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**LA THÈSE A ÉTÉ
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THE SOLUBILITY OF SOME ALUMINOSILICATE MINERALS
IN SUPERCRITICAL WATER -
AN EXPERIMENTAL AND THERMODYNAMIC STUDY

by

Stephen William Adcock

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfillment of
the requirements for the degree of
Doctor of Philosophy

Department of Geology

Carleton University

Ottawa, Ontario

July, 1985

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Carleton University

December, 1985

"thermodynamics is intellectual masturbation -
concentrate on plate tectonics"

quote from New Scientist,
29th January 1981, p276

ABSTRACT

Aqueous solubility data have been obtained using a "dynamic flow" technique at temperatures in the range 400 to 600°C and pressures in the range 0.5 to 3.5 kbar. Pure water was used as the solvent. Quartz, albite, K-feldspar, labradorite, nepheline, leucite and mixtures of these minerals were used as starting solids. The data were collected over several years (1963 to 1980 by K. L. Currie and 1979 to 1981 by S. W. Adcock), and are of variable quality. Experiments under carefully controlled conditions yield aqueous concentrations of Si, Al, Na and K which are reproducible to $\pm 5\%$. Poorly controlled experiments yield concentrations which may vary by $\pm 50\%$ from the mean value.

The hypothesis that most of the solutions attained thermodynamic equilibrium with respect to the starting material was investigated and found to be reasonable. The data were interpreted thermodynamically in terms of a simple aqueous solution model, involving mononuclear species. Values for the apparent molal Gibbs free energy of $\text{AlO}_{1.5}(\text{aq})$ were obtained. Predictions of corundum solubility using these values were too high by one or two orders of magnitude. This failure of the model led to the development of more complex models. Additional experimental data from a variety of sources were used to constrain the models. The data were sufficient to precisely constrain the new models only at 600°C and 2 kbar.

The first model investigated involved the charged hydroxyl species $\text{Al}(\text{OH})_4^-$ and $\text{Si}(\text{OH})_5^-$. This model could be constrained to fit the experimental data, but only by allowing the activity coefficients for charged aqueous species to drop to well below unity. This is an indication that some kind of strong interaction, or complex formation, is occurring in the solution.

The second model investigated involved the neutral polynuclear species KH_2AlO_3 , KH_3SiO_4 , NaH_2AlO_3 , and NaH_3SiO_4 . This model was found to be consistent with most of the experimental data, using a simple activity model, wherein all activity coefficients plus the activity of water were set equal to unity.

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The only major failure of this model at 600°C and 2 kbar concerns the prediction of Al concentrations in solutions equilibrated with quartz plus other (Na,K)-Al-Si-bearing phases. In the experimental solutions, Al concentration is higher than the predicted concentrations by up to an order of magnitude.

This shortcoming may be explained by complex activity model corrections. However, these corrections cannot be accurately developed without highly accurate experimental data, and they have little theoretical basis.

Some suggestions for future experiments are given, which will help to resolve these problems.

A computer code for interpreting aqueous solubility experiments in terms of dissociation equilibria has been developed. This code makes it very easy to quantitatively assess alternative aqueous speciation/activity models, using experimental solubility data.

The analysis of the experimental data resulted in values of the Gibbs free energies of the aqueous species $\text{Al}(\text{OH})_3$, $\text{Si}(\text{OH})_4$, NaH_2AlO_3 , NaH_3SiO_4 , KH_2AlO_3 and KH_3SiO_4 at 600°C and 2 kbar. Some simple applications to geological problems, using these derived thermodynamic data, are given. Given an appropriate bulk composition, Al can be a dominant constituent of the aqueous phase. The thermodynamic data can be incorporated into a general aqueous speciation computer code to enable predictions of water-rock interaction at high temperatures and pressures.

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Many people have contributed both materially and intellectually to this study. Four people should be singled out for special mention. Professor W. S. MacKenzie gave me the opportunity to come to Canada to work at the Geological Survey. My supervisor, Prof. G. B. Skippen gave support and encouragement and the freedom to pursue my own ideas. Dr. K. L. Currie gave me freedom to use his large amount of unpublished data, and much support in the use of his experimental laboratory. Prof. G. M. Anderson gave me permission to use unpublished data obtained in his laboratory. Open discussions with him led to major improvements and clarifications of several concepts presented within the thesis.

Last, but by every means most, to my wife, Jane, a huge thank-you for five years of support, both moral and financial. Without her, this thesis would not have been started, let alone finished.

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Chapter 1 Introduction and conventions

As an igneous intrusion cools down and solidifies, the magma may become saturated with water and a separate fluid phase may form. At the same time, the country rock and any fluid within it will become hotter.

A convection cell involving the fluid will be set up. In general, the fluid will enter the igneous body, rise up through it, then spread out and descend back (schematically shown in figure 1-1, taken from Wickman and Rickard, 1981). Evidence of very large long-lived convection cells is provided by oxygen isotope data (Taylor, 1977).

As the aqueous phase migrates through the rock, it will attempt to attain chemical equilibrium with the host rock. The equilibrium composition of the aqueous phase will depend on its original composition, the ambient temperature and pressure, and the compositions of the minerals in the host rock. Elements will be dissolved and precipitated at different points in the cycle.

To fully understand the process of water-rock interaction is a formidable problem. Some of the aspects which must be considered are:

- a) chemical composition of the aqueous fluid in the country rock before intrusion,
- b) porosity and permeability of the country rock before intrusion,

Figure 1-1 Schematic illustration of the thermal "mushroom" above a high-level intrusion. Flow lines for convective recharge-discharge system indicated.

(Figure taken from Wickman and Rickard, 1981)

- c) mineralogical composition of the country rock - are the minerals in equilibrium with one another and with the aqueous fluid prior to intrusion?
- d) chemical composition of the magma, which will be a primary control on the crystallisation sequence of the magma and on the composition of any aqueous fluid which may exsolve from it,
- e) development of porosity and permeability within the igneous body as it cools,
- f) variation of temperature and pressure with time relative to fixed points within the country rock and igneous body,
- g) changes in porosity and permeability due to chemical dissolution and precipitation,
- h) rate of reaction of minerals with aqueous fluid relative to flow rates of the fluid,
- i) development of two-fluid phase regions,
- j) the composition of the aqueous fluid in equilibrium with the surrounding minerals.

The complex inter-relationships among these factors are summarised in figure 1-2, taken from Norton (1979). Constraints can be placed on all these factors and a comprehensive model can be produced. Norton (1979) has developed computer programmes which simulate conditions in and around cooling plutons. Figure 1-2 summarises his conceptual model.

Figure 1-2 - Dynamics of hydrothermal systems, relating thermal, mechanical and chemical processes.

(Figure taken from Norton, 1979)

Rectangular boxes with valves represent rates; rectangular boxes represent levels; circles indicate feedback from level to rate; positive signs indicate that feedback augments rate.

Regions 1, 2 and 3 indicate subsets of overall processes which coincide with decoupled equations.

Where dashed lines cross subset boundaries, feedback is approximated by arbitrary functions which estimate magnitude of effects. Analyses of processes in the respective subsets include:

Region 1: Norton, 1972; Ribando et al., 1976;

Norton and Knight, 1977; Cathles, 1977; Norton and Knapp, 1977; Norton, 1977, 1978, 1982.

Region 2: Knapp and Norton, 1981; Roberts, 1970.

Region 3: Helgeson, 1971; Norton, 1972, 1978;

Norton and Taylor, 1978; Hemley and McNabb, 1978.

One of the major restrictions in such models is our poor understanding of the chemical reactions which may occur (factors h) and j)). This dissertation aims to improve our understanding of the chemical reactions by placing some constraints on the composition of the aqueous fluid in equilibrium with Na, K alumino-silicates in the range 400-600°C and 0.75-3.5 kbar, based on experimental data. The experiments reported here all involve a starting fluid phase of pure water.

Granitic and syenitic magmas have water-saturated solidi in the region of 750°C at 1 kbar and 640°C at 5 kbar (Bailey and MacDonald, 1976; Brown, 1963; Burnham, 1979; Edgar, 1974; Gittins, 1979; Tuttle and Bowen, 1958). Hence the experimental data lie in the sub-solidus region, in the supercritical region for pure water.

There is ample fluid inclusion evidence that most fluids in the Earth's crust contain abundant NaCl and/or CO₂ (Roedder, 1981, 1982). An experiment designed to simulate natural systems should involve an aqueous fluid containing these components. However, by introducing these components, the system becomes much more complex relative to one involving only pure water as the initial fluid composition. Interpretation becomes correspondingly more difficult. A safer approach is to first experiment on relatively simple systems. Thermodynamic theory can be used to apply the results to more complex systems. These complex systems can then be investigated experimentally and the data used to refine the thermodynamic theory.

The problem being tackled here is quite immense. Only one paper has been presented to date, which predicts the solution composition in equilibrium with mixtures of minerals at supercritical temperatures and pressures (Frantz et al., 1981; database corrected by Popp, 1981, 1984). [Helgeson et al. (1981, p1471-1481) present a method for predicting solution compositions, but do not go on to present results of actual calculations.] Frantz et al.'s method for calculating the solution composition involved several major assumptions:

- a) their thermodynamic database was based on experiments involving solutions rich in Cl - richer than are commonly found in fluid inclusions. Complementary data for Cl poor solutions would be useful, but cannot be obtained using their experimental technique (Frantz and Eugster, 1973).
- b) they assumed that the only important species of Na, K, Mg and Ca in solution were neutral Cl complexes - this has since been shown to be incorrect (Frantz and Popp, 1981; Frantz and Marshall, 1982, 1983).
- c) they assumed that the solutions contained no Al; that it was all precipitated as corundum. There is ample field and experimental evidence to contradict this assumption, but in the absence of reliable thermodynamic data for Al(aq), the assumption is the most reasonable one to make.

The end result of my work is a somewhat improved version of Frantz et al.'s method, based on all the available experimental data. It is not intended to be highly accurate - the nature of

the experimental data prevents this. However, it is semi-quantitative and an improvement on earlier work. It can be used to provide explanations of some features observed in natural systems and is compatible with the available experimental data. The guiding philosophy is that any model is better than no model.

The data presented here will allow one to perform reaction path calculations analogous to those of Helgeson et al. (1970) at supercritical temperatures and pressures. These calculations could then be integrated into a physico-chemical model such as that of Norton (1979). However, this is beyond the scope of the present study. Instead, the data will be applied to much simpler systems, such as closed system metamorphism and mineral alteration.

Abbreviations

Mineral abbreviations correspond to those recommended by Kretz (1983). The minerals mentioned in this thesis are shown in figures 1-3 and 1-4, together with the recommended abbreviations. Components present in the aqueous phase are referred to by "aq".

To avoid unnecessary repetition of a few oft-quoted references, I have used the following abbreviations in this dissertation:

H+K : Helgeson and Kirkham

HKF : Helgeson, Kirkham and Flowers (1981)

HDNB : Helgeson, Delany, Nesbitt and Bird (1978)

W+H : Walther and Helgeson (1977)

Figure 1-3 Molar K-Al-Si diagram, showing minerals mentioned in this thesis:

Ab	Albite
Als	Al-silicate
And	Andalusite
Anl	Analcime
Bhm	Boehmite
Crn	Corundum
Dsp	Diaspore
Fsp	Feldspar
Gbs	Gibbsite
Kfs	K-feldspar
Kln	Kaolinite
Kls	Kalsilite
Ky	Kyanite
Lab	Labradorite
Lct	Leucite
Mc	Microcline
Ms	Muscovite
Ne	Nepheline
Or	Orthoclase
Pg	Paragonite
Prl	Pyrophyllite
Qtz	Quartz
Sa	Sanidine
Sil	Sillimanite

Figure 1-4 Molar Na-Al-Si diagram, showing minerals mentioned in this thesis:

Ab	Albite
Als	Al-silicate
And	Andalusite
Anl	Analcime
Bhm	Boehmite
Crn	Corundum
Dsp	Diaspore
Fsp	Feldspar
Gbs	Gibbsite
Kfs	K-feldspar
Kln	Kaolinite
Kls	Kalsilite
Ky	Kyanite
Lab	Labradorite
Lct	Leucite
Mc	Microcline
Ms	Muscovite
Ne	Nepheline
Or	Orthoclase
Pg	Paragonite
Prl	Pyrophyllite
Qtz	Quartz
Sa	Sanidine
Sil	Sillimanite

Symbolism

The symbolism employed in the thermodynamic equations follows that of HKF as closely as practicable. The expression " $\Delta G = \Delta G^0 + R T \ln a$ " which appears in Chapter 4 is analogous to the more commonly used symbolism " $\mu = \mu^0 + R T \ln a$ " (see HKF's list of symbols and equations 1 to 18 and 54 to 72)

Definitions

In this paper, the concepts of incongruent dissolution and non-stoichiometric dissolution, which in general usage are synonymous, are given different meanings.

Congruent dissolution: the various components of the solid phase go into solution in their stoichiometric ratios, and a stoichiometric solution results.

Incongruent dissolution: the components of the solid phase dissolve at different rates, giving rise to a non-stoichiometric solution.

Stoichiometric dissolution: the kinetics of dissolution are not considered. No new phases form and the solution reflects the stoichiometry of the solid phase.

Non-stoichiometric dissolution: new phases with different stoichiometry to the original solid phase are produced, and hence the solution composition does not reflect the stoichiometry of the original solid phase.

These distinctions involve the mechanism of dissolution reactions. They are useful when discussing some of the albite dissolution data in Chapter 4. Incongruent dissolution involves

changes in the solid composition, brought about by processes occurring either within the solid or at the solid-liquid interface; new phases may be formed by processes other than precipitation from supersaturated solutions.

Units and physical constants

The units are chosen so as to be consistent with the database of HDNB. Two important diversions from S.I. units are thus involved. To obtain numbers consistent with the S.I. system, the following conversion factors should be used:

$$1 \text{ cal mole}^{-1} = 4.1840 \text{ joule mole}^{-1}$$

$$1 \text{ kbar} = 100 \text{ MPa}$$

The value of the gas constant, R , used in this study, is $1.98719 \text{ cal mole}^{-1} \text{ K}^{-1}$. The molecular weight of H_2O is taken to be 18.0153. The atomic weights used in this study are:

Si	28.0855
Al	26.98154
Na	22.9898
K	39.0983
Ca	40.08
Fe	55.8470 ± 0.003
O	15.99994

Conversion factors from oxides to elements are as follows:

SiO_2	$\rightarrow$	Si	$\times 0.4674$
Al_2O_3	$\rightarrow$	Al	$\times 0.5292$
Na_2O	$\rightarrow$	Na	$\times 0.7419$
K_2O	$\rightarrow$	K	$\times 0.8301$

Standard states

The thermodynamic standard states adopted in this study are identical to those of HDNB. For minerals and water, the standard state is one of unit activity of the pure phase at any pressure and temperature. The solutions considered in this study are all so dilute (< 0.1 molal) that the activity of water is approximated to unity in all calculations. Note that in more concentrated solutions, this approximation may introduce significant errors (Shmulovich et al., 1982, fig. 7; Blencoe et al., 1982). The standard state for aqueous species corresponds to unit activity of the species in a hypothetical one molal solution referenced to infinite dilution at any pressure and temperature. Molality is approximately proportional to mole fraction at low concentrations. Molalities are much easier to calculate than mole fractions, being independent of the concentrations of other species in the solution. At high concentrations, use of the molal standard state may lead to unnecessarily complex expressions for activity coefficients, and a standard state based on mole fractions may yield simpler results. At the concentrations considered in this study, use of a molal standard state should introduce negligible extra complexities. All mineral reactants and products are assumed to be pure end-member phases. Unless otherwise stated, all dissociation constants are based on the molal concentration scale

(see Appendix E).

Chapter 2 Experimental design

Solubility determinations of silicate minerals in water are notoriously difficult to obtain. At low temperatures, very slow reaction rates are the main obstacle. At elevated temperatures and pressures, quench reactions create formidable problems. Even if these can be minimised (e.g. by Eugster, in discussion with Barnes, 1981; Hemley et al., 1977a,b,c, 1980), the amount of solution obtained may be too small to allow accurate analysis of all the major components of the solution (e.g. Hemley et al. could not quantitatively analyse Mg in solution (1977a,b,c) or Al in solution (1980)). To avoid these problems, methods have been devised which allow several millilitres of solution to be sampled while the reaction chamber remains at high temperature and pressure.

Barnes (1971, 1981) has reviewed some of the different experimental techniques available. The reviews are biased strongly in favour of his own particular apparatus which was designed primarily for work on sulphide mineral solubilities at lower temperatures and pressures than those of the present study. In an earlier dissertation (Adcock, 1980), I also reviewed the different techniques. This review is summarised in Appendix D. The conclusion I drew was that the "gold bag" arrangement of Dickson et al. (1963), as modified by Seyfried et al. (1979) was perhaps the most foolproof design. The range of the "gold bag" apparatus has recently been extended to 500°C and 1 kbar, but the extent of the modifications necessary to achieve this was not

described (Bischoff and Rosenhauer, 1983). Hamilton and Manning (1981) tried to construct a similar apparatus for use up to 700°C at 1 kbar, but encountered numerous technical problems (Manning, pers. comm., 1980).

Hence, I opted to use the dynamic flow apparatus of Currie (1968). This apparatus had already been used extensively at temperatures up to 600°C and pressures up to 3.5 kbar. The design is simple and the experimental techniques can be easily mastered. There are numerous possible sources of error in the technique, but with experience, these can be minimised to within acceptable limits. A detailed description of the apparatus, with practical information on its operation, has been given earlier (Adcock, 1980). Here, I will emphasise the general principles and discuss the possible sources of error.

The basic principle of the apparatus is that if water is passed sufficiently slowly over a solid, then the solid and water will stay very close to chemical equilibrium. The experimental arrangement is shown schematically in figure 2-1. Water is leaked out one end of the pressure vessel, and a pump automatically injects more water in the opposite end to maintain constant pressure. The aqueous solutions are analysed by atomic absorption spectrometry.

Figure 2-1 Schematic diagram of the experimental apparatus

The first problem that must be addressed is how slow the flow rate should be. In general, the slower the rate, the closer the system will remain to chemical equilibrium. Practical aspects dictate the minimum rate of collection. At least 20 ml should be collected to ensure accurate analyses of Si, Al, Na and K by atomic absorption spectrophotometry (AAS), which can be routinely performed by analysts at the G.S.C. This amount can be further reduced if "state of the art" AAS techniques and equipment are used. The slowest steady drip rate results in 20 ml being collected within about 4 hours. If the exit valves are closed further, the flow rate stops (presumably due to surface tension forces exceeding the hydraulic force from the pressure vessel). An alternative mode of operation that would result in slower rates of collection would be to open and close the exit valves at fixed intervals. In practice, chemical equilibrium seems to be maintained even with very high flow rates. With extremely high flow rates, solute concentrations should drop to very low levels. Experiments with mixtures of nepheline and albite at 400°C and 1 kbar in which the flow rate was varied from 30 to 200 ml h⁻¹ showed no indication of such an effect (table 2-1). [Runs AC67 and AC68 are both anomalous, and are classified in Chapter 3 as disequilibrium results, but the anomalies are not related to the flow rate.] Currie (1968, figure 2) presented additional evidence that equilibrium was achieved with flow rates much greater than 5 ml h⁻¹.

Table 2-1 Solubility of Ab-Ne as a function of flow rate, at
400°C and 1 kbar (data from Adcock, 1980)

Run no.	Si ppm	Al ppm	Na ppm	K ppm	Flow rate (ml h ⁻¹)	Volume collected (ml)
AC67	192	179	360	219	28	135
AC68	237	207	230	205	147	135
AC69	237	183	157	81	180	135
AC70	233	196	188	68	201	135
AC78	268	203	163	64	31	135
AC79	281	218	190	66	31	135

The apparently rapid rate of equilibration may be attributed to the high solid surface area exposed to reaction. Approximately 80 g of solid particles, 2-5 mm in size, were reacted with water in a reaction vessel with a volume of about 80 ml.

Sample preparation may affect measured solubilities (Holdren and Adams, 1982; Lin and Clemency, 1981; Gardner, 1983; Nitkiewicz et al., 1984). In my experiments, the samples were mechanically crushed, sieved, handpicked to remove any visible impurities, and washed with distilled water prior to the experiment. Ultrasonic cleaning was not done; hence at the beginning of an experiment, the grains were probably coated with numerous fine particles. Surface layers may also have been disrupted by the crushing. Effects due to disrupted surface layers and fine material should be most apparent at the beginning

of an experiment. Once they have been removed by preferential dissolution, the measured solubilities should correspond to those of 2-5 mm particles.

Because the apparatus uses 80 g of material per experiment, natural material must be used. The ideal starting material should be chemically pure, in the stable state of order/disorder for the experimental conditions, and be free of crystallographic defects (see Salje and Wernecke (1982) for a discussion of this last aspect). Natural material fitting these criteria is unknown. Hence, some error is introduced. The magnitude of this error source is unknown. It is assumed that it lies within the range of other known error sources. Structural analysis of the starting materials was limited to routine X-ray powder diffraction, which simply confirmed the mineral identities. Further structural analysis would be hard to justify until a means of assessing the associated errors is developed.

When the starting material dissolves non-stoichiometrically, one or more new phases must be produced. These new phases are very difficult to identify with the present technique. The water:rock ratio is so low that, in general, only very small amounts of the new phase form relative to the starting material. These small amounts cannot be identified using any simple, easily available technique. When the end product of an experiment is examined under a scanning electron microscope, new phases can be readily detected on the surface of the starting material, but they cannot be quantitatively analysed. Techniques such as X-ray

photoelectron spectroscopy (XPS) and scanning Auger microscopy (Riviere, 1982; Haines et al., 1983) could potentially yield accurate chemical analyses of these phases, but these techniques were not available during this study.

An attempt was made to increase the amount of the new phase(s) relative to the starting material, by increasing the water:rock ratio. Five or six fragments of the starting material were loosely wrapped in gold foil and placed in the reaction vessel. This allowed new phases to be identified by conventional X-ray powder diffraction techniques, but the concentrations of the cations in the solution were depressed to considerably below the levels reached in experiments using 80 g of starting material (compare table 3-11 with table 3-10). The slower reaction rate may have been caused by the lower available surface area of the starting material and/or the gold foil acting as a barrier. Such a slow reaction rate is fatal for the dynamic flow technique.

Temperature gradients are a problem when dealing with large reaction vessels - the ones used in this study had outside lengths of 300 mm and outside diameters of 100 mm. The vessel was placed within the furnace such that the thermocouples at each end gave the same readings (to within 2°C). However, the temperature profile within the reaction chamber is unknown. An internal thermocouple is the only reliable way of ascertaining this profile, but such devices are very difficult to maintain. Measurement of the temperature profile when there is no solution or solid within the chamber, and with one or both seals removed,

is not likely to yield a profile similar to that present in the chamber under experimental conditions. One is forced to assume that the temperature inside the chamber is close to that measured by the thermocouples. The large mass of the reaction vessel, and convection within the chamber would tend to remove any temperature gradients.

As a direct consequence of the experimental technique, pressure varies cyclically during solution collection. The magnitude of these variations depends on the sensitivity of the pump. In the present study, pressure variation was within ± 20 bars of the quoted pressure. One way of avoiding such cyclical variations would be to connect a very large (perhaps 2 litres) high pressure reservoir to the inlet end of the reaction chamber. Water could be drawn from this reservoir during sample collection. One problem with this possible modification would be diffusion of dissolved ions back through the apparatus and into the high pressure reservoir.

