3.005
 aluminum        -1.000            0.0          6.780                0.0           9.99900        4.940     2.9600        0.000
    --first tran--                0.00          0.00         temp=2726.8           0.00000       0.000     0.0000        0.000


                                    .....ions.....


                                    .....gases.....

                                                                                        maier-kelley power fun. coef.
  name            coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a         bx10**3      cx10**-5
  ----            -----    --------------   -------------   ----------------   ---------------   -----     -------      --------
 oxygen          -1.000            0.0         49.029                0.0           0.00000        7.160     1.0000       -0.400
 hydrogen        -0.500            0.0         31.234                0.0           0.00000        6.520     0.7800        0.120

                                    .....h2o.....


      --------------------------------------------------------------------------------
                      reaction properties at 25 degrees c and 1 bar
      --------------------------------------------------------------------------------

  enthalpy (cal)    entropy (cal)    free energy (cal)   delta vol (cc/mol)   heat capacity       log k

 -0.237893E+06     -0.624380E+02     -0.219289E+06       0.953600E+01       -0.578220E+00     0.160740E+03

                    fugacity coefficents are listed in this order

                             gas number  1 = oxygen

                             gas number  2 = hydrogen
```

```
           ---------------------------------------------------------------------------------------
                        1.00aluminum + 1.00oxygen + 0.50hydrogen =  1.00boehmite
           ---------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp      delta h(t,p)   delta s(t,p)   delta g(t,p)    log k(t,p)    delta v(t,p)  fug coef
-----------  ------------ ------------    ------------   ------------   ------------    -----------   ------------  ---------

   0.006         0.0      -0.156086E+01  -0.237867E+06  -0.623448E+02  -0.220849E+06   0.176700E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.009         5.0      -0.135185E+01  -0.237874E+06  -0.623712E+02  -0.220537E+06   0.173279E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.012        10.0      -0.114952E+01  -0.237880E+06  -0.623935E+02  -0.220226E+06   0.169978E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.017        15.0      -0.953414E+00  -0.237886E+06  -0.624119E+02  -0.219913E+06   0.166792E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.023        20.0      -0.763109E+00  -0.237890E+06  -0.624267E+02  -0.219601E+06   0.163715E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.032        25.0      -0.578220E+00  -0.237893E+06  -0.624380E+02  -0.219289E+06   0.160740E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.042        30.0      -0.398391E+00  -0.237896E+06  -0.624461E+02  -0.218977E+06   0.157864E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.056        35.0      -0.223298E+00  -0.237897E+06  -0.624512E+02  -0.218665E+06   0.155081E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.074        40.0      -0.526403E-01  -0.237898E+06  -0.624534E+02  -0.218352E+06   0.152387E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.096        45.0       0.113859E+00  -0.237898E+06  -0.624529E+02  -0.218040E+06   0.149778E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01

   0.123        50.0       0.276454E+00  -0.237897E+06  -0.624499E+02  -0.217728E+06   0.147249E+03   0.953600E+01 0.1000E+01
                                                                                                                   0.1000E+01
```

```
0.158       55.0     0.435382E+00  -0.237895E+06  -0.624444E+02  -0.217416E+06   0.144798E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

0.199       60.0     0.590862E+00  -0.237892E+06  -0.624367E+02  -0.217103E+06   0.142420E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

0.250       65.0     0.743095E+00  -0.237889E+06  -0.624267E+02  -0.216791E+06   0.140112E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

0.312       70.0     0.892270E+00  -0.237885E+06  -0.624147E+02  -0.216479E+06   0.137872E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

0.386       75.0     0.103856E+01  -0.237880E+06  -0.624008E+02  -0.216167E+06   0.135696E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

0.474       80.0     0.118213E+01  -0.237875E+06  -0.623849E+02  -0.215855E+06   0.133581E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

0.578       85.0     0.132313E+01  -0.237868E+06  -0.623673E+02  -0.215543E+06   0.131526E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

0.701       90.0     0.146169E+01  -0.237861E+06  -0.623480E+02  -0.215231E+06   0.129528E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

0.845       95.0     0.159796E+01  -0.237854E+06  -0.623271E+02  -0.214920E+06   0.127583E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

1.013      100.0     0.173205E+01  -0.237845E+06  -0.623046E+02  -0.214608E+06   0.125691E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

1.208      105.0     0.186408E+01  -0.237836E+06  -0.622807E+02  -0.214297E+06   0.123849E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

1.432      110.0     0.199416E+01  -0.237826E+06  -0.622554E+02  -0.213985E+06   0.122056E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01

1.690      115.0     0.212237E+01  -0.237816E+06  -0.622287E+02  -0.213674E+06   0.120308E+03   0.953600E+01 0.1000E+01
                                                                                                              0.1000E+01
```

```
 1.985         120.0      0.224883E+01   -0.237805E+06   -0.622007E+02   -0.213363E+06    0.118605E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 2.320         125.0      0.237361E+01   -0.237793E+06   -0.621715E+02   -0.213052E+06    0.116945E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 2.700         130.0      0.249680E+01   -0.237781E+06   -0.621411E+02   -0.212741E+06    0.115326E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 3.129         135.0      0.261848E+01   -0.237768E+06   -0.621096E+02   -0.212430E+06    0.113747E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 3.612         140.0      0.273872E+01   -0.237755E+06   -0.620769E+02   -0.212120E+06    0.112206E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 4.153         145.0      0.285758E+01   -0.237741E+06   -0.620433E+02   -0.211809E+06    0.110702E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 4.757         150.0      0.297514E+01   -0.237726E+06   -0.620086E+02   -0.211499E+06    0.109234E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 5.430         155.0      0.309145E+01   -0.237711E+06   -0.619730E+02   -0.211189E+06    0.107800E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 6.177         160.0      0.320657E+01   -0.237695E+06   -0.619364E+02   -0.210879E+06    0.106399E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 7.003         165.0      0.332055E+01   -0.237678E+06   -0.618990E+02   -0.210569E+06    0.105030E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 7.915         170.0      0.343345E+01   -0.237661E+06   -0.618607E+02   -0.210259E+06    0.103693E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

 8.918         175.0      0.354532E+01   -0.237643E+06   -0.618215E+02   -0.209950E+06    0.102385E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

10.019         180.0      0.365619E+01   -0.237625E+06   -0.617816E+02   -0.209641E+06    0.101106E+03    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01
```

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11.225        185.0      0.376611E+01    -0.237606E+06   -0.617408E+02   -0.209332E+06    0.998551E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

12.542        190.0      0.387512E+01    -0.237587E+06   -0.616994E+02   -0.209023E+06    0.986313E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

13.976        195.0      0.398327E+01    -0.237567E+06   -0.616572E+02   -0.208714E+06    0.974338E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

15.536        200.0      0.409058E+01    -0.237546E+06   -0.616143E+02   -0.208406E+06    0.962616E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

17.229        205.0      0.419710E+01    -0.237525E+06   -0.615707E+02   -0.208097E+06    0.951141E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

19.062        210.0      0.430285E+01    -0.237504E+06   -0.615265E+02   -0.207789E+06    0.939904E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

21.042        215.0      0.440787E+01    -0.237481E+06   -0.614817E+02   -0.207481E+06    0.928898E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

23.178        220.0      0.451218E+01    -0.237459E+06   -0.614362E+02   -0.207173E+06    0.918116E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

25.478        225.0      0.461582E+01    -0.237435E+06   -0.613902E+02   -0.206866E+06    0.907551E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

27.950        230.0      0.471881E+01    -0.237411E+06   -0.613436E+02   -0.206558E+06    0.897197E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

30.603        235.0      0.482117E+01    -0.237387E+06   -0.612964E+02   -0.206251E+06    0.887048E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

33.446        240.0      0.492294E+01    -0.237362E+06   -0.612487E+02   -0.205944E+06    0.877097E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01

36.487        245.0      0.502413E+01    -0.237336E+06   -0.612005E+02   -0.205637E+06    0.867339E+02    0.953600E+01 0.1000E+01
                                                                                                                       0.1000E+01
```

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 39.735      250.0     0.512476E+01  -0.237310E+06  -0.611517E+02  -0.205331E+06   0.857769E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 43.201      255.0     0.522486E+01  -0.237284E+06  -0.611025E+02  -0.205024E+06   0.848380E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 46.893      260.0     0.532444E+01  -0.237256E+06  -0.610528E+02  -0.204718E+06   0.839169E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 50.821      265.0     0.542353E+01  -0.237229E+06  -0.610027E+02  -0.204412E+06   0.830129E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 54.996      270.0     0.552215E+01  -0.237200E+06  -0.609520E+02  -0.204106E+06   0.821257E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 59.429      275.0     0.562030E+01  -0.237171E+06  -0.609010E+02  -0.203800E+06   0.812547E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 64.128      280.0     0.571802E+01  -0.237142E+06  -0.608495E+02  -0.203495E+06   0.803996E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 69.107      285.0     0.581530E+01  -0.237112E+06  -0.607976E+02  -0.203190E+06   0.795598E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 74.376      290.0     0.591217E+01  -0.237082E+06  -0.607453E+02  -0.202885E+06   0.787350E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 79.946      295.0     0.600865E+01  -0.237050E+06  -0.606926E+02  -0.202580E+06   0.779249E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 85.832      300.0     0.610474E+01  -0.237019E+06  -0.606396E+02  -0.202275E+06   0.771289E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 92.044      305.0     0.620046E+01  -0.236987E+06  -0.605861E+02  -0.201971E+06   0.763468E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01

 98.597      310.0     0.629583E+01  -0.236954E+06  -0.605323E+02  -0.201666E+06   0.755781E+02   0.953600E+01 0.1000E+01
                                                                                                               0.1000E+01
```

```
105.505        315.0       0.639084E+01   -0.236921E+06   -0.604782E+02   -0.201362E+06    0.748226E+02    0.953600E+01  0.1018E+01
                                                                                                                         0.1036E+01

112.783        320.0       0.648553E+01   -0.236887E+06   -0.604237E+02   -0.201058E+06    0.740799E+02    0.953600E+01  0.1020E+01
                                                                                                                         0.1039E+01

120.447        325.0       0.657989E+01   -0.236852E+06   -0.603688E+02   -0.200755E+06    0.733497E+02    0.953600E+01  0.1021E+01
                                                                                                                         0.1041E+01

128.514        330.0       0.667394E+01   -0.236817E+06   -0.603137E+02   -0.200451E+06    0.726316E+02    0.953600E+01  0.1023E+01
                                                                                                                         0.1043E+01

137.003        335.0       0.676768E+01   -0.236782E+06   -0.602582E+02   -0.200148E+06    0.719255E+02    0.953600E+01  0.1025E+01
                                                                                                                         0.1046E+01

145.933        340.0       0.686114E+01   -0.236746E+06   -0.602024E+02   -0.199845E+06    0.712309E+02    0.953600E+01  0.1027E+01
                                                                                                                         0.1049E+01

155.328        345.0       0.695431E+01   -0.236709E+06   -0.601463E+02   -0.199542E+06    0.705476E+02    0.953600E+01  0.1030E+01
                                                                                                                         0.1051E+01

165.212        350.0       0.704721E+01   -0.236672E+06   -0.600899E+02   -0.199239E+06    0.698753E+02    0.953600E+01  0.1032E+01
                                                                                                                         0.1054E+01

175.614        355.0       0.713984E+01   -0.236634E+06   -0.600332E+02   -0.198936E+06    0.692138E+02    0.953600E+01  0.1034E+01
                                                                                                                         0.1057E+01

186.568        360.0       0.723221E+01   -0.236596E+06   -0.599762E+02   -0.198634E+06    0.685628E+02    0.953600E+01  0.1037E+01
                                                                                                                         0.1060E+01

198.118        365.0       0.732434E+01   -0.236557E+06   -0.599190E+02   -0.198331E+06    0.679221E+02    0.953600E+01  0.1040E+01
                                                                                                                         0.1064E+01

210.327        370.0       0.741623E+01   -0.236517E+06   -0.598615E+02   -0.198029E+06    0.672913E+02    0.953600E+01  0.1043E+01
                                                                                                                         0.1067E+01
```

TABLE I.5

```
                                                                                                          07/ 5/88
                                                                                                          page  1

              -----------------------------------------------------------------------------
                         1.00aluminum + 1.00oxygen + 0.50hydrogen =  1.00diaspore
              -----------------------------------------------------------------------------

        ------------------------------------------------------------------------------------
                     species properties in their standard state of 25 degrees c and 1 bar
        ------------------------------------------------------------------------------------

                                          .....minerals.....

                                                                                         maier-kelley power fun. coef.
  name            coef.   enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a        bx10**3       cx10**-5
  ----            -----   --------------   -------------   ----------------   ---------------  -----      -------       --------
 diaspore         1.000     -238827.0          8.446          -220082.0          17.76000      14.430     4.2000         0.000
 aluminum        -1.000           0.0          6.780                0.0           9.99900       4.940     2.9600         0.000
     --first tran--              0.00          0.00         temp=2726.8           0.00000      0.000      0.0000         0.000


                                          .....ions.....


                                          .....gases.....

                                                                                         maier-kelley power fun. coef.
  name            coef.   enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a        bx10**3       cx10**-5
  ----            -----   --------------   -------------   ----------------   ---------------  -----      -------       --------
 oxygen          -1.000           0.0         49.029                0.0           0.00000       7.160     1.0000        -0.400
 hydrogen        -0.500           0.0         31.234                0.0           0.00000       6.520     0.7800         0.120

                                          .....h2o.....


        ------------------------------------------------------------------------------------
                              reaction properties at 25 degrees c and 1 bar
        ------------------------------------------------------------------------------------

   enthalpy (cal)      entropy (cal)      free energy (cal)    delta vol (cc/mol)    heat capacity        log k

  -0.238827E+06      -0.629798E+02       -0.220082E+06        0.776100E+01      -0.592242E+00      0.161322E+03

                           fugacity coefficents are listed in this order

                                   gas number  1 = oxygen

                                   gas number  2 = hydrogen
```

```
          --------------------------------------------------------------------------------------------------
                            1.00aluminum + 1.00oxygen + 0.50hydrogen =  1.00diaspore
          --------------------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp     delta h(t,p)  delta s(t,p)  delta g(t,p)    log k(t,p)    delta v(t,p)  fug coef
-----------  ------------ ------------   ------------  ------------  ------------    ----------    ------------  --------

   0.006          0.0    -0.515275E+00  -0.238813E+06 -0.629312E+02 -0.221656E+06  0.177346E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.009          5.0    -0.532261E+00  -0.238816E+06 -0.629407E+02 -0.221341E+06  0.173911E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.012         10.0    -0.548394E+00  -0.238819E+06 -0.629503E+02 -0.221027E+06  0.170597E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.017         15.0    -0.563734E+00  -0.238821E+06 -0.629601E+02 -0.220712E+06  0.167398E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.023         20.0    -0.578333E+00  -0.238824E+06 -0.629699E+02 -0.220397E+06  0.164308E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.032         25.0    -0.592242E+00  -0.238827E+06 -0.629798E+02 -0.220082E+06  0.161322E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.042         30.0    -0.605505E+00  -0.238830E+06 -0.629898E+02 -0.219767E+06  0.158434E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.056         35.0    -0.618164E+00  -0.238833E+06 -0.629998E+02 -0.219452E+06  0.155640E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.074         40.0    -0.630256E+00  -0.238836E+06 -0.630098E+02 -0.219137E+06  0.152935E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.096         45.0    -0.641819E+00  -0.238840E+06 -0.630199E+02 -0.218822E+06  0.150315E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01

   0.123         50.0    -0.652883E+00  -0.238843E+06 -0.630300E+02 -0.218507E+06  0.147776E+03   0.776100E+01 0.1000E+01
                                                                                                                0.1000E+01
```

```
0.158         55.0    -0.663479E+00   -0.238846E+06   -0.630401E+02   -0.218192E+06    0.145314E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

0.199         60.0    -0.673636E+00   -0.238849E+06   -0.630502E+02   -0.217877E+06    0.142927E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

0.250         65.0    -0.683378E+00   -0.238853E+06   -0.630603E+02   -0.217561E+06    0.140610E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

0.312         70.0    -0.692730E+00   -0.238856E+06   -0.630704E+02   -0.217246E+06    0.138360E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

0.386         75.0    -0.701714E+00   -0.238860E+06   -0.630805E+02   -0.216931E+06    0.136175E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

0.474         80.0    -0.710351E+00   -0.238863E+06   -0.630906E+02   -0.216615E+06    0.134052E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

0.578         85.0    -0.718660E+00   -0.238867E+06   -0.631006E+02   -0.216300E+06    0.131988E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

0.701         90.0    -0.726658E+00   -0.238870E+06   -0.631106E+02   -0.215984E+06    0.129981E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

0.845         95.0    -0.734364E+00   -0.238874E+06   -0.631206E+02   -0.215669E+06    0.128028E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

1.013        100.0    -0.741791E+00   -0.238878E+06   -0.631306E+02   -0.215353E+06    0.126128E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

1.208        105.0    -0.748956E+00   -0.238881E+06   -0.631405E+02   -0.215037E+06    0.124277E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

1.432        110.0    -0.755871E+00   -0.238885E+06   -0.631504E+02   -0.214721E+06    0.122475E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01

1.690        115.0    -0.762549E+00   -0.238889E+06   -0.631602E+02   -0.214406E+06    0.120720E+03    0.776100E+01 0.1000E+01
                                                                                                                    0.1000E+01
```

```
  1.985       120.0    -0.769003E+00  -0.238893E+06  -0.631700E+02  -0.214090E+06    0.119009E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  2.320       125.0    -0.775243E+00  -0.238896E+06  -0.631798E+02  -0.213774E+06    0.117341E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  2.700       130.0    -0.781280E+00  -0.238900E+06  -0.631895E+02  -0.213458E+06    0.115715E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  3.129       135.0    -0.787124E+00  -0.238904E+06  -0.631992E+02  -0.213142E+06    0.114128E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  3.612       140.0    -0.792784E+00  -0.238908E+06  -0.632088E+02  -0.212826E+06    0.112579E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  4.153       145.0    -0.798269E+00  -0.238912E+06  -0.632184E+02  -0.212509E+06    0.111068E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  4.757       150.0    -0.803588E+00  -0.238916E+06  -0.632279E+02  -0.212193E+06    0.109592E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  5.430       155.0    -0.808747E+00  -0.238920E+06  -0.632373E+02  -0.211877E+06    0.108151E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  6.177       160.0    -0.813754E+00  -0.238923E+06  -0.632468E+02  -0.211561E+06    0.106743E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  7.003       165.0    -0.818616E+00  -0.238927E+06  -0.632561E+02  -0.211244E+06    0.105367E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  7.915       170.0    -0.823340E+00  -0.238931E+06  -0.632654E+02  -0.210928E+06    0.104022E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

  8.918       175.0    -0.827932E+00  -0.238935E+06  -0.632747E+02  -0.210611E+06    0.102707E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01

 10.019       180.0    -0.832397E+00  -0.238939E+06  -0.632839E+02  -0.210295E+06    0.101421E+03    0.776100E+01 0.1000E+01
                                                                                                                 0.1000E+01
```

```
11.225    185.0    -0.836742E+00   -0.238943E+06   -0.632931E+02   -0.209978E+06   0.100163E+03   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

12.542    190.0    -0.840970E+00   -0.238947E+06   -0.633022E+02   -0.209661E+06   0.989325E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

13.976    195.0    -0.845088E+00   -0.238951E+06   -0.633112E+02   -0.209344E+06   0.977280E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

15.536    200.0    -0.849099E+00   -0.238955E+06   -0.633202E+02   -0.209027E+06   0.965489E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

17.229    205.0    -0.853009E+00   -0.238959E+06   -0.633292E+02   -0.208711E+06   0.953944E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

19.062    210.0    -0.856821E+00   -0.238963E+06   -0.633381E+02   -0.208394E+06   0.942638E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

21.042    215.0    -0.860539E+00   -0.238967E+06   -0.633469E+02   -0.208076E+06   0.931563E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

23.178    220.0    -0.864168E+00   -0.238971E+06   -0.633557E+02   -0.207759E+06   0.920713E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

25.478    225.0    -0.867710E+00   -0.238975E+06   -0.633644E+02   -0.207442E+06   0.910080E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

27.950    230.0    -0.871170E+00   -0.238979E+06   -0.633731E+02   -0.207125E+06   0.899658E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

30.603    235.0    -0.874550E+00   -0.238982E+06   -0.633818E+02   -0.206807E+06   0.889440E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

33.446    240.0    -0.877853E+00   -0.238986E+06   -0.633903E+02   -0.206490E+06   0.879422E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01

36.487    245.0    -0.881083E+00   -0.238990E+06   -0.633989E+02   -0.206172E+06   0.869596E+02   0.776100E+01 0.1000E+01
                                                                                                               0.1000E+01
```

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39.735        250.0      -0.884243E+00  -0.238994E+06  -0.634073E+02  -0.205855E+06     0.859958E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

43.201        255.0      -0.887334E+00  -0.238998E+06  -0.634158E+02  -0.205537E+06     0.850502E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

46.893        260.0      -0.890359E+00  -0.239001E+06  -0.634241E+02  -0.205219E+06     0.841224E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

50.821        265.0      -0.893321E+00  -0.239005E+06  -0.634325E+02  -0.204901E+06     0.832117E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

54.996        270.0      -0.896223E+00  -0.239009E+06  -0.634407E+02  -0.204583E+06     0.823177E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

59.429        275.0      -0.899066E+00  -0.239013E+06  -0.634490E+02  -0.204265E+06     0.814401E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

64.128        280.0      -0.901852E+00  -0.239016E+06  -0.634571E+02  -0.203947E+06     0.805782E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

69.107        285.0      -0.904584E+00  -0.239020E+06  -0.634653E+02  -0.203629E+06     0.797318E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

74.376        290.0      -0.907264E+00  -0.239023E+06  -0.634733E+02  -0.203311E+06     0.789003E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

79.946        295.0      -0.909892E+00  -0.239027E+06  -0.634814E+02  -0.202992E+06     0.780835E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

85.832        300.0      -0.912472E+00  -0.239030E+06  -0.634894E+02  -0.202674E+06     0.772809E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

92.044        305.0      -0.915004E+00  -0.239034E+06  -0.634973E+02  -0.202355E+06     0.764921E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01

98.597        310.0      -0.917491E+00  -0.239037E+06  -0.635052E+02  -0.202036E+06     0.757168E+02     0.776100E+01 0.1000E+01
                                                                                                                        0.1000E+01
```

```
105.505       315.0     -0.919934E+00   -0.239040E+06   -0.635130E+02   -0.201718E+06     0.749546E+02     0.776100E+01 0.1018E+01
                                                                                                                         0.1036E+01

112.783       320.0     -0.922334E+00   -0.239044E+06   -0.635208E+02   -0.201399E+06     0.742053E+02     0.776100E+01 0.1020E+01
                                                                                                                         0.1039E+01

120.447       325.0     -0.924693E+00   -0.239047E+06   -0.635286E+02   -0.201080E+06     0.734684E+02     0.776100E+01 0.1021E+01
                                                                                                                         0.1041E+01

128.514       330.0     -0.927012E+00   -0.239050E+06   -0.635363E+02   -0.200760E+06     0.727437E+02     0.776100E+01 0.1023E+01
                                                                                                                         0.1043E+01

137.003       335.0     -0.929292E+00   -0.239053E+06   -0.635440E+02   -0.200441E+06     0.720309E+02     0.776100E+01 0.1025E+01
                                                                                                                         0.1046E+01

145.933       340.0     -0.931536E+00   -0.239056E+06   -0.635516E+02   -0.200122E+06     0.713297E+02     0.776100E+01 0.1027E+01
                                                                                                                         0.1049E+01

155.328       345.0     -0.933743E+00   -0.239059E+06   -0.635591E+02   -0.199802E+06     0.706398E+02     0.776100E+01 0.1030E+01
                                                                                                                         0.1051E+01

165.212       350.0     -0.935915E+00   -0.239062E+06   -0.635667E+02   -0.199483E+06     0.699609E+02     0.776100E+01 0.1032E+01
                                                                                                                         0.1054E+01

175.614       355.0     -0.938053E+00   -0.239065E+06   -0.635742E+02   -0.199163E+06     0.692927E+02     0.776100E+01 0.1034E+01
                                                                                                                         0.1057E+01

186.568       360.0     -0.940159E+00   -0.239067E+06   -0.635816E+02   -0.198843E+06     0.686351E+02     0.776100E+01 0.1037E+01
                                                                                                                         0.1060E+01

198.118       365.0     -0.942233E+00   -0.239070E+06   -0.635890E+02   -0.198523E+06     0.679877E+02     0.776100E+01 0.1040E+01
                                                                                                                         0.1064E+01

210.327       370.0     -0.944276E+00   -0.239072E+06   -0.635964E+02   -0.198203E+06     0.673504E+02     0.776100E+01 0.1043E+01
                                                                                                                         0.1067E+01
```