The reactant water was purified by distillation. Chemical analyses revealed it to contain only Si in detectable amounts. The Si concentration varied between 10-15 ppm. Other purification methods (de-ionisation with or without distillation) gave identical results. A possible technique for obtaining pure water is given by Hofmann and Mattinson (1972). In the experiments reported here, Si concentrations are usually well in excess of 10-15 ppm, and hence the impure water used should have a negligible effect on the results.

The experimental solution is leaked from the reaction vessel via 600-700 mm of high pressure capillary tubing, directly into a sealed polyethylene bottle. By the time the solution has reached the end of the capillary tubing, it has cooled to room temperature.

One would expect some precipitation to occur on cooling. Precipitation is a major problem with other experimental arrangements (see discussion of Barnes, 1981; also Walther and Orville, 1983). However, no precipitation was observed in the present study. The tubing never became blocked, despite its narrow diameter (0.006"), and occasional sectioning never revealed any precipitates. The collected solutions, whilst obviously supersaturated with respect to many silicate phases, did not show any precipitation. Repeat analyses of the same solutions after they had been allowed to stand for several weeks or months gave results within the error limits of the earlier analyses. The solutions were not treated in any way after they were collected.

Evidently there must be large kinetic energy barriers preventing nucleation of any of the supersaturated phases. Other experimental arrangements may encounter problems because of the presence of "seed crystals" of the supersaturated phases or because of lower kinetic energy barriers to nucleation in the systems being studied.

Bridgman seals are notoriously difficult to take apart after an experiment. One quite successful, but rather involved and

laborious technique is described by Adcock (1980). Subsequently, another seal design was developed (as shown in Adcock, 1980, figure 8, p45). This new design allowed the seals to be dismantled easily, but there have since been three catastrophic failures of the seals, each time causing serious damage to the apparatus. The cause of the failures is unknown, but may be related to the new design.

It is hard to demonstrate that equilibrium has been achieved in this experimental arrangement. The equilibrium solution composition can be approached from either undersaturation or oversaturation by approaching the equilibrium temperature and pressure from either lower or higher conditions. Such experiments yield results consistent with equilibrium having been reached. However, one must always bear in mind that too high a flow rate will lead to disequilibrium.

Generally, the experimental results are reproducible to better than $\pm 10\%$ of the values reported in Chapter 3, and frequently to better than $\pm 2\%$. Runs AM22 to AM25 in table 3-8 give the best indication of how good reproducibility can be in a well-controlled set of experiments, even when some of the elements are present in very small amounts (~ 1 ppm). Some anomalous results indicative of disequilibrium can be readily detected, as described in Chapter 3. Whether or not the experiments gave results consistent with thermodynamic equilibrium will be further discussed in Chapter 4.

Some suggestions for future experiments

Until a technique such as the "gold bag" one is developed for use at temperatures up to 600°C and 2 kbar, the dynamic flow technique will remain the only one capable of yielding complete solubility data (i.e. chemical analyses for all the major components in solution) for sparingly soluble silicate minerals in pure water over a wide range of supercritical temperatures and pressures, with a reproducibility of better than $\pm 10\%$ for each element. [For example, a "sparingly soluble" silicate mineral would be albite at 400°C and 2 kbar, but not albite at 600°C and 6 kbar. At the higher P-T condition, albite is much more soluble, and quench experiments can yield good results (Davis, 1972).]

The design of the experiments reported here was flawed in several ways. With the benefit of hindsight, I would suggest the following procedure for future experimentalists:

Perform a series of experiments (10 would be a reasonable number) at one temperature and pressure, collecting about 20 ml of solution each time, at about 5 ml h⁻¹, at daily intervals, after the solid and water have been allowed 24 hours or more to approach equilibrium. The first few samples of solution may show a wide variation in composition, but this variation should be much less (within the limits of analytical error) in the final solutions collected. [The reasons for the initial variation in composition, readily apparent in table 2-1, include problems with sample preparation, as discussed earlier.]

Use starting materials with well-characterised thermodynamic properties, e.g. Amelia albite, quartz or corundum. Use stable mixtures of solid phases as starting materials (up to the maximum permitted by the phase rule) in order to place additional constraints on the system (e.g. use Ab + Crn or Ab + Qtz, but not Crn + Qtz).

Do not use the same material for another experiment at a different temperature and/or pressure.

Analyse the surface of the material after the experiment, by XPS, SAM or similar "surface-specific" techniques.

Optional modifications to the apparatus would include:

- 1) a return to the original Bridgman seal design, detailed by Adcock (1980, figures 6 and 7, p43-44), or a modification of the present design;
- 2) addition of an internal thermocouple;
- 3) addition of a large volume high pressure reservoir, or some other arrangement to stabilise the pressure.

Chapter 3 Experimental results

Dissolution experiments were carried out on

- a) albite
- b) perthitic microcline
- c) albite + nepheline
- d) leucite
- e) quartz
- f) labradorite
- g) albite + perthitic microcline
- h) quartz + albite + perthitic microcline
- i) quartz + labradorite + perthitic microcline

Data on the starting materials are summarised in table 3-1.

Chemical analyses of the materials are given in table 3-2. The microcline analyses in table 3-2 are both anomalous. The % total for Buckingham microcline is rather low (97.25%). The Richardson microcline contains an anomalously high percentage of SiO_2 , suggesting the presence of quartz. Although quartz was not visible in the experimental samples, the experimental results (table 3-8) are also consistent with its presence (this is further discussed in Chapter 4). The number of digits in table 3-2 (2) allow one to precisely re-generate the percentages in table 3-2 (1), from which they were calculated.

Tables 3-3 to 3-17 give the complete set of experimental results, including Currie's 1968 albite data and additional unpublished data. The number of digits in these tables do NOT reflect the accuracy of the measurements (e.g. temperature is not

accurate to $\pm 0.1^{\circ}\text{C}$). Actual uncertainties for temperature and pressure are about $\pm 5^{\circ}\text{C}$ and ± 20 bars respectively. The original analytical data were obtained sometimes as ppm of the oxides and sometimes as ppm of the elements. Analytical uncertainties (determined by duplicate analyses) are better than the experimental reproducibility, which varies, but is rarely better than $\pm 5\%$. The decimal point was included in the tables to simplify reading of the datafiles by FORTRAN programmes.

A comprehensive treatment of errors is not possible, for three main reasons. Firstly, the experiments were carried out over a period of about 20 years, during which time analytical techniques were greatly improved. Secondly, as a consequence of improved analytical techniques, smaller sample volumes were needed for analysis; hence lower flow rates became feasible. Thirdly, the importance of initial disequilibrium effects in a series of experiments only became clear in the most recent experiments. This factor is clearly seen in runs AM19 to AM25 in table 3-8. This series of seven experiments was performed at 600°C and 1 kbar. The first experiment, AM19 gave clearly anomalous results. The following two experiments, AM20 and AM21, gave slightly anomalous results. The final four experiments showed very good agreement with one another.

XRD analysis of the starting materials confirmed their identities and showed the albite and microcline to be highly ordered. The labradorite gave an "intermediate plagioclase pattern". XRD analysis of the end products generally gave

identical results to those before dissolution. This indicates that the amount of dissolution was insignificant relative to the amount of starting material. The only exceptions were as follows:

- a) Microcline was detected by XRD in the end product from leucite dissolution runs AC37-AC52.
- b) Disequilibrium runs with albite dissolution produced nepheline (Currie, 1968).
- c) In microcline dissolution experiments, the microcline was more disordered at the end of the experiments, according to the criteria of Kroll and Ribbe (1983).

In every case where a product phase has been identified, that phase has turned out to be a complex aluminosilicate.

Some of the results given in the tables are classed as disequilibrium results. One common result, indicating "disequilibrium" in feldspar dissolution experiments, is that Si concentration is high, whilst Na, K and Al concentrations are low, relative to the "equilibrium" value. Such a pattern can be seen, for example, in the "disequilibrium" results of table 3-3, relative to the "equilibrium" results. The increase in Si concentration is opposite to what one would expect intuitively, and appears to be a general phenomenon, associated with the alkali feldspars. The phenomenon was first described by Currie (1968) and has recently been described under different experimental conditions by Moore et al. (1983). A hypothesis to explain it is given in Chapter 4. Several of the experiments

designated as disequilibrium runs in tables 3-3 to 3-17 were designated according to this criterion. The remaining disequilibrium experiments were designated as such because Na, K, Al and Si all had anomalously low solubilities.

Na, K, Al and Si all have concentrations in the range 0 - 3000 ppm. The highest equilibrium concentration (excluding the labradorite data, which are highly variable, and the experiments involving quartz in the starting material) is Si = 1496 ppm (run PA56, table 3-3). The Na:K ratio in solution is almost always greater than in the starting material. Concentrations of Na, K, Al and Si usually increase with increasing temperature and always increase with increasing pressure. Dissolution is always non-stoichiometric, and the degree of non-stoichiometry varies strongly as a f(P,T). This aspect is highlighted in figures 3-1 to 3-5, where the molal ratios Si:Al, Si:(Na+K) and (Na+K):Al in solution are plotted for the single mineral dissolution experiments.

In albite dissolution, the ratio $m_{Si}:(m_{Na} + m_K)$ (shown in figures 3-1(a) and 3-2(a)) hovers above and below the stoichiometric value of 3.0 except at low pressures and high temperatures, where it greatly exceeds the stoichiometric value. Figure 3-1(a) shows a gradual increase in $m_{Si}:(m_{Na} + m_K)$ as temperature increases. This trend does not appear in figure 3-2(a). The ratio $(m_{Na} + m_K):m_{Al}$ is almost always greater than the stoichiometric value (1.0), but rarely greater than 2.0. There are no clear trends with pressure or temperature. The

ratio $m_{\text{Si}}:m_{\text{Al}}$ is also almost always greater than the stoichiometric value (3.0), and markedly so at high temperatures and low pressures; there are no other clear trends with pressure or temperature. The high $m_{\text{Si}}:m_{\text{Al}}$ ratio at 600°C shown in figure 3-1(c) is not repeated in figure 3-2(c).

Ratios of elements in solution for Davis's data show no trends with either temperature or pressure. The ratio $(m_{\text{Na}} + m_{\text{K}}):m_{\text{Al}}$ varies between 1.0 and 1.5; $m_{\text{Si}}:(m_{\text{Na}} + m_{\text{K}})$ varies between 2.8 and 3.4; and $m_{\text{Si}}:m_{\text{Al}}$ varies between 3.3 and 4.5.

The molal ratio patterns for microcline dissolution (figure 3-3) are very similar to those for albite dissolution.

Figures 3-6 to 3-9 show the data plotted on graphs of $\ln m_X$ vs. $\ln V_{\text{H}_2\text{O}}$ (where $X = \text{Na}, \text{K}, \text{Al}$ or Si ; $V_{\text{H}_2\text{O}}$ = molar volume of water at P and T of experiment). The reasons for choosing this kind of plot will be made clear in Chapter 4. The data in table 3-3 were plotted in numerous different ways; only $\ln m_X$ vs. $\ln V_{\text{H}_2\text{O}}$ gave linear graphs.

The results for albite dissolution (tables 3-3, 3-4 and 3-5, figures 3-6 and 3-7) show good agreement. Davis's (1972) data are given in table 3-18 and figure 3-9. Where Davis's results overlap those of tables 3-3, 3-4 and 3-5, they are in general agreement within the limits of experimental error, as shown in figure 3-10. The one exception is the Al concentrations at 600°C given in table 3-3 (Currie's 1968 data); these are systematically lower than the other 600°C data, possibly because of analytical problems (Currie, 1985, pers. comm.).

The results for microcline dissolution (tables 3-6, 3-7 and 3-8) show rather more scatter. The anomalous results in table 3-8 (high Si, low Na, K, Al) suggest that there may have been some quartz accidentally included in the starting material. The Si concentrations in table 3-8 are very similar to those obtained in experiments where quartz was known to be present (e.g. tables 3-12, 3-15, 3-16, 3-17 and 4-2).

Figures 3-6 to 3-9 can be overlaid in order to compare the different sets of data.

The trends in the plots of $\ln m_X$ vs. $\ln V_{H_2O}$ are much more regular than the trends in the molar ratio diagrams. Taking ratios leads to a compounding of errors. This is very clearly seen in the 600°C albite dissolution data, for which there is good evidence that Currie's 1968 Al analyses are too low (compare figures 3-1, 3-2 and 3-10).

There are relatively few results for Ne-Ab and leucite dissolution. They are of the same order of magnitude as the albite and microcline results. The data for labradorite show wide scatter. The reasons for the scatter are not known, but may be linked to the complex microstructures found in plagioclase solid solutions.

The Qtz-Fsp dissolution data (tables 3-15 and 3-16) give Si concentrations very similar to those obtained with quartz dissolution (table 4-2). Na, K and Al concentrations are lower than in feldspar dissolution experiments.

The data in table 3-14 (dissolution of a mixture of Amelia

albize and Buckingham microcline) are very similar to the results in table 3-6 (Buckingham microcline dissolution).

Plots of $\ln m_X$ vs. $1/T$ at constant pressure are curvilinear and are not presented here. There is some indication (see Appendix E) that with V_{H_2O} held constant, plots of $\ln m_X$ vs. $1/T$ may be linear, but the data were not collected at constant V_{H_2O} .

Experimental "reversals", where the equilibrium composition was approached from a P-T condition with a more concentrated equilibrium composition, can be identified in tables 3-7, 3-9 and 3-10. These are the only sets of experiments for which "reversal" data are available. Within each of these tables, the run numbers increase in the order in which the experiments were performed. The data are too limited to permit detailed interpretation, but some of the clearer examples may be mentioned:

- a) in table 3-7, collection of AM9 following collection of AM8
- b) in table 3-9, collection of AC74 following collection of AC73
 in table 3-9, collection of AC76 following collection of AC75
 " " " " " AC80 " " " AC79
- c) in table 3-10, collection of AC42 following collection of AC41
 " " " " " AC45 " " " AC44

The above experiments are highlighted in table 4-1 (page 118).

Table 3-1 Details of starting material used in tables 3-3 to 3-17

Experimental results listed in table:	Number of assumed equilibrium results	Starting material	Source of starting material
3-3	54	Ab	Amelia albite (Amelia County, Court House, Virginia; obtained via Wards). See Harlow and Brown (1980) for details on its structure.
3-4	61	Ab	Amelia albite (separate batch from that used for table 3-3)
3-5	2	Ab	Same as for table 3-4
3-6	59	Mc	Perthitic microcline. Obtained from Buckingham, Quebec (de Schmid, 1916, p31-32; Spence, 1932, p65-70)
3-7	9	Mc	Same as for table 3-6
3-8	12	Mc	Perthitic microcline. Obtained from Richardson Mine, Ontario (de Schmid, 1916, p12-14; Spence, 1932, p38)
3-9	13	Ab-Nc	Intergrown Ab and Nc. Obtained from Bancroft, Ontario, via Wards
3-10	14	Lct	Euhedral crystals. Obtained from Ariccia, Rome, Italy, via

				Wards
3-11	0	Lct	Same as for table 3-10	
3-12	4	Qtz	Obtained from Black Rapids, Ontario (Harrison and Fortier, 1944)	
3-13	0	Lab	Obtained from G.S.C. stocks	
3-14	18	Ab-Mc	Ab:Mc ratio of 1:1 (weight %) Same as for tables 3-4 and 3-6	
3-15	32	Qtz-Ab-Mc	Qtz:Ab:Mc ratio of 1:1:1 (weight %). Same as for tables 3-4, 3-6 and 3-12.	
3-16	8	Qtz-Ab-Mc	Same as for table 3-15	
3-17	0	Qtz-Lab-Mc	Qtz:Lab:Mc ratio of 1:1:1 (weight %). Same as for tables 3-6, 3-12 and 3-13.	

286 total number of assumed equilibrium runs

Note - Wards Natural Science Establishment, Inc.,
Rochester, New York, U.S.A.

Table 3-2 Chemical analyses of starting material

(1) Weight %

	Albite table 3-3	Albite tables 3-4 to 3-17	Buckingham microcline	Richardson microcline	Albite- Nepheline	Leucite	Labradorite
SiO ₂	68.0	61.3	61.7	68.6	55.8	55.8	54.60
TiO ₂	n.d.	0.04	0.02	0.01	0.01	0.05	0.01
Al ₂ O ₃	19.8	24.2	20.1	16.7	26.1	22.6	27.92
Fe ₂ O ₃	0.09	n.d.	n.d.	0.1	0.0	0.5	0.28
FeO	n.d.	n.d.	n.d.	0.0	0.1	0.0	0.57
MnO	n.d.	n.d.	n.d.	0.01	0.00	0.01	0.01
MgO	0.04	1.1	n.d.	0.11	0.00	0.01	0.48
CaO	0.22	0.4	0.1	0.20	0.94	0.24	9.16
Na ₂ O	11.42	10.78	2.43	1.7	13.0	0.5	4.60
K ₂ O	0.32	0.19	12.90	11.2	3.03	18.47	0.98
H ₂ O	0.03	n.d.	n.d.	0.2	1.2	1.9	0.5
Total	99.9	98.0	97.25	99.0	100.2	100.2	101.1

n.d. not determined

(2) Mole % (normalised to 24 O)

TiO₂ grouped with SiO₂

Fe₂O₃ grouped with Al₂O₃

FeO, MnO, MgO grouped with CaO

H₂O neglected

	Albite table 3-3	Albite tables 3-4 to 3-17	Buckingham microcline	Richardson microcline	Albite- Nepheline	Leucite	Labradorite
Si	8.933	8.265	8.730	9.354	7.724	8.134	7.509
Al	3.076	3.845	3.352	2.694	4.259	3.936	4.556
Ca	0.039	0.279	0.015	0.052	0.151	0.040	1.449
Na	2.908	2.816	0.666	0.449	3.488	0.142	1.226
K	0.054	0.032	2.327	1.948	0.536	3.433	0.172
							An54.17

Table 3-3 Albite solubility experiments (Currie, 1968)

54 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
PA14	400.0	.75	172.5	47.6	79.0	.3
PA15	400.0	1.00	229.0	67.2	89.0	.5
PA16	400.0	1.25	304.3	84.7	112.0	.7
PA17	400.0	1.50	363.6	97.9	140.0	1.1
PA18	400.0	1.75	411.3	113.8	152.0	1.5
PA19	400.0	2.00	475.3	121.7	170.0	1.6
PA26	400.0	2.50	571.6	147.6	218.0	2.0
PA27	400.0	3.00	657.6	160.9	231.0	2.2
PA28	400.0	3.50	843.7	171.5	280.0	3.1
PA20	450.0	.75	175.3	54.5	62.0	.5
PA21	450.0	1.00	267.4	82.0	94.0	.8
PA22	450.0	1.25	363.6	109.5	125.0	1.2
PA23	450.0	1.50	441.7	135.5	150.0	1.5
PA24	450.0	1.75	530.5	159.3	177.0	1.7
PA25	450.0	2.00	607.6	173.6	200.0	1.8
PA29	450.0	2.50	755.8	232.8	241.0	2.4
PA30	450.0	3.00	919.4	272.5	290.0	2.6
PA31	450.0	3.50	1140.5	320.7	346.0	2.9
PA32	500.0	.75	144.9	28.0	33.0	1.0
PA33	500.0	1.00	268.3	66.7	76.0	1.2
PA34	500.0	1.25	383.7	111.1	111.0	1.7
PA38	500.0	1.50	518.8	137.1	157.0	1.8
PA39	500.0	1.75	588.9	165.6	189.0	3.8
PA40	500.0	2.00	750.2	210.1	230.0	6.5
PA54	500.0	2.75	1118.5	288.4	325.0	6.9
PA55	500.0	3.00	1191.9	317.5	346.0	7.3
PA56	500.0	3.50	1496.1	390.5	545.0	7.6
PA43	550.0	.75	127.1	14.3	23.0	1.8
PA44	550.0	1.00	236.0	46.0	67.0	2.2
PA45	550.0	1.25	371.6	84.7	102.0	2.6
PA46	550.0	1.50	537.5	128.6	148.0	2.9
PA47	550.0	1.75	655.8	164.1	178.0	3.7
PA48	550.0	2.00	822.6	217.0	214.0	4.2
PA49	550.0	2.25	972.2	253.5	263.0	4.9

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
PA50	550.0	2.50	1128.8	281.5	310.0	5.1
PA51	550.0	2.75	1304.0	310.6	355.0	5.3
PA58	600.0	.75	136.0	5.8	15.0	3.4
PA42	600.0	1.00	257.1	19.1	40.0	3.6
PA59	600.0	1.25	386.5	45.0	77.0	4.1
PA69	600.0	1.50	532.8	84.1	134.0	5.0
PA61	600.0	1.75	743.2	114.8	165.0	5.3
PA62	600.0	2.00	965.2	148.7	230.0	5.3
PA63	600.0	2.25	1122.2	188.9	286.0	5.9
PA64	600.0	2.50	1290.0	211.7	319.0	6.6
PA70	500.0	2.00	720.3	221.2	215.0	4.8
PA71	500.0	2.00	724.5	214.9	231.0	5.1
PA72	500.0	2.00	731.5	218.0	216.0	6.1
PA73	500.0	2.00	727.7	211.2	233.0	5.3
PA41	600.0	1.00	242.1	19.6	36.0	2.9
PA66	400.0	1.00	224.8	65.6	89.0	.6
PA67	400.0	1.50	339.8	96.8	124.0	1.0
PA68	400.0	2.00	464.1	114.3	161.0	1.4
M+H	500.0	1.00	254.3	71.4	88.0	.0
M+H	500.0	2.00	743.6	230.7	221.0	.0

Disequilibrium results

PA35	500.0	1.50	1318.1	49.2	51.0	.0
PA36	500.0	1.50	970.3	74.6	83.0	.8
PA37	600.0	2.00	1979.9	51.3	99.0	1.1
PA52	500.0	2.25	1872.9	79.9	149.0	1.4
PA53	500.0	2.50	3225.1	14.3	17.0	.0
PA57	600.0	.75	218.3	9.0	13.0	.0
PA60	500.0	1.50	732.4	98.4	137.0	1.5
PA62	600.0	2.00	2185.1	104.3	176.0	3.6
PA65	600.0	2.00	1204.0	132.8	209.0	5.3
PA69	400.0	2.50	939.9	121.2	190.0	.0

Table 3-4 Albite solubility experiments (Currie, unpublished)

61 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
A1	400.0	1.00	257.0	68.0	65.5	1.7
A55	400.0	1.00	291.0	70.0	80.4	3.1
PP19B	400.0	1.00	258.0	78.3	65.7	1.2
PP19C	400.0	1.00	285.0	79.4	76.3	1.9
PP41A	400.0	1.00	262.0	78.0	87.0	1.6
PP19D	400.0	1.25	333.0	90.4	89.3	1.4
PP41B	400.0	1.25	349.0	96.0	97.0	1.9
A5	400.0	1.50	419.0	109.0	114.0	1.3
A6	400.0	1.50	381.0	106.6	100.0	1.4
PP41C	400.0	1.50	399.0	108.0	107.0	2.2
A61	400.0	1.50	395.0	102.0	105.0	2.5
A7	400.0	1.75	490.0	129.0	124.0	2.1
A8	400.0	1.75	442.0	117.0	125.0	2.0
A54	400.0	2.00	542.0	138.0	141.0	2.1
PP19E	400.0	2.00	538.0	118.0	127.0	2.3
PP41D	400.0	2.00	584.0	138.0	134.0	2.6
PP19G	400.0	2.50	560.0	148.0	132.5	4.1
A56	450.0	0.50	197.0	38.0	56.2	4.5
A57	450.0	0.50	153.0	14.0	23.5	2.1
A11	450.0	1.00	247.0	106.0	95.0	5.0
PP19J	450.0	1.00	294.0	82.1	71.0	3.5
PP41E	450.0	1.00	270.0	71.0	69.0	1.3
PP19K	450.0	1.25	336.0	94.5	93.5	1.8
A15	450.0	1.50	318.0	148.0	95.0	6.0
A22	500.0	1.00	273.0	71.0	66.0	1.4
PP20A	500.0	1.00	267.0	76.0	71.2	2.3
PP20B	500.0	1.00	237.0	71.4	59.5	1.2
A59	500.0	1.00	261.0	61.0	65.0	1.7
PP42A	500.0	1.00	268.0	71.0	66.0	1.3
PP20C	500.0	1.25	299.0	77.0	74.2	1.7
PP22A	500.0	1.25	309.0	77.2	80.9	2.2
PP22B	500.0	1.50	528.0	106.0	95.0	5.0

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
A27	500.0	1.75	635.0	111.0	96.0	11.0
A28	500.0	1.75	682.0	148.0	95.0	6.0
PP20E	500.0	1.75	589.0	172.0	150.0	2.6
PP42B	500.0	1.75	629.0	180.0	160.0	3.7
PP20F	500.0	2.00	771.0	189.0	182.0	6.5
PP20G	500.0	2.00	720.0	173.0	170.0	4.3
PP42C	500.0	2.00	805.0	197.0	198.0	4.5
PP20J	500.0	2.00	836.0	205.0	215.0	2.6
PP20L	500.0	2.25	799.0	233.0	204.0	3.3
PP20O	550.0	1.00	225.0	75.0	68.5	2.9
PP20R	550.0	1.75	631.0	180.0	160.0	4.9
PP20S	550.0	1.75	841.0	246.0	223.0	5.6
PP20T	550.0	2.00	823.0	236.0	204.0	3.7
PP42D	550.0	2.00	830.0	241.0	214.0	4.8
PP20U	550.0	2.25	965.0	276.0	236.0	5.0
PP21A	600.0	0.50	78.5	1.5	1.5	0.2
A62	600.0	0.75	201.5	25.5	29.0	0.7
A41	600.0	1.00	250.0	19.5	20.0	0.6
A42	600.0	1.00	223.0	27.0	27.0	1.5
PP21E	600.0	1.00	223.0	46.3	33.3	1.3
PP43A	600.0	1.00	228.0	28.0	25.0	1.3
PP43B	600.0	1.25	315.0	102.0	81.0	2.0
PP43C	600.0	1.50	490.0	159.0	148.0	4.0
PP21N	600.0	1.65	624.0	193.0	143.0	2.7
A47	600.0	1.75	842.0	245.0	223.0	5.6
PP43D	600.0	1.75	652.0	237.0	218.0	4.0
PP21K	600.0	2.00	1020.0	248.0	250.0	5.3
PP21M	600.0	2.00	953.0	231.0	245.0	4.0
PP43E	600.0	2.00	1019.0	295.0	270.0	5.3

Disequilibrium results

PP19A	400.0	1.00	110.0	29.6	28.5	0.9
PP19F	400.0	2.00	472.0	119.4	116.0	3.2
A13	450.0	1.25	291.0	111.0	96.0	11.0
PP19L	450.0	1.75	316.0	78.0	75.8	2.3
PP20H	500.0	2.00	1398.0	81.0	73.0	4.5
PP20I	500.0	2.00	421.0	114.0	111.0	2.0

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
PP20M	500.0	2.40	1161.0	289.0	310.0	
PP21F	600.0	1.00	315.0	88.0	80.6	2.0
PP21G	600.0	1.25	467.0	141.0	128.0	3.0
PP21J	600.0	1.50	654.0	238.0	218.0	4.9

Table 3-5 Albite solubility experiments (Adcock, unpublished)

2 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	VC	RoC	ET
C3	500.0	1.00	223.0	30.0	32.0	10.3	104	16	*
C5	500.0	2.00	835.0	220.0	201.0	12.3	193	29	*

VC volume collected (ml)

RoC rate of collection (ml h⁻¹)

ET equilibration time (h)

* denotes first run of a series; taken to P-T and left
15-20 hours before collection began

Table 3-6 Microcline solubility experiments (Currie, unpublished)

59 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
PP26A	400.0	0.75	151.0	23.0	19.1	16.1
M1	400.0	1.00	278.0	66.0	44.8	36.2
M2	400.0	1.00	364.0	61.0	49.2	34.0
PP23A	400.0	1.00	282.0	71.0	47.1	43.8
PP23B	400.0	1.00	332.0	24.0	13.6	16.8
PP23C	400.0	1.00	241.0	31.0	19.5	17.8
M3	400.0	1.25	319.0	78.0	60.4	47.3
M4	400.0	1.25	349.0	75.0	65.3	43.2
PP26D	400.0	1.25	320.0	74.4	47.8	47.9
PP26E	400.0	1.25	324.0	80.0	47.4	49.5
PP25D	400.0	1.25	322.0	74.0	46.2	46.4
PP25E	400.0	1.25	314.0	71.0	46.4	49.8
M5	400.0	1.50	409.0	93.0	64.6	55.8
PP23D	400.0	1.50	401.0	107.0	63.6	72.1
PP26F	400.0	1.50	393.0	62.0	61.8	38.9
M7	400.0	1.75	480.0	105.0	77.9	59.4
PP26G	400.0	1.75	496.0	70.0	50.4	33.8
M10	400.0	2.00	574.0	109.0	94.9	70.1
PP26H	400.0	2.00	557.0	152.0	88.7	110.0
PP26J	400.0	2.50	737.0	185.0	109.0	155.0
M11	450.0	1.00	299.0	69.0	54.3	51.0
PP23E	450.0	1.00	307.0	68.0	45.8	43.2
M13	450.0	1.25	400.0	103.0	98.6	73.1
M14	450.0	1.25	390.0	92.0	64.2	54.0
M16	450.0	1.50	505.0	119.0	82.4	80.2
PP23F	450.0	1.50	463.0	107.0	64.2	75.0
PP23G	450.0	1.50	472.0	112.0	78.6	60.0
M18	450.0	1.75	553.0	145.0	103.0	92.0
PP23H	450.0	1.75	556.0	137.0	77.4	88.6
PP23I	450.0	1.75	558.0	131.0	93.5	62.5
M20	450.0	2.00	598.0	154.0	127.0	193.0
PP23J	450.0	2.00	664.0	163.0	85.7	140.0
M21	500.0	1.00	243.0	63.8	28.6	54.8
M22	500.0	1.00	396.0	40.0	35.2	27.1

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
M24	500.0	1.25	422.0	100.0	107.0	63.3
PP24A	500.0	1.25	365.0	94.0	40.9	80.6
PP24B	500.0	1.50	463.0	116.0	54.0	106.0
M26	500.0	1.50	515.0	130.0	88.1	91.0
M27	500.0	1.75	680.0	162.0	113.0	111.0
M28	500.0	1.75	656.0	146.0	105.0	66.0
PP24C	500.0	2.00	825.0	202.0	139.0	133.0
M31	550.0	1.00	243.0	57.0	34.9	36.1
M32	550.0	1.00	241.0	31.0	19.5	17.8
M33	550.0	1.25	359.0	86.0	57.8	64.7
M34	550.0	1.25	401.0	107.0	63.6	72.1
M35	550.0	1.50	535.0	141.0	83.2	99.6
M36	550.0	1.50	557.0	152.0	88.7	110.0
M37	550.0	1.75	689.0	181.0	113.0	134.0
M38	550.0	1.75	737.0	185.0	109.0	155.0
PP24E	550.0	2.00	773.0	204.0	93.0	205.0
PP25A	600.0	1.00	278.0	66.0	44.8	36.2
M43	600.0	1.25	353.0	82.0	51.1	46.3
M44	600.0	1.25	312.0	84.0	49.1	45.8
M45	600.0	1.50	516.0	133.0	83.2	83.0
PP25B	600.0	1.50	574.0	109.0	94.9	70.1
M47	600.0	1.75	731.0	188.0	119.0	125.0
PP25C	600.0	1.75	699.0	169.0	114.2	120.0
M49	600.0	2.00	791.0	205.0	122.0	149.0
M50	600.0	2.00	1092.0	273.0	176.0	180.0

Disequilibrium results

PP26B	400.0	1.00	443.0	37.0	32.5	19.4
PP26C	400.0	1.25	250.0	52.0	35.9	26.7
M9	400.0	2.00	217.0	57.0	22.3	53.9
PP26I	400.0	2.00	518.0	81.0	70.5	46.6
PP26K	450.0	1.00	272.0	39.3	26.7	19.2
PP26L	450.0	1.25	521.0	40.7	30.3	17.3
PP26M	450.0	1.50	558.0	46.3	33.5	19.6
PP26N	450.0	1.75	744.0	60.3	36.8	17.5
PP26O	450.0	2.00	648.0	36.2	40.4	28.6
PP26P	450.0	2.00	836.0	39.0	44.7	19.3

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
M41	600.0	1.00	388.0	13.0	21.1	22.3

Table 3-7 Buckingham Mc solubility experiments (Adcock, unpublished)

9 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	VC	RoC	ET
AM1	400.0	1.00	580.0	19.0	46.0	39.0	140	25	*
AM2	400.0	1.00	550.0	36.0	33.0	28.0	120	27	65
AM5	400.0	1.00	300.0	83.0	77.0	50.0	120	30	94
AM3	500.0	1.00	340.0	29.0	29.0	22.0	120	30	43
AM4	600.0	1.00	250.0	11.0	17.0	16.0	120	34	117
AM9	600.0	1.00	340.0	24.0	17.0	24.0	115	23	45
AM6	400.0	2.00	740.0	136.0	117.0	97.0	135	34	114
AM7	500.0	2.00	880.0	195.0	158.0	138.0	100	24	44
AM8	600.0	2.00	1070.0	251.0	182.0	178.0	120	37	69

VC volume collected (ml)

RoC rate of collection (ml h⁻¹)

ET equilibration time (h)

* denotes first run of a series; taken to P-T and left 15-20 hours before collection began

Table 3-8 Richardson Mc solubility experiments (Adcock, unpublished)

12 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	VC	RoC	ET
AM11	400.0	1.00	900.0	7.2	38.5	33.4	60	13	*
AM12	400.0	1.00	905.0	12.3	18.1	15.8	60	17	140
AM15	500.0	1.00	1160.0	5.2	5.6	6.8	56	10	21
AM16	500.0	1.00	1170.0	5.1	4.3	4.8	63	12	18
AM17	500.0	1.00	1240.0	5.3	4.7	5.0	62	11	19
AM18	500.0	1.00	1190.0	5.1	4.3	4.8	55	12	19
AM20	600.0	1.00	1405.0	1.7	1.2	2.1	62	12	22
AM21	600.0	1.00	1425.0	1.8	1.2	1.6	62	10	67
AM22	600.0	1.00	1365.0	1.6	0.9	1.0	65	15	21
AM23	600.0	1.00	1315.0	1.5	0.9	1.0	64	13	20
AM24	600.0	1.00	1330.0	1.7	0.9	0.9	64	12	19
AM25	600.0	1.00	1350.0	1.7	0.8	1.0	65	16	19

Disequilibrium results

AM14	500.0	1.00	1140.0	3.4	35.7	38.2	62	22	*
AM19	600.0	1.00	1360.0	1.9	24.0	30.1	64	27	*

VC volume collected (ml)
 RoC rate of collection (ml h⁻¹)
 ET equilibration time (h)

* denotes first run of a series; taken to P-T and left
 15-20 hours before collection began

Table 3-9 Ab-Ne solubility experiments (Adcock, MSc thesis)

13 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	VC	RoC	ET
AC69	400.0	1.00	237.0	183.0	157.0	81.0	135	180	0
AC70	400.0	1.00	233.0	196.0	188.0	68.0	135	201	2
AC78	400.0	1.00	268.0	203.0	163.0	64.0	135	31	18
AC79	400.0	1.00	281.0	218.0	190.0	66.0	135	31	68
AC72	500.0	1.00	272.0	64.0	62.0	35.0	45	19	0
AC73	500.0	1.00	244.0	58.0	61.0	36.0	135	26	17
AC76	500.0	1.00	268.0	61.0	42.0	34.0	135	26	19
AC77	500.0	1.00	255.0	62.0	43.0	32.0	135	23	18
AC74	600.0	1.00	338.0	17.0	44.0	36.0	135	28	67
AC75	600.0	1.00	345.0	19.0	18.0	18.0	135	26	19
AC80	600.0	1.00	352.0	22.0	40.0	17.0	135	23	20
AC81	600.0	1.00	345.0	17.0	22.0	11.0	135	23	18
AC82	600.0	1.00	347.0	16.0	18.0	12.0	135	20	19

Disequilibrium results

AC67	400.0	1.00	192.0	179.0	360.0	219.0	135	28	*
AC68	400.0	1.00	237.0	207.0	230.0	205.0	135	147	19
AC71	500.0	1.00	224.0	47.0	122.0	54.0	135	32	20

VC volume collected (ml)
 RoC rate of collection (ml h⁻¹)
 ET equilibration time (h)

* denotes first run of a series; taken to P-T and left 15-20 hours before collection began

Table 3-10 Leucite solubility experiments (Adcock, MSc thesis)

14 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	VC	RoC	ET
AC38	400.0	1.00	267.0	240.0	186.0	317.0	140	22	18
AC45	400.0	1.00	231.0	240.0	143.0	437.0	135	21	18
AC48	400.0	1.00	243.0	235.0	112.0	454.0	130	26	*
AC39	500.0	1.00	191.0	142.0	79.0	146.0	135	19	66
AC42	500.0	1.00	192.0	133.0	60.0	161.0	135	20	18
AC40	600.0	1.00	196.0	24.0	18.0	41.0	135	19	17
AC44	400.0	2.00	500.0	506.0	320.0	999.0	135	25	66
AC46	400.0	2.00	432.0	388.0	229.0	848.0	130	29	18
AC49	400.0	2.00	483.0	426.0	171.0	970.0	130	24	19
AC43	500.0	2.00	543.0	715.0	314.0	946.0	135	22	17
AC47	500.0	2.00	523.0	634.0	213.0	999.0	100	25	20
AC51	500.0	2.00	565.0	540.0	122.0	921.0	130	32	18
AC52	500.0	2.00	553.0	587.0	122.0	1052.0	90	32	67
AC41	600.0	2.00	623.0	557.0	213.0	659.0	140	24	17

Disequilibrium results

AC37	400.0	1.00	285.0	144.0	173.0	269.0	135	22	*
AC50	500.0	1.00	141.0	98.0	27.0	164.0	130	32	21

VC volume collected (ml)
 RoC rate of collection (ml h⁻¹)
 ET equilibration time (h)

* denotes first run of a series; taken to P-T and left 15-20 hours before collection began

Table 3-11 Leucite solubility experiments (Adcock, unpublished)

Disequilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	VC	RoC	ET
LL1	500.0	1.00	201.0	43.0	10.0	83.0	65	14	*
LL2	500.0	1.00	170.0	64.0	6.6	120.0	65	11	140
LL3	500.0	1.00	133.0	50.0	2.3	88.0	65	10	18

Note - these data were obtained from experiments using small amounts of leucite loosely wrapped in gold foil (see Chapter 2 for details)

VC volume collected (ml)
 RoC rate of collection (ml h⁻¹)
 ET equilibration time (h)

* denotes first run of a series; taken to P-T and left 15-20 hours before collection began

Table 3-12 Quartz solubility experiments (Adcock, unpublished)

4 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	VC	RoC	ET
Q1	400.0	1.00	910.0	135	54	*
Q2	400.0	1.00	980.0	140	37	47
Q3	400.0	1.00	910.0	135	85	66
Q4	400.0	1.00	950.0	50	67	0

VC volume collected (ml)

RoC rate of collection (ml h⁻¹)

ET equilibration time (h)

* denotes first run of a series; taken to P-T and left
15-20 hours before collection began

Table 3-13 Labradorite solubility experiments (Currie, unpublished)

68 results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	Ca (ppm)
P1A	400.0	1.00	192.0	16.3	23.5		0.8
P1	400.0	1.00	397.0	11.5	47.9		0.0
P2	400.0	1.00	484.0	3.9	19.8		1.6
PR1	400.0	1.00	830.0	28.0	61.8		5.4
P3	400.0	1.25	457.0	44.8	43.8		0.8
P4	400.0	1.25	283.0	38.7	56.1		0.0
PR2	400.0	1.25	765.0	98.0	77.8		1.1
P5A	400.0	1.50	361.0	58.2	84.8		2.2
P5	400.0	1.50	297.0	22.0	49.3		0.0
P6	400.0	1.50	479.0	93.0	73.1		0.6
PR3	400.0	1.50	900.0	120.0	113.4		1.1
PP27A	400.0	1.50	149.0	3.0	1.8		1.1
P7	400.0	1.75	481.0	99.0	104.0		0.4
P8	400.0	1.75	713.0	84.8	97.7		1.3
PR4	400.0	1.75	1080.0	132.0	138.4		1.6
P9A	400.0	2.00	1083.0	85.9	155.0		3.1
PP27B	400.0	2.00	238.0	24.0	45.3		1.5
P10	400.0	2.00	560.0	128.0	128.0		0.6
PR5	400.0	2.00	1060.0	180.0	144.6		0.8
P11	450.0	1.00	435.0	27.5	25.7		0.6
PR6	450.0	1.00	1040.0	6.0	36.0		1.5
P13	450.0	1.25	491.0	65.0	51.7		0.3
PR7	450.0	1.25	1870.0	25.0	62.0		1.3
P15	450.0	1.50	496.0	91.0	78.6		0.2
PR8	450.0	1.50	2500.0	100.0	92.0		1.3
P17	450.0	1.75	538.0	142.0	110.0		0.0
PR9	450.0	1.75	2200.0	205.0	128.0		2.7
P19	450.0	2.00	605.0	164.0	135.0		0.1
PR10	450.0	2.00	1830.0	248.0	152.0		1.0
P21	500.0	1.00	390.0	72.0	47.9		0.3
P22A	500.0	1.00	1386.0	71.1	119.0		2.4
P22	500.0	1.00	899.0	9.7	16.8		1.9
P22B	500.0	1.00	183.0	48.6	39.5		1.7
PR11	500.0	1.00	2460.0	29.0	21.6		2.3

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	Ca (ppm)
P23	500.0	1.25	431.0	94.0	76.8		0.6
23	500.0	1.25	852.0	101.0	109.0		2.4
PR12	500.0	1.25	2620.0	111.0	65.0		5.8
P25	500.0	1.50	498.0	130.0	92.6		0.0
P26	500.0	1.50	489.0	113.0	96.2		0.1
PR13	500.0	1.50	2300.0	181.0	111.0		3.0
P27	500.0	1.75	531.0	141.0	98.1		0.0
P28	500.0	1.75	911.0	132.0	126.0		1.2
PR14	500.0	1.75	2800.0	263.0	145.0		2.2
P29	500.0	2.00	620.0	144.0	140.0		0.6
P30	500.0	2.00	1375.0	161.0	176.0		2.6
PR15	500.0	2.00	2560.0	356.0	183.0		0.9
P31	550.0	1.00	651.0	34.2	44.8		0.6
P33	550.0	1.25	890.0	87.0	107.0		0.5
P35	550.0	1.50	1516.0	145.0	178.0		3.1
P37	550.0	1.75	947.0	156.0	150.0		1.8
P39	550.0	2.00	1067.0	170.0	185.0		3.0
P41	600.0	1.00	313.0	63.0	51.0	15.0	
P43	600.0	1.25	388.0	89.0	75.0	21.0	
P45	600.0	1.50	519.0	122.0	97.0	30.0	
P47	600.0	1.75	593.0	158.0	116.0	37.0	
P49	600.0	2.00	902.0	184.0	144.0	71.0	
PP36A	500.0	1.00	486.0	34.0	37.0	28.0	1.1
PP36B	500.0	1.25	495.0	71.0	64.0	42.0	2.3
PP36C	500.0	1.50	505.0	100.0	88.0	56.0	0.1
PP36D	500.0	1.75	552.0	126.0	106.0	66.0	0.5
PP36F	510.0	2.00	715.0	158.0	139.0	83.0	0.9
PP36G	550.0	1.00	416.0	18.0	29.0	36.0	2.1
PP36H	550.0	1.00	430.0	5.0	6.0	12.0	0.6
PP36I	550.0	1.25	486.0	25.0	22.0	18.0	0.1
PP36J	550.0	1.25	411.0	53.0	53.0	35.0	0.0
PP36K	550.0	1.50	533.0	114.0	95.0	65.0	0.0
PP36L	550.0	1.75	612.0	148.0	114.0	80.0	0.0
PP36M	550.0	2.00	790.0	192.0	153.0	103.0	0.0

Note - the data are highly variable;
no attempt is made to separate equilibrium from
disequilibrium results.

Table 3-14 Ab-Mc solubility experiments (Currie, unpublished)

18 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
F1	400.0	1.00	338.0	62.0	48.0	36.0
F2	400.0	1.00	354.0	47.0	30.0	24.0
F3	400.0	1.25	382.0	76.0	64.0	37.0
F5	400.0	1.50	409.0	86.0	77.0	42.0
F7	400.0	1.75	447.0	93.0	89.0	44.0
F11	450.0	1.00	417.0	61.0	38.0	37.0
F12	450.0	1.00	438.0	89.0	66.4	44.0
F13	450.0	1.25	395.0	80.0	74.0	46.0
PP33B	450.0	1.25	509.0	111.0	84.5	51.0
F15	450.0	1.50	418.0	92.0	80.0	55.0
F16	450.0	1.50	538.0	128.0	100.0	57.0
F17	450.0	1.75	492.0	110.0	98.0	61.0
F18	450.0	1.75	593.0	137.0	114.0	62.0
F19	450.0	2.00	535.0	125.0	113.0	65.0
PP34A	500.0	1.25	509.0	62.0	48.0	37.0
PP34B	500.0	1.50	523.0	111.0	76.0	57.0
PP34C	500.0	1.75	668.0	163.0	106.0	87.0
PP34D	500.0	2.00	818.0	199.0	134.0	110.0

Disequilibrium results

PP33A	400.0	1.00	707.0	37.0	31.0	24.0
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Table 3-15 Qtz-Ab-Mc solubility experiments (Currie, unpublished)

32 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
G1	400.0	1.00	752.0	31.0	25.0	19.0
G2	400.0	1.00	521.0	40.7	30.3	17.3
G3	400.0	1.25	832.0	47.0	31.0	25.0
G4	400.0	1.25	558.0	46.3	33.5	19.6
PP31B	400.0	1.25	787.0	22.3	30.1	22.1
PP31C	400.0	1.25	793.0	53.0	47.8	27.0
G5	400.0	1.50	1009.0	47.0	38.0	26.0
G6	400.0	1.50	744.0	60.3	36.8	17.5
PP31D	400.0	1.50	956.0	43.0	32.9	21.1
PP31E	400.0	1.75	984.0	53.0	41.9	27.0
PP31F	400.0	1.75	1093.0	51.0	37.9	23.1
PP31G	400.0	2.00	1004.0	68.0	45.4	31.4
G11	450.0	1.00	384.0	36.2	18.9	19.8
PP31H	450.0	1.00	956.0	16.0	14.3	13.4
G13	450.0	1.25	787.0	22.3	30.1	22.1
PP31I	450.0	1.25	1092.0	26.5	16.3	13.8
G15	450.0	1.50	956.0	53.0	41.9	27.0
PP31K	450.0	1.50	1248.0	41.0	25.2	18.5
G17	450.0	1.75	1093.0	51.0	37.9	23.1
PP31L	450.0	1.75	1319.0	52.0	33.3	25.8
PP31M	450.0	2.00	1568.0	77.0	51.0	36.9
G21	500.0	1.00	1098.0	24.0	16.3	13.8
G22	500.0	1.00	956.0	16.0	14.3	13.4
G23	500.0	1.25	1248.0	41.0	25.2	18.5
G25	500.0	1.50	1319.0	52.0	33.0	25.8
G27	500.0	1.75	1568.0	77.0	51.0	36.9
G29	500.0	2.00	1587.0	117.0	59.0	40.0
PP32A	500.0	2.00	1589.0	62.0	44.0	33.0
G31	550.0	1.00	1452.0	18.0	16.0	13.0
G33	550.0	1.25	1800.0	32.0	18.0	16.0
G35	550.0	1.50	2159.0	55.0	30.0	28.0
G41	600.0	1.00	1717.0	8.5	7.0	9.0

Disequilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
PP31A	400.0	1.00	384.0	36.2	18.9	14.8
G7	400.0	1.75	742.0	37.6	42.5	23.9
G9	400.0	2.00	793.0	53.0	47.8	27.0

Table 3-16 Qtz-Ab-Mc solubility experiments (Currie, unpublished)

8 equilibrium results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
KG9	500.0	1.25	1110.0	6.0	8.0	5.0
KG1	500.0	1.50	1666.0	20.0	25.0	27.0
KG2	500.0	1.50	1814.0	32.0	21.0	18.0
KG3	500.0	2.00	2668.0	65.0	47.0	31.0
KG10	500.0	2.00	2600.0	64.0	44.0	37.0
KG11	600.0	1.00	1540.0	3.0	7.0	4.0
KG12	600.0	1.25	1990.0	3.0	4.0	3.0
KG13	600.0	1.50	2800.0	12.0	7.0	7.0

Table 3-17 Qtz-Lab-Mc solubility experiments (Currie, unpublished)

5 results

Run no.	T (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	Ca (ppm)
PP39A	400.0	1.00	603.0	13.0	36.0	39.0	0.7
PP39B	400.0	1.25	668.0	20.0	26.0	22.0	0.0
PP39C	400.0	1.50	738.0	26.0	31.0	17.0	0.0
PP39D	400.0	1.75	729.0	30.0	37.0	19.0	0.0
PP39F	400.0	2.00	832.0	33.0	42.0	17.0	0.0

Note - because of the difficulties apparent in table 3-13 with regard to labradorite solubility, the results presented here are of limited value.