TABLE I.6

```
                                                                                                   07/ 6/88
                                                                                                   page  1


             ----------------------------------------------------------------------------
                               2.00aluminum + 1.50oxygen =  1.00corundum
             ----------------------------------------------------------------------------

         ------------------------------------------------------------------------------------
                    species properties in their standard state of 25 degrees c and 1 bar
         ------------------------------------------------------------------------------------

                                            .....minerals.....

                                                                                     maier-kelley power fun. coef.
   name             coef.   enthalpy (cal)  entropy (cal)  free energy(cal)  volume (cc/mol)     a       bx10**3        cx10**-5
   ----             -----   --------------  -------------  ----------------  ---------------   -----     -------        --------
  corundum          1.000     -400511.0       12.180         -378185.0         25.57500       27.490     2.8200          -8.380
  aluminum         -2.000           0.0        6.780               0.0          9.99900        4.940     2.9600           0.000
      --first tran--               0.00        0.00       temp=2726.8          0.00000        0.000     0.0000           0.000


                                             .....ions.....


                                             .....gases.....

                                                                                     maier-kelley power fun. coef.
   name             coef.   enthalpy (cal)  entropy (cal)  free energy(cal)  volume (cc/mol)     a       bx10**3        cx10**-5
   ----             -----   --------------  -------------  ----------------  ---------------   -----     -------        --------
  oxygen           -1.500           0.0       49.029               0.0          0.00000        7.160     1.0000          -0.400

                                              .....h2o.....


         ------------------------------------------------------------------------------------
                                 reaction properties at 25 degrees c and 1 bar
         ------------------------------------------------------------------------------------

   enthalpy (cal)      entropy (cal)       free energy (cal)    delta vol (cc/mol)    heat capacity          log k

  -0.400511E+06       -0.749235E+02        -0.378185E+06          0.557700E+01       -0.325354E+01        0.277212E+03

                             fugacity coefficents are listed in this order

                                       gas number  1 = oxygen
```

```
          ------------------------------------------------------------------------------------------
                             2.00aluminum + 1.50oxygen =  1.00corundum
          ------------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp      delta h(t,p)  delta s(t,p)  delta g(t,p)   log k(t,p)    delta v(t,p)  fug coef
-----------  ------------  ------------  ------------  ------------  ------------   ----------    ------------  --------

   0.006         0.0       -0.481392E+01 -0.400411E+06 -0.745725E+02 -0.380054E+06  0.304079E+03  0.557700E+01 0.1000E+01

   0.009         5.0       -0.446540E+01 -0.400434E+06 -0.746566E+02 -0.379681E+06  0.298320E+03  0.557700E+01 0.1000E+01

   0.012        10.0       -0.413639E+01 -0.400456E+06 -0.747332E+02 -0.379308E+06  0.292764E+03  0.557700E+01 0.1000E+01

   0.017        15.0       -0.382555E+01 -0.400476E+06 -0.748029E+02 -0.378934E+06  0.287400E+03  0.557700E+01 0.1000E+01

   0.023        20.0       -0.353164E+01 -0.400494E+06 -0.748661E+02 -0.378560E+06  0.282220E+03  0.557700E+01 0.1000E+01

   0.032        25.0       -0.325354E+01 -0.400511E+06 -0.749235E+02 -0.378185E+06  0.277212E+03  0.557700E+01 0.1000E+01

   0.042        30.0       -0.299022E+01 -0.400527E+06 -0.749754E+02 -0.377810E+06  0.272370E+03  0.557700E+01 0.1000E+01

   0.056        35.0       -0.274072E+01 -0.400541E+06 -0.750223E+02 -0.377435E+06  0.267684E+03  0.557700E+01 0.1000E+01

   0.074        40.0       -0.250417E+01 -0.400554E+06 -0.750645E+02 -0.377060E+06  0.263149E+03  0.557700E+01 0.1000E+01

   0.096        45.0       -0.227976E+01 -0.400566E+06 -0.751023E+02 -0.376685E+06  0.258755E+03  0.557700E+01 0.1000E+01

   0.123        50.0       -0.206675E+01 -0.400577E+06 -0.751362E+02 -0.376309E+06  0.254497E+03  0.557700E+01 0.1000E+01

   0.158        55.0       -0.186444E+01 -0.400587E+06 -0.751664E+02 -0.375933E+06  0.250369E+03  0.557700E+01 0.1000E+01

   0.199        60.0       -0.167220E+01 -0.400596E+06 -0.751931E+02 -0.375557E+06  0.246365E+03  0.557700E+01 0.1000E+01

   0.250        65.0       -0.148944E+01 -0.400604E+06 -0.752167E+02 -0.375181E+06  0.242479E+03  0.557700E+01 0.1000E+01

   0.312        70.0       -0.131560E+01 -0.400611E+06 -0.752372E+02 -0.374805E+06  0.238707E+03  0.557700E+01 0.1000E+01
```

```
 0.386      75.0   -0.115019E+01  -0.400617E+06  -0.752551E+02  -0.374429E+06   0.235042E+03   0.557700E+01 0.1000E+01

 0.474      80.0   -0.992717E+00  -0.400622E+06  -0.752703E+02  -0.374053E+06   0.231482E+03   0.557700E+01 0.1000E+01

 0.578      85.0   -0.842754E+00  -0.400627E+06  -0.752832E+02  -0.373676E+06   0.228020E+03   0.557700E+01 0.1000E+01

 0.701      90.0   -0.699885E+00  -0.400630E+06  -0.752939E+02  -0.373300E+06   0.224654E+03   0.557700E+01 0.1000E+01

 0.845      95.0   -0.563729E+00  -0.400634E+06  -0.753026E+02  -0.372923E+06   0.221380E+03   0.557700E+01 0.1000E+01

 1.013     100.0   -0.433928E+00  -0.400636E+06  -0.753093E+02  -0.372547E+06   0.218193E+03   0.557700E+01 0.1000E+01

 1.208     105.0   -0.310148E+00  -0.400638E+06  -0.753142E+02  -0.372170E+06   0.215090E+03   0.557700E+01 0.1000E+01

 1.432     110.0   -0.192076E+00  -0.400639E+06  -0.753175E+02  -0.371794E+06   0.212068E+03   0.557700E+01 0.1000E+01

 1.690     115.0   -0.794208E-01  -0.400640E+06  -0.753193E+02  -0.371417E+06   0.209124E+03   0.557700E+01 0.1000E+01

 1.985     120.0    0.280915E-01  -0.400640E+06  -0.753196E+02  -0.371040E+06   0.206256E+03   0.557700E+01 0.1000E+01

 2.320     125.0    0.130718E+00  -0.400639E+06  -0.753186E+02  -0.370664E+06   0.203459E+03   0.557700E+01 0.1000E+01

 2.700     130.0    0.228699E+00  -0.400638E+06  -0.753164E+02  -0.370287E+06   0.200731E+03   0.557700E+01 0.1000E+01

 3.129     135.0    0.322261E+00  -0.400637E+06  -0.753130E+02  -0.369910E+06   0.198070E+03   0.557700E+01 0.1000E+01

 3.612     140.0    0.411617E+00  -0.400635E+06  -0.753085E+02  -0.369534E+06   0.195474E+03   0.557700E+01 0.1000E+01

 4.153     145.0    0.496967E+00  -0.400633E+06  -0.753030E+02  -0.369157E+06   0.192940E+03   0.557700E+01 0.1000E+01

 4.757     150.0    0.578499E+00  -0.400630E+06  -0.752966E+02  -0.368781E+06   0.190466E+03   0.557700E+01 0.1000E+01

 5.430     155.0    0.656390E+00  -0.400627E+06  -0.752894E+02  -0.368404E+06   0.188049E+03   0.557700E+01 0.1000E+01

 6.177     160.0    0.730807E+00  -0.400623E+06  -0.752813E+02  -0.368028E+06   0.185688E+03   0.557700E+01 0.1000E+01
```

```
  7.003   165.0   0.801908E+00  -0.400619E+06  -0.752725E+02  -0.367651E+06   0.183382E+03   0.557700E+01 0.1000E+01
  7.915   170.0   0.869842E+00  -0.400615E+06  -0.752630E+02  -0.367275E+06   0.181127E+03   0.557700E+01 0.1000E+01
  8.918   175.0   0.934749E+00  -0.400610E+06  -0.752529E+02  -0.366898E+06   0.178922E+03   0.557700E+01 0.1000E+01
 10.019   180.0   0.996763E+00  -0.400605E+06  -0.752422E+02  -0.366522E+06   0.176767E+03   0.557700E+01 0.1000E+01
 11.225   185.0   0.105601E+01  -0.400600E+06  -0.752309E+02  -0.366145E+06   0.174658E+03   0.557700E+01 0.1000E+01
 12.542   190.0   0.111260E+01  -0.400594E+06  -0.752192E+02  -0.365769E+06   0.172595E+03   0.557700E+01 0.1000E+01
 13.976   195.0   0.116666E+01  -0.400589E+06  -0.752069E+02  -0.365393E+06   0.170576E+03   0.557700E+01 0.1000E+01
 15.536   200.0   0.121829E+01  -0.400582E+06  -0.751942E+02  -0.365017E+06   0.168600E+03   0.557700E+01 0.1000E+01
 17.229   205.0   0.126759E+01  -0.400576E+06  -0.751812E+02  -0.364641E+06   0.166665E+03   0.557700E+01 0.1000E+01
 19.062   210.0   0.131466E+01  -0.400569E+06  -0.751677E+02  -0.364264E+06   0.164770E+03   0.557700E+01 0.1000E+01
 21.042   215.0   0.135959E+01  -0.400562E+06  -0.751540E+02  -0.363888E+06   0.162914E+03   0.557700E+01 0.1000E+01
 23.178   220.0   0.140246E+01  -0.400555E+06  -0.751399E+02  -0.363512E+06   0.161095E+03   0.557700E+01 0.1000E+01
 25.478   225.0   0.144335E+01  -0.400548E+06  -0.751255E+02  -0.363136E+06   0.159313E+03   0.557700E+01 0.1000E+01
 27.950   230.0   0.148235E+01  -0.400540E+06  -0.751109E+02  -0.362760E+06   0.157567E+03   0.557700E+01 0.1000E+01
 30.603   235.0   0.151953E+01  -0.400532E+06  -0.750961E+02  -0.362385E+06   0.155855E+03   0.557700E+01 0.1000E+01
 33.446   240.0   0.155496E+01  -0.400524E+06  -0.750810E+02  -0.362009E+06   0.154176E+03   0.557700E+01 0.1000E+01
 36.487   245.0   0.158871E+01  -0.400516E+06  -0.750658E+02  -0.361633E+06   0.152530E+03   0.557700E+01 0.1000E+01
 39.735   250.0   0.162084E+01  -0.400507E+06  -0.750504E+02  -0.361257E+06   0.150915E+03   0.557700E+01 0.1000E+01
```

```
  43.201     255.0     0.165140E+01   -0.400499E+06   -0.750348E+02   -0.360882E+06    0.149331E+03    0.557700E+01 0.1000E+01

  46.893     260.0     0.168047E+01   -0.400490E+06   -0.750191E+02   -0.360506E+06    0.147777E+03    0.557700E+01 0.1000E+01

  50.821     265.0     0.170810E+01   -0.400481E+06   -0.750033E+02   -0.360130E+06    0.146251E+03    0.557700E+01 0.1000E+01

  54.996     270.0     0.173433E+01   -0.400472E+06   -0.749874E+02   -0.359755E+06    0.144754E+03    0.557700E+01 0.1000E+01

  59.429     275.0     0.175922E+01   -0.400462E+06   -0.749714E+02   -0.359379E+06    0.143284E+03    0.557700E+01 0.1000E+01

  64.128     280.0     0.178282E+01   -0.400453E+06   -0.749553E+02   -0.359004E+06    0.141840E+03    0.557700E+01 0.1000E+01

  69.107     285.0     0.180517E+01   -0.400443E+06   -0.749392E+02   -0.358628E+06    0.140422E+03    0.557700E+01 0.1000E+01

  74.376     290.0     0.182632E+01   -0.400434E+06   -0.749230E+02   -0.358253E+06    0.139030E+03    0.557700E+01 0.1000E+01

  79.946     295.0     0.184631E+01   -0.400424E+06   -0.749067E+02   -0.357878E+06    0.137662E+03    0.557700E+01 0.1000E+01

  85.832     300.0     0.186518E+01   -0.400414E+06   -0.748905E+02   -0.357503E+06    0.136318E+03    0.557700E+01 0.1000E+01

  92.044     305.0     0.188296E+01   -0.400403E+06   -0.748742E+02   -0.357127E+06    0.134997E+03    0.557700E+01 0.1000E+01

  98.597     310.0     0.189970E+01   -0.400393E+06   -0.748579E+02   -0.356752E+06    0.133699E+03    0.557700E+01 0.1000E+01

 105.505     315.0     0.191544E+01   -0.400383E+06   -0.748416E+02   -0.356377E+06    0.132423E+03    0.557700E+01 0.1018E+01

 112.783     320.0     0.193020E+01   -0.400372E+06   -0.748253E+02   -0.356002E+06    0.131169E+03    0.557700E+01 0.1020E+01

 120.447     325.0     0.194401E+01   -0.400361E+06   -0.748091E+02   -0.355627E+06    0.129935E+03    0.557700E+01 0.1021E+01

 128.514     330.0     0.195691E+01   -0.400350E+06   -0.747928E+02   -0.355252E+06    0.128722E+03    0.557700E+01 0.1023E+01

 137.003     335.0     0.196893E+01   -0.400339E+06   -0.747766E+02   -0.354877E+06    0.127529E+03    0.557700E+01 0.1025E+01

 145.933     340.0     0.198010E+01   -0.400328E+06   -0.747605E+02   -0.354501E+06    0.126355E+03    0.557700E+01 0.1027E+01
```

```
155.328      345.0     0.199044E+01  -0.400317E+06  -0.747443E+02  -0.354126E+06   0.125201E+03   0.557700E+01 0.1030E+01

165.212      350.0     0.199999E+01  -0.400306E+06  -0.747283E+02  -0.353751E+06   0.124065E+03   0.557700E+01 0.1032E+01

175.614      355.0     0.200876E+01  -0.400295E+06  -0.747122E+02  -0.353376E+06   0.122947E+03   0.557700E+01 0.1034E+01

186.568      360.0     0.201677E+01  -0.400283E+06  -0.746963E+02  -0.353002E+06   0.121846E+03   0.557700E+01 0.1037E+01

198.118      365.0     0.202407E+01  -0.400271E+06  -0.746804E+02  -0.352627E+06   0.120763E+03   0.557700E+01 0.1040E+01

210.327      370.0     0.203066E+01  -0.400260E+06  -0.746646E+02  -0.352252E+06   0.119697E+03   0.557700E+01 0.1043E+01
```

TABLE I.7

```
           -------------------------------------------------------------------------------
                     0.50oxygen + 1.00hydrogen =  1.00oh- + 1.00h+
           -------------------------------------------------------------------------------

      ---------------------------------------------------------------------------------------
                species properties in their standard state of 25 degrees c and 1 bar
      ---------------------------------------------------------------------------------------

                                 .....minerals.....


                                   .....ions.....

  name            coef.    enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----            -----    --------------   -------------   -----------------   ---------------
h+                1.000             0.0           0.0                  0.0            0.0000
oh-               1.000        -54977.0          -2.6             -37595.0           -4.1812

  name              a1            a2            a3            a4           c1            c2         wprtr
  ----              --            --            --            --           --            --         -----
h+             0.00000E+00   0.00000E+00   0.00000E+00   0.00000E+00  0.00000E+00   0.00000E+00   0.00000E+00
oh-            0.12527E+00   0.73800E+01   0.18423E+01  -0.27821E+05  0.41500E+01  -0.10346E+06   0.17246E+06

                                   .....gases.....

                                                                                           maier-kelley power fun. coef.
  name            coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)   a       bx10**3       cx10**-5
  ----            -----    --------------   -------------   ----------------   ---------------  -----   -------       --------
oxygen           -0.500             0.0         49.029                0.0          0.00000       7.160   1.0000         -0.400
hydrogen         -1.000             0.0         31.234                0.0          0.00000       6.520   0.7800          0.120

                                    .....h2o.....


      ---------------------------------------------------------------------------------------
                          reaction properties at 25 degrees c and 1 bar
      ---------------------------------------------------------------------------------------

 enthalpy (cal)     entropy (cal)     free energy (cal)   delta vol (cc/mol)   heat capacity        log k

-0.549761E+05      -0.583083E+02      -0.375941E+05        -0.418121E+01      -0.431576E+02     0.275567E+02

                       fugacity coefficents are listed in this order

                              gas number  1 = oxygen
```