Table 3-18 Albite solubility experiments (Davis, 1972)

30 results

Run no.	T. (°C)	P (kbar)	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)	Ca (ppm)
40N	498.0	2.00	817.1	224.9	216.3	12.8	6.9
44N	499.0	5.58	2343.8	571.1	641.9	40.9	22.6
25N	502.0	5.95	3244.8	747.2	844.4	19.0	17.0
38N	502.0	6.69	3790.6	818.0	957.3	39.3	11.8
46N	602.0	2.04	1043.2	291.8	281.3	20.2	9.4
37N	603.0	3.00	1863.5	515.2	488.8	16.0	15.8
58S	598.0	3.00	2094.2	609.1	560.0	17.6	15.6
53S	600.0	4.00	3279.5	869.9	832.0	2.4	26.0
57S	600.0	4.00	3293.3	948.0	875.6	12.5	26.6
35N	599.0	4.10	3193.1	813.5	829.8	44.4	13.7
18N	599.0	4.95	4104.6	1086.7	1016.9	20.4	21.0
19N	598.0	4.98	4146.8	1063.6	1054.5	25.7	17.7
22N	608.0	5.88	5357.1	1366.6	1380.2	55.8	27.5
52S	600.0	5.57	5479.6	1565.7	1519.9	20.9	45.7
17N	609.0	5.90	5717.1	1486.6	1508.6	35.6	30.7
55S	600.0	6.02	5592.9	1565.5	1545.4	.0	36.6
14N	601.0	6.14	5980.3	1515.1	1555.6	41.5	39.6
49N	600.0	6.74	6624.5	1720.4	1779.3	26.5	47.0
47N	600.0	7.27	7537.1	1859.3	1896.9	64.9	54.3
50S	598.0	7.55	8566.9	2198.0	2357.4	38.5	29.4
9N	600.0	7.58	8067.7	2097.3	1920.4	67.7	70.3
56N	601.0	7.76	8240.8	2270.3	2202.4	49.9	59.0
10N	604.0	7.89	9343.1	2297.4	2397.6	64.5	71.4
23N	598.0	8.41	10072.1	2764.9	2465.8	75.4	58.4
36N	699.0	3.00	2663.2	726.7	750.1	20.9	24.4
27N	699.0	3.96	4191.5	1178.0	1121.5	52.1	23.8
28N	703.0	4.02	4623.0	1133.4	1138.3	40.8	24.4
30N	695.0	4.93	6694.6	1826.7	1616.4	65.0	34.4
31N	704.0	5.00	6542.8	1804.9	1566.6	65.3	56.3
39N	705.0	5.77	9266.2	2407.0	2314.0	96.6	65.3

Figure 3-1 Molar ratios of elements in solution for
table 3-3 data (Currie's 1968 albite dissolution
experiments)

Where there are duplicate experiments for the same
P and T, the plotted points correspond to the
average ratio. The vertical bars cover the range
of measured ratios.

The molar ratio values are subject to large
uncertainties, especially where total solubility is
low and/or dissolution is markedly non-
stoichiometric. The "kinks" in figures 3-1 to 3-5
may be due to experimental error.

Figure 3-2 Molar ratios of elements in solution for table 3-4 data (Currie's unpublished albite dissolution experiments)

The plotted points correspond to the average ratio for a given P and T. Range bars (as given in figures 3-1 and 3-4) are not shown, for the sake of clarity. However, it should be noted that they are often very wide. Hence, the graphs should be interpreted very cautiously.

Figure 3-3 Molar ratios of elements in solution for
table 3-6 data (Currie's unpublished microcline
dissolution experiments)

The plotted points correspond to the average ratio
for a given P and T. Range bars (as given in
figures 3-1 and 3-4) are not shown, for the sake of
clarity. However, it should be noted that they are
often very wide. Hence, the graphs should be
interpreted very cautiously.

Figure 3-4 Molar ratios of elements in solution for
table 3-9 data (nepheline + albite dissolution
experiments, all at 1 kbar)

Where there are duplicate experiments for the same
P and T, the plotted points correspond to the
average ratio. The vertical bars cover the range
of measured ratios.

The molar ratio values are subject to large
uncertainties, especially where total solubility is
low and/or dissolution is markedly non-
stoichiometric. The "kinks" in figures 3-1 to 3-5
may be due to experimental error.

Figure 3-5 Molar ratios of elements in solution for

table 3-10 data (leucite dissolution experiments, at
either 1 or 2 kbar).

The plotted points correspond to the average ratio
for a given P and T. Range bars (as given in

figures 3-1 and 3-4) are not shown, for the sake of
clarity. However, it should be noted that they are

often very wide. Hence, the graphs should be
interpreted very cautiously.

Figure 3-6(a) Graph of $\ln m_{Si}$ vs. $\ln V_{H_2O}$ at constant temperature for table 3-3 data (Currie's 1968 albite dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-6(b) Graph of $\ln m_{Al}$ vs. $\ln V_{H_2O}$ at constant temperature for table 3-3 data (Currie's 1968 albite dissolution experiments).
(Straight lines fitted by linear regression)

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Figure 3-6(c) Graph of $\ln m_{\text{Na}}$ vs. $\ln V_{\text{H}_2\text{O}}$ at constant,
temperature for table 3-3 data (Currie's 1968
allite dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-6(d) Graph of $\ln m_K$ vs. $\ln V_{H_2O}$ at constant temperature for table 3-3 data (Currie's 1968 albite dissolution experiments).

(Straight lines fitted by linear regression)

Figure 3-7(a) Graph of $\ln m_{\text{Si}}$ vs. $\ln V_{\text{H}_2\text{O}}$ at constant temperature for table 3-4 data (Carrie's unpublished albite dissolution experiments) (Straight lines fitted by linear regression)

Figure 3-7(b) Graph of $\ln m_{Al}$ vs. $\ln V_{H_2O}$ at constant temperature for table 3-4 data (Currie's unpublished albite dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-7(c) Graph of $\ln m_{\text{Na}}$ vs. $\ln V_{\text{H}_2\text{O}}$ at constant temperature for table 3-4 data (Currie's unpublished albite dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-7(d) Graph of $\ln m_K$ vs. $\ln V_{H_2O}$ at constant temperature for table 3-4 data (Currie's unpublished albite dissolution experiments)

Figure 3-8(a) Graph of $\ln m_{\text{Si}}$ vs. $\ln V_{\text{H}_2\text{O}}$ at constant temperature for table 3-6 data (Currie's unpublished microcline dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-8(b) Graph of $\ln m_{Al}$ vs. $\ln V_{H_2O}$ at constant temperature for table 3-6 data (Currie's unpublished microcline dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-8(c) . Graph of $\ln m_{\text{Na}}$ vs. $\ln V_{\text{H}_2\text{O}}$ at constant temperature for table 3-6 data (Currie's unpublished microcline dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-8(d) Graph of $\ln m_K$ vs. $\ln V_{H_2O}$ at constant temperature for table 3-6 data (Currie's unpublished microcline dissolution experiments) (Straight lines fitted by linear regression)

Figure 3-9(a) Graph of $\ln m_{Si}$ vs. $\ln V_{H_2O}$ at constant temperature for table 3-18 data (Davis's 1972 albite dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-9(b) Graph of $\ln m_{\text{Al}}$ vs. $\ln V_{\text{H}_2\text{O}}$ at constant temperature for table 3-18 data (Davis's 1972 albite dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-9(c) Graph of $\ln m_{\text{Na}}$ vs. $\ln V_{\text{H}_2\text{O}}$ at constant temperature for table 3-18 data (Davis's 1972 albite dissolution experiments)
(Straight lines fitted by linear regression)

Figure 3-10(a) Comparison of albite dissolution data at
500°C and 600°C

Graph of $\ln m_{\text{Si}}$ vs. $\ln V_{\text{H}_2\text{O}}$

Table 3-3 Currie's 1968 data

Table 3-4 Currie's unpublished data

Table 3-5 Adcock's unpublished data

Table 3-18 Davis's 1972 data

$\ln m_{Si}$ vs. $\ln V_{H_2O}$

Figure 3-10(b) Comparison of albite dissolution data at
500°C and 600°C

Graph of $\ln m_{\text{Al}}$ vs. $\ln V_{\text{H}_2\text{O}}$

Table 3-3 Currie's 1968 data

Table 3-4 Currie's unpublished data

Table 3-5 Adcock's unpublished data

Table 3-18 Davis's 1972 data

$\ln m_{Al}$ vs. $\ln V_{H_2O}$

Figure 3-10(c) Comparison of albite dissolution data at
500°C and 600°C

Graph of $\ln m_{\text{Na}}$ vs. $\ln V_{\text{H}_2\text{O}}$

Table 3-3 Currie's 1968 data

Table 3-4 Currie's unpublished data

Table 3-5 Adcock's unpublished data

Table 3-18 Davis's 1972 data

$\ln m_{\text{Na}}$ vs. $\ln V_{\text{H}_2\text{O}}$

Chapter 4 Thermodynamic interpretation of the results

In Chapter 3, it was shown that the "equilibrium" experimental results are reproducible. They were shown to be independent of flow rate at low flow rates.

In this chapter, the results are critically analysed, and then interpreted in terms of a general model for supercritical aqueous solutions. The initial theoretical model was developed independently of detailed analysis of the results. Fitting the results to the model then became a test of the model and led to improvements.

The initial model is developed in considerable detail (in steps 5 to 8), despite ultimately being rejected. By starting with the simplest possible model, even one with obvious failings, some useful insights can be gained, which might otherwise be overlooked when developing more complex models.

When reading this chapter, it is possible to ignore steps 5 to 8. They are retained because of their historical and philosophical importance in terms of the present study.

In future years, models will be developed, based on knowledge of the actual structure of the solution and/or a rigorous statistical mechanical theory for aqueous solutions (Pitzer, 1977, 1981). In the meantime, one must be content with models which are merely internally consistent and fit the data, and which do not necessarily represent the physical chemistry of the system. In order to interpret the results thermodynamically, it is not necessary to know any details of the "microscopic"

chemistry. However, such knowledge would allow simpler and/or more accurate activity-composition (a-X) models to be produced. In the absence of such constraints, an infinite number of models could be chosen, all of which would be internally consistent and fit the data. One's choice between the models would then be dependent on their simplicity, utility, and predictive powers.

In the following pages, the terms "species" and "complex" are used to describe the cations in solution. These terms imply a precise physical form, but this implication is not necessarily correct. In what follows, the term "species" is used without any physical implication. Any proposed "species" and "speciation scheme" are merely mathematical conveniences to allow construction of simple a-X models. The term "complex" is used where an actual physical structure is implied.

The number of digits given in the calculations in this chapter is not intended to reflect the accuracy of the experimental values used. It is an effort to facilitate exact reproduction by other workers.

Outline of the theoretical developmentGiven

Chemical analyses of aqueous solutions.

Step 1

Do the results represent thermodynamic equilibrium?

Step 2

Thermodynamic treatment of the aqueous solution.

Step 3

Write balanced chemical "reactions".

Step 4

Construct a thermodynamic database.

Step 5

Run each "reaction" through a computer programme, to calculate $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$.

Step 6

Analyse values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$.

Step 7

Run "best" set of values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ through regression programme to obtain fit to general equation.

Step 8

Prediction of corundum solubility.

Step 9

Additional experimental constraints on the model

Step 10

Development of a better model - theoretical considerations

Step 11

Thermodynamic data for $\text{Al}(\text{OH})_3(\text{aq})$

Step 12

Thermodynamic data for $\text{Si}(\text{OH})_4(\text{aq})$

Step 13

Development of a charged, mononuclear model

Step 14

Development of an uncharged, polynuclear model

Given

The experiments yield chemical analyses of solutions which have been in contact with one or more known solid phases and possibly one or more unknown phases. Only four cations dissolve in significant amounts (i.e. > 1 ppm): Si, Al, Na and K.

Step 1 Do the results represent thermodynamic equilibrium?

Numerous arguments can be proposed both for and against equilibrium having been achieved. These arguments and their counter-arguments are covered here in point form. The arguments are summarised with particular respect to albite, but can generally be applied to the results obtained using other minerals.

1. For: The results are reproducible i.e. experiments at different times with the same starting mineral give the same results. This implies some kind of "equilibrium" in the general sense of the word, but not necessarily thermodynamic equilibrium with respect to albite.

Against: (a) The reproducibility could be due to equilibrium with respect to phases other than albite. This can be illustrated by reference to figure 4-1. This figure summarises the observed behaviour of Si during albite dissolution.

Figure 4-1 Variation of Si concentration in solution as a function of "time" (= flow rate), in feldspar dissolution experiments, and a potential explanation (see text for discussion)

According to this hypothesis, the pronounced decrease in Si solubility is due to rapid precipitation of unknown phases, with which the solution is in equilibrium. The albite carries on dissolving (unless it is shielded from the solution by the precipitates) and may eventually either reach equilibrium or dissolve entirely, to be replaced by more stable phases.

- (b) Flow rate can be treated as an inverse function of time when considering its effect on the reaction kinetics. The "equilibrium" solutions are obtained from the region which shows little or no change in Si concentration as a function of time. However, Si concentration may be steadily changing, but at a rate too slow to be detected in the experiments.

(c) Davis's (1972) results for albite solubility (reproduced in table 3-18) are systematically higher than those of Currie (1968). The results were obtained using a "static" technique as opposed to the "dynamic" technique of Currie. Currie's lower results may have been caused by:

- i) precipitation in the exit tubes (see Becker et al., 1983), or
- ii) too high a flow rate.

Reply: a) The extremely high Si concentrations are associated with formation of Si-rich nepheline (Currie, 1968; Dollase and Thomas, 1978) which is clearly a kinetic

phenomenon (the composition of the nepheline lies well within the Ne-Ab miscibility gap (for which the experimental data are summarised by HDNB p151)).

Apparently, the Si is being removed very efficiently from the albite framework; this removal is facilitated possibly by the formation of an "activated Si-OH complex" both on the surface of the solid phase and within it. The importance of hydroxyl ions as kinetic agents could be assessed by varying a_{OH^-} in the solution.

The fall in Si concentration depicted in figure 4-1 may be due to steadily increasing amounts of Na, Al and K in the solution, leading to supersaturation of the solution with respect to multi-cation phases. The albite (or Si-rich nepheline) would adjust to a more stable structure by either re-absorbing Si or dissolving more Na, Al and K.

The situation is more complex when considering dissolution of Qtz-Fsp mixtures (tables 3-15 and 3-16). The analyses show the same pattern as that just described for alkali feldspar (e.g. compare runs G11 and PP31H). Quartz is present at equilibrium and therefore the Si analysis should correspond to that of quartz solubility (see table 4-2) (assuming that the simple solution model proposed in step 2 is applicable). This implies that run PP31H (higher Si.

(2045 ppm SiO_2); lower Na, K, Al, compared to G11) is the equilibrium result. Why, then, should Na, K, and Al concentrations be lower in run PP31H than in run G11?

The solution may have equilibrated first with respect to the feldspar (run G11). Continued dissolution of Si to the level of quartz saturation would then lead to a decrease in the concentration of Na, K and Al, according to the law of mass action, in order to maintain equilibrium with respect to the feldspar (see point 4).

(b) SEM photographs of feldspar after dissolution show very localised surface precipitates, with most of the feldspar surface remaining accessible to the solution. The experimental evidence is summarised by Aagaard and Helgeson (1982).

(c) Other experimental studies on high pressure / temperature silicate mineral solubilities all report apparent equilibration times of only a few hours or days, regardless of the experimental technique. The interpretation of the Qtz-Ab-Mc solubility data presented above, suggests that feldspar reaches equilibrium with the solution more rapidly than quartz. Wood and Walther (1983) report similar dissolution rates for many silicates in the presence of a fluid of moderate to high pH. They derived a general Arrhenius relationship, $\log_{10}K \approx \frac{-2900}{T} - 6.85$, where T is

temperature (in Kelvins) and K has the units gram-atoms of oxygen per square centimetre per second.

(d) Davis's (1972) data overlap with the present compilation at only two conditions: 500°C, 2 kbar and 600°C, 2 kbar. In these two cases, his results are slightly higher than those of Currie (1968), but are similar to data in tables 3-4 and 3-5. The results are in agreement within the limits of experimental uncertainty. See figure 3-10.

3. For: The solution composition can be approached from over- or under-saturated conditions. The equilibrium solution composition can thus be "bracketed". There are only a few "bracketed" compositions, for only three starting materials (nepheline + albite, Buckingham microcline, and leucite; tables 3-7, 3-9 and 3-10).

The data are summarised in table 4-1.

In table 4-1, states B and D are at identical pressures and temperatures. They are approached from states A and C respectively, which are at different pressures and temperatures. Some solute concentrations decrease and others increase in going from A to B and C to D.

If there is no run given for state A, then state B was the first run of a series.

Table 4-1 Experimental data obtained by approaching from
(partially) supersaturated conditions

State	Run no.	T °C	P kbar	Si ppm	Al ppm	Na ppm	K ppm	flow rate cm ³ h ⁻¹
Microcline dissolution								
A	AM3	500	1.0	340	29	29	22	30
B	AM4	600	1.0	250	11	17	16	34
C	AM8	600	2.0	1070	251	182	178	37
D	AM9	600	1.0	340	24	17	24	23
Albite - nepheline dissolution								
A	AC79	400	1.0	281	218	190	66	31
B	AC80	600	1.0	352	22	40	17	23
C	AC73	500	1.0	244	58	61	36	26
D	AC74	600	1.0	338	17	44	36	28
B	AC72	500	1.0	272	64	62	35	19
C	AC75	600	1.0	345	19	18	18	26
D	AC76	500	1.0	268	61	42	34	26
A	AC73	500	1.0	244	58	61	36	26
B	AC74	600	1.0	338	17	44	36	28
C	AC79	400	1.0	281	218	190	66	31
D	AC80	600	1.0	352	22	40	17	23
Leucite dissolution								
A	AC38	400	1.0	267	240	186	317	22
B	AC39	500	1.0	191	142	79	146	19
C	AC41	600	2.0	623	557	213	659	24
D	AC42	500	1.0	192	133	60	161	20
B	AC38	400	1.0	267	240	186	317	22
C	AC44	400	2.0	500	506	320	999	25
D	AC45	400	1.0	231	240	143	437	21

Against: The "brackets" are rather wide. Solutions obtained from initially oversaturated conditions are typically 10-15% more concentrated than those obtained from initially undersaturated conditions. Reproducibility when pressure and temperature are held constant, for several days, allowing several solutions to be collected, is generally within 5%.

Reply: Prolonged supersaturation may be causing the wide "brackets". Future attempts to approach a state from supersaturated conditions should take advantage of the observation that all solute concentrations decrease as pressure decreases at constant temperature, whereas some increase and some decrease as temperature decreases at constant pressure.

4. For: Experiments with Qtz-Fsp mixtures lead to an increase in Si concentration and decreases in Na, Al concentrations, relative to experiments on pure albite. This is consistent with equilibrium being achieved with respect to one or more multi-cation phases (not just simple oxides or hydroxides).

Against: The Si concentration should rise to the level of quartz saturation, if the a-X model for $\text{SiO}_2(\text{aq})$ presented in step 2 is correct.

If additional multi-cation complexes form (e.g. NaH_3SiO_4) then Si solubility may rise above that of quartz. It actually varies both above and below that

value (see table 4-2).

Reply: The experimental data for "granite" solubility show wide variability. The Si concentrations for quartz solubility are generally within the error limits for "granite" solubility. Without more accurate data, no quantitative analysis can be attempted.

5. For: The results can be interpreted thermodynamically to yield a consistent set of numbers and graphs:-

(a) Graphs of $\ln m_X$ vs. $\ln V_{H_2O}$ (where $X = Si, Al, Na$ or K), using Currie's 1968 data and H+K's (1974a) values of V_{H_2O} produce remarkably straight lines (figure 3-6). This is consistent with other workers' results (Marshall, 1972) and is discussed further in step 2.

(b) Consistent values of $\Delta G_{AlO_{1.5}(aq)}^{\circ}$ are obtained, (in steps 5 and 6) from data on Ab, Mc, Ne and Lct dissolution.

Against: (a) Even if one accepts the relationship of $\ln m_X$ vs. $\ln V_{H_2O}$ as evidence of thermodynamic equilibrium; that equilibrium may be with respect to any phase, not necessarily albite.

(b) Sensitivity analyses of the data suggest that they are also compatible with equilibrium with respect to other phases. Values obtained for $\Delta G_{AlO_{1.5}(aq)}^{\circ}$ later in this chapter cluster around -180.0 to -190.0 kcal mole⁻¹ for all the phases concerned.

Table 4-2 Comparison of SiO₂ concentrations (in ppm) in solutions equilibrated with:

a) pure quartz

b) "granitic" assemblages

QUARTZ SOLUBILITIES							"GRANITE" SOLUBILITIES				
T (°C)	P (kbar)	Table 3-12	Ke	M+H	W+F	A+B	W+O	SPP	BS	Table 3-15	Table 3-16
400	1.0	2097	1740	1550	1700		1721		1140	1609	
	1.5			2070	2080					2159	
	2.0			2330	2480		2439		2000	2148	
500	1.0		2380	2600	2400	2400	2465		1600	2349	
	1.5			4040	3720	3600			2100	2822	3881
	2.0			4990	4560	4100	4240	5800	2990	3400	5708
600	1.0			2960		2600				3674	3295
	2.0			7650		7200		7900			

Sources of data:

Ke : Kennedy (1950)

M+H : Morey and Hesselgesser (1951)

W+F : Veill and Fyfe (1964)

A+B : Anderson and Burnham (1965)

W+O : Walther and Orville (1983)

SPP : Spruce Pine pegmatite (Clark, 1966, p433; see also Burnham, 1967, p50 and Anderson and Burnham, 1983, p293)

BS : Belleoram Stock (Ermanovics et al., 1967)

Conclusion: The evidence points in favour of thermodynamic

equilibrium having been achieved. It is less clear whether or not this equilibrium was with respect to albite or some other phase. The evidence is equivocal. Alternative scenarios will be presented, assuming equilibrium with respect to various phases, as identified in figures 1-3 and 1-4. The possibility of the formation of "non-geological" phases should also be considered. When new phases have been identified, they have always turned out to be either "geologically reasonable" phases (e.g. nepheline, paragonite, leucite, mentioned by Anderson and Burnham, 1983; muscovite, mentioned by Eugster, 1981, p476; microcline, mentioned by Adcock, 1980) or closely related to "geologically reasonable" phases (e.g. Si-rich nepheline, Dollase and Thomas, 1978; K-analcime, Roux and MacKenzie, 1978).

Step 2 Thermodynamic treatment of the aqueous solution

Simple solubility experiments cannot provide unequivocal evidence as to the physical nature of an aqueous solution. However, they can provide compositional data which any model must account for.

Corundum, quartz, sodium hydroxide and potassium hydroxide all dissolve in pure water to varying degrees. Therefore, Al, Si, Na and K are all capable of existing in solution in significant amounts, surrounded only by O and H atoms.

If more than one of these cations (Al, Si, Na and K) are present in the same solution, there will be some interaction. This interaction will probably be a complex function of the solution composition. Aqueous "complexes" may form if there is strong interaction. For example, Na and Al may be strongly attracted to one another, to form some kind of Na-Al complex. An individual complex may have a very short lifespan, but as it breaks up, new ones may form elsewhere in the solution. This interaction can be envisaged as part of a continuum. At any given moment, some Na and Al will be wholly separate, with minimal interaction; some will be wholly together (very strong interaction) and some will be in between. The environment around an individual ion may change extremely rapidly.

Given this potential enormous complexity and our inability to make direct observations, what can we do? From a strict thermodynamic point of view, the actual structure of the solution is irrelevant. Thermodynamic principles can be applied without

knowledge of the structure. However, such an approach may lead to extremely complex a-X models. If the structure of the solution is considered, simpler a-X models may be produced. These structurally based models have the additional advantage of more justifiable extrapolation and interpolation.

Theoretical studies of cation hydrolysis suggest that at high temperatures, neutral mononuclear species become dominant in aqueous solutions (Baes and Mesmer, 1981).

The approach adopted here is to initially assume that the Na, K, Al and Si do not interact strongly with one another in dilute aqueous solutions. This is the simplest possible assumption. If the model cannot explain the observations, then the next step is to invoke significant interaction between pairs of ions. Mathematically, this could be handled in either of two ways (or a combination of the two):

- a) modify the a-X relationships for each of Na, K, Al and Si by incorporating interaction parameters,
- b) create new "species", which ideally should correspond to "complexes" within the solution.

Can the straight-line graphs of $\ln m_X$ vs. $\ln V_{H_2O}$ (figures 3-6 to 3-9) be used to place any constraints on the physical chemistry of the solutions? The following argument is based on the work of Marshall (1972):

Consider the general equilibrium:

$$\bar{G}_{Si}^{solid} = \bar{G}_{Si}^{solution}$$

We can write:

$$\ln K = \ln \frac{a_{Si,solution}}{a_{Si,solid}}$$

If we assume:

$$a_{Si,solution} = k_1 m_{Si,solution}$$

$$a_{Si,solid} \approx \text{constant}$$

then:

$$\ln K = \ln m_{Si} - k_2$$

At constant T, we observe:

$$\begin{aligned} \ln m_{Si} &\propto - \ln V \\ &= - k_3 \ln V + k_4 \end{aligned}$$

Hence:

$$\ln K = - k_3 \ln V + k_5$$

Differentiating w.r.t. P:

$$\begin{aligned} \frac{\partial \ln K}{\partial P} &= - k_3 \frac{\partial \ln V}{\partial P} \\ &= - \frac{k_3}{V} \frac{\partial V}{\partial P} \\ &= k_3 \beta \end{aligned}$$

where β = isothermal compressibility
of water

If we choose a standard state where $P(\text{standard state}) = P(\text{system})$

we can write:

$$\frac{\partial \ln K}{\partial P} = - \frac{\Delta V}{RT}$$

where ΔV is the volume change
associated with the dissolution of Si

Hence:

$$- \frac{\Delta V}{RT} = k_3 \beta$$

Analogous arguments to the one presented for Si can also be made for Al and Na (if we accept that $a_{Al} = k_1 m_{Al}$ and $a_{Na} = k_1 m_{Na}$).

The proportionality of $\ln K$ to $\ln V_{H_2O}$ (where K is the equilibrium constant for a dissolution reaction) is a general relationship which has been shown to hold true for many systems (Marshall, 1972; Marshall and Mesmer, 1981; Fournier and Marshall, 1983). However, the reason the relationship holds true is unclear.

H+K (1976, p116) note that β is roughly linearly related to $\frac{1}{\epsilon} \left(\frac{\partial \ln \epsilon}{\partial P} \right)$ over wide ranges of temperature and pressure (see H+K, 1976, fig.8, p117). Based on this observation, they explained the straight line plots as follows:

The Born equation (H+K, 1976, p119) can be written as

$$\Delta G_s^0 = \frac{\eta Z^2}{r_e} \left(\frac{1}{\epsilon} - 1 \right)$$

where ΔG_s^0 = Gibbs free energy of

solvation of a cation

(H+K, 1976, p118-122)

η = Born constant

Z = charge on the cation

r_e = effective electrostatic
radius of the cation

ϵ = dielectric constant of
 H_2O

Differentiating with respect to pressure at constant temperature leads to the Drude-Nernst equation (H+K, 1976, p121):

$$\Delta V_S^0 = -\frac{\eta Z^2}{r_e} \frac{1}{\epsilon} \left(\frac{\partial \ln \epsilon}{\partial P} \right)$$

where ΔV_S^0 = volume of solvation of
a cation

Assuming that the Born equation represents roughly the solvation process, ΔV_S^0 should show a rough linear dependence on β .

H+K (1976, p118) represent the partial molal volume of an ion in aqueous solution by

$$V^0 = V_i^0 + \Delta V_C^0 + \Delta V_S^0$$

where V_i^0 = intrinsic partial
molal volume (constant)

ΔV_C^0 = partial molal
volume of solvent
collapse

If ΔV_S^0 is dominant over ΔV_C^0 , then V^0 will be an almost linear $f(\beta)$, which is consistent with what we observe.

An additional complexity is the suggestion of a slight curve, concave upwards, in some of the graphs of $\ln m_X$ vs. $\ln V_{H_2O}$. This is most pronounced for Si concentrations at 550°C and 600°C (figures 3-6(a) and 3-10(a)). Accepting H+K's

explanation for the straight line plots, two possible explanations for this curvature are:

- 1) a breakdown in the linear correlation of $\frac{1}{\epsilon} \frac{\partial \ln \epsilon}{\partial P}$ with β in certain P-T regions. This possibility cannot be fully assessed because of incomplete knowledge of ϵ as a f(P,T). However, note that the graphs of $\ln m_X$ vs. $\ln V_{H_2O}$ for Na and Al do not show such curvature and hence, this possibility alone cannot explain the curvature.

- 2) a significant and varying contribution of ΔV_C^0 to V^0 .

One can attempt to quantitatively analyse the data in figure 3-6. Numerical results of the linear regression analysis are given in table 4-3. The slopes are similar to one another, but not identical. Note that the data for K are of much lower statistical significance than for Na, Al and Si.

From

$$\Delta V = -k_3 RT \beta$$

where k_3 = slope, as given in table 4-3
(dimensionless)

one can calculate the molar volume of dissolution for given β and T. Setting β equal to 10^{-3} bar^{-1} and T equal to 773.15 K, we obtain

For $k_3 = -3.0$	$\Delta V = -192.8 \text{ cm}^3 \text{ mole}^{-1}$
$= -4.0$	$\Delta V = -257.1 \text{ " "}$
$= -5.0$	$\Delta V = -321.4 \text{ " "}$
$= -6.0$	$\Delta V = -385.7 \text{ " "}$

Table 4-3 Linear regression statistics for graphs of $\ln m_X$ vs. $\ln V_{H_2O}$

		Correlation (R)	R Squared	Significance	Std err of est	Intercept (A)	Slope (B)
400°C	Si	-0.99723	0.99446	0.00001	0.03661	12.537	-5.321
	Al	-0.99426	0.98855	0.00001	0.04357	8.301	-4.391
	Na	-0.98812	0.97638	0.00001	0.06501	9.263	-4.534
	K	-0.98872	0.97757	0.00001	0.10692	13.749	-7.657
450°C	Si	-0.99759	0.99519	0.00001	0.04440	10.139	-4.373
	Al	-0.99779	0.99559	0.00001	0.04085	8.424	-4.203
	Na	-0.99890	0.99781	0.00001	0.02747	8.074	-4.014
	K	-0.99551	0.99103	0.00001	0.05836	3.444	-4.200
500°C	Si	-0.99446	0.98896	0.00001	0.06869	8.870	-3.829
	Al	-0.99773	0.99547	0.00001	0.04868	9.012	-4.250
	Na	-0.99263	0.98532	0.00001	0.08689	9.082	-4.193
	K	-0.92666	0.85870	0.00000	0.28534	4.240	-4.071
550°C	Si	-0.99146	0.98299	0.00001	0.10794	7.062	-3.169
	Al	-0.99965	0.99930	0.00001	0.02865	9.098	-4.181
	Na	-0.99840	0.99680	0.00001	0.05250	7.344	-3.581
	K	-0.95583	0.91361	0.00003	0.12361	-3.963	-1.552
600°C	Si	-0.98959	0.97928	0.00001	0.12013	5.815	-2.703
	Al	-0.99887	0.99774	0.00001	0.06316	9.641	-4.339
	Na	-0.99662	0.99325	0.00001	0.09329	8.032	-3.704
	K	-0.90245	0.81441	0.00043	0.12764	-5.874	-0.875

Figure 4-2 Variation of k_3 as a f(T) (data from table

3)

Setting β equal to 10^{-4} bar^{-1} would reduce the above values of ΔV by an order of magnitude.

The variation of k_3 as a $f(T)$ for Na, Al and Si is shown in figure 4-2. β varies from $49.72 \times 10^{-6} \text{ bar}^{-1}$ at 400°C and 3500 bars to $1604.8 \times 10^{-6} \text{ bar}^{-1}$ at 600°C and 750 bars.

The physical meaning of the values of ΔV thus obtained is unclear. Interpretation would be dependent on conceptual models of cation hydrolysis, and will not be attempted here.

It is noted in passing that, if dissolution was stoichiometric, a straight line relationship of $\ln m_{\text{Si}}$ vs. $\ln V_{\text{H}_2\text{O}}$ would force $\ln m_{\text{Al}}$ vs. $\ln V_{\text{H}_2\text{O}}$ and $\ln m_{\text{Na}}$ vs. $\ln V_{\text{H}_2\text{O}}$ also to be straight lines. Only one aqueous species, $\text{NaAlSi}_3\text{O}_8(\text{aq})$, would then be needed to explain the albite data. Extra species would be needed, though, to explain the nepheline, leucite and microcline data.

What does the relationship, $\Delta V = -k_3RT\beta$, tell us about the factors affecting albite solubility? It allows us to predict albite solubility as a $f(P)$, given two albite solubilities at different pressures at the temperature of interest, and knowing only $V_{\text{H}_2\text{O}}$ as a $f(P,T)$. The underlying control on the equilibrium phase composition is maximisation of the entropy of the system, which corresponds to minimisation of the Gibbs free energy when pressure and temperature are the variables. As the dissolution reaction proceeds, it may run into local minima in the Gibbs free energy before reaching the absolute minimum. If a local minimum is substantial enough, the reaction may halt there indefinitely

(a metastable equilibrium) (analogous to studying Ky-Sil within the And stability field). Apparently, one such minimum is predictable based on the graphs of $\ln m_X$ vs. $\ln V_{H_2O}$; and in this sense, the solution composition is controlling the phase assemblage.

One might predict that, in general, the phase assemblage will control the solution composition. For example, if the stable phase assemblage for a bulk composition lying on the $NaAlSi_3O_8-H_2O$ join, at a particular temperature and pressure, is Ab-Pg-Crn-aq, then the molal Na:Si ratio in solution will be fixed at 1:3, whilst the molality of Al in solution will be variable, but always less than the molality of Na in solution. These ratios will be fixed wholly independently of the nature of the aqueous solution. They offer no insights regarding the stoichiometry of possible complexes. [Note that the above phase assemblage is stable only along a unique line in P-T space (see HDNB fig. 67B)].

However, when albite dissolves in water under certain P-T conditions, paragonite is produced, and not other phases such as quartz, nepheline or analcime. This does provide some constraints on the stoichiometry of the dominant complexes.

Note that since thermodynamic theory yields meaningful results with Currie's results, some kind of equilibrium is suggested. The equilibrium may be a metastable one. To reach the stable assemblage, an energy barrier (the "activation energy") must be overcome. This barrier may be prohibitively

large. From the Arrhenius equation

$$k' = A \exp(-E_a/RT)$$

the Boltzmann factor, $\exp(-E_a/RT)$, is the fraction of molecules that manage to obtain the energy necessary to react. The derivation of the Arrhenius equation assumes that the activation energy, E_a , is not a function of temperature. When the activation energy is zero, all the molecules will react at any temperature. For half the molecules to react, we can write at 25°C,

$$0.5 = \exp(-E_a / (1.98719 \times 298.15))$$

$$E_a = 411 \text{ calories}$$

at 600°C,

$$E_a = 1203 \text{ calories}$$

For a reaction with a specific value of E_a , increasing temperature will lead to a higher proportion of reacting molecules; i.e. increasing temperature makes it easier for molecules to overcome activation energy barriers.

The corundum solubility data of Becker et al. (1983) can also be expressed as a simple $f(V_{H_2O})$. Considering only the 670°C data and neglecting the anomalously low solubilities at 2.5 kbar and 4.5 kbar, the following regression curve results:

$$\log_{10} m_{Al} = -2.725 + 4.813 \log_{10} \rho$$

where ρ = density of water (g cm^{-3})

correlation coefficient, $R = 0.974$

The data also show a good correlation with pressure:

$$C_{\text{Al}_2\text{O}_3, \text{ppm}} = -11.97 + 7.70 P$$

where C = concentration of Al_2O_3 (in ppm)

P = pressure (in kbar)

correlation coefficient, $R = 0.953$

In a similar vein, Fournier and Potter (1983) developed an equation which describes quartz solubility over a wide range of pressure and temperature as a $f(T, V_{\text{H}_2\text{O}})$.

Anderson and Burnham (1983) have interpreted a large body of experimental aqueous solubility data in terms of possible aqueous complexes. They concluded that mixed cation complexes must be present in significant amounts in solutions obtained by dissolution of Na, K alumino-silicates. Their arguments will be discussed here in some detail.

They noted that corundum is apparently insoluble relative to alkali feldspars, i.e. solutions in equilibrium with alkali feldspars contain more Al than solutions in equilibrium with corundum. If the aqueous Al is in the same form in both cases, then the alkali feldspar solution must be supersaturated with respect to corundum. Anderson and Burnham argue that the Al must be in different forms in the two solutions. The most obvious possibility would be the formation of mixed cation complexes in the alkali feldspar solutions.

Table 4-4 gives a summary of all the available corundum solubility data in the range 350°C to 900°C and 1 kbar to 6 kbar. The best documented and most internally consistent data are those

of Becker et al. (1983). The data of Anderson and Burnham (1967) can be ignored (based on their own admission that their experimental technique was inadequate for solubilities below 1000 ppm). Similarly, the data of Ganeyev and Rumyantsev (1974) are judged to be unreliable, because of wide scatter in the data (Becker et al., 1983). The data of Ragnarsdottir and Walther (1983, 1985) are in good agreement with the data of Morey and Becker et al. However, the experimental errors in their study are hard to assess because of the lack of multiple results at one pressure and temperature.

It is clear that corundum solubility in pure water is considerably lower than the Al concentrations recorded in Chapter 3.

Table 4-4 Corundum solubility data in the range 350°C to 900°C
and 1 kbar to 6 kbar

Temperature (°C)	Pressure (kbar)	Al ₂ O ₃ concentration (ppm)	Source
350	1.0	124	Ganeyev and Rumyantsev (1974)
	2.0	185	" " " "
400	1.0	34	" " " "
	1.5	46	" " " "
	2.0	45	" " " "
500	1.0	16	" " " "
	1.5	14	" " " "
500	1.04	1.8	Morey (1957)
500	6.0	35 ± 14	Burnham et al. (1973)
600	6.0	23 ± 12	" " " "
700	6.0	17 ± 8	" " " "
800	6.0	24 ± 13	" " " "
700	2.5	2.7	Becker et al. (1983)
	3.0	10.7	" " " "
	3.5	14.5	" " " "
	4.0	19.5	" " " "
	4.5	16.6	" " " "
	5.0	26.7	" " " "
	6.0	33.3	" " " "
700	6.0	960.	Anderson and Burnham (1967)
		880	" " " "
800	6.0	590	" " " "
900	6.0	1050.	" " " "
400	2.0	4.76	Ragnarsdottir and Walther (1983)
450		5.73	" " " "
500		5.10	" " " "
550		4.76	" " " "
600		3.78	" " " "
700		4.76	" " " "

Table 4-4 Corundum solubility data in the range 350°C to 900°C
and 1 kbar to 6 kbar (continued)

Temperature (°C)	Pressure (kbar)	Al ₂ O ₃ concentration (ppm)	Source			
555	2.009	2.8	Ragnarsdottir and Walther (1985)			
608	2.022	1.4	"	"	"	"
600	2.018	2.0	"	"	"	"
400	2.039	2.5	"	"	"	"
400	1.899	2.8	"	"	"	"
550	1.850	3.2	"	"	"	"
685	1.900	2.2	"	"	"	"
698	1.630	2.2	"	"	"	"
700	1.041	2.4	"	"	"	"
400	2.040	1.7	"	"	"	"
485	1.920	3.1	"	"	"	"
590	2.080	1.5	"	"	"	"
690	2.120	2.1	"	"	"	"
720	1.140	1.0	"	"	"	"
450	2.950	3.7	"	"	"	"
450	2.000	2.2	"	"	"	"
460	1.445	3.4	"	"	"	"
450	3.000	3.6	"	"	"	"
450	2.110	3.6	"	"	"	"
450	1.440	3.1	"	"	"	"
450	1.000	2.7	"	"	"	"
450	0.730	2.5	"	"	"	"
497	2.370	4.2	"	"	"	"
455	3.120	2.4	"	"	"	"
400	1.950	2.5	"	"	"	"
400	1.250	2.6	"	"	"	"
550	1.970	1.8	"	"	"	"
550	1.500	1.6	"	"	"	"
550	1.170	1.1	"	"	"	"
550	0.940	1.1	"	"	"	"
550	0.770	1.3	"	"	"	"

If the aqueous Al complex is the same in solutions equilibrated with respect to feldspar or corundum, then most of the experimental solutions reported in Chapter 3 plus the solutions reported by Anderson and Burnham (1983) must be supersaturated with respect to corundum. At room temperature and pressure, the solutions reported in Chapter 3 remain supersaturated with respect to many phases for indefinite lengths of time (> 3 years). Crystallisation may be kinetically very difficult because of the very dilute solutions.

Anderson and Burnham also note that the solubilities of quartz and corundum in KOH or NaOH solutions are greater than in pure water. They again explain this in terms of multi-cation complexes.

However, adding an electrolyte to an aqueous solution may change the thermodynamic properties of the solution quite significantly. HKF (1981, p1305) summarised available data showing how the dielectric constant of an electrolyte solution is a function of the ionic strength, I , at 25°C and 1 atm. As an example, they state "Increasing the concentration of an NaCl solution from 0.1 to ~ 6 m at 1.5°C and 1 bar causes the dielectric constant of the solution to decrease by ~ 45 , which is equal to the decrease in the dielectric constant of H_2O accompanying a temperature increase from 25° to $\sim 200^{\circ}\text{C}$ at pressures corresponding to the liquid-vapor equilibrium curve for H_2O ". If one accepts their explanation for the origin of the straight line plots of $\ln m_X$ vs. $\ln V_{\text{H}_2\text{O}}$, then varying ϵ could

clearly have a major effect on the solubility of elements in aqueous solutions.

Fournier (1983a) produced a simple model to explain increased SiO_2 solubility in NaCl solutions relative to pure water. He allowed the activity of water to vary with solution composition. The activity was related to the "effective" density of the water, which is given by the product of the density of the NaCl solution times the mass fraction of water in the solution. The "effective" density of water in a NaCl solution is greater than the density of pure water at the same temperature and pressure (see table 4-5). By allowing a_{water} to vary, no complexes other than $\text{SiO}_2 \cdot n\text{H}_2\text{O}$ were needed to explain the solubility results (note that this is not the case with Na_2SO_4 solutions (Fournier and Marshall, 1983; Fournier, 1983b)).

Table 4-5 "Effective" density of water at 500°C and 1 kbar

	density of solution (g cm^{-3})	"effective" density of water (g cm^{-3})	data source
pure water	0.53	0.53	H&K (1974a)
13 wt% NaCl	0.70	0.61	Potter and Brown (1977)
25 wt% NaCl	0.842	0.63	" " " "

Much of the earlier discussion on straight line plots of $\ln m_X$ vs. $\ln V_{H_2O}$ applies to Fournier's model. His model is purely empirical and has no theoretical justification. If we accept H+K's (1976) theoretical explanation, then knowledge of the dielectric constants of NaOH-H₂O and KOH-H₂O solutions as $f(P,T,i)$ would be essential for understanding changes in quartz and corundum solubility.

On examination of Anderson and Burnham's data (1983, fig. 1) one can see that the effect of adding NaOH or KOH is much more drastic than adding NaCl or KCl. The P-V-T properties of NaOH-H₂O and KOH-H₂O solutions would have to change much more than for chloride solutions for Fournier's model to work satisfactorily. An additional factor may be the formation of hydroxyl complexes. This possibility is elaborated on in detail in steps 10 to 14.

Anderson and Burnham's (1983) arguments in support of multi-cation complexes are persuasive, but not conclusive. The experimental data are not good enough or complete enough to quantify the effects. From a modelling aspect, introduction of extra species to account for possible complexing brings with it the risk of "overfitting" the data. The approach adopted here is to maintain the initial approximation that Na, K, Al, Si interactions are negligible. If this can be shown to be inadequate, then a more complex model allowing for such interactions can be developed. By avoiding overfitting the data, gaps and inconsistencies within the data set may be revealed more clearly. Experiments can then be designed to remedy the

situation.

Summary: In the absence of direct measurements on the solution at the pressure and temperature of the experiment (such as conductivity (Frantz and Marshall, 1982) or laser Raman spectroscopy (Frantz, 1981)) definite conclusions as to the nature of the aqueous solution cannot be drawn. In reality, there will be interactions between all the elements in the solution, though many interactions may be very weak. We must settle for the simplest hypothetical model which can quantitatively explain the data. The simplest model to try initially is one involving no interaction between the Na, K, Al and Si.