gas number 2 = hydrogen

```
            ----------------------------------------------------------------------------------------------------
                                  0.50oxygen + 1.00hydrogen =  1.00oh- + 1.00h+
            ----------------------------------------------------------------------------------------------------

 pres (bars)  temp (deg c)   delta cp     delta h(t,p)   delta s(t,p)   delta g(t,p)    log k(t,p)    delta v(t,p)  fug coef
 -----------  ------------  ------------  ------------   ------------   ------------    ----------    ------------  --------

    0.006          0.0     -0.733718E+02 -0.536096E+05 -0.535031E+02 -0.389979E+05   0.312020E+02  -0.675206E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.009          5.0     -0.631954E+02 -0.539496E+05 -0.547369E+02 -0.387272E+05   0.304285E+02  -0.595682E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.012         10.0     -0.558290E+02 -0.542462E+05 -0.557940E+02 -0.384508E+05   0.296778E+02  -0.533805E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.017         15.0     -0.503783E+02 -0.545111E+05 -0.567213E+02 -0.381695E+05   0.289495E+02  -0.485394E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.023         20.0     -0.462820E+02 -0.547523E+05 -0.575513E+02 -0.378838E+05   0.282427E+02  -0.447583E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.032         25.0     -0.431724E+02 -0.549756E+05 -0.583066E+02 -0.375941E+05   0.275567E+02  -0.418354E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.042         30.0     -0.408006E+02 -0.551852E+05 -0.590040E+02 -0.373008E+05   0.268908E+02  -0.396250E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.056         35.0     -0.389927E+02 -0.553845E+05 -0.596561E+02 -0.370042E+05   0.262441E+02  -0.380204E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.074         40.0     -0.376244E+02 -0.555759E+05 -0.602722E+02 -0.367043E+05   0.256158E+02  -0.369423E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.096         45.0     -0.366051E+02 -0.557613E+05 -0.608597E+02 -0.364015E+05   0.250052E+02  -0.363313E+01 0.1000E+01
                                                                                                                 0.1000E+01

    0.123         50.0     -0.358678E+02 -0.559424E+05 -0.614245E+02 -0.360958E+05   0.244115E+02  -0.361433E+01 0.1000E+01
                                                                                                                 0.1000E+01
```

```
0.158      55.0    -0.353621E+02  -0.561204E+05  -0.619711E+02  -0.357873E+05    0.238341E+02   -0.363453E+01 0.1000E+01
                                                                                                              0.1000E+01

0.199      60.0    -0.350501E+02  -0.562964E+05  -0.625032E+02  -0.354761E+05    0.232723E+02   -0.369134E+01 0.1000E+01
                                                                                                              0.1000E+01

0.250      65.0    -0.349029E+02  -0.564712E+05  -0.630240E+02  -0.351623E+05    0.227253E+02   -0.378309E+01 0.1000E+01
                                                                                                              0.1000E+01

0.312      70.0    -0.348986E+02  -0.566456E+05  -0.635361E+02  -0.348459E+05    0.221927E+02   -0.390870E+01 0.1000E+01
                                                                                                              0.1000E+01

0.386      75.0    -0.350206E+02  -0.568204E+05  -0.640416E+02  -0.345269E+05    0.216738E+02   -0.406757E+01 0.1000E+01
                                                                                                              0.1000E+01

0.474      80.0    -0.352565E+02  -0.569960E+05  -0.645425E+02  -0.342055E+05    0.211680E+02   -0.425954E+01 0.1000E+01
                                                                                                              0.1000E+01

0.578      85.0    -0.355974E+02  -0.571730E+05  -0.650403E+02  -0.338815E+05    0.206748E+02   -0.448482E+01 0.1000E+01
                                                                                                              0.1000E+01

0.701      90.0    -0.360371E+02  -0.573520E+05  -0.655366E+02  -0.335551E+05    0.201937E+02   -0.474395E+01 0.1000E+01
                                                                                                              0.1000E+01

0.845      95.0    -0.365718E+02  -0.575335E+05  -0.660327E+02  -0.332262E+05    0.197242E+02   -0.503783E+01 0.1000E+01
                                                                                                              0.1000E+01

1.013     100.0    -0.371996E+02  -0.577178E+05  -0.665299E+02  -0.328948E+05    0.192658E+02   -0.536764E+01 0.1000E+01
                                                                                                              0.1000E+01

1.208     105.0    -0.379205E+02  -0.579054E+05  -0.670294E+02  -0.325609E+05    0.188181E+02   -0.573486E+01 0.1000E+01
                                                                                                              0.1000E+01

1.432     110.0    -0.387361E+02  -0.580969E+05  -0.675323E+02  -0.322246E+05    0.183807E+02   -0.614132E+01 0.1000E+01
                                                                                                              0.1000E+01

1.690     115.0    -0.396495E+02  -0.582927E+05  -0.680398E+02  -0.318857E+05    0.179531E+02   -0.658911E+01 0.1000E+01
                                                                                                              0.1000E+01
```

```
   1.985       120.0    -0.406652E+02  -0.584932E+05  -0.685530E+02  -0.315443E+05    0.175350E+02   -0.708071E+01 0.1000E+01
                                                                                                                    0.1000E+01

   2.320       125.0    -0.417894E+02  -0.586990E+05  -0.690730E+02  -0.312003E+05    0.171259E+02   -0.761891E+01 0.1000E+01
                                                                                                                    0.1000E+01

   2.700       130.0    -0.430295E+02  -0.589106E+05  -0.696010E+02  -0.308536E+05    0.167256E+02   -0.820691E+01 0.1000E+01
                                                                                                                    0.1000E+01

   3.129       135.0    -0.443947E+02  -0.591287E+05  -0.701384E+02  -0.305044E+05    0.163337E+02   -0.884831E+01 0.1000E+01
                                                                                                                    0.1000E+01

   3.612       140.0    -0.458958E+02  -0.593538E+05  -0.706863E+02  -0.301524E+05    0.159499E+02   -0.954718E+01 0.1000E+01
                                                                                                                    0.1000E+01

   4.153       145.0    -0.475453E+02  -0.595866E+05  -0.712461E+02  -0.297977E+05    0.155738E+02   -0.103081E+02 0.1000E+01
                                                                                                                    0.1000E+01

   4.757       150.0    -0.493408E+02  -0.598378E+05  -0.718180E+02  -0.294508E+05    0.152105E+02   -0.111362E+02 0.1000E+01
                                                                                                                    0.1000E+01

   5.430       155.0    -0.512378E+02  -0.600832E+05  -0.723937E+02  -0.290905E+05    0.148490E+02   -0.120326E+02 0.1000E+01
                                                                                                                    0.1000E+01

   6.177       160.0    -0.532210E+02  -0.603323E+05  -0.729717E+02  -0.287273E+05    0.144944E+02   -0.130030E+02 0.1000E+01
                                                                                                                    0.1000E+01

   7.003       165.0    -0.552836E+02  -0.605847E+05  -0.735509E+02  -0.283611E+05    0.141463E+02   -0.140530E+02 0.1000E+01
                                                                                                                    0.1000E+01

   7.915       170.0    -0.574250E+02  -0.608401E+05  -0.741308E+02  -0.279917E+05    0.138045E+02   -0.151894E+02 0.1000E+01
                                                                                                                    0.1000E+01

   8.918       175.0    -0.596507E+02  -0.610985E+05  -0.747116E+02  -0.276192E+05    0.134688E+02   -0.164198E+02 0.1000E+01
                                                                                                                    0.1000E+01

  10.019       180.0    -0.619715E+02  -0.613603E+05  -0.752942E+02  -0.272434E+05    0.131390E+02   -0.177533E+02 0.1000E+01
                                                                                                                    0.1000E+01
```

```
11.225      185.0     -0.644044E+02  -0.616258E+05  -0.758799E+02  -0.268641E+05    0.128147E+02    -0.191999E+02 0.1000E+01
                                                                                                                  0.1000E+01

12.542      190.0     -0.669731E+02  -0.618960E+05  -0.764707E+02  -0.264812E+05    0.124957E+02    -0.207715E+02 0.1000E+01
                                                                                                                  0.1000E+01

13.976      195.0     -0.697089E+02  -0.621719E+05  -0.770691E+02  -0.260947E+05    0.121817E+02    -0.224813E+02 0.1000E+01
                                                                                                                  0.1000E+01

15.536      200.0     -0.727963E+02  -0.624885E+05  -0.777444E+02  -0.257064E+05    0.118737E+02    -0.242452E+02 0.1000E+01
                                                                                                                  0.1000E+01

17.229      205.0     -0.763166E+02  -0.628550E+05  -0.785128E+02  -0.253168E+05    0.115714E+02    -0.260447E+02 0.1000E+01
                                                                                                                  0.1000E+01

19.062      210.0     -0.801763E+02  -0.632388E+05  -0.793087E+02  -0.249235E+05    0.112738E+02    -0.279897E+02 0.1000E+01
                                                                                                                  0.1000E+01

21.042      215.0     -0.844193E+02  -0.636414E+05  -0.801349E+02  -0.245262E+05    0.109805E+02    -0.300943E+02 0.1000E+01
                                                                                                                  0.1000E+01

23.178      220.0     -0.890970E+02  -0.640647E+05  -0.809942E+02  -0.241250E+05    0.106913E+02    -0.323747E+02 0.1000E+01
                                                                                                                  0.1000E+01

25.478      225.0     -0.942710E+02  -0.645106E+05  -0.818901E+02  -0.237197E+05    0.104062E+02    -0.348493E+02 0.1000E+01
                                                                                                                  0.1000E+01

27.950      230.0     -0.100014E+03  -0.649814E+05  -0.828262E+02  -0.233100E+05    0.101248E+02    -0.375392E+02 0.1000E+01
                                                                                                                  0.1000E+01

30.603      235.0     -0.106415E+03  -0.654798E+05  -0.838069E+02  -0.228960E+05    0.984713E+01    -0.404693E+02 0.1000E+01
                                                                                                                  0.1000E+01

33.446      240.0     -0.113579E+03  -0.660086E+05  -0.848370E+02  -0.224772E+05    0.957285E+01    -0.436682E+02 0.1000E+01
                                                                                                                  0.1000E+01

36.487      245.0     -0.121636E+03  -0.665715E+05  -0.859221E+02  -0.220537E+05    0.930182E+01    -0.471695E+02 0.1000E+01
                                                                                                                  0.1000E+01
```

```
39.735      250.0     -0.130743E+03   -0.671724E+05   -0.870688E+02   -0.216250E+05     0.903385E+01    -0.510128E+02 0.1000E+01
                                                                                                                      0.1000E+01

43.201      255.0     -0.141094E+03   -0.678159E+05   -0.882845E+02   -0.211911E+05     0.876876E+01    -0.552452E+02 0.1000E+01
                                                                                                                      0.1000E+01

46.893      260.0     -0.152930E+03   -0.685075E+05   -0.895783E+02   -0.207515E+05     0.850635E+01    -0.599226E+02 0.1000E+01
                                                                                                                      0.1000E+01

50.821      265.0     -0.166549E+03   -0.692539E+05   -0.909607E+02   -0.203061E+05     0.824642E+01    -0.651126E+02 0.1000E+01
                                                                                                                      0.1000E+01

54.996      270.0     -0.182331E+03   -0.700626E+05   -0.924439E+02   -0.198544E+05     0.798876E+01    -0.708965E+02 0.1000E+01
                                                                                                                      0.1000E+01

59.429      275.0     -0.200752E+03   -0.709431E+05   -0.940431E+02   -0.193961E+05     0.773316E+01    -0.773740E+02 0.1000E+01
                                                                                                                      0.1000E+01

64.128      280.0     -0.222428E+03   -0.719066E+05   -0.957762E+02   -0.189307E+05     0.747939E+01    -0.846673E+02 0.1000E+01
                                                                                                                      0.1000E+01

69.107      285.0     -0.248152E+03   -0.729668E+05   -0.976651E+02   -0.184577E+05     0.722719E+01    -0.929283E+02 0.1000E+01
                                                                                                                      0.1000E+01

74.376      290.0     -0.278966E+03   -0.741405E+05   -0.997364E+02   -0.179766E+05     0.697631E+01    -0.102347E+03 0.1000E+01
                                                                                                                      0.1000E+01

79.946      295.0     -0.316253E+03   -0.754485E+05   -0.102023E+03   -0.174866E+05     0.672644E+01    -0.113165E+03 0.1000E+01
                                                                                                                      0.1000E+01

85.832      300.0     -0.361874E+03   -0.769170E+05   -0.104567E+03   -0.169870E+05     0.647727E+01    -0.125691E+03 0.1000E+01
                                                                                                                      0.1000E+01

92.044      305.0     -0.418378E+03   -0.785790E+05   -0.107420E+03   -0.164769E+05     0.622843E+01    -0.140324E+03 0.1000E+01
                                                                                                                      0.1000E+01

98.597      310.0     -0.489318E+03   -0.804769E+05   -0.110648E+03   -0.159553E+05     0.597952E+01    -0.157593E+03 0.1000E+01
                                                                                                                      0.1000E+01
```

```
105.505     315.0     -0.579752E+03   -0.826655E+05   -0.114337E+03   -0.154207E+05    0.573005E+01   -0.178202E+03 0.1018E+01
                                                                                                                     0.1036E+01

112.783     320.0     -0.697054E+03   -0.852171E+05   -0.118601E+03   -0.148717E+05    0.547948E+01   -0.203109E+03 0.1020E+01
                                                                                                                     0.1039E+01

120.447     325.0     -0.852269E+03   -0.882286E+05   -0.123589E+03   -0.143065E+05    0.522717E+01   -0.233646E+03 0.1021E+01
                                                                                                                     0.1041E+01

128.514     330.0     -0.106246E+04   -0.918321E+05   -0.129507E+03   -0.137228E+05    0.497234E+01   -0.271700E+03 0.1023E+01
                                                                                                                     0.1043E+01

137.003     335.0     -0.135495E+04   -0.962116E+05   -0.136638E+03   -0.131179E+05    0.471408E+01   -0.320025E+03 0.1025E+01
                                                                                                                     0.1046E+01

145.933     340.0     -0.177530E+04   -0.101630E+06   -0.145387E+03   -0.124884E+05    0.445126E+01   -0.382746E+03 0.1027E+01
                                                                                                                     0.1049E+01

155.328     345.0     -0.240287E+04   -0.108468E+06   -0.156339E+03   -0.118301E+05    0.418250E+01   -0.466246E+03 0.1030E+01
                                                                                                                     0.1051E+01

165.212     350.0     -0.338171E+04   -0.117292E+06   -0.170355E+03   -0.111379E+05    0.390618E+01   -0.580708E+03 0.1032E+01
                                                                                                                     0.1054E+01

175.614     355.0     -0.234771E+05   -0.245900E+06   -0.379174E+03   -0.772382E+04    0.268727E+01   -0.220362E+04 0.1034E+01
                                                                                                                     0.1057E+01

186.568     360.0     -0.513019E+05   -0.335683E+06   -0.520319E+03   -0.624595E+04    0.215593E+01   -0.354226E+04 0.1037E+01
                                                                                                                     0.1060E+01

198.118     365.0     -0.154671E+06   -0.534829E+06   -0.831303E+03   -0.433587E+04    0.148490E+01   -0.674787E+04 0.1040E+01
                                                                                                                     0.1064E+01

210.327     370.0     -0.101124E+07   -0.123178E+07   -0.191295E+04   -0.146515E+04    0.497866E+00   -0.191418E+05 0.1043E+01
                                                                                                                     0.1067E+01
```

TABLE I.8

ESTIMATES OF LOG K_W BETWEEN 0 AND 350°C ALONG THE SATURATION SURFACE OF WATER

T,°C	Pressure, bars	Sweeton, et al. (1974)	Helgeson et al. (1981)	Marshall and Franck (1981)	Tanger (1986)	Tanger and Helgeson (1988) SUPCRT'87
0	0.006	-14.941	-14.934	14.938	-14.933	14.940
25	0.032	-13.993	-13.988	13.955	-13.989	13.995
50	0.123	-13.272	-13.264	13.275	-13.266	13.271
60	0.199	—	-13.020	—	-13.023	13.027
75	0.386	-12.709	-12.694	12.712	-12.700	12.704
100	1.013	-12.264	-12.240	12.265	-12.255	12.259
125	2.320	-11.914	-11.879	—	-11.908	11.910
150	4.757	-11.642	-11.594	11.638	-11.641	11.637
175	8.918	-11.441	-11.376	—	-11.447	11.439
200	15.536	-11.302	-11.219	11.289	-11.305	11.305
225	25.478	-11.222	-11.122	—	-11.221	11.221
250	39.735	-11.196	-11.083	11.191	-11.194	11.194
275	59.429	-11.224	-11.132	—	-11.227	11.226
300	85.832	-11.301	-11.285	11.406	-11.328	11.327
325	120.447	—	-11.619	—	-11.523	11.521
350	165.212	—	-12.356	12.30	-11.875	11.874

TABLE I.9

```
                                                                                          07/15/88
                                                                                          page  1

            ------------------------------------------------------------------------------
                                  1.00h2o =  1.00oh- + 1.00h+
            ------------------------------------------------------------------------------

        ---------------------------------------------------------------------------------------
                    species properties in their standard state of 25 degrees c and 1 bar
        ---------------------------------------------------------------------------------------

                                      .....minerals.....


                                        .....ions.....

   name             coef.   enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
   ----             -----   --------------   -------------   -----------------   ---------------
 h+                 1.000            0.0            0.0                0.0             0.0000
 oh-                1.000       -54977.0           -2.6           -37595.0            -4.1812

   name             a1           a2           a3           a4           c1           c2           wprtr
   ----             --           --           --           --           --           --           -----
 h+           0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00  0.00000E+00
 oh-          0.12527E+00  0.73800E+01  0.18423E+01 -0.27821E+05  0.41500E+01 -0.10346E+06  0.17246E+06

                                        .....gases.....


                                         .....h2o.....

   name             coef.   enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
   ----             -----   --------------   -------------   -----------------   ---------------
 water             -1.000       -68315.7           16.7           -56686.8            18.0692


        ---------------------------------------------------------------------------------------
                               reaction properties at 25 degrees c and 1 bar
        ---------------------------------------------------------------------------------------


        enthalpy (cal)    entropy (cal)    free energy (cal)   delta vol (cc/mol)   heat capacity        log k

        0.133397E+05     -0.192722E+02      0.190927E+05        -0.222504E+02      -0.507801E+02    -0.139951E+02
```

```
          ----------------------------------------------------------------------------------------
                                        1.00h2o =  1.00oh- + 1.00h+
          ----------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp     delta h(t,p)  delta s(t,p)  delta g(t,p)   log k(t,p)   delta v(t,p)  fugacity
-----------  ------------  ------------  ------------  ------------  ------------  ----------   ------------  --------

   0.006         0.0      -0.812400E+02  0.148982E+05 -0.137940E+02  0.186729E+05 -0.149401E+02 -0.247714E+02  0.610990E-02

   0.009         5.0      -0.709298E+02  0.145192E+05 -0.151691E+02  0.187454E+05 -0.147285E+02 -0.239731E+02  0.872790E-02

   0.012        10.0      -0.635018E+02  0.141841E+05 -0.163634E+02  0.188243E+05 -0.145293E+02 -0.233589E+02  0.122784E-01

   0.017        15.0      -0.580237E+02  0.138810E+05 -0.174248E+02  0.189089E+05 -0.143413E+02 -0.228856E+02  0.170562E-01

   0.023        20.0      -0.539139E+02  0.136016E+05 -0.183861E+02  0.189985E+05 -0.141635E+02 -0.225239E+02  0.233701E-01

   0.032        25.0      -0.507949E+02  0.133402E+05 -0.192705E+02  0.190927E+05 -0.139951E+02 -0.222527E+02  0.316655E-01

   0.042        30.0      -0.484136E+02  0.130924E+05 -0.200946E+02  0.191911E+05 -0.138352E+02 -0.220572E+02  0.423811E-01

   0.056        35.0      -0.465948E+02  0.128551E+05 -0.208711E+02  0.192936E+05 -0.136834E+02 -0.219263E+02  0.561843E-01

   0.074        40.0      -0.452150E+02  0.126257E+05 -0.216095E+02  0.193998E+05 -0.135390E+02 -0.218517E+02  0.736189E-01

   0.096        45.0      -0.441843E+02  0.124023E+05 -0.223172E+02  0.195097E+05 -0.134017E+02 -0.218274E+02  0.956318E-01

   0.123        50.0      -0.434370E+02  0.121834E+05 -0.230000E+02  0.196230E+05 -0.132710E+02 -0.218486E+02  0.123004E+00

   0.158        55.0      -0.429236E+02  0.119675E+05 -0.236627E+02  0.197397E+05 -0.131465E+02 -0.219120E+02  0.156721E+00

   0.199        60.0      -0.426069E+02  0.117538E+05 -0.243092E+02  0.198596E+05 -0.130279E+02 -0.220151E+02  0.198193E+00

   0.250        65.0      -0.424582E+02  0.115412E+05 -0.249426E+02  0.199827E+05 -0.129148E+02 -0.221562E+02  0.248524E+00

   0.312        70.0      -0.424560E+02  0.113289E+05 -0.255655E+02  0.201090E+05 -0.128071E+02 -0.223340E+02  0.309531E+00
```

```
0.386      75.0   -0.425836E+02  0.111164E+05  -0.261804E+02  0.202384E+05  -0.127043E+02  -0.225479E+02  0.382523E+00

0.474      80.0   -0.428285E+02  0.109029E+05  -0.267891E+02  0.203708E+05  -0.126064E+02  -0.227977E+02  0.469240E+00

0.578      85.0   -0.431817E+02  0.106879E+05  -0.273934E+02  0.205062E+05  -0.125130E+02  -0.230837E+02  0.571573E+00

0.701      90.0   -0.436366E+02  0.104709E+05  -0.279950E+02  0.206446E+05  -0.124241E+02  -0.234062E+02  0.692524E+00

0.845      95.0   -0.441892E+02  0.102514E+05  -0.285951E+02  0.207861E+05  -0.123393E+02  -0.237663E+02  0.833606E+00

1.013     100.0   -0.448375E+02  0.100289E+05  -0.291951E+02  0.209305E+05  -0.122585E+02  -0.241650E+02  0.997909E+00

1.208     105.0   -0.455813E+02  0.980289E+04  -0.297964E+02  0.210779E+05  -0.121816E+02  -0.246040E+02  0.118756E+01

1.432     110.0   -0.464220E+02  0.957299E+04  -0.304000E+02  0.212282E+05  -0.121084E+02  -0.250849E+02  0.140532E+01

1.690     115.0   -0.473627E+02  0.933866E+04  -0.310072E+02  0.213816E+05  -0.120388E+02  -0.256101E+02  0.165472E+01

1.985     120.0   -0.484079E+02  0.909942E+04  -0.316191E+02  0.215380E+05  -0.119727E+02  -0.261818E+02  0.193866E+01

2.320     125.0   -0.495636E+02  0.885472E+04  -0.322371E+02  0.216975E+05  -0.119098E+02  -0.268031E+02  0.226018E+01

2.700     130.0   -0.508376E+02  0.860401E+04  -0.328622E+02  0.218600E+05  -0.118502E+02  -0.274770E+02  0.262365E+01

3.129     135.0   -0.522390E+02  0.834670E+04  -0.334958E+02  0.220257E+05  -0.117938E+02  -0.282074E+02  0.303172E+01

3.612     140.0   -0.537789E+02  0.808214E+04  -0.341392E+02  0.221944E+05  -0.117403E+02  -0.289983E+02  0.348862E+01

4.153     145.0   -0.554701E+02  0.780963E+04  -0.347939E+02  0.223664E+05  -0.116898E+02  -0.298544E+02  0.399822E+01

4.757     150.0   -0.573102E+02  0.751852E+04  -0.354599E+02  0.225311E+05  -0.116367E+02  -0.307808E+02  0.456450E+01

5.430     155.0   -0.592551E+02  0.723307E+04  -0.361292E+02  0.227096E+05  -0.115919E+02  -0.317790E+02  0.519103E+01

6.177     160.0   -0.612899E+02  0.694352E+04  -0.368003E+02  0.228914E+05  -0.115498E+02  -0.328545E+02  0.588234E+01
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   7.003      165.0    -0.634081E+02   0.665042E+04  -0.374719E+02   0.230766E+05  -0.115104E+02  -0.340132E+02   0.664261E+01

   7.915      170.0    -0.656094E+02   0.635403E+04  -0.381439E+02   0.232653E+05  -0.114736E+02  -0.352619E+02   0.747609E+01

   8.918      175.0    -0.678997E+02   0.605429E+04  -0.388163E+02   0.234577E+05  -0.114394E+02  -0.366086E+02   0.838621E+01

  10.019      180.0    -0.702903E+02   0.575092E+04  -0.394902E+02   0.236538E+05  -0.114078E+02  -0.380622E+02   0.937882E+01

  11.225      185.0    -0.727985E+02   0.544334E+04  -0.401668E+02   0.238537E+05  -0.113787E+02  -0.396332E+02   0.104564E+02

  12.542      190.0    -0.754487E+02   0.513074E+04  -0.408483E+02   0.240576E+05  -0.113520E+02  -0.413334E+02   0.116241E+02

  13.976      195.0    -0.782725E+02   0.481195E+04  -0.415372E+02   0.242656E+05  -0.113279E+02  -0.431764E+02   0.128860E+02

  15.536      200.0    -0.814550E+02   0.445198E+04  -0.423030E+02   0.244757E+05  -0.113052E+02  -0.450783E+02   0.142463E+02

  17.229      205.0    -0.850782E+02   0.404165E+04  -0.431617E+02   0.246875E+05  -0.112838E+02  -0.470208E+02   0.157075E+02

  19.062      210.0    -0.890492E+02   0.361352E+04  -0.440480E+02   0.249034E+05  -0.112647E+02  -0.491141E+02   0.172766E+02

  21.042      215.0    -0.934125E+02   0.316596E+04  -0.449647E+02   0.251236E+05  -0.112479E+02  -0.513727E+02   0.189543E+02

  23.178      220.0    -0.982206E+02   0.269715E+04  -0.459147E+02   0.253481E+05  -0.112334E+02  -0.538129E+02   0.207437E+02

  25.478      225.0    -0.103536E+03   0.220504E+04  -0.469014E+02   0.255771E+05  -0.112211E+02  -0.564536E+02   0.226525E+02

  27.950      230.0    -0.109432E+03   0.168728E+04  -0.479287E+02   0.258108E+05  -0.112111E+02  -0.593165E+02   0.246823E+02

  30.603      235.0    -0.115999E+03   0.114123E+04  -0.490009E+02   0.260493E+05  -0.112033E+02  -0.624265E+02   0.268337E+02

  33.446      240.0    -0.123343E+03   0.563843E+03  -0.501230E+02   0.262927E+05  -0.111978E+02  -0.658130E+02   0.291124E+02

  36.487      245.0    -0.131595E+03  -0.484004E+02  -0.513008E+02   0.265414E+05  -0.111947E+02  -0.695101E+02   0.315212E+02

  39.735      250.0    -0.140915E+03  -0.699568E+03  -0.525407E+02   0.267954E+05  -0.111938E+02  -0.735581E+02   0.340629E+02
```

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  43.201     255.0   -0.151498E+03  -0.139441E+04  -0.538506E+02   0.270551E+05  -0.111953E+02  -0.780046E+02   0.367404E+02

  46.893     260.0   -0.163587E+03  -0.213851E+04  -0.552394E+02   0.273208E+05  -0.111992E+02  -0.829065E+02   0.395560E+02

  50.821     265.0   -0.177484E+03  -0.293846E+04  -0.567177E+02   0.275926E+05  -0.112055E+02  -0.883320E+02   0.425120E+02

  54.996     270.0   -0.193570E+03  -0.380211E+04  -0.582982E+02   0.278710E+05  -0.112144E+02  -0.943637E+02   0.456106E+02

  59.429     275.0   -0.212328E+03  -0.473888E+04  -0.599960E+02   0.281564E+05  -0.112259E+02  -0.101102E+03   0.488535E+02

  64.128     280.0   -0.234375E+03  -0.576013E+04  -0.618291E+02   0.284491E+05  -0.112401E+02  -0.108671E+03   0.522425E+02

  69.107     285.0   -0.260513E+03  -0.687968E+04  -0.638196E+02   0.287498E+05  -0.112571E+02  -0.117224E+03   0.557790E+02

  74.376     290.0   -0.291789E+03  -0.811453E+04  -0.659946E+02   0.290589E+05  -0.112771E+02  -0.126953E+03   0.594643E+02

  79.946     295.0   -0.329595E+03  -0.948570E+04  -0.683873E+02   0.293772E+05  -0.113003E+02  -0.138101E+03   0.632930E+02

  85.832     300.0   -0.375804E+03  -0.110195E+05  -0.710393E+02   0.297053E+05  -0.113268E+02  -0.150979E+03   0.672784E+02

  92.044     305.0   -0.432978E+03  -0.127492E+05  -0.740031E+02   0.300443E+05  -0.113570E+02  -0.165990E+03   0.714151E+02

  98.597     310.0   -0.504690E+03  -0.147175E+05  -0.773453E+02   0.303952E+05  -0.113911E+02  -0.183667E+03   0.757035E+02

 105.505     315.0   -0.596023E+03  -0.169794E+05  -0.811526E+02   0.307592E+05  -0.114296E+02  -0.204716E+03   0.801358E+02

 112.783     320.0   -0.714386E+03  -0.196078E+05  -0.855382E+02   0.311379E+05  -0.114728E+02  -0.230104E+03   0.847276E+02

 120.447     325.0   -0.870873E+03  -0.227000E+05  -0.906535E+02   0.315332E+05  -0.115213E+02  -0.261168E+03   0.894622E+02

 128.514     330.0   -0.108262E+04  -0.263887E+05  -0.967042E+02   0.319472E+05  -0.115758E+02  -0.299806E+03   0.943566E+02

 137.003     335.0   -0.137706E+04  -0.308590E+05  -0.103976E+03   0.323827E+05  -0.116371E+02  -0.348783E+03   0.994019E+02

 145.933     340.0   -0.179991E+04  -0.363741E+05  -0.112873E+03   0.328431E+05  -0.117063E+02  -0.412242E+03   0.104587E+03
```

```
155.328        345.0     -0.243084E+04  -0.433180E+05  -0.123985E+03   0.333325E+05  -0.117847E+02  -0.496593E+03   0.109931E+03

165.212        350.0     -0.341443E+04  -0.522577E+05  -0.138177E+03   0.338562E+05  -0.118737E+02  -0.612056E+03   0.115423E+03

175.614        355.0     -0.235171E+05  -0.180995E+06  -0.347191E+03   0.371019E+05  -0.129085E+02  -0.223819E+04   0.121049E+03

186.568        360.0     -0.513542E+05  -0.270930E+06  -0.488561E+03   0.384117E+05  -0.132587E+02  -0.357637E+04   0.126832E+03

198.118        365.0     -0.154750E+06  -0.470261E+06  -0.799821E+03   0.401540E+05  -0.137515E+02  -0.678411E+04   0.132744E+03

210.327        370.0     -0.101140E+07  -0.116747E+07  -0.188185E+04   0.428572E+05  -0.145631E+02  -0.191815E+05   0.138810E+03
```

TABLE I.10

```
                                                                                    07/ 6/88
                                                                                    page  1

          ------------------------------------------------------------------
                     1.00gibbsite =  1.00boehmite + 1.00h2o
          ------------------------------------------------------------------

      --------------------------------------------------------------------------
            species properties in their standard state of 25 degrees c and 1 bar
      --------------------------------------------------------------------------

                                  .....minerals.....

                                                                                      maier-kelley power fun. coef.
 name          coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)      a      bx10**3      cx10**-5
 ----          -----    --------------   -------------   ----------------   ---------------    -----    -------      --------
gibbsite      -1.000      -309065.0         16.358          -276025.0          31.95600        8.650    45.6000         0.000
boehmite       1.000      -237893.0          8.988          -219289.0          19.53500       12.905    20.7000        -3.005


                                   .....ions.....


                                   .....gases.....


                                   .....h2o.....
 name          coef.    enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
 ----          -----    --------------   -------------   -----------------   ---------------
water          1.000       -68315.3          16.7            -56686.4            18.0684


      --------------------------------------------------------------------------
                      reaction properties at 25 degrees c and 1 bar
      --------------------------------------------------------------------------

enthalpy (cal)     entropy (cal)     free energy (cal)   delta vol (cc/mol)   heat capacity        log k

0.285666E+04       0.934226E+01      0.496289E+02        0.564740E+01         0.114636E+02     -0.363783E-01
```

```
          ------------------------------------------------------------------------------------------
                                    1.00gibbsite =  1.00boehmite + 1.00h2o
          ------------------------------------------------------------------------------------------

pres (bars)   temp (deg c)    delta cp     delta h(t,p)   delta s(t,p)   delta g(t,p)    log k(t,p)    delta v(t,p)    fugacity
-----------   ------------  ------------   ------------   ------------   ------------    ----------    ------------    --------

   0.006          0.0       0.116366E+02   0.256898E+04   0.833492E+01   0.270815E+03  -0.216678E+00   0.559831E+01   0.610990E-02

   0.009          5.0       0.115321E+02   0.262687E+04   0.854492E+01   0.228584E+03  -0.179601E+00   0.559532E+01   0.872790E-02

   0.012         10.0       0.114919E+02   0.268441E+04   0.874995E+01   0.185316E+03  -0.143034E+00   0.559984E+01   0.122784E-01

   0.017         15.0       0.114787E+02   0.274183E+04   0.895098E+01   0.141033E+03  -0.106966E+00   0.561069E+01   0.170562E-01

   0.023         20.0       0.114729E+02   0.279921E+04   0.914839E+01   0.957549E+02  -0.713861E-01   0.562702E+01   0.233701E-01

   0.032         25.0       0.114648E+02   0.285656E+04   0.934237E+01   0.494982E+02  -0.362825E-01   0.564819E+01   0.316655E-01

   0.042         30.0       0.114506E+02   0.291385E+04   0.953293E+01   0.228050E+01  -0.164405E-02   0.567372E+01   0.423811E-01

   0.056         35.0       0.114298E+02   0.297105E+04   0.972008E+01  -0.458811E+02   0.325397E-01   0.570325E+01   0.561643E-01

   0.074         40.0       0.114030E+02   0.302814E+04   0.990384E+01  -0.949694E+02   0.662787E-01   0.573649E+01   0.736189E-01

   0.096         45.0       0.113717E+02   0.308508E+04   0.100842E+02  -0.144967E+03   0.995821E-01   0.577322E+01   0.956318E-01

   0.123         50.0       0.113372E+02   0.314186E+04   0.102613E+02  -0.195858E+03   0.132459E+00   0.581327E+01   0.123004E+00

   0.158         55.0       0.113007E+02   0.319845E+04   0.104351E+02  -0.247625E+03   0.164917E+00   0.585650E+01   0.156721E+00

   0.199         60.0       0.112632E+02   0.325487E+04   0.106057E+02  -0.300252E+03   0.196965E+00   0.590280E+01   0.198193E+00

   0.250         65.0       0.112253E+02   0.331109E+04   0.107732E+02  -0.353723E+03   0.228611E+00   0.595208E+01   0.248524E+00

   0.312         70.0       0.111873E+02   0.336713E+04   0.109376E+02  -0.408022E+03   0.259862E+00   0.600427E+01   0.309531E+00
```

```
0.386     75.0    0.111495E+02  0.342297E+04  0.110992E+02  -0.463134E+03  0.290725E+00  0.605932E+01  0.382523E+00

0.474     80.0    0.111120E+02  0.347863E+04  0.112579E+02  -0.519044E+03  0.321209E+00  0.611719E+01  0.469240E+00

0.578     85.0    0.110747E+02  0.353410E+04  0.114138E+02  -0.575739E+03  0.351320E+00  0.617785E+01  0.571573E+00

0.701     90.0    0.110376E+02  0.358939E+04  0.115670E+02  -0.633203E+03  0.381066E+00  0.624128E+01  0.692524E+00

0.845     95.0    0.110006E+02  0.364449E+04  0.117177E+02  -0.691424E+03  0.410452E+00  0.630747E+01  0.833606E+00

1.013    100.0    0.109636E+02  0.369940E+04  0.118658E+02  -0.750388E+03  0.439486E+00  0.637641E+01  0.997909E+00

1.208    105.0    0.109265E+02  0.375413E+04  0.120114E+02  -0.810081E+03  0.468174E+00  0.644813E+01  0.118756E+01

1.432    110.0    0.108895E+02  0.380868E+04  0.121546E+02  -0.870492E+03  0.496522E+00  0.652263E+01  0.140532E+01

1.690    115.0    0.108525E+02  0.386303E+04  0.122954E+02  -0.931607E+03  0.524537E+00  0.659994E+01  0.165472E+01

1.985    120.0    0.108155E+02  0.391721E+04  0.124340E+02  -0.993414E+03  0.552224E+00  0.668010E+01  0.193866E+01

2.320    125.0    0.107788E+02  0.397119E+04  0.125703E+02  -0.105590E+04  0.579588E+00  0.676314E+01  0.226018E+01

2.700    130.0    0.107426E+02  0.402500E+04  0.127045E+02  -0.111906E+04  0.606636E+00  0.684912E+01  0.262365E+01

3.129    135.0    0.107069E+02  0.407862E+04  0.128365E+02  -0.118287E+04  0.633373E+00  0.693809E+01  0.303172E+01

3.612    140.0    0.106722E+02  0.413206E+04  0.129664E+02  -0.124733E+04  0.659804E+00  0.703012E+01  0.348862E+01

4.153    145.0    0.106387E+02  0.418532E+04  0.130943E+02  -0.131242E+04  0.685934E+00  0.712528E+01  0.399822E+01

4.757    150.0    0.106067E+02  0.423842E+04  0.132203E+02  -0.137813E+04  0.711768E+00  0.722368E+01  0.456450E+01

5.430    155.0    0.105765E+02  0.429135E+04  0.133444E+02  -0.144446E+04  0.737311E+00  0.732539E+01  0.519103E+01

6.177    160.0    0.105486E+02  0.434413E+04  0.134667E+02  -0.151138E+04  0.762568E+00  0.743053E+01  0.588234E+01
```

```
  7.003      165.0     0.105234E+02  0.439677E+04  0.135871E+02  -0.157890E+04  0.787543E+00  0.753922E+01  0.664261E+01

  7.915      170.0     0.105013E+02  0.444928E+04  0.137059E+02  -0.164700E+04  0.812240E+00  0.765158E+01  0.747609E+01

  8.918      175.0     0.104826E+02  0.450167E+04  0.138231E+02  -0.171566E+04  0.836665E+00  0.776777E+01  0.838621E+01

 10.019      180.0     0.104680E+02  0.455396E+04  0.139387E+02  -0.178489E+04  0.860821E+00  0.788794E+01  0.937882E+01

 11.225      185.0     0.104579E+02  0.460617E+04  0.140527E+02  -0.185467E+04  0.884712E+00  0.801226E+01  0.104564E+02

 12.542      190.0     0.104528E+02  0.465832E+04  0.141654E+02  -0.192499E+04  0.908344E+00  0.814092E+01  0.116241E+02

 13.976      195.0     0.104532E+02  0.471043E+04  0.142767E+02  -0.199585E+04  0.931719E+00  0.827413E+01  0.128860E+02

 15.536      200.0     0.104599E+02  0.476253E+04  0.143867E+02  -0.206722E+04  0.954842E+00  0.841212E+01  0.142463E+02

 17.229      205.0     0.104733E+02  0.481464E+04  0.144956E+02  -0.213912E+04  0.977717E+00  0.855514E+01  0.157075E+02

 19.062      210.0     0.104943E+02  0.486679E+04  0.146033E+02  -0.221152E+04  0.100035E+01  0.870345E+01  0.172766E+02

 21.042      215.0     0.105236E+02  0.491902E+04  0.147100E+02  -0.228441E+04  0.102274E+01  0.885737E+01  0.189543E+02

 23.178      220.0     0.105619E+02  0.497136E+04  0.148157E+02  -0.235780E+04  0.104489E+01  0.901722E+01  0.207437E+02

 25.478      225.0     0.106102E+02  0.502385E+04  0.149206E+02  -0.243167E+04  0.106681E+01  0.918336E+01  0.226525E+02

 27.950      230.0     0.106696E+02  0.507654E+04  0.150248E+02  -0.250602E+04  0.108850E+01  0.935621E+01  0.246823E+02

 30.603      235.0     0.107411E+02  0.512946E+04  0.151282E+02  -0.258083E+04  0.110997E+01  0.953620E+01  0.268337E+02

 33.446      240.0     0.108261E+02  0.518267E+04  0.152312E+02  -0.265610E+04  0.113121E+01  0.972383E+01  0.291124E+02

 36.487      245.0     0.109260E+02  0.523622E+04  0.153336E+02  -0.273183E+04  0.115224E+01  0.991965E+01  0.315212E+02

 39.735      250.0     0.110426E+02  0.529017E+04  0.154358E+02  -0.280801E+04  0.117305E+01  0.101243E+02  0.340629E+02
```

```
  43.201     255.0    0.111777E+02  0.534459E+04  0.155377E+02  -0.288462E+04  0.119364E+01  0.103384E+02  0.367404E+02

  46.893     260.0    0.113338E+02  0.539955E+04  0.156395E+02  -0.296167E+04  0.121403E+01  0.105628E+02  0.395560E+02

  50.821     265.0    0.115134E+02  0.545513E+04  0.157414E+02  -0.303915E+04  0.123422E+01  0.107984E+02  0.425120E+02

  54.996     270.0    0.117198E+02  0.551143E+04  0.158435E+02  -0.311705E+04  0.125420E+01  0.110461E+02  0.456106E+02

  59.429     275.0    0.119568E+02  0.556853E+04  0.159460E+02  -0.319537E+04  0.127399E+01  0.113072E+02  0.488535E+02

  64.128     280.0    0.122292E+02  0.562655E+04  0.160490E+02  -0.327410E+04  0.129358E+01  0.115829E+02  0.522425E+02

  69.107     285.0    0.125424E+02  0.568563E+04  0.161528E+02  -0.335324E+04  0.131298E+01  0.118747E+02  0.557790E+02

  74.376     290.0    0.129037E+02  0.574590E+04  0.162576E+02  -0.343278E+04  0.133219E+01  0.121846E+02  0.594643E+02

  79.946     295.0    0.133218E+02  0.580753E+04  0.163637E+02  -0.351272E+04  0.135121E+01  0.125145E+02  0.632930E+02

  85.832     300.0    0.138078E+02  0.587072E+04  0.164713E+02  -0.359305E+04  0.137006E+01  0.128669E+02  0.672784E+02

  92.044     305.0    0.143762E+02  0.593570E+04  0.165808E+02  -0.367377E+04  0.138872E+01  0.132450E+02  0.714151E+02

  98.597     310.0    0.150459E+02  0.600274E+04  0.166926E+02  -0.375488E+04  0.140721E+01  0.136523E+02  0.757035E+02

 105.505     315.0    0.158422E+02  0.607216E+04  0.168072E+02  -0.383637E+04  0.142552E+01  0.140933E+02  0.801358E+02

 112.783     320.0    0.168000E+02  0.614437E+04  0.169253E+02  -0.391823E+04  0.144367E+01  0.145739E+02  0.847276E+02

 120.447     325.0    0.179682E+02  0.621988E+04  0.170475E+02  -0.400047E+04  0.146165E+01  0.151011E+02  0.894622E+02

 128.514     330.0    0.194182E+02  0.629931E+04  0.171748E+02  -0.408309E+04  0.147947E+01  0.156844E+02  0.943566E+02

 137.003     335.0    0.212584E+02  0.638350E+04  0.173084E+02  -0.416608E+04  0.149713E+01  0.163366E+02  0.994019E+02

 145.933     340.0    0.236608E+02  0.647357E+04  0.174501E+02  -0.424943E+04  0.151463E+01  0.170752E+02  0.104587E+03
```

```
155.328         345.0       0.269172E+02   0.657112E+04   0.176021E+02  -0.433316E+04   0.153198E+01   0.179257E+02   0.109931E+03

165.212         350.0       0.315627E+02   0.667847E+04   0.177681E+02  -0.441726E+04   0.154918E+01   0.189270E+02   0.115423E+03

175.614         355.0       0.386955E+02   0.679936E+04   0.179535E+02  -0.450173E+04   0.156624E+01   0.201430E+02   0.121049E+03

186.568         360.0       0.509656E+02   0.694032E+04   0.181683E+02  -0.458658E+04   0.158316E+01   0.216904E+02   0.126832E+03

198.118         365.0       0.767094E+02   0.711489E+04   0.184331E+02  -0.467182E+04   0.159995E+01   0.238211E+02   0.132744E+03

210.327         370.0       0.160720E+03   0.736104E+04   0.188056E+02  -0.475747E+04   0.161661E+01   0.272815E+02   0.138810E+03
```

TABLE I.11

```
                                                                                                    07/ 6/88
                                                                                                    page  1

              ------------------------------------------------------------------------------------
                                      1.00boehmite =  1.00diaspore
              ------------------------------------------------------------------------------------

         ----------------------------------------------------------------------------------------------
                    species properties in their standard state of 25 degrees c and 1 bar
         ----------------------------------------------------------------------------------------------

                                        .....minerals.....

                                                                                         maier-kelley power fun. coef.
  name            coef.   enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)      a        bx10**3       cx10**-5
  ----            -----   --------------   -------------   ----------------   ---------------    -----      -------       --------
diaspore          1.000      -238827.0          8.446          -220082.0          17.76000       14.430      4.2000          0.000
boehmite         -1.000      -237893.0          8.988          -219289.0          19.53500       12.905     20.7000         -3.005


                                          .....ions.....


                                          .....gases.....


                                          .....h2o.....


         ----------------------------------------------------------------------------------------------
                                 reaction properties at 25 degrees c and 1 bar
         ----------------------------------------------------------------------------------------------

   enthalpy (cal)      entropy (cal)      free energy (cal)   delta vol (cc/mol)    heat capacity         log k

  -0.934000E+03       -0.541800E+00       -0.793000E+03       -0.177500E+01        -0.140224E-01        0.581274E+00
```

```
          ----------------------------------------------------------------------------------
                                    1.00boehmite =  1.00diaspore
          ----------------------------------------------------------------------------------

pres  (bars)  temp (deg c)    delta cp     delta h(t,p)   delta s(t,p)   delta g(t,p)    log k(t,p)    delta v(t,p)
------------  ------------  ------------  ------------   ------------   ------------    ----------    ------------