Step 3 Write balanced chemical "reactions"

Let us assume that one or more of the following 21 phases (or polymorphs) (listed in figures 1-3 and 1-4) are present in each experiment when it reaches "thermodynamic equilibrium":-

Crn Qtz Bhm Dsp Gbs Anl Dehyd Anl Ab Low Ab High Ab
Kfs Max Mc High San Ne Kls Kln Prl Ms Pg Als Lct

An energy balance ("reaction") can be written involving each of these phases and the aqueous solution. For example,

At least one of the 21 balances should be a valid representation of the system. It does not affect the validity of the method if additional phases, not listed above, are present.

Step 4 Construct a thermodynamic database

All the phases listed in figures 1-3 and 1-4 are included in HDNB's database, with the exception of leucite. Data for leucite were taken from the database of Robie, Hemingway and Fisher (1979). However, these two databases are incompatible.

Hemingway, Haas and Robinson (1982) presented revised data for minerals in the system $\text{Al}_2\text{O}_3\text{-CaO-SiO}_2\text{-H}_2\text{O}$, which are consistent with Robie et al.'s database. They also investigated the source of the discrepancy between Robie et al.'s and HDNB's databases.

They noted that the addition of -6.5 kJ per mole of Al to the enthalpy and free energy values of the Al-bearing phases (except gibbsite) reported by HDNB eliminates most of the discrepancy.

They concluded that the discrepancy is a consequence of a redefinition of the Al reference state within the data set HDNB considered.

Hence, HDNB's database was modified according to Hemingway et al.'s recommendation. Because this modification was applied to the whole database, it does not affect the database's internal consistency. Corrections to the database as suggested by Helgeson (SUPCRT update notices, Feb. 8th, 1982, Jan. 31st, 1983, and June 26th, 1984) were also incorporated into my database (the final form of which is given in Appendix B).

The thermodynamic database thus generated gave a P-T slope for

of about 17°C per kbar and an intercept at 1 bar of 481°C. The

intercept agrees well with Scarfe et al.'s (1966) experimentally derived value of 490°C, but the slope agrees poorly with their value of about 30°C per kbar. This discrepancy was resolved by allowing for the anomalously high thermal expansion of leucite. Details are given in Appendix G.

The equilibrium

gave an intercept at 1 bar of 809°C. This is contrary to experimental observations, which indicate that K-feldspar is stable up to 1150°C (± 20°C), where it breaks down to give leucite and liquid (Schairer and Bowen, 1955). The cause of this discrepancy remains unresolved. It is discussed briefly in Appendix G.

The thermodynamic properties of water were calculated using the equations of Haar, Gallagher and Kell (1984).

Figure 4-3 Phase equilibria in the system $\text{KAlSiO}_4\text{-SiO}_2$
as $f(P,T)$

The curves are calculated using the thermodynamic database derived in step 4 (with provision for expansion and compression of leucite and quartz), with the exception of the $\text{Kfs} = \text{Lct} + \text{liquid}$ curve, which is plotted using experimental data summarised by Deer, Howie and Zussman (1966), and is well constrained only at 1 bar and 5 kbar.

HDNB obtained satisfactory fits to experimental solubility data at temperatures up to 400°C, by assuming that Na^+ , K^+ and $\text{SiO}_2(\text{aq})$ were present in the aqueous solution. The thermodynamic data for Na^+ and K^+ were derived theoretically and independently of phase equilibrium data, by HKF. The data for $\text{SiO}_2(\text{aq})$ were derived principally from silica solubility data by W+H, using HKF's theoretical model. Above 400°C, HDNB present only a few data points involving either Na^+ or K^+ (HDNB, figures 63, 65 and 68), all from the work of Montoya and Hemley (1975). Agreement between experimental and predicted values is good where Na^+/K^+ exchange equilibria are involved, but poor where only Na^+ or K^+ are involved. In these cases, HKF's model predicts higher values of $\log_{10}(a_{\text{K}^+}/a_{\text{H}^+})$ and $\log_{10}(a_{\text{Na}^+}/a_{\text{H}^+})$ than were deduced by Montoya and Hemley. Interpretation of the experimental data is very difficult. Almost all researchers assume that activity ratios involving monovalent ions are identical to the molality ratios. Knowledge of $\log_{10}K$ for dissociation reactions such as $\text{H}_2\text{O} \rightleftharpoons \text{H}^+ + \text{OH}^-$ and $\text{KCl} = \text{K}^+ + \text{Cl}^-$ is needed to evaluate the experimental data. Montoya and Hemley took $\log_{10}K$ for HCl dissociation at 500°C and 1 kbar to equal -3.5. The equations of Frantz and Marshall (1984) give a value of -4.2. Using this updated value, the discrepancy between the predicted and experimental values at 500°C disappears (see Appendix E).

HKF's thermodynamic data for Na^+ , K^+ , and $\text{SiO}_2(\text{aq})$ will be used here. HDNB did not test HKF's high pressure / temperature data for Al^{3+} against any phase equilibrium data. HKF's data for

Al^{3+} are poorly constrained by experimental evidence, and it seems improbable that Al^{3+} is present in significant amounts at supercritical conditions. Hence, their data for $\text{Al}^{3+}(\text{aq})$ were not used in the initial model, and the Gibbs free energy of the aqueous Al species was treated as an unknown.

Following HKF, $\Delta G^\circ_{\text{H}^+} = 0.0$ at all temperatures and pressures, by convention (see the discussion of a paper by Grjotheim (1981) for an insight into the thermodynamic validity of this convention). Marshall and Franck's (1981) expression for $\log_{10} K_{\text{H}_2\text{O}}$ as a $f(T, V_{\text{H}_2\text{O}})$ (given in Appendix E) was used to obtain $\Delta G^\circ_{\text{OH}^-}$, using the relationship

$$\Delta G^\circ_{\text{H}_2\text{O}} - \Delta G^\circ_{\text{OH}^-} - \Delta G^\circ_{\text{H}^+} = R T \ln K$$

The Gibbs free energy of each aqueous species is related to the standard state Gibbs free energy of that species by:

$$\Delta G = \Delta G^\circ + RT \ln a$$

where a = activity

$$= \gamma_m$$

m = molality

γ = activity coefficient

The Al and Si species were both modelled as mononuclear neutral species which obey Henry's Law, thus allowing γ_{Al} and γ_{Si} to be set equal to unity. All the Al and Si were assumed to be present as $\text{AlO}_{1.5}(\text{aq})$ and $\text{SiO}_2(\text{aq})$ respectively.

In order to maintain consistency with HDNB and HKF, Na and K were modelled as mixtures of charged cations ($\text{Na}^+(\text{aq})$ and $\text{K}^+(\text{aq})$) and neutral hydroxyl species (NaOH and KOH).

The solutions listed in tables 3-1 to 3-17 are all very dilute. Hence, the activity coefficients for charged species can be calculated according to the Debye-Huckel equation:

$$\log_{10} \gamma_j = \frac{-A_\gamma z_j^2 \sqrt{I}}{1 + a_{B_\gamma} \sqrt{I}} - \log_{10} (1 + 0.0180153 m^*)$$

A_γ, B_γ = electrostatic Debye-Huckel parameters

(calculated using equations of H+K, 1974b)

z = ionic charge

a = ion size parameter

I = "true" ionic strength of an electrolyte solution (HKF eq 83, p1284)

m^* = sum of the molalities of all solute species in an electrolyte solution

The value of a is calculated using:

$$a = a_{\text{NaOH}} \left(\frac{m_{\text{Na}, \text{total}}}{m_{\text{Na}, \text{total}} + m_{\text{K}, \text{total}}} \right) + a_{\text{KOH}} \left(\frac{m_{\text{K}, \text{total}}}{m_{\text{Na}, \text{total}} + m_{\text{K}, \text{total}}} \right)$$

This allows a to range smoothly between a_{NaOH} for solutions which contain no K, and a_{KOH} for solutions which contain no Na.

Following HKF (table 2, p1298) a_{NaOH} is set equal to 3.31

Angstroms and a_{KOH} is set equal to 3.67 Angstroms. [Note - this

treatment of a leads to inconsistencies with thermodynamic theory and was abandoned at a later stage in the modelling process. (See step 10 and Appendix F.)]

In order to divide the Na and K between Na^+ , K^+ and NaOH, KOH, a set of non-linear simultaneous equations was solved. The equations are:

- 1) $\log_{10} K_{\text{NaOH}} = \log_{10} [\gamma_{\text{Na}^+} m_{\text{Na}^+}] + \log_{10} [\gamma_{\text{OH}^-} m_{\text{OH}^-}] - \log_{10} [\gamma_{\text{NaOH}} m_{\text{NaOH}}]$
- 2) $\log_{10} K_{\text{KOH}} = \log_{10} [\gamma_{\text{K}^+} m_{\text{K}^+}] + \log_{10} [\gamma_{\text{OH}^-} m_{\text{OH}^-}] - \log_{10} [\gamma_{\text{KOH}} m_{\text{KOH}}]$
- 3) $\log_{10} K_{\text{H}_2\text{O}} = \log_{10} [\gamma_{\text{H}^+} m_{\text{H}^+}] + \log_{10} [\gamma_{\text{OH}^-} m_{\text{OH}^-}] - \log_{10} [a_{\text{H}_2\text{O}}]$
- 4) charge balance: $m_{\text{Na}^+} + m_{\text{K}^+} + m_{\text{H}^+} = m_{\text{OH}^-}$
- 5) Na total molality: $m_{\text{Na},\text{total}} = m_{\text{Na}^+} + m_{\text{NaOH}}$
- 6) K total molality: $m_{\text{K},\text{total}} = m_{\text{K}^+} + m_{\text{KOH}}$

The six unknowns solved for are m_{Na^+} , m_{K^+} , m_{H^+} , m_{OH^-} , m_{NaOH} and m_{KOH} . γ_{NaOH} and γ_{KOH} are assumed to be equal to unity (because they are neutral "species"). The activity of water is assumed to be equal to unity (because the solutions are very dilute). The Debye-Huckel expression for activity coefficients, in conjunction with the above equation for γ leads to

$$\gamma_{\text{Na}^+} = \gamma_{\text{K}^+} = \gamma_{\text{H}^+} = \gamma_{\text{OH}^-}$$

for a specific composition. K_{NaOH} , K_{KOH} and $K_{\text{H}_2\text{O}}$ were obtained from expressions given in Appendix E.

Details of the mathematical technique used to solve the equations are given in Appendix A.

Step 5 Calculation of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$

The balanced chemical "reactions" generated by step 3 are run through a computer programme, to calculate $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ (the "apparent standard molal Gibbs free energy of formation"). For example, assume that albite is in equilibrium with one of the experimental solutions. Then we can write, for the pressure and temperature of the experiment:

The only unknown in this equation is $\Delta G_{\text{AlO}_{1.5}(\text{aq})}$. We can further break down $\Delta G_{\text{AlO}_{1.5}(\text{aq})}$ as follows:

$$\Delta G_{\text{AlO}_{1.5}(\text{aq})} = \Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ} + RT \ln a_{\text{AlO}_{1.5}}$$

$$\text{where } a_{\text{AlO}_{1.5}} = m_{\text{AlO}_{1.5}}$$

[Henry's Law constant = 1]

Hence, for each phase in figures 1-3 and 1-4, and for each experimental solution, and for each datafile we obtain a value of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$. The datafiles correspond to tables 3-3 to 3-17.

Tables 3-13 (labradorite solubility), 3-17 (Qtz-Lab-Mc solubility), 3-12 (quartz solubility) and 3-11 (leucite disequilibrium results) were excluded from the calculation.

Also, analyses indicative of disequilibrium (as identified in tables 3-3 to 3-17) were excluded from the calculation. A total of 282 analyses remained. No values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ can be obtained by assuming equilibrium between the solution and quartz, since Al is not involved in this energy balance. The phases

considered (including polymorphs) were:

Crn Bhm Dsp Gbs Anl Dehyd Anl Ab Low Ab High Ab
Kfs Max Mc High San Ne Kls Kln Prl Ms Pg Als Lct

This resulted in 5640 values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ (20 phases x 282 analyses).

Step 6 Analyse the values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$

The complete set of values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ is not presented here. Instead, tables 4-6 to 4-12 were compiled to illustrate the general pattern of the results.

Several features can be noted in the results:

1. The values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ show a narrow total range of -175.0 to -200.0 kcal mole⁻¹. These values are reasonable and lie in between the values for Na⁺ (about -70.0 kcal mole⁻¹, HKF p1442) and SiO₂(aq) (about -200.0 kcal mole⁻¹, W+H p1346).
2. Within each datafile, the values show consistent P-T trends. These trends are best shown by table 3-3 (Currie's 1968 experiments), assuming equilibrium with albite (table 4-6, figures 4-4 and 4-5).
3. Values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ for individual minerals, in all the datafiles, show low high ranges of less than 20 kcals.
4. Values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ using the various dissolution datafiles show good agreement.
5. Detailed numerical analysis

If two or more of the 20 phases were in equilibrium with the same solution, they should yield identical values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$.

Tables 4-7 to 4-12 list the values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ obtained at six different P-T conditions, assuming equilibration of the solution with respect to the 20 different phases for the various datafiles (tables 3-3 to 3-17).

Table 4-6 Standard state Gibbs free energy of $\text{AlO}_{1.5}(\text{aq})$ (kcal mole^{-1})

Values obtained using table 3-3 data, assuming equilibrium with respect to albite

Temperature (Celsius)	Pressure (bars)											
	750	1000	1250	1500	1750	2000	2250	2500	2750	3000	3250	3500
400	-185.15	-184.90	-185.50	-185.50	-185.72	-185.65		-185.90		-185.41		-185.82
450	-187.23	-186.69	-186.82	-186.79	-186.93	-186.86		-186.89		-186.94		-187.27
500	-189.87	-188.32	-187.75	-187.91	-187.47	-187.91			-188.10	-187.87		-188.96
550	-195.63	-190.52	-188.70	-188.53	-187.91	-188.06	-188.14	-188.19	-188.31			
600	-198.88	-190.72	-187.90	-187.25	-186.90	-187.21	-187.13	-186.83				

500°C, 2 kbar values:

-188.04
-187.75
-187.92
-187.82
-187.94
-188.03

500°C, 2 kbar values:
 -188.04
 -187.75
 -187.92
 -187.82
 -187.94
 -188.03

For a given experiment, the differences in values for $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ are often so small that they lie within the error range both of the thermodynamic data and of solid solution effects. [Solid solutions will lead to more negative values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ than are obtained assuming pure end-member phases.] It is apparent that the values obtained for $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ are very critically dependent on the values of ΔG° for the other aqueous species and solid phases involved in the assumed equilibrium.

The values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ obtained assuming equilibrium with respect to the starting solids, are emphasised by **bold print** in tables 4-7 to 4-12. The values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ in **bold print** show systematic differences between tables 3-3 to 3-17 at fixed temperature and pressure. Values obtained assuming equilibrium with respect to albite are almost invariably 0.75 to 2.0 kcal mole⁻¹ less negative than values obtained assuming equilibrium with respect to microcline, when both albite and microcline were present in the starting material. The values obtained for leucite when leucite was present in the starting material are several kcal mole⁻¹ more negative than the other **bold print** values.

Table 4-7* Values of $-\Delta G_{AlO_{1.5}(aq)}^0$ at 400°C and 1 kbar (in kcal mole⁻¹), calculated assuming equilibrium with respect to different phases

Table Run no.	3-3 PA15	3-4 Al	3-6 MI	3-7 AM1	3-8 AM11	3-9 AC69	3-10 AC38	3-14 Fl	3-15 Gd
Crn	184.91	184.93	184.89	183.22	181.92	186.25	186.61	184.80	183.88
Bhm	184.69	184.70	184.66	183.00	181.70	186.03	186.39	184.58	183.65
Dsp	184.70	184.72	184.68	183.01	181.71	186.04	186.40	184.59	183.66
Gbs	180.06	180.08	180.04	178.37	177.07	181.40	181.77	179.95	179.03
Anl	185.37	184.97	184.62	185.01	184.46	188.36	189.77	185.20	184.82
Dehy Anl	180.73	180.33	179.98	180.36	179.82	183.72	185.13	180.56	180.18
Ab	184.95	184.71	184.47	185.83	185.88	187.99	189.56	185.31	186.00
Low Ab	184.87	184.63	184.39	185.75	185.80	187.91	189.48	185.23	185.92
Hlgh Ab	184.12	183.87	183.63	185.00	185.04	187.16	188.73	184.47	185.16
Kfs	179.67	181.47	185.83	187.26	187.34	188.73	191.88	186.57	187.29
Max Mc	179.57	181.38	185.73	187.16	187.24	188.64	191.78	186.48	187.19
Hlgh San	179.20	181.01	185.37	186.80	186.87	188.27	191.41	186.11	186.83
Ne	184.47	183.91	183.46	182.86	181.73	187.41	188.66	183.78	182.33
Kls	179.06	180.56	184.70	184.16	183.07	188.03	190.86	184.92	183.50
Kln	183.06	183.23	183.29	182.61	181.90	184.44	184.97	183.47	183.61
Pr1	181.78	182.10	182.27	182.57	182.45	183.21	183.89	182.71	183.92
Ms	184.56	185.18	186.60	185.97	185.13	188.48	189.77	186.79	186.42
Pg	185.75	185.68	185.57	184.92	184.07	187.66	188.42	185.80	185.41
Als	184.58	184.68	184.69	183.51	182.51	185.95	186.39	184.73	184.34
Qtz	178.80	180.46	184.71	185.16	184.65	187.82	190.81	185.19	184.84

Values in bold type correspond to those obtained by assuming equilibrium with respect to the starting material

Table 4-8 Values of $\Delta G_{AlO_1.5(aq)}^\circ$ at 400°C and 2 kbar (in kcal mole⁻¹), calculated assuming equilibrium with respect to different phases

Table Run no.	3-3 PA19	3-4 A54	3-6 M10	3-7 AM6	3-10 AC44	3-15 PP31G
Crn	185.40	185.57	185.25	185.55	187.31	184.62
Bhm	185.30	185.47	185.15	185.45	187.21	184.52
Dsp	185.36	185.53	185.21	185.51	187.26	184.58
Gbs	180.96	181.13	180.81	181.11	182.86	180.18
An1	185.82	185.90	185.15	186.67	190.26	184.18
Dehy An1	180.80	180.87	180.13	181.64	185.23	179.15
Ab	185.80	186.05	185.38	187.24	190.30	185.16
Low Ab	185.72	185.97	185.30	187.16	190.22	185.08
High Ab	184.96	185.20	184.54	186.40	189.46	184.31
Kfs	181.35	182.22	186.77	188.78	193.55	186.47
Max Mc	181.26	182.12	186.68	188.68	193.46	186.38
High San	180.88	181.75	186.30	188.31	193.08	186.00
Nc	184.33	184.23	183.41	184.59	188.70	181.69
Kls	179.83	180.35	184.75	186.08	191.90	182.95
Kin	184.28	184.62	184.38	185.02	186.25	184.50
Prl	183.43	183.95	183.78	184.76	185.47	184.65
Ms	185.59	185.99	187.30	188.17	190.93	186.78
Pg	186.50	186.69	186.20	187.08	189.27	185.76
Als	185.28	185.54	185.26	185.53	187.22	185.00
Lct	179.94	180.63	185.11	186.77	192.07	184.06

Values in bold type correspond to those obtained by assuming equilibrium with respect to the starting material.

Table 4-9 Values of $-ΔG_{AlO_{1.5}(aq)}^{00}$ at 500°C and 1 kbar (in kcal mole⁻¹), calculated assuming equilibrium with respect to different phases

Table Run no.	3-3 PA33	3-4 A21	3-5 C3	3-6 M21	3-7 AM3	3-8 AM15	3-9 AC72	3-10 AC39	3-15 G21
Crn	185.40	185.41	184.17	184.38	184.12	181.48	185.34	186.56	183.83
Bhm	184.45	184.46	183.23	184.38	183.17	180.53	184.39	185.61	182.88
Dsp	184.15	184.16	182.92	184.08	182.87	180.23	184.09	185.31	182.58
Gbs	178.30	178.31	177.08	178.24	177.02	174.38	178.24	179.47	176.73
Anl	188.64	188.35	184.92	186.56	186.10	183.12	188.35	189.30	188.00
Dehy' Anl	184.87	184.58	181.15	182.79	182.33	179.35	184.58	185.52	184.23
Ab	188.23	187.94	184.23	186.00	186.05	184.97	187.96	188.37	189.76
Low Ab	188.00	187.72	184.00	185.78	185.83	184.74	187.73	188.14	189.53
Hlgh Ab	187.56	187.27	183.56	185.34	185.39	184.30	187.29	187.70	189.09
Kfs	182.96	182.87	183.62	188.12	186.76	186.43	188.19	190.39	190.65
Max Mc	182.70	182.61	183.36	187.86	186.50	186.17	187.93	190.12	190.39
Hlgh San	182.67	182.59	183.33	187.83	186.47	186.15	187.90	190.10	190.36
Ne	188.95	188.66	185.51	187.02	186.04	181.18	188.64	190.13	186.15
Kls	183.52	183.44	184.75	188.98	186.59	182.50	188.71	191.99	186.88
Kln	181.54	181.55	180.03	181.32	180.63	179.87	181.50	182.18	182.14
Prl	180.16	180.17	178.37	179.79	179.61	180.74	180.14	180.28	182.92
Ms	185.35	185.33	184.76	187.03	185.77	183.90	187.05	188.60	186.87
Pg	186.49	186.40	184.33	185.70	184.91	182.78	186.35	187.31	185.95
Als	184.98	184.99	183.62	184.84	183.89	182.19	184.93	185.88	184.50
Lct	183.25	183.17	184.20	188.56	186.69	184.48	188.46	191.20	188.78

Values in bold type correspond to those obtained by assuming equilibrium with respect to the starting material

Table 4-10 Values of $-\Delta G_{AlO_1.5(aq)}^0$ at 500°C and 2 kbar ($\ln \text{ kcal mole}^{-1}$), calculated assuming equilibrium with respect to different phases

Table Run no.	3-3 PA40	3-4 PP20F	3-5 C5	3-6 PP24C	3-7 ^a AM7	3-10 AC43	3-14 PP34D	3-15 G29	3-16 KG3
Crn	186.86	186.69	186.93	186.80	186.74	188.74	186.77	185.96	185.05
Bhm	186.10	185.93	186.17	186.04	185.98	187.98	186.01	185.20	184.29
Dsp	185.84	185.67	185.91	185.78	185.72	187.72	185.75	184.94	184.03
Gbs	180.35	180.18	180.42	180.28	180.23	182.23	180.26	179.45	178.54
Anl	187.88	187.21	187.96	187.24	187.67	190.26	187.05	186.06	186.12
Dehy Anl	183.61	182.94	183.68	182.96	183.40	185.99	182.77	181.78	181.85
Ab	188.04	187.41	188.28	187.54	188.07	189.92	187.33	187.36	188.23
Low Ab	187.81	187.18	188.05	187.31	187.84	189.69	187.11	187.14	188.40
High Ab	187.36	186.73	187.60	186.86	187.40	189.24	186.66	186.69	187.55
Kfs	184.07	183.82	185.51	188.99	189.38	192.98	188.56	188.36	189.20
Max Mc	183.81	183.56	185.25	188.73	189.12	192.72	188.30	188.10	188.94
High San	183.77	183.53	185.21	188.70	189.08	192.69	188.27	188.07	188.90
Ne	187.20	186.49	187.11	186.41	186.74	190.08	186.23	184.22	183.49
Kls	183.15	182.82	184.26	187.78	187.96	193.06	187.37	185.14	184.38
Kln	184.14	184.02	184.37	184.22	184.27	185.52	184.19	184.39	184.29
Pr1	183.41	183.33	183.81	183.64	183.79	184.30	183.60	184.82	185.51
Ms	186.87	186.69	187.40	188.48	188.57	191.10	188.32	187.71	187.38
Pg	187.57	187.25	187.70	187.36	187.51	189.45	187.28	186.75	186.43
Als	186.81	186.67	186.97	186.83	186.82	188.45	186.80	186.49	185.99
Lct	183.52	183.23	184.80	188.30	188.58	192.93	187.88	186.66	186.70

Values in bold type correspond to those obtained by assuming equilibrium with respect to the starting material.