   0.006           0.0      0.104559E+01  -0.946498E+03  -0.586407E+00  -0.806859E+03  0.645564E+00  -0.177500E+01

   0.009           5.0      0.819589E+00  -0.941839E+03  -0.569496E+00  -0.803971E+03  0.631690E+00  -0.177500E+01

   0.012          10.0      0.601127E+00  -0.938290E+03  -0.556845E+00  -0.801157E+03  0.618364E+00  -0.177500E+01

   0.017          15.0      0.389680E+00  -0.935816E+03  -0.548178E+00  -0.798397E+03  0.605540E+00  -0.177500E+01

   0.023          20.0      0.184776E+00  -0.934383E+03  -0.543240E+00  -0.795670E+03  0.593179E+00  -0.177500E+01

   0.032          25.0     -0.140224E-01  -0.933959E+03  -0.541800E+00  -0.792959E+03  0.581244E+00  -0.177500E+01

   0.042          30.0     -0.207114E+00  -0.934515E+03  -0.543642E+00  -0.790247E+03  0.569702E+00  -0.177500E+01

   0.056          35.0     -0.394865E+00  -0.936022E+03  -0.548569E+00  -0.787518E+03  0.558523E+00  -0.177500E+01

   0.074          40.0     -0.577616E+00  -0.938456E+03  -0.556398E+00  -0.784758E+03  0.547679E+00  -0.177500E+01

   0.096          45.0     -0.755677E+00  -0.941792E+03  -0.566960E+00  -0.781952E+03  0.537144E+00  -0.177500E+01

   0.123          50.0     -0.929337E+00  -0.946008E+03  -0.580100E+00  -0.779086E+03  0.526895E+00  -0.177500E+01

   0.158          55.0     -0.109886E+01  -0.951081E+03  -0.595672E+00  -0.776149E+03  0.516911E+00  -0.177500E+01

   0.199          60.0     -0.126450E+01  -0.956993E+03  -0.613543E+00  -0.773129E+03  0.507171E+00  -0.177500E+01

   0.250          65.0     -0.142647E+01  -0.963724E+03  -0.633588E+00  -0.770014E+03  0.497659E+00  -0.177500E+01

   0.312          70.0     -0.158500E+01  -0.971257E+03  -0.655691E+00  -0.766794E+03  0.488357E+00  -0.177500E+01
```

```
0.386     75.0   -0.174027E+01  -0.979574E+03  -0.679743E+00  -0.763460E+03   0.479250E+00  -0.177500E+01

0.474     80.0   -0.189248E+01  -0.988661E+03  -0.705645E+00  -0.760001E+03   0.470324E+00  -0.177500E+01

0.578     85.0   -0.204179E+01  -0.998503E+03  -0.733301E+00  -0.756408E+03   0.461566E+00  -0.177500E+01

0.701     90.0   -0.218835E+01  -0.100908E+04  -0.762626E+00  -0.752674E+03   0.452964E+00  -0.177500E+01

0.845     95.0   -0.233233E+01  -0.102039E+04  -0.793535E+00  -0.748791E+03   0.444507E+00  -0.177500E+01

1.013    100.0   -0.247385E+01  -0.103242E+04  -0.825953E+00  -0.744750E+03   0.436184E+00  -0.177500E+01

1.208    105.0   -0.261304E+01  -0.104514E+04  -0.859808E+00  -0.740544E+03   0.427986E+00  -0.177500E+01

1.432    110.0   -0.275003E+01  -0.105856E+04  -0.895032E+00  -0.736167E+03   0.419904E+00  -0.177500E+01

1.690    115.0   -0.288492E+01  -0.107266E+04  -0.931562E+00  -0.731612E+03   0.411931E+00  -0.177500E+01

1.985    120.0   -0.301783E+01  -0.108743E+04  -0.969338E+00  -0.726873E+03   0.404057E+00  -0.177500E+01

2.320    125.0   -0.314886E+01  -0.110286E+04  -0.100830E+01  -0.721944E+03   0.396277E+00  -0.177500E+01

2.700    130.0   -0.327808E+01  -0.111895E+04  -0.104841E+01  -0.716818E+03   0.388584E+00  -0.177500E+01

3.129    135.0   -0.340561E+01  -0.113567E+04  -0.108960E+01  -0.711492E+03   0.380972E+00  -0.177500E+01

3.612    140.0   -0.353150E+01  -0.115304E+04  -0.113183E+01  -0.705959E+03   0.373435E+00  -0.177500E+01

4.153    145.0   -0.365585E+01  -0.117103E+04  -0.117506E+01  -0.700215E+03   0.365967E+00  -0.177500E+01

4.757    150.0   -0.377873E+01  -0.118964E+04  -0.121925E+01  -0.694256E+03   0.358565E+00  -0.177500E+01

5.430    155.0   -0.390020E+01  -0.120887E+04  -0.126435E+01  -0.688076E+03   0.351223E+00  -0.177500E+01

6.177    160.0   -0.402032E+01  -0.122870E+04  -0.131033E+01  -0.681671E+03   0.343937E+00  -0.177500E+01
```

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  7.003      165.0    -0.413917E+01  -0.124914E+04  -0.135715E+01  -0.675038E+03   0.336704E+00  -0.177500E+01
  7.915      170.0    -0.425679E+01  -0.127017E+04  -0.140479E+01  -0.668172E+03   0.329519E+00  -0.177500E+01
  8.918      175.0    -0.437325E+01  -0.129178E+04  -0.145320E+01  -0.661070E+03   0.322379E+00  -0.177500E+01
 10.019      180.0    -0.448858E+01  -0.131399E+04  -0.150236E+01  -0.653728E+03   0.315281E+00  -0.177500E+01
 11.225      185.0    -0.460285E+01  -0.133677E+04  -0.155225E+01  -0.646143E+03   0.308222E+00  -0.177500E+01
 12.542      190.0    -0.471609E+01  -0.136012E+04  -0.160282E+01  -0.638311E+03   0.301199E+00  -0.177500E+01
 13.976      195.0    -0.482836E+01  -0.138404E+04  -0.165406E+01  -0.630230E+03   0.294210E+00  -0.177500E+01
 15.536      200.0    -0.493968E+01  -0.140853E+04  -0.170595E+01  -0.621897E+03   0.287251E+00  -0.177500E+01
 17.229      205.0    -0.505011E+01  -0.143358E+04  -0.175846E+01  -0.613308E+03   0.280322E+00  -0.177500E+01
 19.062      210.0    -0.515967E+01  -0.145918E+04  -0.181156E+01  -0.604461E+03   0.273419E+00  -0.177500E+01
 21.042      215.0    -0.526841E+01  -0.148533E+04  -0.186524E+01  -0.595353E+03   0.266541E+00  -0.177500E+01
 23.178      220.0    -0.537635E+01  -0.151204E+04  -0.191948E+01  -0.585982E+03   0.259686E+00  -0.177500E+01
 25.478      225.0    -0.548353E+01  -0.153928E+04  -0.197426E+01  -0.576345E+03   0.252851E+00  -0.177500E+01
 27.950      230.0    -0.558998E+01  -0.156707E+04  -0.202955E+01  -0.566441E+03   0.246037E+00  -0.177500E+01
 30.603      235.0    -0.569572E+01  -0.159540E+04  -0.208535E+01  -0.556266E+03   0.239240E+00  -0.177500E+01
 33.446      240.0    -0.580079E+01  -0.162426E+04  -0.214163E+01  -0.545820E+03   0.232460E+00  -0.177500E+01
 36.487      245.0    -0.590521E+01  -0.165366E+04  -0.219839E+01  -0.535099E+03   0.225695E+00  -0.177500E+01
 39.735      250.0    -0.600900E+01  -0.168358E+04  -0.225560E+01  -0.524102E+03   0.218944E+00  -0.177500E+01
```

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  43.201      255.0    -0.611219E+01   -0.171403E+04   -0.231325E+01   -0.512827E+03    0.212205E+00   -0.177500E+01

  46.893      260.0    -0.621480E+01   -0.174500E+04   -0.237132E+01   -0.501272E+03    0.205479E+00   -0.177500E+01

  50.821      265.0    -0.631686E+01   -0.177650E+04   -0.242981E+01   -0.489436E+03    0.198763E+00   -0.177500E+01

  54.996      270.0    -0.641837E+01   -0.180852E+04   -0.248870E+01   -0.477317E+03    0.192057E+00   -0.177500E+01

  59.429      275.0    -0.651937E+01   -0.184105E+04   -0.254797E+01   -0.464914E+03    0.185360E+00   -0.177500E+01

  64.128      280.0    -0.661987E+01   -0.187410E+04   -0.260763E+01   -0.452224E+03    0.178671E+00   -0.177500E+01

  69.107      285.0    -0.671989E+01   -0.190766E+04   -0.266765E+01   -0.439248E+03    0.171989E+00   -0.177500E+01

  74.376      290.0    -0.681944E+01   -0.194173E+04   -0.272802E+01   -0.425982E+03    0.165314E+00   -0.177500E+01

  79.946      295.0    -0.691854E+01   -0.197631E+04   -0.278874E+01   -0.412427E+03    0.158645E+00   -0.177500E+01

  85.832      300.0    -0.701721E+01   -0.201140E+04   -0.284979E+01   -0.398580E+03    0.151981E+00   -0.177500E+01

  92.044      305.0    -0.711547E+01   -0.204699E+04   -0.291117E+01   -0.384442E+03    0.145322E+00   -0.177500E+01

  98.597      310.0    -0.721332E+01   -0.208310E+04   -0.297286E+01   -0.370010E+03    0.138668E+00   -0.177500E+01

 105.505      315.0    -0.731078E+01   -0.211970E+04   -0.303486E+01   -0.355284E+03    0.132017E+00   -0.177500E+01

 112.783      320.0    -0.740786E+01   -0.215680E+04   -0.309716E+01   -0.340262E+03    0.125370E+00   -0.177500E+01

 120.447      325.0    -0.750458E+01   -0.219441E+04   -0.315975E+01   -0.324945E+03    0.118725E+00   -0.177500E+01

 128.514      330.0    -0.760095E+01   -0.223252E+04   -0.322262E+01   -0.309332E+03    0.112084E+00   -0.177500E+01

 137.003      335.0    -0.769698E+01   -0.227112E+04   -0.328577E+01   -0.293421E+03    0.105444E+00   -0.177500E+01

 145.933      340.0    -0.779267E+01   -0.231022E+04   -0.334918E+01   -0.277213E+03    0.988073E-01   -0.177500E+01
```

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155.328      345.0    -0.788805E+01  -0.234983E+04  -0.341286E+01  -0.260706E+03   0.921723E-01  -0.177500E+01

165.212      350.0    -0.798312E+01  -0.238992E+04  -0.347679E+01  -0.243902E+03   0.855391E-01  -0.177500E+01

175.614      355.0    -0.807789E+01  -0.243052E+04  -0.354096E+01  -0.226799E+03   0.789078E-01  -0.177500E+01

186.568      360.0    -0.817237E+01  -0.247161E+04  -0.360538E+01  -0.209398E+03   0.722783E-01  -0.177500E+01

198.118      365.0    -0.826657E+01  -0.251319E+04  -0.367004E+01  -0.191699E+03   0.656509E-01  -0.177500E+01

210.327      370.0    -0.836050E+01  -0.255528E+04  -0.373492E+01  -0.173705E+03   0.590259E-01  -0.177500E+01
```

TABLE I.12

```
                                                                                07/ 6/88
                                                                                page  1

      ------------------------------------------------------------------------
                  1.00gibbsite + 1.00oh- =  1.00alo2- + 2.00h2o
      ------------------------------------------------------------------------

   --------------------------------------------------------------------------------
           species properties in their standard state of 25 degrees c and 1 bar
   --------------------------------------------------------------------------------

                               .....minerals.....

                                                                                    maier-kelley power fun. coef.
  name         coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)     a        bx10**3       cx10**-5
  ----         -----    --------------   -------------   ----------------   ---------------   -----      -------       --------
 gibbsite     -1.000      -309065.0         16.358          -276025.0          31.95600        8.650     45.6000          0.000


                                 .....ions.....

  name         coef.    enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----         -----    --------------   -------------   -----------------   ---------------
 oh-          -1.000      -54977.0           -2.6            -37595.0           -4.1799
 alo2-         1.000     -220928.0           -3.8           -198506.0            6.0190

  name           a1            a2            a3            a4            c1            c2          wprtr
  ----           --            --            --            --            --            --          -----
 oh-         0.12527E+00   0.73800E+01   0.18423E+01  -0.27821E+05   0.41500E+01  -0.10346E+06   0.17246E+06
 alo2-       0.31586E+00   0.30566E+03  -0.21559E+01  -0.29053E+05   0.13331E+02  -0.60750E+05   0.16866E+06

                                 .....gases.....


                                  .....h2o.....

  name         coef.    enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----         -----    --------------   -------------   -----------------   ---------------
 water         2.000      -68315.3          16.7            -56686.4            18.0684


   --------------------------------------------------------------------------------
                        reaction properties at 25 degrees c and 1 bar
   --------------------------------------------------------------------------------

   enthalpy (cal)    entropy (cal)     free energy (cal)   delta vol (cc/mol)   heat capacity        log k

   0.648329E+04      0.158165E+02      0.174124E+04        0.143797E+02         0.319904E+02     -0.127634E+01
```

```
          ------------------------------------------------------------------------------------------------
                                    1.00gibbsite + 1.00oh- =  1.00alo2- + 2.00h2o
          ------------------------------------------------------------------------------------------------

pres (bars)   temp (deg c)   delta cp       delta h(t,p)   delta s(t,p)   delta g(t,p)   log k(t,p)     delta v(t,p)   fugacity
-----------   ------------   ------------   ------------   ------------   ------------   ----------     ------------   --------

   0.006          0.0        0.457825E+02   0.554771E+04   0.125318E+02   0.209859E+04   -0.167907E+01  0.127986E+02   0.610990E-02

   0.009          5.0        0.413324E+02   0.576489E+04   0.133198E+02   0.203386E+04   -0.159803E+01  0.132063E+02   0.872790E-02

   0.012         10.0        0.380606E+02   0.596298E+04   0.140258E+02   0.196541E+04   -0.151698E+01  0.135547E+02   0.122784E-01

   0.017         15.0        0.355625E+02   0.614678E+04   0.146693E+02   0.189359E+04   -0.143618E+01  0.138600E+02   0.170582E-01

   0.023         20.0        0.335896E+02   0.631948E+04   0.152635E+02   0.181868E+04   -0.135584E+01  0.141335E+02   0.233701E-01

   0.032         25.0        0.319854E+02   0.648329E+04   0.158176E+02   0.174091E+04   -0.127610E+01  0.143830E+02   0.316655E-01

   0.042         30.0        0.306490E+02   0.663978E+04   0.163381E+02   0.166045E+04   -0.119705E+01  0.146144E+02   0.423811E-01

   0.056         35.0        0.295136E+02   0.679011E+04   0.168300E+02   0.157746E+04   -0.111877E+01  0.148320E+02   0.561643E-01

   0.074         40.0        0.285337E+02   0.693517E+04   0.172970E+02   0.149208E+04   -0.104132E+01  0.150392E+02   0.736189E-01

   0.096         45.0        0.276776E+02   0.707566E+04   0.177421E+02   0.140443E+04   -0.964740E+00  0.152384E+02   0.956318E-01

   0.123         50.0        0.269224E+02   0.721212E+04   0.181676E+02   0.131460E+04   -0.889060E+00  0.154319E+02   0.123004E+00

   0.158         55.0        0.262507E+02   0.734502E+04   0.185757E+02   0.122269E+04   -0.814301E+00  0.156212E+02   0.156721E+00

   0.199         60.0        0.256495E+02   0.747475E+04   0.189680E+02   0.112878E+04   -0.740476E+00  0.158077E+02   0.198193E+00

   0.250         65.0        0.251082E+02   0.760163E+04   0.193460E+02   0.103295E+04   -0.667591E+00  0.159925E+02   0.248524E+00

   0.312         70.0        0.246181E+02   0.772593E+04   0.197108E+02   0.935263E+03   -0.595652E+00  0.161765E+02   0.309531E+00
```

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0.386     75.0   0.241723E+02  0.784789E+04  0.200636E+02   0.835792E+03  -0.524656E+00   0.163605E+02  0.382523E+00

0.474     80.0   0.237649E+02  0.796773E+04  0.204053E+02   0.734591E+03  -0.454599E+00   0.165453E+02  0.469240E+00

0.578     85.0   0.233907E+02  0.808561E+04  0.207366E+02   0.631714E+03  -0.385477E+00   0.167313E+02  0.571573E+00

0.701     90.0   0.230458E+02  0.820170E+04  0.210584E+02   0.527213E+03  -0.317280E+00   0.169192E+02  0.692524E+00

0.845     95.0   0.227265E+02  0.831613E+04  0.213712E+02   0.421135E+03  -0.250000E+00   0.171093E+02  0.833606E+00

1.013    100.0   0.224299E+02  0.842903E+04  0.216756E+02   0.313525E+03  -0.183625E+00   0.173022E+02  0.997909E+00

1.208    105.0   0.221537E+02  0.854049E+04  0.219721E+02   0.204424E+03  -0.118144E+00   0.174981E+02  0.118756E+01

1.432    110.0   0.218959E+02  0.865062E+04  0.222612E+02   0.938730E+02  -0.535445E-01   0.176976E+02  0.140532E+01

1.690    115.0   0.216550E+02  0.875950E+04  0.225433E+02  -0.180904E+02   0.101857E-01   0.179009E+02  0.165472E+01

1.985    120.0   0.214297E+02  0.886722E+04  0.228187E+02  -0.131430E+03   0.730600E-01   0.181085E+02  0.193866E+01

2.320    125.0   0.212192E+02  0.897385E+04  0.230878E+02  -0.246112E+03   0.135092E+00   0.183206E+02  0.226018E+01

2.700    130.0   0.210230E+02  0.907945E+04  0.233510E+02  -0.362103E+03   0.196295E+00   0.185376E+02  0.262365E+01

3.129    135.0   0.208406E+02  0.918411E+04  0.236085E+02  -0.479372E+03   0.256682E+00   0.187598E+02  0.303172E+01

3.612    140.0   0.206721E+02  0.928789E+04  0.238607E+02  -0.597889E+03   0.316268E+00   0.189877E+02  0.348862E+01

4.153    145.0   0.205175E+02  0.939085E+04  0.241079E+02  -0.717624E+03   0.375066E+00   0.192215E+02  0.399822E+01

4.757    150.0   0.203763E+02  0.949358E+04  0.243501E+02  -0.838001E+03   0.432806E+00   0.194618E+02  0.456450E+01

5.430    155.0   0.202457E+02  0.959484E+04  0.245873E+02  -0.960087E+03   0.490069E+00   0.197086E+02  0.519103E+01

6.177    160.0   0.201245E+02  0.969516E+04  0.248194E+02  -0.108331E+04   0.546585E+00   0.199624E+02  0.588234E+01
```

```
  7.003     165.0    0.200120E+02  0.979454E+04  0.250466E+02 -0.120765E+04  0.602367E+00  0.202236E+02  0.664261E+01

  7.915     170.0    0.199080E+02  0.989298E+04  0.252691E+02 -0.133308E+04  0.657428E+00  0.204925E+02  0.747609E+01

  8.918     175.0    0.198122E+02  0.999049E+04  0.254869E+02 -0.145958E+04  0.711781E+00  0.207697E+02  0.838621E+01

 10.019     180.0    0.197248E+02  0.100871E+05  0.257002E+02 -0.158712E+04  0.765440E+00  0.210557E+02  0.937882E+01

 11.225     185.0    0.196462E+02  0.101829E+05  0.259093E+02 -0.171569E+04  0.818418E+00  0.213510E+02  0.104564E+02

 12.542     190.0    0.195770E+02  0.102779E+05  0.261144E+02 -0.184527E+04  0.870727E+00  0.216563E+02  0.116241E+02

 13.976     195.0    0.195182E+02  0.103722E+05  0.263156E+02 -0.197584E+04  0.922380E+00  0.219723E+02  0.128860E+02

 15.536     200.0    0.194785E+02  0.104675E+05  0.265167E+02 -0.210727E+04  0.973337E+00  0.222944E+02  0.142463E+02

 17.229     205.0    0.194610E+02  0.105645E+05  0.267186E+02 -0.223951E+04  0.102360E+01  0.226217E+02  0.157075E+02

 19.062     210.0    0.194596E+02  0.106613E+05  0.269180E+02 -0.237266E+04  0.107324E+01  0.229597E+02  0.172766E+02

 21.042     215.0    0.194749E+02  0.107580E+05  0.271149E+02 -0.250671E+04  0.112226E+01  0.233091E+02  0.189543E+02

 23.178     220.0    0.195076E+02  0.108548E+05  0.273097E+02 -0.264163E+04  0.117067E+01  0.236703E+02  0.207437E+02

 25.478     225.0    0.195582E+02  0.109516E+05  0.275024E+02 -0.277741E+04  0.121849E+01  0.240440E+02  0.226525E+02

 27.950     230.0    0.196276E+02  0.110486E+05  0.276933E+02 -0.291402E+04  0.126572E+01  0.244308E+02  0.246823E+02

 30.603     235.0    0.197163E+02  0.111458E+05  0.278824E+02 -0.305146E+04  0.131238E+01  0.248313E+02  0.268337E+02

 33.446     240.0    0.198251E+02  0.112433E+05  0.280700E+02 -0.318970E+04  0.135846E+01  0.252464E+02  0.291124E

 36.487     245.0    0.199545E+02  0.113412E+05  0.282562E+02 -0.332873E+04  0.140399E+01  0.256766E+02  0.3

 39.735     250.0    0.201049E+02  0.114395E+05  0.284411E+02 -0.346852E+04  0.144897E+01  0.261227E+0
```

```
  43.201      255.0     0.202764E+02  0.115382E+05  0.286249E+02 -0.360906E+04   0.149341E+01  0.265855E+02  0.367404E+02

  46.893      260.0     0.204687E+02  0.116376E+05  0.288076E+02 -0.375033E+04   0.153732E+01  0.270657E+02  0.395560E+02

  50.821      265.0     0.206809E+02  0.117376E+05  0.289895E+02 -0.389232E+04   0.158069E+01  0.275641E+02  0.425120E+02

  54.996      270.0     0.209108E+02  0.118382E+05  0.291704E+02 -0.403500E+04   0.162355E+01  0.280811E+02  0.456106E+02

  59.429      275.0     0.211546E+02  0.119395E+05  0.293506E+02 -0.417836E+04   0.166590E+01  0.286172E+02  0.488535E+02

  64.128      280.0     0.214057E+02  0.120414E+05  0.295298E+02 -0.432238E+04   0.170774E+01  0.291727E+02  0.522425E+02

  69.107      285.0     0.216531E+02  0.121440E+05  0.297082E+02 -0.446702E+04   0.174908E+01  0.297473E+02  0.557790E+02

  74.376      290.0     0.218792E+02  0.122471E+05  0.298853E+02 -0.461228E+04   0.178992E+01  0.303400E+02  0.594643E+02

  79.946      295.0     0.220550E+02  0.123505E+05  0.300608E+02 -0.475813E+04   0.183027E+01  0.309488E+02  0.632930E+02

  85.832      300.0     0.221338E+02  0.124537E+05  0.302341E+02 -0.490453E+04   0.187013E+01  0.315700E+02  0.672784E+02

  92.044      305.0     0.220392E+02  0.125563E+05  0.304040E+02 -0.505145E+04   0.190949E+01  0.321971E+02  0.714151E+02

  98.597      310.0     0.216441E+02  0.126571E+05  0.305689E+02 -0.519885E+04   0.194836E+01  0.328189E+02  0.757035E+02

 105.505      315.0     0.207335E+02  0.127547E+05  0.307261E+02 -0.534668E+04   0.198673E+01  0.334170E+02  0.801358E+02

 112.783      320.0     0.189340E+02  0.128463E+05  0.308713E+02 -0.549488E+04   0.202459E+01  0.339603E+02  0.847276E+02

 120.447      325.0     0.155747E+02  0.129276E+05  0.309974E+02 -0.564336E+04   0.206191E+01  0.343958E+02  0.894622E+02

 128.514      330.0     0.940049E+01  0.129914E+05  0.310925E+02 -0.579200E+04   0.209868E+01  0.346312E+02  0.943566E+02

 [illegible]  335.0    -0.206282E+01  0.130248E+05  0.311362E+02 -0.594064E+04   0.213484E+01  0.344993E+02  0.994019E+02
```

```
155.328       345.0    -0.684524E+02   0.128844E+05   0.308842E+02  -0.623675E+04   0.220499E+01   0.315471E+02   0.109931E+03

165.212       350.0    -0.166124E+03   0.125685E+05   0.303642E+02  -0.638316E+04   0.223865E+01   0.266900E+02   0.115423E+03

175.614       355.0     0.590991E+03   0.180897E+05   0.393668E+02  -0.666887E+04   0.232023E+01   0.938320E+02   0.121049E+03

186.568       360.0     0.122862E+04   0.203325E+05   0.428768E+02  -0.684527E+04   0.236280E+01   0.126411E+03   0.126832E+03

198.118       365.0     0.355775E+04   0.250522E+05   0.502290E+02  -0.703177E+04   0.240816E+01   0.201293E+03   0.132744E+03

210.327       370.0     0.225994E+05   0.408838E+05   0.747779E+02  -0.724003E+04   0.246020E+01   0.481290E+03   0.138810E+03
```

TABLE I.13

```
                                                                                                       07/ 6/ι
                                                                                                       page  1

              ----------------------------------------------------------------------------------
                                 1.00bayerite + 1.00oh- =  1.00alo2- + 2.00h2o
              ----------------------------------------------------------------------------------

          ---------------------------------------------------------------------------------------------
                     species properties in their standard state of 25 degrees c and 1 bar
          ---------------------------------------------------------------------------------------------

                                           .....minerals.....

                                                                                             maier-kelley power fun. coef.
  name             coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a        bx10**3       cx10**-5
  ----             -----    --------------   -------------   ----------------   ---------------   -----     -------       --------
bayerite          -1.000      -307829.0         18.972          -275570.0         31.95600        8.650     45.6000          0.000


                                             .....ions.....

  name             coef.    enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----             -----    --------------   -------------   -----------------   ---------------
oh-               -1.000       -54977.0          -2.6            -37595.0            -4.1799
alo2-              1.000      -220928.0          -3.8           -198506.0             6.0190

  name              a1           a2           a3            a4          c1            c2           wprtr
  ----              --           --           --            --          --            --           -----
oh-            0.12527E+00  0.73800E+01  0.18423E+01  -0.27821E+05  0.41500E+01  -0.10346E+06  0.17246E+06
alo2-          0.31586E+00  0.30566E+03 -0.21559E+01  -0.29053E+05  0.13331E+02  -0.60750E+05  0.16866E+06

                                             .....gases.....


                                              .....h2o.....

  name             coef.    enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----             -----    --------------   -------------   -----------------   ---------------
water              2.000       -68315.3          16.7            -56686.4            18.0684


          ---------------------------------------------------------------------------------------------
                                  reaction properties at 25 degrees c and 1 bar
          ---------------------------------------------------------------------------------------------

          enthalpy (cal)     entropy (cal)      free energy (cal)   delta vol (cc/mol)   heat capacity        log k

          0.524729E+04        0.132025E+02       0.128624E+04        0.143797E+02        0.319904E+02      -0.942823E+00
```

```
          ---------------------------------------------------------------------------------------
                              1.00bayerite + 1.00oh- =  1.00alo2- + 2.00h2o
          ---------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp      delta h(t,p)  delta s(t,p)  delta g(t,p)   log k(t,p)    delta v(t,p)  fugacity
-----------  ------------  ------------  ------------  ------------  ------------   ----------    ------------  --------

   0.006          0.0      0.457825E+02  0.431171E+04  0.991780E+01  0.157824E+04  -0.126274E+01  0.127986E+02  0.610990E-02

   0.009          5.0      0.413324E+02  0.452889E+04  0.107058E+02  0.152658E+04  -0.119945E+01  0.132063E+02  0.872790E-02

   0.012         10.0      0.380606E+02  0.472698E+04  0.114118E+02  0.147120E+04  -0.113553E+01  0.135547E+02  0.122784E-01

   0.017         15.0      0.355625E+02  0.491078E+04  0.120553E+02  0.141245E+04  -0.107127E+01  0.138600E+02  0.170562E-01

   0.023         20.0      0.335896E+02  0.508348E+04  0.126495E+02  0.135061E+04  -0.100689E+01  0.141335E+02  0.233701E-01

   0.032         25.0      0.319854E+02  0.524729E+04  0.132036E+02  0.128591E+04  -0.942579E+00  0.143830E+02  0.316655E-01

   0.042         30.0      0.306490E+02  0.540378E+04  0.137241E+02  0.121852E+04  -0.878452E+00  0.146144E+02  0.423811E-01

   0.056         35.0      0.295136E+02  0.555411E+04  0.142160E+02  0.114860E+04  -0.814613E+00  0.148320E+02  0.561643E-01

   0.074         40.0      0.285337E+02  0.569917E+04  0.146830E+02  0.107629E+04  -0.751141E+00  0.150392E+02  0.736189E-01

   0.096         45.0      0.276776E+02  0.583966E+04  0.151281E+02  0.100171E+04  -0.688100E+00  0.152384E+02  0.956318E-01

   0.123         50.0      0.269224E+02  0.597612E+04  0.155536E+02  0.924947E+03  -0.625540E+00  0.154319E+02  0.123004E+00

   0.158         55.0      0.262507E+02  0.610902E+04  0.159617E+02  0.846105E+03  -0.563501E+00  0.156212E+02  0.156721E+00

   0.199         60.0      0.256495E+02  0.623875E+04  0.163540E+02  0.765266E+03  -0.502013E+00  0.158077E+02  0.198193E+00

   0.250         65.0      0.251082E+02  0.636563E+04  0.167320E+02  0.682506E+03  -0.441103E+00  0.159925E+02  0.248524E+00

   0.312         70.0      0.246181E+02  0.648993E+04  0.170968E+02  0.597893E+03  -0.380787E+00  0.161765E+02  0.309531E+00
```

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0.386     75.0    0.241723E+02  0.661189E+04  0.174496E+02   0.511492E+03  -0.321081E+00   0.163605E+02   0.382523E+00
0.474     80.0    0.237649E+02  0.673173E+04  0.177913E+02   0.423361E+03  -0.261996E+00   0.165453E+02   0.469240E+00
0.578     85.0    0.233907E+02  0.684961E+04  0.181226E+02   0.333554E+03  -0.203537E+00   0.167313E+02   0.571573E+00
0.701     90.0    0.230458E+02  0.696570E+04  0.184444E+02   0.242123E+03  -0.145711E+00   0.169192E+02   0.692524E+00
0.845     95.0    0.227265E+02  0.708013E+04  0.187572E+02   0.149115E+03  -0.885195E-01   0.171093E+02   0.833606E+00
1.013    100.0    0.224299E+02  0.719303E+04  0.190616E+02   0.545746E+02  -0.319631E-01   0.173022E+02   0.997909E+00
1.208    105.0    0.221537E+02  0.730449E+04  0.193581E+02  -0.414561E+02   0.239589E-01   0.174981E+02   0.118756E+01
1.432    110.0    0.218959E+02  0.741462E+04  0.196472E+02  -0.138937E+03   0.792486E-01   0.176976E+02   0.140532E+01
1.690    115.0    0.216550E+02  0.752350E+04  0.199293E+02  -0.237830E+03   0.133909E+00   0.179009E+02   0.165472E+01
1.985    120.0    0.214297E+02  0.763122E+04  0.202047E+02  -0.338100E+03   0.187945E+00   0.181085E+02   0.193866E+01
2.320    125.0    0.212192E+02  0.773785E+04  0.204738E+02  -0.439712E+03   0.241360E+00   0.183206E+02   0.226018E+01
2.700    130.0    0.210230E+02  0.784345E+04  0.207370E+02  -0.542633E+03   0.294159E+00   0.185376E+02   0.262365E+01
3.129    135.0    0.208406E+02  0.794811E+04  0.209945E+02  -0.646832E+03   0.346349E+00   0.187598E+02   0.303172E+01
3.612    140.0    0.206721E+02  0.805189E+04  0.212467E+02  -0.752279E+03   0.397937E+00   0.189877E+02   0.348862E+01
4.153    145.0    0.205175E+02  0.815485E+04  0.214939E+02  -0.858944E+03   0.448927E+00   0.192215E+02   0.399822E+01
4.757    150.0    0.203763E+02  0.825758E+04  0.217361E+02  -0.966251E+03   0.499043E+00   0.194618E+02   0.456450E+01
5.430    155.0    0.202457E+02  0.835884E+04  0.219733E+02  -0.107527E+04   0.548862E+00   0.197086E+02   0.519103E+01
6.177    160.0    0.201245E+02  0.845916E+04  0.222054E+02  -0.118542E+04   0.598105E+00   0.199624E+02   0.588234E+01
```

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  7.003        165.0     0.200120E+02  0.855854E+04  0.224326E+02  -0.129669E+04  0.646779E+00  0.202236E+02  0.664261E+01

  7.915        170.0     0.199080E+02  0.865698E+04  0.226551E+02  -0.140905E+04  0.694894E+00  0.204925E+02  0.747609E+01

  8.918        175.0     0.198122E+02  0.875449E+04  0.228729E+02  -0.152248E+04  0.742455E+00  0.207697E+02  0.838621E+01

 10.019        180.0     0.197248E+02  0.885112E+04  0.230862E+02  -0.163695E+04  0.789472E+00  0.210557E+02  0.937882E+01

 11.225        185.0     0.196462E+02  0.894691E+04  0.232953E+02  -0.175245E+04  0.835953E+00  0.213510E+02  0.104564E+02

 12.542        190.0     0.195770E+02  0.904190E+04  0.235004E+02  -0.186896E+04  0.881905E+00  0.216563E+02  0.116241E+02

 13.976        195.0     0.195182E+02  0.913616E+04  0.237016E+02  -0.198646E+04  0.927338E+00  0.219723E+02  0.128860E+02

 15.536        200.0     0.194785E+02  0.923153E+04  0.239027E+02  -0.210482E+04  0.972206E+00  0.222944E+02  0.142463E+02

 17.229        205.0     0.194610E+02  0.932848E+04  0.241046E+02  -0.222399E+04  0.101651E+01  0.226217E+02  0.157075E+02

 19.062        210.0     0.194596E+02  0.942530E+04  0.243040E+02  -0.234407E+04  0.106031E+01  0.229597E+02  0.172766E+02

 21.042        215.0     0.194749E+02  0.952205E+04  0.245009E+02  -0.246505E+04  0.110361E+01  0.233091E+02  0.189543E+02

 23.178        220.0     0.195076E+02  0.961881E+04  0.246957E+02  -0.258690E+04  0.114642E+01  0.236703E+02  0.207437E+02

 25.478        225.0     0.195582E+02  0.971564E+04  0.248884E+02  -0.270961E+04  0.118875E+01  0.240440E+02  0.226525E+02

 27.950        230.0     0.196276E+02  0.981263E+04  0.250793E+02  -0.283315E+04  0.123060E+01  0.244308E+02  0.246823E+02

 30.603        235.0     0.197163E+02  0.990983E+04  0.252684E+02  -0.295752E+04  0.127198E+01  0.248313E+02  0.268337E+02

 33.446        240.0     0.198251E+02  0.100073E+05  0.254560E+02  -0.308269E+04  0.131289E+01  0.252464E+02  0.291124E+02

 36.487        245.0     0.199545E+02  0.101052E+05  0.256422E+02  -0.320865E+04  0.135335E+01  0.256766E+02  0.315212E+02

 39.735        250.0     0.201049E+02  0.102035E+05  0.258271E+02  -0.333537E+04  0.139335E+01  0.261227E+02  0.340629E+02
```

```
  43.201     255.0    0.202764E+02  0.103022E+05  0.260109E+02  -0.346284E+04  0.143291E+01  0.265855E+02  0.367404E+02

  46.893     260.0    0.204687E+02  0.104016E+05  0.261936E+02  -0.359104E+04  0.147202E+01  0.270657E+02  0.395560E+02

  50.821     265.0    0.206809E+02  0.105015E+05  0.263755E+02  -0.371996E+04  0.151070E+01  0.275641E+02  0.425120E+02

  54.996     270.0    0.209108E+02  0.106022E+05  0.265564E+02  -0.384957E+04  0.154894E+01  0.280811E+02  0.456106E+02

  59.429     275.0    0.211546E+02  0.107035E+05  0.267366E+02  -0.397986E+04  0.158676E+01  0.286172E+02  0.488535E+02

  64.128     280.0    0.214057E+02  0.108054E+05  0.269158E+02  -0.411081E+04  0.162415E+01  0.291727E+02  0.522425E+02

  69.107     285.0    0.216531E+02  0.109080E+05  0.270942E+02  -0.424238E+04  0.166112E+01  0.297473E+02  0.557790E+02

  74.376     290.0    0.218792E+02  0.110111E+05  0.272713E+02  -0.437457E+04  0.169767E+01  0.303400E+02  0.594643E+02

  79.946     295.0    0.220550E+02  0.111145E+05  0.274468E+02  -0.450735E+04  0.173381E+01  0.309488E+02  0.632930E+02

  85.832     300.0    0.221338E+02  0.112177E+05  0.276201E+02  -0.464068E+04  0.176952E+01  0.315700E+02  0.672784E+02

  92.044     305.0    0.220392E+02  0.113203E+05  0.277900E+02  -0.477453E+04  0.180482E+01  0.321971E+02  0.714151E+02

  98.597     310.0    0.216441E+02  0.114211E+05  0.279549E+02  -0.490886E+04  0.183968E+01  0.328189E+02  0.757035E+02

 105.505     315.0    0.207335E+02  0.115187E+05  0.281121E+02  -0.504362E+04  0.187412E+01  0.334170E+02  0.801358E+02

 112.783     320.0    0.189340E+02  0.116103E+05  0.282573E+02  -0.517875E+04  0.190811E+01  0.339603E+02  0.847276E+02

 120.447     325.0    0.155747E+02  0.116916E+05  0.283834E+02  -0.531416E+04  0.194163E+01  0.343958E+02  0.894622E+02

 128.514     330.0    0.940049E+01  0.117554E+05  0.284785E+02  -0.544973E+04  0.197466E+01  0.346312E+02  0.943566E+02

 137.003     335.0   -0.206282E+01  0.117888E+05  0.285222E+02  -0.558530E+04  0.200714E+01  0.344993E+02  0.994019E+02

 145.933     340.0   -0.240268E+02  0.117684E+05  0.284768E+02  -0.572061E+04  0.203901E+01  0.336838E+02  0.104587E+03
```

```
155.328      345.0   -0.684524E+02  0.116484E+05  0.282702E+02 -0.585527E+04  0.207012E+01  0.315471E+02  0.109931E+03

165.212      350.0   -0.166124E+03  0.113325E+05  0.277502E+02 -0.598861E+04  0.210028E+01  0.266900E+02  0.115423E+03

175.614      355.0    0.590991E+03  0.168537E+05  0.367528E+02 -0.626125E+04  0.217841E+01  0.938320E+02  0.121049E+03

186.568      360.0    0.122862E+04  0.190965E+05  0.402628E+02 -0.642458E+04  0.221759E+01  0.126411E+03  0.126832E+03

198.118      365.0    0.355775E+04  0.238162E+05  0.476150E+02 -0.659801E+04  0.225961E+01  0.201293E+03  0.132744E+03

210.327      370.0    0.225994E+05  0.396478E+05  0.721639E+02 -0.679320E+04  0.230837E+01  0.481290E+03  0.138810E+03
```

TABLE I.14

```
                                                                                   07/ 6/88
                                                                                   page  1

        -------------------------------------------------------------------------
                   1.00boehmite + 1.00oh- =  1.00alo2- + 1.00h2o
        -------------------------------------------------------------------------

     ------------------------------------------------------------------------------
            species properties in their standard state of 25 degrees c and 1 bar
     ------------------------------------------------------------------------------

                                    .....minerals.....

                                                                                       maier-kelley power fun. coef.
   name           coef.   enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)     a       bx10**3       cx10**-5
   ----           -----   --------------   -------------   ----------------   ---------------   -----    -------      --------
 boehmite        -1.000      -237893.0         8.988          -219289.0          19.53500       12.905   20.7000        -3.005


                                     .....ions.....

   name           coef.   enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
   ----           -----   --------------   -------------   -----------------   ---------------
 oh-             -1.000       -54977.0          -2.6           -37595.0           -4.1799
 alo2-            1.000      -220928.0          -3.8          -198506.0            6.0190

   name             a1            a2            a3            a4            c1            c2          wprtr
   ----             --            --            --            --            --            --          -----
 oh-            0.12527E+00   0.73800E+01   0.18423E+01  -0.27821E+05   0.41500E+01  -0.10346E+06   0.17246E+06
 alo2-          0.31586E+00   0.30566E+03  -0.21559E+01  -0.29053E+05   0.13331E+02  -0.60750E+05   0.16866E+06

                                     .....gases.....


                                      .....h2o.....

   name           coef.   enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
   ----           -----   --------------   -------------   -----------------   ---------------
 water            1.000       -68315.3          16.7           -56688.4           18.0684

     ------------------------------------------------------------------------------
                      reaction properties at 25 degrees c and 1 bar
     ------------------------------------------------------------------------------

     enthalpy (cal)     entropy (cal)      free energy (cal)   delta vol (cc/mol)    heat capacity          log k

     0.362663E+04        0.647424E+01       0.169161E+04        0.873235E+01         0.205268E+02       -0.123996E+01
```

```
          ------------------------------------------------------------------------------------
                                1.00boehmite + 1.00oh- =  1.00alo2- + 1.00h2o
          ------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp      delta h(t,p)   delta s(t,p)   delta g(t,p)    log k(t,p)    delta v(t,p)   fugacity
-----------  ------------  ------------  ------------   ------------   ------------    ----------    ------------   --------

   0.006         0.0       0.341459E+02  0.297873E+04   0.419689E+01   0.182777E+04  -0.146239E+01   0.720027E+01   0.610990E-02

   0.009         5.0       0.298003E+02  0.313803E+04   0.477492E+01   0.180527E+04  -0.141843E+01   0.761095E+01   0.872790E-02

   0.012        10.0       0.265688E+02  0.327857E+04   0.527581E+01   0.178009E+04  -0.137394E+01   0.795485E+01   0.122784E-01

   0.017        15.0       0.240838E+02  0.340495E+04   0.571829E+01   0.175256E+04  -0.132922E+01   0.824936E+01   0.170562E-01

   0.023        20.0       0.221167E+02  0.352027E+04   0.611511E+01   0.172293E+04  -0.128446E+01   0.850650E+01   0.233701E-01

   0.032        25.0       0.205207E+02  0.362673E+04   0.647524E+01   0.169141E+04  -0.123981E+01   0.873485E+01   0.316655E-01

   0.042        30.0       0.191984E+02  0.372593E+04   0.680522E+01   0.165817E+04  -0.119540E+01   0.894070E+01   0.423811E-01

   0.056        35.0       0.180838E+02  0.381906E+04   0.710993E+01   0.162335E+04  -0.115131E+01   0.912877E+01   0.561643E-01

   0.074        40.0       0.171307E+02  0.390703E+04   0.739315E+01   0.158705E+04  -0.110760E+01   0.930266E+01   0.736189E-01

   0.096        45.0       0.163059E+02  0.399058E+04   0.765782E+01   0.154939E+04  -0.106432E+01   0.946520E+01   0.956318E-01

   0.123        50.0       0.155851E+02  0.407026E+04   0.790634E+01   0.151045E+04  -0.102152E+01   0.961862E+01   0.123004E+00

   0.158        55.0       0.149500E+02  0.414657E+04   0.814065E+01   0.147031E+04  -0.979218E+00   0.976469E+01   0.156721E+00

   0.199        60.0       0.143863E+02  0.421988E+04   0.836237E+01   0.142903E+04  -0.937440E+00   0.990488E+01   0.198193E+00

   0.250        65.0       0.138829E+02  0.429054E+04   0.857283E+01   0.138667E+04  -0.896202E+00   0.100404E+02   0.248524E+00

   0.312        70.0       0.134309E+02  0.435880E+04   0.877320E+01   0.134328E+04  -0.855513E+00   0.101722E+02   0.309531E+00
```

```
0.386      75.0    0.130228E+02  0.442492E+04  0.896445E+01  0.129893E+04  -0.815381E+00  0.103012E+02  0.382523E+00

0.474      80.0    0.126529E+02  0.448910E+04  0.914742E+01  0.125363E+04  -0.775809E+00  0.104281E+02  0.469240E+00

0.578      85.0    0.123160E+02  0.455151E+04  0.932285E+01  0.120745E+04  -0.736797E+00  0.105535E+02  0.571573E+00

0.701      90.0    0.120082E+02  0.461232E+04  0.949136E+01  0.116042E+04  -0.698346E+00  0.106779E+02  0.692524E+00

0.845      95.0    0.117259E+02  0.467165E+04  0.965353E+01  0.111256E+04  -0.660452E+00  0.108018E+02  0.833606E+00

1.013     100.0    0.114664E+02  0.472963E+04  0.980984E+01  0.106391E+04  -0.623111E+00  0.109258E+02  0.997909E+00

1.208     105.0    0.112272E+02  0.478636E+04  0.996074E+01  0.101451E+04  -0.586318E+00  0.110500E+02  0.118756E+01

1.432     110.0    0.110064E+02  0.484194E+04  0.101066E+02  0.964365E+03  -0.550067E+00  0.111750E+02  0.140532E+01

1.690     115.0    0.108025E+02  0.489647E+04  0.102478E+02  0.913517E+03  -0.514351E+00  0.113010E+02  0.165472E+01

1.985     120.0    0.106142E+02  0.495001E+04  0.103847E+02  0.861984E+03  -0.479164E+00  0.114284E+02  0.193866E+01

2.320     125.0    0.104404E+02  0.500265E+04  0.105175E+02  0.809790E+03  -0.444496E+00  0.115574E+02  0.226018E+01

2.700     130.0    0.102804E+02  0.505446E+04  0.106466E+02  0.756954E+03  -0.410342E+00  0.116884E+02  0.262365E+01

3.129     135.0    0.101337E+02  0.510550E+04  0.107721E+02  0.703497E+03  -0.376691E+00  0.118217E+02  0.303172E+01

3.612     140.0    0.999992E+01  0.515583E+04  0.108943E+02  0.649438E+03  -0.343536E+00  0.119575E+02  0.348862E+01

4.153     145.0    0.987886E+01  0.520553E+04  0.110135E+02  0.594793E+03  -0.310868E+00  0.120962E+02  0.399822E+01

4.757     150.0    0.976962E+01  0.525516E+04  0.111298E+02  0.540129E+03  -0.278963E+00  0.122381E+02  0.456450E+01

5.430     155.0    0.966912E+01  0.530349E+04  0.112429E+02  0.484368E+03  -0.247242E+00  0.123832E+02  0.519103E+01

6.177     160.0    0.957582E+01  0.535103E+04  0.113527E+02  0.428070E+03  -0.215983E+00  0.125319E+02  0.588234E+01
```

```
 7.003    165.0    0.948862E+01  0.539777E+04  0.114595E+02  0.371248E+03  -0.185176E+00  0.126843E+02  0.664261E+01

 7.915    170.0    0.940671E+01  0.544370E+04  0.115631E+02  0.313916E+03  -0.154812E+00  0.128409E+02  0.747609E+01

 8.918    175.0    0.932954E+01  0.548883E+04  0.116638E+02  0.256086E+03  -0.124883E+00  0.130019E+02  0.838621E+01

10.019    180.0    0.925678E+01  0.553317E+04  0.117616E+02  0.197769E+03  -0.953805E-01  0.131678E+02  0.937882E+01

11.225    185.0    0.918832E+01  0.557674E+04  0.118566E+02  0.138977E+03  -0.662946E-01  0.133388E+02  0.104564E+02

12.542    190.0    0.912426E+01  0.561958E+04  0.119490E+02  0.797193E+02  -0.376170E-01  0.135154E+02  0.116241E+02

13.976    195.0    0.906496E+01  0.566173E+04  0.120389E+02  0.200052E+02  -0.933901E-02  0.136981E+02  0.128860E+02

15.536    200.0    0.901859E+01  0.570500E+04  0.121300E+02 -0.400418E+02   0.184951E-01  0.138823E+02  0.142463E+02

17.229    205.0    0.898769E+01  0.574984E+04  0.122230E+02 -0.100389E+03   0.458844E-01  0.140665E+02  0.157075E+02

19.062    210.0    0.896533E+01  0.579451E+04  0.123147E+02 -0.161143E+03   0.728908E-01  0.142563E+02  0.172766E+02

21.042    215.0    0.895138E+01  0.583903E+04  0.124049E+02 -0.222293E+03   0.995210E-01  0.144517E+02  0.189543E+02

23.178    220.0    0.894568E+01  0.588345E+04  0.124940E+02 -0.283827E+03   0.125782E+00  0.146531E+02  0.207437E+02

25.478    225.0    0.894800E+01  0.592779E+04  0.125818E+02 -0.345735E+03   0.151679E+00  0.148606E+02  0.226525E+02

27.950    230.0    0.895800E+01  0.597209E+04  0.126685E+02 -0.408006E+03   0.177220E+00  0.150746E+02  0.246823E+02

30.603    235.0    0.897523E+01  0.601637E+04  0.127542E+02 -0.470630E+03   0.202409E+00  0.152951E+02  0.268337E+02

33.446    240.0    0.899902E+01  0.606065E+04  0.128388E+02 -0.533596E+03   0.227254E+00  0.155225E+02  0.291124E+02

36.487    245.0    0.902848E+01  0.610496E+04  0.129226E+02 -0.596893E+03   0.251758E+00  0.157569E+02  0.315212E+02

39.735    250.0    0.906229E+01  0.614929E+04  0.130053E+02 -0.660509E+03   0.275928E+00  0.159984E+02  0.340629E+02
```

```
   43.201     255.0     0.909865E+01  0.619365E+04  0.130872E+02 -0.724435E+03  0.299768E+00  0.162471E+02  0.367404E+02