Table 4-11 Values of $-\Delta G_{101.5}^{\circ}(\text{aq})$ at 600°C and 1 kbar (in kcal mole⁻¹), calculated assuming equilibrium with respect to different phases

Table Run no.	3-3 PA42	3-4 A41	3-6 PP25A	3-7 AM4	3-8 AM20	3-9 AC74	3-10 AC40	3-15 G41	3-16 KG11
Crn	183.91	183.95	186.06	182.95	179.71	183.71	184.31	182.50	180.70
Bhm	182.14	182.17	184.29	181.18	177.94	181.94	182.53	180.73	178.93
Dsp	181.52	181.56	183.67	180.56	177.32	181.32	181.92	180.12	178.31
Gbs	174.50	174.54	176.65	173.54	170.30	174.30	174.90	173.10	171.29
An1	191.27	189.74	194.02	188.58	185.21	192.31	189.35	192.95	190.61
Dehy An1	188.52	187.00	191.27	185.84	182.47	189.56	186.61	190.21	187.86
Ab	190.97	189.39	193.85	188.24	187.86	192.48	188.58	195.95	193.41
Low Ab	190.51	188.94	193.40	187.78	187.40	192.02	188.13	195.49	192.96
High Ab	190.42	188.84	193.30	187.69	187.31	191.93	188.03	195.40	192.86
Kfs	187.50	183.99	194.21	188.82	189.41	192.86	190.72	197.04	193.09
Max Hc	187.02	183.51	193.73	188.34	188.93	192.38	190.25	196.56	192.61
High Sam	187.33	183.82	194.04	188.66	189.25	192.69	190.56	196.88	192.92
Ne	192.96	191.49	195.58	190.33	183.97	193.53	191.52	191.36	189.20
Kls	189.37	185.95	195.81	190.79	185.39	193.78	193.53	192.32	188.74
Kln	177.89	177.88	180.18	176.88	176.64	178.16	177.81	179.78	177.78
Pr1	176.38	176.32	178.80	175.33	178.08	177.13	175.83	181.57	179.38
Ms	185.18	184.04	188.86	184.99	183.02	186.84	186.52	187.43	184.91
Pg	185.65	185.15	188.05	184.11	181.82	186.02	185.12	186.38	184.33
Als	183.19	183.20	185.40	182.20	180.46	183.22	183.35	183.43	181.53
Lct	189.02	185.55	195.59	190.39	187.98	193.90	192.71	195.26	191.50

Values in bold type correspond to those obtained by assuming equilibrium with respect to the starting material

Table 4-12 Values of $-\Delta G_{\text{AlO}_{1.5}}^{\circ}(\text{aq})$ at 600°C and 2 kbar (in kcal mole⁻¹), calculated assuming equilibrium with respect to different phases

Table Run no.	3-3 PA14	3-4 Al	3-6 Ml	3-7 AM1	3-8 AM11
Crn	187.16	188.05	187.72	188.07	189.46
Bhm	185.67	186.56	186.23	186.58	187.96
Dsp	185.10	185.98	185.65	186.00	187.39
Gbs	178.61	179.50	179.17	179.52	180.90
Anl	187.05	188.33	185.66	188.00	188.18
Dehy Anl	183.62	184.90	182.23	184.57	184.75
Ab	187.21	188.59	185.48	188.34	187.59
Low Ab	186.75	188.13	185.02	187.88	187.13
High Ab	186.65	188.03	184.92	187.78	187.03
Kfs	181.86	183.08	187.05	189.47	190.61
Max Mc	181.38	182.60	186.57	188.99	190.13
High San	181.69	182.91	186.88	189.30	190.43
Ne	187.49	188.68	186.44	188.26	189.38
Kls	182.08	183.11	187.96	189.33	192.34
Kln	182.54	183.53	182.76	183.63	184.08
Pr1	181.68	182.76	181.55	182.95	182.46
Ms	185.72	186.71	187.82	188.86	190.16
Pg	186.81	187.86	186.60	187.79	188.46
Als	186.85	187.79	187.24	187.85	188.77
Lct	182.45	183.58	187.99	189.88	191.96

Values in bold type correspond to those obtained by assuming equilibrium with respect to the starting material

If

- a) the thermodynamic model is good,
- b) the solutions reached equilibrium with respect to the starting material,
- c) the thermodynamic data are accurate,

then the values in **bold** print within each table should be very similar. This is, very approximately, true. But the values obtained assuming equilibrium with respect to other phases within each table are also very similar, and the variation in values between tables is very small. In principle, if conditions a) and c) above are satisfied, this kind of comparison may indicate which phases the solution is most likely to have equilibrated with. In practice, the values in tables 4-7 to 4-12 show too much scatter to allow a detailed comparison.

6. Error analysis

A very simplistic error analysis is presented here. The data necessary for a thorough analysis are not available. HDNB and HKF do not provide error estimates for their thermodynamic data. No error estimates for $\log K_{\text{KOH}}$ or $\log K_{\text{NaOH}}$ are presented in Appendix E. The values of $\log K_{\text{NaOH}}$ are entirely suppositive.

An error in $\log K_{\text{NaOH}}$ may lead to a major error in the derived value of m_{Na^+} . This in turn can lead to a major error in ΔG_{Na^+} , as can be seen from the expression

$$\Delta G = \Delta G^{\circ} + RT \ln \gamma + RT \ln m$$

At 500°C, $m = .10^{-3}$ $RT \ln m = -10.613 \text{ kcal mole}^{-1}$

" 500°C, $m = 10^{-6}$ $RT \ln m = -21.226 \text{ kcal mole}^{-1}$

It can be seen in table 4-6 that the derived values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ show random fluctuations at constant temperature. These fluctuations are probably due to experimental error. Values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ at 500°C and 2 kbar show a range of 0.3 kcal mole⁻¹ which gives an indication of the experimental error.

The values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ at constant pressure increase with increasing temperature up to 550°C. Above 550°C and with $P > 1$ kbar, $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ decreases slightly. This may be due to the anomalously low Al concentrations in Currie's 1968 600°C experiments (see figure 3-10).

Summary

The derived values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ are highly sensitive to measured solution compositions, and much less sensitive to the assumed equilibrium mineral. Considering this sensitivity, the measure of agreement in tables 4-7 to 4-12 is good and lends support to the applicability of the solution model. The variation in values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ within each of tables 4-7 to 4-12 may be largely ascribed to

- i) experimental error. This can be reduced to less than 0.3 kcal mole⁻¹ on the evidence of the table 3-3, 500°C, 2 kbar data, but probably rises to several kcal mole⁻¹ in some of the experiments.
- ii) inaccurate values of $\log K_{\text{NaOH}}$ and/or $\log K_{\text{KOH}}$, again leading

to potential errors of a few kcal mole⁻¹.

The values of $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ calculated assuming albite equilibrium with the solutions in table 3-3 are taken as reference values (table 4-6), to which values obtained from other datafiles can be compared. This is justifiable because:

- i) The data in table 3-3 are internally consistent, as evidenced by the straight line plots of $\ln m_x$ vs. $\ln V_{\text{H}_2\text{O}}$.
- ii) The data in table 3-3 define a more closely spaced P-T grid than is available in the other tables.
- iii) The starting material (Amelia albite) is better characterised thermodynamically than the other starting materials.

Step 7 Data regression

The data in table 4-6 were fitted to HKF's equation 276, using a non-linear regression computer programme. Details of the programme are given in Appendix A. The resultant parameters have no physical significance, but do allow one to calculate $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ analogously to other species in HKF's database. Other data were not included in the regression analysis, because by doing so, errors may have been introduced due to poorly characterised starting material and inaccurate thermodynamic data. HKF's equation 276 is given below:

$$\begin{aligned} \Delta G_{\text{P,T}}^{\circ} = & \Delta G_{\text{f}}^{\circ} - S_{\text{P,T}}^{\circ} (T - T_{\text{r}}) \\ & - c_1 (T \ln(T/T_{\text{r}}) - T + T_{\text{r}}) \\ & + c_2 (T - T_{\text{r}} - (T - \theta) \ln((T - \theta)/(T_{\text{r}} - \theta))) \\ & + \frac{2(a_1(T - \theta) + a_3 T)(P - P_{\text{r}}) + (a_2(T - \theta) + a_4 T)(P^2 - P_{\text{r}}^2)}{2(T - \theta)} \\ & - \omega (Z_{\text{P,T}} - Z_{\text{P,T}_{\text{r}}} - V_{\text{P,T}_{\text{r}}}(T - T_{\text{r}})) \end{aligned}$$

The "fit" parameters for $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ are:

$$\Delta G_{\text{f}}^{\circ} = -1.50642858\text{E}+05$$

$$S_{\text{P,T}_{\text{r}}}^{\circ} = 2.33881761\text{E}+02$$

$$c_1 = 9.98113169\text{E}+00$$

$$c_2 = -1.33461941\text{E}+02$$

$$a_1 = -3.02780057\text{E}+01$$

$$a_2 = 5.38574100\text{E}-03$$

$$a_3 = 1.77749184\text{E}+01$$

$$a_4 = -2.81360697\text{E}-03$$

$$\omega = -9.61042828\text{E}+04$$

$$Z_{P_r, T_r} = -0.012744$$

$$Y_{P_r, T_r} = -0.000058017$$

[θ was taken to be equal to θ for Al^{3+} (229.6). This avoided problems caused by $(T_r - \theta)$ becoming negative, and hence $\ln \left(\frac{T_r - \theta}{T_r - \theta} \right)$ becoming undefined.]

The curves in figures 4-4 and 4-5 were calculated using these parameters.

In theory, $\Delta G_{AlO_{1.5}}^{\circ}(aq)$ could be broken down into enthalpy, entropy and volume terms. This is not done here because of

- a) numerical difficulties in maintaining consistency with HKF's model,
- b) lack of good uses for the resultant data.

Figure 4-4 $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ as a f(T) at constant P
(curves calculated using HKF's equation 276 and
constants listed in the text)

Figure 4-5 $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ as a f(P) at constant T
(points calculated from table 3-3 data (Currie's
1968 albite dissolution experiments); curves
calculated using HKF's equation 276 and constants
listed in the text)

3

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(ANSI and ISO TEST CHART No. 2)

Step 8 Prediction of corundum solubility

The "fit" parameters generated in step 7 can be used to predict corundum solubility in pure water. Predicted values are given in table 4-13.

Table 4-13 Predicted solubilities of corundum (in ppm Al)

	400°C	500°C	600°C
1 kbar	67.7	449.5	1489.8
2 kbar	128.9	406.9	154.2
3 kbar	166.7	702.4	220.2

In step 2 it was suggested that the experimental solutions presented in Chapter 3 may have been supersaturated with respect to corundum. The predicted values in table 4-13 contradict this suggestion. This implies a serious flaw in the model.

Although the simple model led to apparently reasonable and consistent values of $\Delta G^\circ_{\text{AlO}_{1.5}(\text{aq})}$, it can now be seen that these numbers have no predictive value, and hence no real usefulness. The model is completely superceded in the following steps by more complex models, but it formed the basis on which they were built. Hence, it would be very misleading to omit its development from this thesis.

Step 9 Additional experimental constraints on the model

A major reason for initially attempting to interpret only the data in Chapter 3 was that those experimental solutions are very dilute. Hence, one could not reasonably blame activity coefficient errors for the failure of the model. When one considers concentrated solutions, uncertainties with respect to activity coefficients become significant and lead to potential major error sources.

However, in order to adequately constrain improved models, it became necessary to consider additional experimental data, involving concentrated (up to 1.5m) electrolyte solutions in equilibrium with either corundum or quartz. The data involving corundum, from the work of Anderson and Burnham (1967) and Pascal (1984), are given in table 4-14.

Anderson and Burnham (1983) noted that corundum solubility increases in KOH solutions according to

$$m_{Al} \approx 0.8 m_{KOH}$$

at 600°C, and is independent of pressure in the range 2 to 6 kbar. Pascal (1984) obtained

$$m_{Al} = 0.89 m_{KOH}$$

at 600°C and 2 kbar, based on seven experiments between 0.1m KOH and 1.0m KOH.

Quartz solubility in KOH solutions shows a very similar linear increase as a function of m_{KOH} (Anderson and Burnham, 1983). In addition, NaOH solutions have effects very similar to KOH solutions, on both corundum and quartz solubilities.

In summary, these effects can be written as:

$$m_{Al} = m_{CW} + N m_X$$

where m_{Al} = molality of Al in solution

m_{CW} = corundum solubility in pure water

(expressed as molality of Al),

negligible when $m_X > 0.1$

m_X = molality of either KOH or NaOH

N = constant

$$m_{Si} = m_{QW} + N m_X$$

where m_{Si} = molality of Si in solution

m_{QW} = quartz solubility in pure water

(expressed as molality of Si),

m_X = molality of either KOH or NaOH

N = constant

N for Crn-KOH experiments equals 0.89 at 600°C, 2 kbar, and 0.94 at 700°C, 2 kbar (Pascal, 1984). N is roughly equal to 0.9 for Crn-KOH, Crn-NaOH, Qtz-KOH and Qtz-NaOH experiments at temperatures between 600°C and 900°C and pressures between 2 kbar and 6 kbar (Anderson and Burnham, 1967, 1983).

These constraints, with particular reference to the system Al_2O_3 - H_2O -KOH, at 600°C and 2 kbar, are invoked in step 10.

The data of Pascal on quartz solubility in KOH and NaOH solutions (Pascal's table 2-1) are not considered here, because of experimental problems (Anderson, pers. comm., 1985).

Table 4-14. Experimental data on corundum solubility in pure water and electrolyte solutions

Run no.	T (°C)	P (kbar)	Initial solution	Al (mmol)	Notes
AB-1	700.0	6.00	pure water	18.8	a
AB-2	700.0	6.00	pure water	17.3	a
AB-3	800.0	6.00	pure water	11.6	a
AB-4*	800.0	5.70	pure water	8.4	a c
AB-5	900.0	6.00	pure water	20.6	a
AB-6	900.0	6.75	pure water	14.1	a
AB-7	800.0	6.17	4.571m KCl	29.4	a
AB-8	800.0	6.00	4.571m KCl	25.5	a
AB-9	800.0	6.00	0.9006m NaCl	18.0	a
AB-10	600.0	2.00	0.346m KOH	307.9	a
AB-11	600.0	2.00	0.346m KOH	311.9	a
AB-12	600.0	3.00	0.346m KOH	319.7	a
AB-13	600.0	4.00	0.346m KOH	255.0	a
AB-14	600.0	4.00	0.346m KOH	335.4	a
AB-15	600.0	6.00	0.346m KOH	286.4	a
AB-16*	600.0	6.00	0.346m KOH	298.1	a c
AB-17	800.0	5.00	0.346m KOH	341.3	a
AB-18	900.0	6.00	0.346m KOH	317.7	a
AB-19	900.0	6.00	0.346m KOH	311.9	a
AB-20*	600.0	6.00	0.720m KOH	566.8	a c
AB-21	600.0	6.00	0.720m KOH	531.5	a
AB-22*	900.0	6.00	0.720m KOH	625.7	a c
AB-23	900.0	6.00	0.720m KOH	621.7	a
AB-24	600.0	6.00	1.480m KOH	1172.9	a
AB-25*	600.0	6.00	1.480m KOH	1220.0	a c
AB-26	900.0	6.00	1.480m KOH	1343.5	a
AB-27	900.0	6.00	1.480m KOH	1404.3	a
AB-28	800.0	6.13	0.113m NaOH	127.5	a
AB-29	900.0	6.00	0.113m NaOH	125.5	a
MLP-C1	500.0	1.86	0.4795m KOH	432.3	b
MLP-C2	500.0	2.00	0.7944m KOH	710.5	b
MLP-C3	610.0	2.07	0.1007m KOH	90.8	b
MLP-C4	602.0	2.00	0.2033m KOH	182.6	b
MLP-C5	600.0	2.28	0.4061m KOH	363.2	b
MLP-C6	600.0	2.21	0.4805m KOH	425.2	b

MLP-C7	602.0	2.13	0.6296m KOH	553.8	b
MLP-C8	602.0	2.07	0.8297m KOH	746.8	b
MLP-C9	602.0	2.00	1.0110m KOH	894.8	b
MLP-C10	598.0	2.00	0.1189m NaOH	105.6	b
MLP-C11	601.0	2.00	0.1267m NaOH	112.5	b
MLP-C12	602.0	2.14	0.4025m NaOH	350.7	b
MLP-C13	600.0	2.14	0.4698m NaOH	405.2	b
MLP-C14	600.0	2.14	0.8713m NaOH	754.7	b
MLP-C15	698.0	2.62	0.2087m KOH	191.7	b
MLP-C16	698.0	2.65	0.4679m KOH	458.5	b
MLP-C17	700.0	2.62	0.6958m KOH	656.0	b
MLP-C18	700.0	2.62	0.1091m NaOH	100.7	b
MLP-C19	700.0	2.41	0.3041m NaOH	273.3	b
MLP-C20	700.0	2.38	0.5962m NaOH	525.9	b
MLP-C21	700.0	2.55	0.8714m NaOH	811.4	b
MLP-C22	700.0	2.34	0.9431m NaOH	814.5	b

Notes

- a) Anderson and Burnham (1967)
- b) Pascal (1984, table 2-5)
- c) Run developed a slow pressure leak. The quoted pressure is the initial pressure.

See table 4-4 for additional data on corundum solubility in pure water.

Additional data, not used to constrain the models, but useful for comparison with predicted solution compositions, are given in table 4-15.

A plot of $\log m_{Al}$ vs. $\log (m_{Na} + m_K)$ for all of the data in tables 4-14 and 4-15, plus Davis's (1972) data (table 3-18) gives a remarkable straight line for the Cl-free solutions (figures 4-6 and 4-7). This relationship was first pointed out by Anderson (pers. comm., 1985). The linear relationship suggests that the solution chemistry may be modelled quite simply. Activity coefficients which were complex functions of solution composition, would lead to a breakdown in the linearity, unless there was a fortuitous cancelling of effects. The reservations expressed above, concerning uncertainties involving activity coefficients, are reduced as a result of this relationship, which extends from dilute to concentrated solutions.

Table 4-15 Experimental data on mineral solubilities in supercritical aqueous solutions

Run no.	T (°C)	P (kbar)	Initial solids	Initial solution	Si (mmol)	Al (mmol)	Na (mmol)	K (mmol)	Notes
MLP-103	600.0	2.00	Qtz Ms Kfs	pure water	90.00	1.01	.32	1.78	a
MLP-106	600.0	2.00	Qtz Ms Kfs	pure water	107.00	1.49	.43	1.25	a
JR-1	600.0	2.00	Qtz Ms Kfs	pure water	107.00	1.33	.00	1.00	b i j
JR-7	600.0	2.00	Qtz Ms Kfs	0.1m KCl	111.60	.53	.72	100.00	b j
JR-6	600.0	2.00	Qtz Ms Kfs	0.5m KCl	74.30	.85	.00	500.00	b r j
JR-8	600.0	2.00	Qtz Ms Kfs	1.0m KCl	93.05	.71	1.46	1000.00	b j
JR-9	600.0	2.00	Qtz Ms Kfs Ab	1.0m NaCl	91.72	.96	899.25	1.79	
JR-2	600.0	2.00	Qtz Ms Kfs Ab	1.0m NaCl	83.66	.75	1000.00	.00	
JR-4	500.0	2.38	Qtz Ms Kfs	pure water	59.80	2.22	.00	.00	b i j
JR-12	500.0	2.00	Qtz Ms Kfs	H2O-CO2	87.68	1.48	.22	1.74	b
MLP-52	500.0	2.00	Qtz Ms And	0.0435m KCl	78.00	1.60	.00	43.50	a i j
MLP-51	600.0	2.00	Qtz Ms And	0.0427m KCl	93.00	.91	.00	42.70	a i j
				+ 0.000572m HCl					
MLP-60	600.0	2.00	Qtz Ms And	0.4018m KCl	129.00	1.90	.00	401.80	a i j
				+ 0.00643m HCl					
MLP-179	700.0	2.00	Qtz Kfs And	pure water	135.00	.93	.34	.68	a k
MLP-179	700.0	2.00	Qtz Kfs And	pure water	135.00	.93	.00	.60	a i j
MLP-62	700.0	2.00	Qtz Kfs And	0.319m KCl	130.00	1.60	.00	319.00	a i j
				+ 0.00790m HCl					
MLP-64	700.0	2.00	Qtz Kfs And	0.0435m KCl	164.00	1.10	.00	43.50	a i j
MLP-180	650.0	2.00	Kfs Ms And	pure water	28.30	5.30	.80	3.52	a k
MLP-180	650.0	2.00	Kfs Ms And	pure water	28.30	5.30	.30	3.10	a i
MLP-178	700.0	2.00	Kfs And Crn	pure water	57.60	2.70	.37	2.64	a k
MLP-178	700.0	2.00	Kfs And Crn	pure water	57.60	2.70	.20	2.45	a i
MLP-178b	700.0	2.00	Kfs And Crn	pure water	48.80	4.42	.91	3.51	a k
MLP-178b	700.0	2.00	Kfs And Crn	pure water	48.80	4.42	.90	3.47	a i
MLP-61	700.0	2.00	Ms And Crn	0.0435m KCl	57.00	1.80	.00	43.50	a i j
MLP-65	700.0	2.00	Ms And Crn	0.0435m KCl	71.70	1.10	.00	43.50	a i j
MLP-177b	700.0	2.00	Kfs Lct Crn	pure water	26.60	10.30	1.32	10.10	a
JR-11	600.0	2.00	Ms Lct Crn	pure water	30.42	8.78	.51	10.02	b
JR-3	600.0	2.00	Ms Lct Crn	pure water	16.50	22.15	.00	.00	b i j
MLP-68	600.0	2.00	Ms Lct Crn	0.0435m KCl	12.60	12.50	.00	43.50	a i j
JR-13	550.0	2.00	Ms Lct Crn	H2O-CO2	31.96	9.81	10.45	.38	b
JR-14	500.0	2.00	Ms Lct Crn	pure water	15.63	17.88	3.87	5.20	b
JR-5	600.0	4.00	Qtz Kfs Ms Ab	1.0m NaCl	167.70	8.77	1000.00	.00	b i j
JR-10	300.0	2.00	Qtz Kfs Ms Ab	1.0m NaCl	14.04	0.21	896.04	1.37	b