   46.893     260.0     0.913496E+01  0.623804E+04  0.131681E+02 -0.788658E+03  0.323283E+00  0.165029E+02  0.395560E+02

   50.821     265.0     0.916752E+01  0.628242E+04  0.132481E+02 -0.853167E+03  0.346476E+00  0.167657E+02  0.425120E+02

   54.996     270.0     0.919102E+01  0.632674E+04  0.133269E+02 -0.917948E+03  0.369352E+00  0.170349E+02  0.456106E+02

   59.429     275.0     0.919777E+01  0.637093E+04  0.134046E+02 -0.982988E+03  0.391914E+00  0.173100E+02  0.488535E+02

   64.128     280.0     0.917653E+01  0.641487E+04  0.134808E+02 -0.104827E+04  0.414165E+00  0.175898E+02  0.522425E+02

   69.107     285.0     0.911069E+01  0.645838E+04  0.135553E+02 -0.111378E+04  0.436106E+00  0.178725E+02  0.557790E+02

   74.376     290.0     0.897544E+01  0.650120E+04  0.136276E+02 -0.117950E+04  0.457738E+00  0.181554E+02  0.594643E+02

   79.946     295.0     0.873319E+01  0.654293E+04  0.136971E+02 -0.124541E+04  0.479062E+00  0.184344E+02  0.632930E+02

   85.832     300.0     0.832602E+01  0.658301E+04  0.137628E+02 -0.131148E+04  0.500075E+00  0.187031E+02  0.672784E+02

   92.044     305.0     0.766300E+01  0.662059E+04  0.138232E+02 -0.137768E+04  0.520776E+00  0.189521E+02  0.714151E+02

   98.597     310.0     0.659823E+01  0.665441E+04  0.138763E+02 -0.144397E+04  0.541155E+00  0.191666E+02  0.757035E+02

  105.505     315.0     0.489134E+01  0.668252E+04  0.139189E+02 -0.151032E+04  0.561207E+00  0.193236E+02  0.801358E+02

  112.783     320.0     0.213401E+01  0.670191E+04  0.139460E+02 -0.157665E+04  0.580916E+00  0.193864E+02  0.847276E+02

  120.447     325.0    -0.239349E+01  0.670776E+04  0.139499E+02 -0.164289E+04  0.600261E+00  0.192948E+02  0.894622E+02

  128.514     330.0    -0.100177E+02  0.669211E+04  0.139178E+02 -0.170891E+04  0.619208E+00  0.189468E+02  0.943568E+02

  137.003     335.0    -0.233212E+02  0.664134E+04  0.138277E+02 -0.177456E+04  0.637710E+00  0.181627E+02  0.994019E+02

  145.933     340.0    -0.476876E+02  0.653083E+04  0.136408E+02 -0.183959E+04  0.655687E+00  0.166086E+02  0.104587E+03
```

```
155.328     345.0   -0.953695E+02  0.631333E+04  0.132821E+02 -0.190359E+04  0.673012E+00  0.136214E+02  0.109931E+03

165.212     350.0   -0.197686E+03  0.589002E+04  0.125961E+02 -0.196590E+04  0.689466E+00  0.776293E+01  0.115423E+03

175.614     355.0    0.552295E+03  0.112903E+05  0.214133E+02 -0.216713E+04  0.753989E+00  0.736889E+02  0.121049E+03

186.568     360.0    0.117765E+04  0.133922E+05  0.247084E+02 -0.225869E+04  0.779639E+00  0.104720E+03  0.126832E+03

198.118     365.0    0.348104E+04  0.179373E+05  0.317959E+02 -0.235995E+04  0.808207E+00  0.177471E+03  0.132744E+03

210.327     370.0    0.224387E+05  0.335228E+05  0.559722E+02 -0.248256E+04  0.843587E+00  0.454008E+03  0.138810E+03
```

TABLE I.15

```
          -----------------------------------------------------------------------------
                    1.00diaspore + 1.00oh- =  1.00alo2- + 1.00h2o
          -----------------------------------------------------------------------------

     -------------------------------------------------------------------------------------
                species properties in their standard state of 25 degrees c and 1 bar
     -------------------------------------------------------------------------------------

                                        .....minerals.....

                                                                                               maier-kelley power fun. coef.
  name            coef.    enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a        bx10**3      cx10**-5
  ----            -----    --------------   -------------   ----------------   ---------------  -----      -------      --------
 diaspore        -1.000       -238827.0         8.446           -220082.0         17.76000     14.430      4.2000        0.000


                                          .....ions.....

  name            coef.    enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----            -----    --------------   -------------   -----------------   ---------------
 oh-             -1.000       -54977.0          -2.6            -37595.0            -4.1799
 alo2-            1.000      -220928.0          -3.8           -198506.0             6.0190

  name             a1             a2            a3            a4           c1            c2           wprtr
  ----             --             --            --            --           --            --           -----
 oh-          0.12527E+00   0.73800E+01   0.18423E+01  -0.27821E+05   0.41500E+01  -0.10346E+06   0.17246E+06
 alo2-        0.31586E+00   0.30566E+03  -0.21559E+01  -0.29053E+05   0.13331E+02  -0.60750E+05   0.16866E+06

                                          .....gases.....


                                           .....h2o.....

  name            coef.    enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----            -----    --------------   -------------   -----------------   ---------------
 water            1.000       -68315.3          16.7            -56686.4            18.0684


     -------------------------------------------------------------------------------------
                           reaction properties at 25 degrees c and 1 bar
     -------------------------------------------------------------------------------------


     enthalpy (cal)     entropy (cal)      free energy (cal)  delta vol (cc/mol)   heat capacity        log k

     0.456063E+04       0.701604E+01       0.248461E+04        0.105073E+02        0.205409E+02      -0.182124E+01
```

```
        ---------------------------------------------------------------------------------------
                           1.00diaspore + 1.00oh- =  1.00alo2- + 1.00h2o
        ---------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp     delta h(t,p)  delta s(t,p)  delta g(t,p)   log k(t,p)   delta v(t,p)  fugacity
-----------  ------------  ------------  ------------  ------------  ------------  -----------  ------------  --------

   0.006         0.0       0.331003E+02  0.392523E+04  0.478329E+01  0.263463E+04  -0.210795E+01  0.897527E+01  0.610990E-02

   0.009         5.0       0.289807E+02  0.407987E+04  0.534441E+01  0.260925E+04  -0.205012E+01  0.938595E+01  0.872790E-02

   0.012        10.0       0.259677E+02  0.421686E+04  0.583265E+01  0.258125E+04  -0.199231E+01  0.972985E+01  0.122784E-01

   0.017        15.0       0.236941E+02  0.434077E+04  0.626647E+01  0.255095E+04  -0.193476E+01  0.100244E+02  0.170562E-01

   0.023        20.0       0.219319E+02  0.445465E+04  0.665835E+01  0.251860E+04  -0.187764E+01  0.102815E+02  0.233701E-01

   0.032        25.0       0.205347E+02  0.456069E+04  0.701704E+01  0.248437E+04  -0.182106E+01  0.105098E+02  0.316655E-01

   0.042        30.0       0.194055E+02  0.466044E+04  0.734886E+01  0.244842E+04  -0.176510E+01  0.107157E+02  0.423811E-01

   0.056        35.0       0.184787E+02  0.475508E+04  0.765850E+01  0.241086E+04  -0.170983E+01  0.109038E+02  0.561643E-01

   0.074        40.0       0.177083E+02  0.484549E+04  0.794954E+01  0.237181E+04  -0.165528E+01  0.110777E+02  0.736189E-01

   0.096        45.0       0.170616E+02  0.493237E+04  0.822478E+01  0.233135E+04  -0.160147E+01  0.112402E+02  0.956318E-01

   0.123        50.0       0.165145E+02  0.501627E+04  0.848644E+01  0.228954E+04  -0.154841E+01  0.113936E+02  0.123004E+00

   0.158        55.0       0.160489E+02  0.509765E+04  0.873633E+01  0.224646E+04  -0.149613E+01  0.115397E+02  0.156721E+00

   0.199        60.0       0.156508E+02  0.517688E+04  0.897591E+01  0.220216E+04  -0.144461E+01  0.116799E+02  0.198193E+00

   0.250        65.0       0.153094E+02  0.525426E+04  0.920642E+01  0.215668E+04  -0.139386E+01  0.118154E+02  0.248524E+00

   0.312        70.0       0.150159E+02  0.533006E+04  0.942889E+01  0.211008E+04  -0.134387E+01  0.119472E+02  0.309531E+00
```

```
0.386       75.0     0.147631E+02  0.540450E+04  0.964419E+01  0.206239E+04  -0.129463E+01  0.120762E+02  0.382523E+00

0.474       80.0     0.145453E+02  0.547776E+04  0.985307E+01  0.201364E+04  -0.124613E+01  0.122031E+02  0.469240E+00

0.578       85.0     0.143578E+02  0.555001E+04  0.100561E+02  0.196386E+04  -0.119836E+01  0.123285E+02  0.571573E+00

0.701       90.0     0.141965E+02  0.562140E+04  0.102540E+02  0.191309E+04  -0.115131E+01  0.124529E+02  0.692524E+00

0.845       95.0     0.140582E+02  0.569204E+04  0.104471E+02  0.186135E+04  -0.110496E+01  0.125768E+02  0.833606E+00

1.013      100.0     0.139402E+02  0.576204E+04  0.106358E+02  0.180866E+04  -0.105929E+01  0.127008E+02  0.997909E+00

1.208      105.0     0.138402E+02  0.583150E+04  0.108205E+02  0.175505E+04  -0.101430E+01  0.128250E+02  0.118756E+01

1.432      110.0     0.137565E+02  0.590050E+04  0.110016E+02  0.170053E+04  -0.969971E+00  0.129500E+02  0.140532E+01

1.690      115.0     0.136874E+02  0.596913E+04  0.111794E+02  0.164513E+04  -0.926282E+00  0.130760E+02  0.165472E+01

1.985      120.0     0.136320E+02  0.603744E+04  0.113540E+02  0.158886E+04  -0.883221E+00  0.132034E+02  0.193866E+01

2.320      125.0     0.135892E+02  0.610552E+04  0.115258E+02  0.153173E+04  -0.840774E+00  0.133324E+02  0.226018E+01

2.700      130.0     0.135685E+02  0.617341E+04  0.116950E+02  0.147377E+04  -0.798926E+00  0.134634E+02  0.262365E+01

3.129      135.0     0.135393E+02  0.624117E+04  0.118617E+02  0.141499E+04  -0.757663E+00  0.135967E+02  0.303172E+01

3.612      140.0     0.135314E+02  0.630887E+04  0.120262E+02  0.135540E+04  -0.716971E+00  0.137325E+02  0.348862E+01

4.153      145.0     0.135347E+02  0.637656E+04  0.121886E+02  0.129501E+04  -0.676836E+00  0.138712E+02  0.399822E+01

4.757      150.0     0.135483E+02  0.644481E+04  0.123490E+02  0.123438E+04  -0.637528E+00  0.140131E+02  0.456450E+01

5.430      155.0     0.135693E+02  0.651236E+04  0.125072E+02  0.117244E+04  -0.598465E+00  0.141582E+02  0.519103E+01

6.177      160.0     0.135961E+02  0.657974E+04  0.126631E+02  0.110974E+04  -0.559920E+00  0.143069E+02  0.588234E+01
```

```
  7.003     165.0   0.136278E+02  0.664691E+04  0.128166E+02  0.104629E+04 -0.521879E+00  0.144593E+02  0.664261E+01

  7.915     170.0   0.136635E+02  0.671387E+04  0.129679E+02  0.982088E+03 -0.484331E+00  0.146159E+02  0.747609E+01

  8.918     175.0   0.137028E+02  0.678061E+04  0.131170E+02  0.917155E+03 -0.447262E+00  0.147769E+02  0.838621E+01

 10.019     180.0   0.137454E+02  0.684715E+04  0.132639E+02  0.851497E+03 -0.410661E+00  0.149428E+02  0.937882E+01

 11.225     185.0   0.137912E+02  0.691351E+04  0.134088E+02  0.785120E+03 -0.374517E+00  0.151138E+02  0.104564E+02

 12.542     190.0   0.138404E+02  0.697970E+04  0.135518E+02  0.718031E+03 -0.338816E+00  0.152904E+02  0.116241E+02

 13.976     195.0   0.138933E+02  0.704578E+04  0.136929E+02  0.650235E+03 -0.303549E+00  0.154731E+02  0.128860E+02

 15.536     200.0   0.139583E+02  0.711353E+04  0.138359E+02  0.581855E+03 -0.268756E+00  0.156573E+02  0.142463E+02

 17.229     205.0   0.140378E+02  0.718342E+04  0.139815E+02  0.512919E+03 -0.234437E+00  0.158415E+02  0.157075E+02

 19.062     210.0   0.141250E+02  0.725368E+04  0.141262E+02  0.443317E+03 -0.200528E+00  0.160313E+02  0.172766E+02

 21.042     215.0   0.142198E+02  0.732436E+04  0.142702E+02  0.373060E+03 -0.167020E+00  0.162267E+02  0.189543E+02

 23.178     220.0   0.143220E+02  0.739548E+04  0.144134E+02  0.302155E+03 -0.133904E+00  0.164281E+02  0.207437E+02

 25.478     225.0   0.144315E+02  0.746707E+04  0.145560E+02  0.230610E+03 -0.101172E+00  0.166356E+02  0.226525E+02

 27.950     230.0   0.145480E+02  0.753916E+04  0.146981E+02  0.158434E+03 -0.688169E-01  0.168496E+02  0.246823E+02

 30.603     235.0   0.146710E+02  0.761177E+04  0.148395E+02  0.856362E+02 -0.368305E-01  0.170701E+02  0.268337E+02

 33.446     240.0   0.147998E+02  0.768492E+04  0.149805E+02  0.122239E+02 -0.520604E-02  0.172975E+02  0.291124E+02

 36.487     245.0   0.149337E+02  0.775861E+04  0.151209E+02 -0.617937E+02  0.260634E-01  0.175319E+02  0.315212E+02

 39.735     250.0   0.150713E+02  0.783287E+04  0.152609E+02 -0.136407E+03  0.569842E-01  0.177734E+02  0.340629E+02
```

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  43.201      255.0     0.152108E+02  0.790768E+04  0.154004E+02  -0.211608E+03   0.875625E-01  0.180221E+02  0.367404E+02

  46.893      260.0     0.153498E+02  0.798304E+04  0.155394E+02  -0.287386E+03   0.117804E+00  0.182779E+02  0.395560E+02

  50.821      265.0     0.154844E+02  0.805892E+04  0.156779E+02  -0.363730E+03   0.147713E+00  0.185407E+02  0.425120E+02

  54.996      270.0     0.156094E+02  0.813526E+04  0.158156E+02  -0.440630E+03   0.177295E+00  0.188099E+02  0.456106E+02

  59.429      275.0     0.157171E+02  0.821198E+04  0.159526E+02  -0.518074E+03   0.206555E+00  0.190850E+02  0.488535E+02

  64.128      280.0     0.157964E+02  0.828897E+04  0.160884E+02  -0.596046E+03   0.235494E+00  0.193648E+02  0.522425E+02

  69.107      285.0     0.158306E+02  0.836604E+04  0.162230E+02  -0.674534E+03   0.264117E+00  0.196475E+02  0.557790E+02

  74.376      290.0     0.157949E+02  0.844293E+04  0.163557E+02  -0.753519E+03   0.292424E+00  0.199304E+02  0.594643E+02

  79.946      295.0     0.156517E+02  0.851924E+04  0.164859E+02  -0.832981E+03   0.320416E+00  0.202094E+02  0.632930E+02

  85.832      300.0     0.153432E+02  0.859441E+04  0.166126E+02  -0.912897E+03   0.348094E+00  0.204781E+02  0.672784E+02

  92.044      305.0     0.147785E+02  0.866759E+04  0.167344E+02  -0.993236E+03   0.375452E+00  0.207271E+02  0.714151E+02

  98.597      310.0     0.138115E+02  0.873750E+04  0.168492E+02  -0.107396E+04   0.402487E+00  0.209416E+02  0.757035E+02

 105.505      315.0     0.122021E+02  0.880221E+04  0.169538E+02  -0.115503E+04   0.429190E+00  0.210986E+02  0.801358E+02

 112.783      320.0     0.954188E+01  0.885871E+04  0.170432E+02  -0.123639E+04   0.455546E+00  0.211614E+02  0.847276E+02

 120.447      325.0     0.511109E+01  0.890217E+04  0.171097E+02  -0.131794E+04   0.481535E+00  0.210698E+02  0.894622E+02

 128.514      330.0    -0.241677E+01  0.892463E+04  0.171404E+02  -0.139958E+04   0.507125E+00  0.207218E+02  0.943566E+02

 137.003      335.0    -0.156242E+02  0.891246E+04  0.171135E+02  -0.148114E+04   0.532265E+00  0.199377E+02  0.994019E+02

 145.933      340.0    -0.398950E+02  0.884106E+04  0.169899E+02  -0.156237E+04   0.556879E+00  0.183836E+02  0.104587E+03
```

```
155.328      345.0    -0.874815E+02  0.866315E+04  0.166949E+02 -0.164289E+04  0.580839E+00  0.153964E+02  0.109931E+03

165.212      350.0    -0.189703E+03  0.827994E+04  0.160729E+02 -0.172200E+04  0.603926E+00  0.953793E+01  0.115423E+03

175.614      355.0     0.560373E+03  0.137208E+05  0.249543E+02 -0.194034E+04  0.675081E+00  0.754639E+02  0.121049E+03

186.568      360.0     0.118582E+04  0.158638E+05  0.283138E+02 -0.204930E+04  0.707360E+00  0.106495E+03  0.126832E+03

198.118      365.0     0.348931E+04  0.204505E+05  0.354659E+02 -0.216825E+04  0.742556E+00  0.179246E+03  0.132744E+03

210.327      370.0     0.224470E+05  0.360780E+05  0.597072E+02 -0.230885E+04  0.784561E+00  0.455783E+03  0.138810E+03
```

TABLE I.16

```
          ---------------------------------------------------------------------------------
                      0.50corundum + 1.00oh- =  1.00alo2- + 0.50h2o
          ---------------------------------------------------------------------------------

     -------------------------------------------------------------------------------------------
                      species properties in their standard state of 25 degrees c and 1 bar
     -------------------------------------------------------------------------------------------

                                        .....minerals.....

                                                                                                 maier-kelley power fun. coef.
  name              coef.   enthalpy (cal)   entropy (cal)   free energy(cal)   volume (cc/mol)    a        bx10**3      cx10**-5
  ----              -----   --------------   -------------   ----------------   ---------------  -----      -------      --------
  corundum         -0.500     -400511.0         12.180          -378185.0          25.57500      27.490     2.8200        -8.380


                                          .....ions.....

  name              coef.   enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----              -----   --------------   -------------   -----------------   ---------------
  oh-              -1.000      -54977.0          -2.6            -37595.0            -4.1812
  alo2-             1.000     -220928.0          -3.8           -198506.0             6.0178

  name               a1            a2            a3            a4           c1            c2           wprtr
  ----               --            --            --            --           --            --           -----
  oh-           0.12527E+00   0.73800E+01   0.18423E+01  -0.27821E+05  0.41500E+01  -0.10346E+06  0.17246E+06
  alo2-         0.31586E+00   0.30566E+03  -0.21559E+01  -0.29053E+05  0.13331E+02  -0.60750E+05  0.16866E+06

                                          .....gases.....


                                          .....h2o.....

  name              coef.   enthalpy (cal)   entropy (cal)   free energy (cal)   volume (cc/mol)
  ----              -----   --------------   -------------   -----------------   ---------------
  water             0.500      -68315.7          16.7            -56686.8            18.0692


     -------------------------------------------------------------------------------------------
                              reaction properties at 25 degrees c and 1 bar
     -------------------------------------------------------------------------------------------


     enthalpy (cal)     entropy (cal)     free energy (cal)   delta vol (cc/mol)   heat capacity        log k

     0.146614E+03       0.101618E+01      -0.161914E+03       0.644607E+01         0.177654E+02     0.118684E+00
```

```
          ------------------------------------------------------------------------------------------------------
                                    0.50corundum + 1.00oh- =  1.00alo2- + 0.50h2o
          ------------------------------------------------------------------------------------------------------

pres (bars)  temp (deg c)   delta cp      delta h(t,p)   delta s(t,p)   delta g(t,p)    log k(t,p)    delta v(t,p)   fugacity
-----------  ------------  ------------   ------------   ------------   ------------    ----------    ------------   --------

   0.006         0.0       0.310578E+02  -0.428562E+03  -0.100714E+01  -0.158943E+03   0.127170E+00   0.493812E+01   0.610990E-02

   0.009         5.0       0.268140E+02  -0.284432E+03  -0.484135E+00  -0.155265E+03   0.121994E+00   0.535030E+01   0.872790E-02

   0.012        10.0       0.236511E+02  -0.158635E+03  -0.358081E-01  -0.154007E+03   0.118868E+00   0.569193E+01   0.122784E-01

   0.017        15.0       0.212205E+02  -0.467099E+02   0.356089E+00  -0.154842E+03   0.117439E+00   0.598101E+01   0.170562E-01

   0.023        20.0       0.193035E+02   0.544187E+02   0.704081E+00  -0.157523E+03   0.117434E+00   0.622999E+01   0.233701E-01

   0.032        25.0       0.177580E+02   0.146939E+03   0.101706E+01  -0.161852E+03   0.118639E+00   0.644775E+01   0.316655E-01

   0.042        30.0       0.164887E+02   0.232454E+03   0.130152E+01  -0.167672E+03   0.120878E+00   0.664084E+01   0.423811E-01

   0.056        35.0       0.154298E+02   0.312173E+03   0.156236E+01  -0.174853E+03   0.124009E+00   0.681414E+01   0.561643E-01

   0.074        40.0       0.145348E+02   0.387022E+03   0.180332E+01  -0.183287E+03   0.127915E+00   0.697142E+01   0.736189E-01

   0.096        45.0       0.137700E+02   0.457735E+03   0.202735E+01  -0.192881E+03   0.132496E+00   0.711559E+01   0.956318E-01

   0.123        50.0       0.131103E+02   0.524895E+03   0.223681E+01  -0.203557E+03   0.137666E+00   0.724898E+01   0.123004E+00

   0.158        55.0       0.125368E+02   0.588980E+03   0.243360E+01  -0.215247E+03   0.143353E+00   0.737344E+01   0.156721E+00

   0.199        60.0       0.120349E+02   0.650382E+03   0.261929E+01  -0.227891E+03   0.149496E+00   0.749048E+01   0.198193E+00

   0.250        65.0       0.115931E+02   0.709429E+03   0.279519E+01  -0.241437E+03   0.156040E+00   0.760135E+01   0.248524E+00

   0.312        70.0       0.112022E+02   0.766398E+03   0.296240E+01  -0.255838E+03   0.162938E+00   0.770709E+01   0.309531E+00
```

```
0.386     75.0   0.108550E+02  0.821526E+03  0.312186E+01  -0.271052E+03  0.170149E+00  0.780855E+01  0.382523E+00

0.474     80.0   0.105453E+02  0.875014E+03  0.327436E+01  -0.287044E+03  0.177636E+00  0.790649E+01  0.469240E+00

0.578     85.0   0.102684E+02  0.927039E+03  0.342059E+01  -0.303779E+03  0.185368E+00  0.800154E+01  0.571573E+00

0.701     90.0   0.100201E+02  0.977753E+03  0.356115E+01  -0.321226E+03  0.193316E+00  0.809425E+01  0.692524E+00

0.845     95.0   0.979701E+01  0.102729E+04  0.369656E+01  -0.339359E+03  0.201455E+00  0.818511E+01  0.833606E+00

1.013    100.0   0.959641E+01  0.107577E+04  0.382728E+01  -0.358153E+03  0.209762E+00  0.827455E+01  0.997909E+00

1.208    105.0   0.941593E+01  0.112330E+04  0.395371E+01  -0.377583E+03  0.218218E+00  0.836295E+01  0.118756E+01

1.432    110.0   0.925366E+01  0.116998E+04  0.407621E+01  -0.397629E+03  0.226804E+00  0.845067E+01  0.140532E+01

1.690    115.0   0.910799E+01  0.121589E+04  0.419512E+01  -0.418271E+03  0.235505E+00  0.853803E+01  0.165472E+01

1.985    120.0   0.897763E+01  0.126111E+04  0.431073E+01  -0.439491E+03  0.244306E+00  0.862533E+01  0.193866E+01

2.320    125.0   0.886152E+01  0.130571E+04  0.442329E+01  -0.461273E+03  0.253194E+00  0.871285E+01  0.226018E+01

2.700    130.0   0.875882E+01  0.134977E+04  0.453307E+01  -0.483600E+03  0.262158E+00  0.880088E+01  0.262365E+01

3.129    135.0   0.866889E+01  0.139335E+04  0.464028E+01  -0.506458E+03  0.271186E+00  0.888967E+01  0.303172E+01

3.612    140.0   0.859125E+01  0.143651E+04  0.474514E+01  -0.529835E+03  0.280269E+00  0.897949E+01  0.348862E+01

4.153    145.0   0.852558E+01  0.147932E+04  0.484784E+01  -0.553716E+03  0.289399E+00  0.907060E+01  0.399822E+01

4.757    150.0   0.847081E+01  0.152234E+04  0.494850E+01  -0.577541E+03  0.298285E+00  0.916327E+01  0.456450E+01

5.430    155.0   0.842370E+01  0.156433E+04  0.504679E+01  -0.602393E+03  0.307487E+00  0.925753E+01  0.519103E+01

6.177    160.0   0.838252E+01  0.160580E+04  0.514270E+01  -0.627717E+03  0.316715E+00  0.935362E+01  0.588234E+01
```

7.003	165.0	0.834597E+01	0.164673E+04	0.523625E+01	-0.653504E+03	0.325963E+00	0.945174E+01	0.664261E+01
7.915	170.0	0.831305E+01	0.168710E+04	0.532747E+01	-0.679745E+03	0.335226E+00	0.955213E+01	0.747609E+01
8.918	175.0	0.828298E+01	0.172693E+04	0.541641E+01	-0.706432E+03	0.344501E+00	0.965506E+01	0.838621E+01
10.019	180.0	0.825520E+01	0.176620E+04	0.550314E+01	-0.733558E+03	0.353782E+00	0.976079E+01	0.937882E+01
11.225	185.0	0.822936E+01	0.180494E+04	0.558776E+01	-0.761116E+03	0.363066E+00	0.986963E+01	0.104564E+02
12.542	190.0	0.820531E+01	0.184317E+04	0.567037E+01	-0.789101E+03	0.372352E+00	0.998193E+01	0.116241E+02
13.976	195.0	0.818312E+01	0.188092E+04	0.575108E+01	-0.817506E+03	0.381636E+00	0.100981E+02	0.128860E+02
15.536	200.0	0.817068E+01	0.191998E+04	0.583350E+01	-0.846213E+03	0.390862E+00	0.102132E+02	0.142463E+02
17.229	205.0	0.817020E+01	0.196078E+04	0.591842E+01	-0.875193E+03	0.400021E+00	0.103260E+02	0.157075E+02
19.062	210.0	0.817440E+01	0.200158E+04	0.600235E+01	-0.904555E+03	0.409162E+00	0.104416E+02	0.172766E+02
21.042	215.0	0.818281E+01	0.204239E+04	0.608536E+01	-0.934292E+03	0.418285E+00	0.105600E+02	0.189543E+02
23.178	220.0	0.819483E+01	0.208322E+04	0.616748E+01	-0.964397E+03	0.427385E+00	0.106815E+02	0.207437E+02
25.478	225.0	0.820979E+01	0.212409E+04	0.624874E+01	-0.994862E+03	0.436461E+00	0.108059E+02	0.226525E+02
27.950	230.0	0.822684E+01	0.216501E+04	0.632919E+01	-0.102568E+04	0.445510E+00	0.109335E+02	0.246823E+02
30.603	235.0	0.824496E+01	0.220597E+04	0.640882E+01	-0.105684E+04	0.454528E+00	0.110640E+02	0.268337E+02
33.446	240.0	0.826285E+01	0.224698E+04	0.648764E+01	-0.108834E+04	0.463515E+00	0.111976E+02	0.291124E+02
36.487	245.0	0.827885E+01	0.228802E+04	0.656565E+01	-0.112017E+04	0.472468E+00	0.113341E+02	0.315212E+02
39.735	250.0	0.829084E+01	0.232908E+04	0.664281E+01	-0.115232E+04	0.481383E+00	0.114733E+02	0.340629E+02

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 43.201   255.0    0.829601E+01  0.237012E+04  0.671906E+01  -0.118479E+04  0.490259E+00  0.116149E+02  0.367404E+02
 46.893   260.0    0.829063E+01  0.241109E+04  0.679433E+01  -0.121755E+04  0.499093E+00  0.117585E+02  0.395560E+02
 50.821   265.0    0.826964E+01  0.245193E+04  0.686850E+01  -0.125062E+04  0.507882E+00  0.119035E+02  0.425120E+02
 54.996   270.0    0.822615E+01  0.249255E+04  0.694142E+01  -0.128396E+04  0.516624E+00  0.120489E+02  0.456106E+02
 59.429   275.0    0.815053E+01  0.253281E+04  0.701286E+01  -0.131758E+04  0.525315E+00  0.121934E+02  0.488535E+02
 64.128   280.0    0.802923E+01  0.257255E+04  0.708252E+01  -0.135145E+04  0.533951E+00  0.123354E+02  0.522425E+02
 69.107   285.0    0.784280E+01  0.261151E+04  0.714998E+01  -0.138557E+04  0.542528E+00  0.124721E+02  0.557790E+02
 74.376   290.0    0.756292E+01  0.264936E+04  0.721469E+01  -0.141992E+04  0.551041E+00  0.126001E+02  0.594643E+02
 79.946   295.0    0.714759E+01  0.268564E+04  0.727584E+01  -0.145448E+04  0.559484E+00  0.127141E+02  0.632930E+02
 85.832   300.0    0.653332E+01  0.271966E+04  0.733232E+01  -0.148922E+04  0.567851E+00  0.128067E+02  0.672784E+02
 92.044   305.0    0.562197E+01  0.275048E+04  0.738255E+01  -0.152412E+04  0.576132E+00  0.128666E+02  0.714151E+02
 98.597   310.0    0.425817E+01  0.277669E+04  0.742422E+01  -0.155914E+04  0.584316E+00  0.128775E+02  0.757035E+02
105.505   315.0    0.218890E+01  0.279618E+04  0.745388E+01  -0.159423E+04  0.592389E+00  0.128140E+02  0.801358E+02
112.783   320.0   -0.101156E+01  0.280574E+04  0.746633E+01  -0.162934E+04  0.600331E+00  0.126365E+02  0.847276E+02
120.447   325.0   -0.608746E+01  0.280030E+04  0.745338E+01  -0.166438E+04  0.608116E+00  0.122813E+02  0.894622E+02
128.514   330.0   -0.144011E+02  0.277158E+04  0.740176E+01  -0.169925E+04  0.615706E+00  0.116416E+02  0.943566E+02
137.003   335.0   -0.285890E+02  0.270554E+04  0.728904E+01  -0.173376E+04  0.623048E+00  0.105314E+02  0.994019E+02
145.933   340.0   -0.541211E+02  0.257700E+04  0.707526E+01  -0.176768E+04  0.630057E+00  0.860804E+01  0.104587E+03
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155.328     345.0   -0.103396E+03   0.233792E+04   0.668451E+01  -0.180061E+04   0.636602E+00   0.519554E+01   0.109931E+03

165.212     350.0   -0.208000E+03   0.188831E+04   0.595952E+01  -0.183187E+04   0.642459E+00  -0.116358E+01   0.115423E+03

175.614     355.0    0.538451E+03   0.725571E+04   0.147278E+02  -0.200208E+04   0.696564E+00   0.641544E+02   0.121049E+03

186.568     360.0    0.115771E+04   0.931485E+04   0.179593E+02  -0.206264E+04   0.711966E+00   0.944122E+02   0.126832E+03

198.118     365.0    0.344826E+04   0.138007E+05   0.249581E+02  -0.213291E+04   0.730454E+00   0.166098E+03   0.132744E+03

210.327     370.0    0.223639E+05   0.292911E+05   0.489918E+02  -0.222454E+04   0.755913E+00   0.440905E+03   0.138810E+03
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APPENDIX J

SUMMARY OF EXPERIMENTAL DATA FROM THE LITERATURE AND CALCULATIONS TO DETERMINE THE SOLUBILITY PRODUCTS OF BAYERITE AND OTHER NON-SPECIFIC ALUMINUM TRI-HYDRATES.

TABLE J.1

BAYERITE SOLUBILITY IN SODIUM HYDROXIDE SOLUTIONS AT 20°C REPORTED BY CHISTYAKOVA (1964)*

No	Na_2O, $g.l^{-1}$	Al_2O_3, $g.l^{-1}$
1	4	5
2	6	12
3	12	3
4	13	8
5	20	5
6/7	30	10
8	40	15
9	50	12
10	90	20
11	115	25
12	150	25
13	165	25
14	170	47
15	185	52
16	200	64
17	240	82
18	310	248
19	318	295
20	344	420

*Data obtained from a figure.

TABLE J.2

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BAYERITE) FROM THE EXPERIMENTAL RESULTS OF CHISTYAKOVA (1964) AT 20°C

No	ρ at 25°C, $g.cm^{-3}$	TDS, $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	$\log[H_2O]$	Ionic Strength	$\log K'_{s4}$
4	1.023	23365	9644	4234	-0.0060	0.4101	-0.197
5	1.030	29930	14837	2646	-0.0093	0.6181	-0.711
6/7	1.048	46953	22256	5293	-0.0142	0.9134	-0.547
8	1.065	63976	29674	7939	-0.0191	1.2000	-0.471
9	1.076	74413	37093	6351	-0.0243	1.4644	-0.698
10	1.131	132626	66767	10585	-0.1474	2.4673	-0.698
11	1.164	169010	85314	13231	-0.0643	3.0302	-0.685
12	1.203	214183	111279	13231	-0.0914	3.7168	-0.783
13	1.219	233543	122407	13231	-0.1044	3.9859	-0.816
14	1.240	258109	126116	24875	-0.1099	4.1889	-0.506
15	1.258	281586	137244	27521	-0.1245	4.4746	-0.483
16	1.281	310826	148372	33872	-0.1407	4.7980	-0.397
17	1.331	377272	377272	178046	-0.1882	5.5428	-0.318
18	1.482	604289	604289	229976	-0.317	8.3182	+0.428
19	1.510	653310	653310	235911	-0.341	9.1944	+0.631
20	1.586	789781	789781	255199	-0.395	12.5394	+1.260

TABLE J.3

BAYERITE AND GIBBSITE SOLUBILITIES REPORTED BY FRICKE (1928) AT 30°C

Agitation Time, days	NaOH, M	Al_2O_3, $g.100\ cm^{-3}$
1. BAYERITE A		
3	3.75	2.89
		2.98
		2.61
2. BAYERITE B		
3	3.75	2.24
		2.64
		2.64
3. SYNTHETIC GIBBSITE		
3	3.75	1.98
		1.95

TABLE J.4

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4} (BAYERITE,GIBBSITE) FROM THE EXPERIMENTAL RESULTS OF FRICKE (1928) AT 30°C

ρ at 25°C, $g.cm^{-3}$	TDSPL $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{3+}, $mg.l^{-1}$	$\log[H_2O]$	Ionic Strength	$\log K'_{s4}$
1. Bayerite A						
1.1685	173769	86205	15295	-0.0648	3.029	-0.609
1.1691	174510		15772	-0.0649	3.034	-0.593
1.1663	171464		13813	-0.0649	3.021	-0.662
2. Bayerite B						
1.1635	168417		11855	-0.0648	3.005	-0.738
1.1666	171711		13972	-0.0648	3.020	-0.656
	171711		13972	-0.0648	3.020	-0.656
3. Synthetic Gibbsite						
1.1616	166277		10479	-0.0648	2.996	-0.799
1.1613	166030		10320	-0.0649	2.996	-0.806

TABLE J.5

SOLUBILITY OF A MIXTURE OF GIBBSITE AND BAYERITE AT 30°C, FROM FRICKE (1929)[1]

Agitation Time, days	NaOH, M	Al_2O_3 g.100 g solution
36[2]	3.73	2.75

[1] Data obtained from a figure.

[2] Equilibrium had not been achieved at this time.

TABLE J.6

CALCULATED DATA FOR THE DETERMINATION OF LOG Q'_{s4} (BAYERITE) FROM THE EXPERIMENTAL RESULTS OF FRICKE (1929)

ρ at 25°C, $g.cm^{-3}$	TDS $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	$\log[H_2O]$	Ionic Strength	$\log Q'_{s4}$
1.1702	175695	85757	17031	-0.06447	3.031	-0.551

TABLE J.7

BAYERITE SEED SOLUBILITIES REPORTED BY HERRMAN AND STIPETIĆ (1950)

T,°C	Na_2O, $g.l^{-1}$	Al_20_3 $g.l^{-1}$
25.0	123.95	20.20
28.5	123.95	23.50

TABLE J.8

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BAYERITE) FROM EXPERIMENTAL RESULTS BY HERRMAN AND STIPETIĆ (1950)

T,°C	ρ at 25°C, $g.cm^{-3}$	TDS $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	$\log[H_2O]$	Ionic Strength	Log K'_{s4}
25.0	1.1707	176609	91957	10691	−0.0704	3.166	−0.816
28.5	1.1731	179326	91951	12436	−0.0704	3.168	−0.739

TABLE J.9

BAYERITE SOLUBILITIES REPORTED BY LYAPUNOV ET AL. (1973)

T,°C	Na_2O, $g.l^{-1}$	Al_20_3 $g.l^{-1}$
40	132.4	49.9
50	122.5	56.1
50	122.0	58.2
50	140.4	66.8
60	141.4	82.5
60	147.4	91.5

TABLE J.10

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(BAYERITE) FROM EXPERIMENTAL RESULTS BY LYAPUNOV ET AL. (1973)

T,°C	ρ at 25°C, $g.cm^{-3}$	TDS $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	$\log[H_2O]$	Ionic Strength	Log K'_{s4}
40	1.202	211967	98222	26408	−0.0769	3.417	−0.363
50	1.195	204294	90888	29692	−0.0695	3.245	−0.257
50	1.196	205378	90510	30804	−0.0692	3.244	−0.232
50	1.222	236206	104158	35355	−0.0831	3.639	−0.212
60	1.234	250423	104904	43665	−0.0839	3.738	−0.075
60	1.246	265577	109351	48428	−0.0881	3.899	−0.024

TABLE J.11

β TRIHYDRATE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS REPORTED BY RUSSELL ET AL. (1955)

T,°C	Equilibration Time, hr	ρ at 25°C, $g.ml^{-1}$	Na_2O, $g.l^{-1}$	Al_2O_3, $g.l^{-1}$
40	148	1.021	15.1	4.8
		1.055	35.9	10.1
90	120	1.021	14.8	6.1
		1.056	36.0	13.0
60	96	1.021	14.7	6.8
		1.057	35.8	15.0
70	48	1.022	15.0	8.0
		1.060	35.2	18.3
80	16	1.021	15.1	9.2
		1.060	35.2	21.8
90	5.5	1.026	15.0	10.5
		1.065	35.1	25.3
100	5.5	1.026	16.0	12.8
		1.063	35.5	29.1

TABLE J.12

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4}(β TRIHYDRATE) FROM EXPERIMENTAL RESULTS BY RUSSELL ET AL. (1955)

T,°C	TDS $mg.l^{-1}$	Na^+, $mg.l^{-1}$	Al^{+++}, $mg.l^{-1}$	$\log[H_2O]$	Ionic Strength	Log K'_{s4}
40	23441	11202	2540	−0.00704	0.4718	−0.590
40	54650	26633	5345	−0.0171	1.0760	−0.629
50	24124	10980	3228	−0.0069	0.4639	−0.445
50	57167	26707	6880	−0.0172	1.0838	−0.493
60	24571	10905	3599	−0.0069	0.4613	−0.376
60	58556	26559	7939	−0.0171	1.0809	−0.407
70	25947	11128	4234	−0.0070	0.4712	−0.286
70	60498	26113	9685	−0.0168	1.0673	−0.276
80	27064	11202	4869	−0.0071	0.4758	−0.196
80	63380	26113	11538	−0.0168	1.0745	−0.157
90	28005	11128	5557	−0.0071	0.4715	−0.095
90	66132	26039	13390	−0.0167	1.0734	−0.044
100	31189	11870	6774	−0.0075	0.5047	−0.014
100	69777	26336	15401	−0.0170	1.0946	−0.064

APPENDIX K

EVALUATION OF BAUXITE SOLUBILITIES IN SODIUM HYDROXIDE SOLUTIONS FROM DATA GIVEN BY TAYLOR ET AL. (1927)

Taylor et al. (1927) conducted as part of a broader study of aluminum hydroxide solubilities in alkali media, five measurements of bauxite solubilities at 150°C in 160 $g.l^{-1}$ NaOH solution. Because the bauxite samples were selected on the basis of their dominant hydroxide phases, it is of interest to see how their solubilities compare with the solubilities of pure minerals. The available data is summarized in Table K.1. These data were used to calculate the appropriate input for the EQ3 code, which calculated data necessary to evaluate log K'_{s4}. Log K'_{s4} at ionic strength = 0, was determined by empirical extrapolation, using log K'_{s4} versus I plots The results are given in Table K.2

Comparison of the calculated values of K_{s4} with the corresponding values for gibbsite, boehmite and diaspore at 150°C suggest that the Dalmatian, Istrian and Surinam bauxites behave similarily to boehmite. The diaspore clay does not appear to have saturated with respect to diaspore, whereas the Arkansas bauxite falls between gibbsite and boehmite in solubility.

TABLE K.1

SOLUBILITIES OF BAUXITES IN SODIUM HYDROXIDE SOLUTION
REPORTED BY TAYLOR ET AL. (1927)

T,°C	NaOH, $g.l^{-1}$	Al_2O_3, wt%	Comments
150	160	10.86	Arkansas bauxite
150	160	6.72	Dalmatian bauxite
150	160	6.83	Istrian bauxite
150	160	8.14	Surinam bauxite
150	160	2.52	diaspore clay

TABLE K.2

CALCULATED DATA FOR THE DETERMINATION OF LOG K'_{s4} FROM SOLUBILITIES OF BAUXITES IN SODIUM HYDROXIDE SOLUTION, FROM TAYLOR, ET AL. (1927)

Sample	T°C	ρ at 25°C, g.cm^{-3}	TDS mg.l^{-1}	Na^+, mg.l^{-1}	Al^{+++}, mg.l^{-1}	log[H_2O]	Ionic Strength	log K'_{s4}(gib)	log K'_{s4}(boe/dia)	log K_{s4}(gibb)	log K_{s4}(boe/dia)
Arkansas bauxite	150	1.249	271683	4.020	2.687	-.0692	3.5618	0.5229	+0.5921	+0.08	≈+0.11
Dalmatian bauxite	150	1.213	227142	4.020	1.589	-.0692	3.2559		+0.0830		-0.26
Istrian bauxite	150	1.214	228295	4.020	1.617	-.0692	3.2630		+0.0960		-0.24
Surinam bauxite	150	1.225	242126	4.020	1.955	-.0692	3.3519	0.1808	+0.2500	-0.17	-0.14
Diaspore clay	150	1.177	184495	4.020	0.570	-.0692	3.0152		-0.5986		-0.85