Run no	T (°C)	P (kbar)	Initial solids	Initial solution	Si (mmol)	Al (mmol)	Na (mmol)	K (mmol)	Notes
SPP-1	500.0	2.00		pure water	96.52	7.85	4.52	1.91	d
SPP-2	600.0	2.00		pure water	131.47	10.98	5.49	2.76	d
SPP-3	650.0	2.00		pure water	149.78	10.40	4.84	2.34	d
SPP-4	700.0	2.20		pure water	201.37	3.73	2.58	1.06	d
SPP-5	600.0	3.00		pure water	184.73	9.22	6.45	3.40	d
SPP-6	500.0	4.00		pure water	136.47	15.10	10.33	4.25	d
SPP-7	600.0	4.00		pure water	249.63	18.63	14.20	6.79	d
SPP-8	700.0	4.00		pure water	374.45	33.34	20.65	11.68	d
SPP-9	700.0	5.70		pure water	562.50	84.34	61.32	31.85	d
SPP-10	500.0	2.00		2.12 % HCl	103.18	14.91	254.94	99.79	d
SPP-11	600.0	2.00		2.12 % HCl	111.50	12.55	280.76	152.86	d
SPP-12	700.0	2.00		2.12 % HCl	164.76	11.77	261.39	199.57	d
SPP-13	500.0	4.00		2.12 % HCl	126.48	4.90	316.25	133.76	d
SPP-14	600.0	4.00		2.12 % HCl	174.74	9.02	290.44	140.13	d
SPP-15	700.0	4.00		2.12 % HCl	304.55	11.57	309.80	178.34	d
SPP-16	500.0	6.00		2.12 % HCl	109.84	2.75	261.39	104.03	d
SPP-17	600.0	6.00		2.12 % HCl	203.03	7.06	271.08	121.02	d
SPP-18	700.0	6.00		2.12 % HCl	302.89	12.16	300.12	131.63	d
SPP-19	600.0	2.00		0.21 % HCl	119.82	1.29	35.50	23.35	d
SPP-20	600.0	4.10		0.21 % HCl	179.73	4.71	45.18	23.35	d
SPP-21	600.0	6.10		0.21 % HCl	239.65	16.67	58.09	23.35	d
SPP-1	500.0	2.00		pure water	96.52	7.85	4.52	1.91	d m
SPP-2	600.0	2.00		pure water	131.47	10.98	5.49	2.76	d m
SPP-3	650.0	2.00		pure water	149.78	10.40	4.84	2.34	d m
SPP-4	700.0	2.20		pure water	201.37	3.73	2.58	1.06	d m
SPP-5	600.0	3.00		pure water	184.73	9.22	6.45	3.40	d m
SPP-6	500.0	4.00		pure water	136.47	15.10	10.33	4.25	d m
SPP-7	600.0	4.00		pure water	249.63	18.63	14.20	6.79	d m
SPP-8	700.0	4.00		pure water	374.45	33.34	20.65	11.68	d m
SPP-9	700.0	5.70		pure water	562.50	84.34	61.32	31.85	d m
SPP-10	500.0	2.00		2.12 % HCl	103.18	27.46	254.94	99.79	d m
SPP-11	600.0	2.00		2.12 % HCl	111.50	10.79	280.76	152.86	d m
SPP-12	700.0	2.00		2.12 % HCl	164.76	11.18	261.39	199.57	d m
SPP-13	500.0	4.00		2.12 % HCl	126.48	2.55	316.25	133.76	d m
SPP-14	600.0	4.00		2.12 % HCl	174.74	5.30	290.44	140.13	d m
SPP-15	700.0	4.00		2.12 % HCl	304.55	8.43	309.80	178.34	d m

Run no.	T (°C)	P (kbar)	Initial solids	Initial solution	Si (mmol)	Al (mmol)	Na (mmol)	K (mmol)	Notes
SPP-16	500.0	6.00		2.12 % HCl	109.84	1.26	261.39	104.03	d m
SPP-17	600.0	6.00		2.12 % HCl	203.03	3.53	271.08	121.02	d m
SPP-18	700.0	6.00		2.12 % HCl	302.89	7.06	300.12	131.63	d m
SPP-19	600.0	2.00		0.21 % HCl	119.82	1.20	35.50	23.35	d m
SPP-20	600.0	4.10		0.21 % HCl	179.73	3.14	45.18	23.35	d m
SPP-21	600.0	6.10		0.21 % HCl	239.65	13.14	58.09	23.35	d m
H-1	650.0	2.90		pure water	209.69	27.46	14.20	5.95	e
H-2	550.0	3.00		pure water	196.38	35.30	11.30	5.52	e
H-3	600.0	3.50		pure water	289.57	47.07	18.39	8.49	e
H-4	550.0	5.50		pure water	277.92	39.23	20.01	7.22	e
H-5	600.0	5.70		pure water	452.66	84.34	41.95	15.71	e
H-6	650.0	5.70		pure water	441.01	92.18	61.32	18.90	e
H-7	650.0	7.90		pure water	906.99	209.86	129.08	38.22	e
H-8	600.0	9.60		pure water	805.48	168.67	109.72	36.09	e
H-9	650.0	9.70		pure water	1116.68	253.01	171.04	42.46	e
H-10	700.0	9.90		pure water	1561.02	372.65	229.12	65.82	e
BELL-1	500.0	2.00		pure water	49.76	3.00	3.17	1.15	e
BELL-2	500.0	1.00		pure water	26.63	11.98	.81	.23	e
BELL-3	400.0	1.00		pure water	18.97	.90	.86	.30	e
BELL-4	400.0	2.00		pure water	33.28	2.53	2.57	.88	e
BELL-5	500.0	1.50		pure water	34.95	2.48	1.91	.77	e
BELL-6	500.0	2.50		pure water	64.07	7.65	6.13	2.35	e
SPENG-1	845.0	2.00	Sa	pure water	76.55	3.92	.00	8.49	f i
SPENG-2	840.0	3.00	Sa	pure water	111.50	19.61	.00	21.23	f i
SPENG-3	850.0	3.50	Sa	pure water	174.74	37.26	.00	31.85	f i
SPENG-4	850.0	4.00	Sa	pure water	271.27	66.69	.00	61.57	f i
SPENG-5	830.0	5.00	Sa	pure water	416.05	117.68	.00	101.91	f i
SPENG-6	760.0	6.00	Sa	pure water	532.55	174.56	.00	167.73	f i
SPENG-7	840.0	3.00	Lct	pure water	131.47	49.03	.00	50.95	f i
SPENG-8	850.0	4.00	Lct	pure water	232.99	133.37	.00	152.86	f i
SPENG-9	795.0	5.00	Lct	pure water	347.82	304.01	.00	256.90	f i
SPENG-10	740.0	6.60	Lct	pure water	617.42	584.48	.00	454.35	f i
MHMC-1	500.0	1.00	Mc	pure water	8.49	2.50	.00	2.60	g i
MHMC-2	500.0	2.00	Mc	pure water	28.15	7.77	.00	8.33	g i

Notes for table 4-15

- a) Pascal (1984)
- b) Rao and Anderson (Anderson, pers. comm., 1985)
- c) Harding pegmatite (Clark, 1966, p432)
- d) Spruce Pine pegmatite (Clark, 1966, p433-434)
The feldspars were completely altered in many of the
HCl-bearing experiments (Anderson, pers. comm., 1985)
- e) Belleoram Stock (Ermanovics et al., 1967)
- f) Spengler (quoted by Clark, 1966, p434-435)
- g) Morey and Hesselgesser (1951)
- i) Na not determined
- j) K not determined
- k) result taken from Pascal (1984, table 2-16)
- l) result taken from Anderson (pers. comm., 1985)
- m) Al_2O_3 determined "spectrochemically"

Figure 4-6 $\log_{10} m_{Al}$ vs. $\log_{10} m_{Na+K}$ for a large collection of experimental data

Key to symbols

- a) $\square$ Pascal (table 4-15) Where Pascal's data conflict with those of Anderson, Anderson's are preferred (Anderson, pers comm.; see notes k and l in table 4-15)
- b) $\square$ Rao and Anderson (table 4-15)
- c) Δ Harding pegmatite (table 4-15)
- d) $\square$ Spruce Pine pegmatite (table 4-15) The "spectrochemical" Al analyses are not plotted
- e) $+$ Belleoram Stock (table 4-15)
- f) $\diamond$ Spengler (table 4-15)
- g) $+$ Morey and Hesselgesser (table 4-15)
- h) $*$ Anderson and Burnham (table 4-14)
- i) $\times$ Pascal (table 4-14)
- j) ∇ Davis (table 3-18)

Figure 4-7 $\log_{10} m_{Al}$ vs. $\log_{10} m_{Na+K}$ for a large collection of Cl-free experimental data

Key to symbols

- a) $\circ$ Pascal (table 4-15) Where Pascal's data conflict with those of Anderson, Anderson's are preferred (Anderson, pers comm.; see notes k and l in table 4-15)
- b) $\square$ Rao and Anderson (table 4-15)
- c) Δ Harding pegmatite (table 4-15)
- d) $\square$ Spruce Pine pegmatite (table 4-15) The "spectrochemical" Al analyses are not plotted
- e) $+$ Belleoram Stock (table 4-15)
- f) $\diamond$ Spengler (table 4-15)
- g) $+$ Morey and Hesselgesser (table 4-15)
- h) $*$ Anderson and Burnham (table 4-14)
- i) $\times$ Pascal (table 4-14)
- j) ∇ Davis (table 3-18)

This figure is based on a graph first produced by Anderson (pers. comm., 1985)

Step 10. Development of an improved model - theoretical aspects

The simple model explains the data moderately well, but fails in two major areas:

- 1) Predictions of corundum solubility (as given in table 4-13) appear too high by about 1-3 orders of magnitude. They are inconsistent with the earlier hypothesis that the experimental solutions are supersaturated with respect to corundum.
- 2) The model cannot explain the large increase in quartz and corundum solubilities in NaOH or KOH solutions.

After rejecting the simple model, a fundamental decision must be made concerning improved models. Two different approaches could be taken. Either

- 1) refine the activity models for the aqueous species e.g. by letting $\gamma_{\text{AlO}_{1.5}}$ and γ_{SiO_2} depart from unity;
- or
- 2) introduce additional or alternative aqueous species.

From a strict thermodynamic point of view, the choice is arbitrary. However, if we try to make the model correspond as closely as possible to what is considered to be the actual "structure" of the solution, the model may be both simpler and have greater predictive power.

When one talks about ion association involving a strong electrolyte (e.g. KOH or KCl) at room temperature and pressure, the distinction between free ions and ion pairs is somewhat arbitrary (Pitzer, 1981). However, as temperature increases, and the dielectric constant of water decreases, the distinction

should become better defined.

At room temperature and pressure, and at higher temperatures and pressures (up to 250°C at saturated vapour pressure), Al in dilute aqueous solutions has been modelled in terms of

(Kuyunko et al., 1983). As pH increases, the dominant species shifts to the right in this series. The same effect should be observable at higher temperatures and pressures, but the pH range of stability of the neutral species should be much expanded, because of the decrease in ϵ (Baes and Mesmer, 1981).

This suggests that one possible new model to try would involve $\text{Al}(\text{OH})_3$ and $\text{Al}(\text{OH})_4^-$ to explain the Crn-H₂O-KOH data. One can immediately object to this model by noting that the $\text{Al}(\text{OH})_4^-$ species must account for almost all of the Al in solution (assuming that $m_{\text{Al}(\text{OH})_3}$ is constant as $m_{\text{K},\text{total}}$ increases, and hence, from Pascal's (1984) 600°C, 2 kbar data, $m_{\text{Al}(\text{OH})_4^-}$ equals 0.89 $m_{\text{K},\text{total}}$, up to $m_{\text{K},\text{total}} = 1.0$). This would lead to a solution of high ionic strength, contrary to what is theoretically reasonable.

Data for log K for the equilibrium

can be obtained from the literature:

At 25°C, Baes and Mesmer (1976) give $\log K_{\text{Al}(\text{OH})_4^-} = -6.0$

At 25°C, Kuyunko et al. (1983) give $\log K_{\text{Al}(\text{OH})_4^-} = -7.15$

At 150°C, Kuyunko et al. (1983) give $\log K_{\text{Al}(\text{OH})_4^-} = -6.44$

At 250°C, Kuyunko et al. (1983) give $\log K_{\text{Al}(\text{OH})_4^-} = -5.99$

Baes and Mesmer's value of $\log K$ at 25°C seems much more reasonable than that of Kuyunko et al. (it is consistent with $a_{\text{Al}(\text{OH})_3} = a_{\text{Al}(\text{OH})_4^-}$ at $\text{pH} = 8.0$, rather than 6.85). This in turn suggests that Kuyunko et al.'s predictions at higher temperatures are also too negative, though the trend of $\log K$ is consistent with Baes and Mesmer's (1981) theoretical calculations. If the trend continues with increasing temperature and the pressure effect is ignored, then a value of $\log K_{\text{Al}(\text{OH})_4^-}$ in the region of -4.0 may be predicted at 600°C. However, Baes and Mesmer (1981) show that the trend should reverse with increasing temperature, leading to more negative values of $\log K$, i.e. one would expect $\log K$ to be more negative than -4.0 at supercritical conditions. The validity (i.e. existence in terms of the "real" structure of the solution) of this equilibrium cannot be disputed. Only the magnitude of the associated $\log K$ is uncertain.

Pre-empting what is determined later, in step R3, the calculated value of $\log K$ is less negative than would be reasonably expected. This problem with the model is based not on thermodynamic arguments, but on what is felt to be the "real" structure of the solution. A thermodynamic model does not have to reflect the actual structure of the solution, but if it does, then it may lead to simpler and better predictive models.

One can then search for a model involving ion association, but also neutral species, in order to comply with theoretical considerations involving the electrostatic properties of the

solution. One obvious choice is

KH_2AlO_3 is a polynuclear species. Polynuclear complexes of this kind are unknown at room temperature and pressure. "The formation of most polynuclear species results from the almost unique tendency of OH^- among the simple ligands to form bridging linkages between two (or more) cations" (Baes and Mesmer, 1976, p397). "The most favored configurations for polynuclear species appear to be symmetrical ones" (Baes and Mesmer, 1976, p422). Baes and Mesmer concluded (p118) that the polynuclear species formed by Al^{3+} hydrolysis at room temperature and pressure are

They showed (table 6.6, p120) how $\log K$ becomes less negative as temperature increases for these complexes. [K refers to equilibria of the type

Neutral polynuclear complexes have apparently never been invoked to explain cation hydrolysis (Baes and Mesmer, 1976, Chapter 18). Most polynuclear complexes have large positive charges. Only a very few mixed cation polynuclear complexes have been identified. The elements involved include Ti, Fe, V, Cr, Zr, Al, Sn, but no alkali metals, and all have carried positive charges (Burgess, 1978, p304).

One final objection to the polynuclear model is that it predicts $\text{NaOH-Al}(\text{OH})_3$ and $\text{KOH-Al}(\text{OH})_3$ interactions to be very similar, despite the differences in the ionic radii of Na^+ and

K⁺. Why should Na and K behave so similarly?

The principal problem with the polynuclear model is the lack of a theoretical basis for the existence of neutral, mixed cation, polynuclear complexes. Theoretical interpretation of aqueous solutions is based on electrostatic interactions. Why should two neutral complexes - KOH and Al(OH)₃ - interact with one another? The lack of a theoretical basis for this model is disturbing, but considering our very limited understanding of the physical chemistry of supercritical aqueous solutions, it is not an overwhelming objection.

Note that when authors such as Seward (1981, p126) state that "the chemistry of complex equilibria at high temperatures is probably more simple with fewer complexes to consider and a decrease in the importance of polymeric species", they are implicitly referring to charged polymeric species.

We have now raised severe theoretical objections to both models. Neither corresponds to what one would expect the actual structure of the solution to be.

One additional possibility is that corundum solubility increases in KOH solutions because of some indirect effect. For example, the KOH may significantly affect the nature of the particle interactions in the aqueous solution by some unspecified process. This may lead to a lowering of $\gamma_{\text{Al(OH)}_3}$, which would lead to an increase of corundum solubility according to

$$K = \frac{\gamma_{\text{Al}(\text{OH})_3} m_{\text{Al}(\text{OH})_3}}{a_{\text{Al}_2\text{O}_3, \text{Crn}} a_{\text{H}_2\text{O}}}$$

Since this latter hypothesis is rather ad-hoc, and dependent on an unknown physical process, it will not be further discussed here.

Perhaps at high temperatures and pressures a neutral polynuclear symmetrical complex forms, containing only Al, not K.

This line of thinking is highly speculative. It can be analysed analogously to the previous possibility. For example,

$$K = \frac{a_{\text{Al}_2\text{O}_2(\text{OH})_2} a_{\text{H}_2\text{O}}}{a_{\text{Al}(\text{OH})_3}}$$

$a_{\text{Al}(\text{OH})_3}$ is constrained by equilibrium with respect to corundum

$$K \propto \gamma_{\text{Al}_2\text{O}_2(\text{OH})_2} m_{\text{Al}_2\text{O}_2(\text{OH})_2} a_{\text{H}_2\text{O}}$$

Let us assume $\gamma_{\text{Al}_2\text{O}_2(\text{OH})_2}$ is constant

$$K \propto m_{\text{Al}_2\text{O}_2(\text{OH})_2} a_{\text{H}_2\text{O}}$$

Because $m_{\text{Al}_2\text{O}_2(\text{OH})_2}$ must increase linearly as $m_{\text{KOH},T}$ increases, $a_{\text{H}_2\text{O}}$ must decrease linearly. This is plausible, but impossible to prove or disprove with the present database.

Returning to the two initial models, and generalising them to account for the observed corundum and quartz solubility increases in both KOH and NaOH solutions, we have two proposed speciation schemes:

1) mononuclear

charged

2) polynuclear

uncharged

In addition to the above species, both models contain H^+ , OH^- , K^+ , KOH , Na^+ and NaOH .

Before performing detailed calculations for these two models, let us first consider how we might expect them to behave.

First, for the polynuclear model, we can write

$$K_{\text{KH}_2\text{AlO}_3} = \frac{a_{\text{KOH}} a_{\text{Al}(\text{OH})_3}}{a_{\text{KH}_2\text{AlO}_3} a_{\text{H}_2\text{O}}}$$

Let us assume a_{H_2O} is constant

$a_{Al(OH)_3}$ is constrained by
equilibrium with respect to corundum

$$K_{KH_2AlO_3} \propto \frac{a_{KOH}}{a_{KH_2AlO_3}}$$

$$\propto \frac{\gamma_{KOH} m_{KOH}}{\gamma_{KH_2AlO_3} m_{KH_2AlO_3}}$$

Assume $\gamma_{KOH} = \gamma_{KH_2AlO_3} = 1$

$$\propto \frac{m_{KOH}}{m_{KH_2AlO_3}}$$

$m_{K, total}$ = molality of KOH in
initial aqueous solution

$m_{K, total} = m_{K^+} + m_{KOH} + m_{KH_2AlO_3}$
in the equilibrium solution

$$m_{Al, total} = m_{Al(OH)_3} + m_{KH_2AlO_3}$$

Assume m_{K^+} and $m_{Al(OH)_3}$ are negligible

From Pascal's data at 600°C, 2 kbar:

$$m_{Al, total} = 0.89 m_{K, total}$$

$$m_{KH_2AlO_3} = 0.89 (m_{KOH} + m_{KH_2AlO_3})$$

$$m_{KOH} / m_{KH_2AlO_3} = 0.89 / 0.11$$

$$K_{KH_2AlO_3} \propto \frac{0.11}{0.89}$$

$K_{\text{KH}_2\text{AlO}_3}$ is a constant. $0.11/0.89$ also is constant;
 i.e. this proposed model is consistent with the above assumptions
 as $m_{\text{K},\text{total}}$ increases.

The mononuclear, charged model is not so simple:

Combining

$$K_{\text{KOH}} = \frac{a_{\text{K}^+} a_{\text{OH}^-}}{a_{\text{KOH}}}$$

with

$$K_{\text{Al}(\text{OH})_4^-} = \frac{a_{\text{Al}(\text{OH})_3} a_{\text{OH}^-}}{a_{\text{Al}(\text{OH})_4^-}}$$

gives

$$\frac{K_{\text{KOH}}}{K_{\text{Al}(\text{OH})_4^-}} = \frac{a_{\text{K}^+} a_{\text{Al}(\text{OH})_4^-}}{a_{\text{KOH}} a_{\text{Al}(\text{OH})_3}}$$

Assume $a_{\text{Al}(\text{OH})_3}$ is constant

$$\begin{aligned} &= \frac{a_{\text{K}^+} a_{\text{Al}(\text{OH})_4^-}}{a_{\text{Al}(\text{OH})_3}} \\ &\propto \frac{\gamma_{\text{K}^+} m_{\text{K}^+} \gamma_{\text{Al}(\text{OH})_4^-} m_{\text{Al}(\text{OH})_4^-}}{\gamma_{\text{KOH}} m_{\text{KOH}}} \end{aligned}$$

$$m_{\text{K},\text{total}} = m_{\text{K}^+} + m_{\text{KOH}}$$

Assume m_{H^+} , m_{OH^-} and $m_{\text{Al}(\text{OH})_3}$ are negligible. Hence:

$$m_{\text{K}^+} = m_{\text{Al}(\text{OH})_4^-}$$

and from Pascal's data at 600°C , 2 kbar:

$$m_{\text{Al}(\text{OH})_4^-} = 0.89 (m_{\text{K}^+} + m_{\text{KOH}})$$

$$m_{K^+} / m_{KOH} = 0.89/0.11$$

$$\text{Assume } \gamma_{KOH} = 1$$

$$\frac{K_{KOH}}{K_{Al(OH)_4^-}} \propto \frac{\gamma_{K^+} 0.89 m_{KOH} \gamma_{Al(OH)_4^-} m_{Al(OH)_4^-}}{0.11 m_{KOH}}$$

$$\propto \gamma_{K^+} \gamma_{Al(OH)_4^-} m_{Al(OH)_4^-}$$

$$\text{Let us assume } \gamma_{K^+} = \gamma_{Al(OH)_4^-}$$

$$\text{Note that } m_{Al(OH)_4^-} \approx \bar{I}$$

$$\propto [\gamma_{Al(OH)_4^-}]^2 \bar{I}$$

The left hand side of this proportionality is constant.

Therefore, as $\bar{I}$ increases, $\gamma_{Al(OH)_4^-}$ must decrease.

$$\gamma_{Al(OH)_4^-} \propto \bar{I}^{-0.5}$$

This predicted correlation of γ with $\bar{I}^{-0.5}$, subject to the above assumptions, is plausible for solutions of high ionic strength. Detailed calculations, summarised in table 4-21, show that some of the assumptions are not valid under certain circumstances. Most notably, m_{OH^-} may not be negligible.

Both models appear to behave plausibly. Neither one can be rejected in favour of the other at this stage. Both should be examined further.

The strongest argument in favour of the existence of polynuclear complexes is the simplicity of the predicted activity model:-

$$a_{\text{H}_2\text{O}} = \gamma_{\text{KH}_2\text{AlO}_3} = \gamma_{\text{KOH}} = \gamma_{\text{Al}(\text{OH})_3} = 1$$

This argument is expanded below.

The excess molar free energy of a component in solution is defined by

$$\bar{G}_{\text{excess}} = \bar{G} - \bar{G}_{\text{ideal}} = RT \ln \gamma$$

Real solutions become ideal as the mole fractions of the components approach either zero or unity. The activity coefficient, γ , is equal to unity for an ideal solution. The behaviour of γ at intermediate mole fractions may be very complicated. However, if we choose components carefully, to reflect the structure of the solution, the derived values of γ are found to lie closer to unity than for alternative sets of components; i.e. $\bar{G}_{\text{excess}}$ is a minimum for the model which most closely represents the structure of the solution. This is an empirical observation, borne out by many studies of solid solutions (Froese, 1976, p8-10). We can apply it to other solutions as a constraint on the relative "reasonableness" of different solution models.

Before applying this criterion to the two proposed aqueous solution models, we must first decide on what components to choose. The number of aqueous species in any model is always at least equal to, and usually greater than, the number of components. However, the two proposed models each contain some

species greatly in excess of the other species. For corundum solubility in KOH solutions, these are:

Case 1) $\text{Al}(\text{OH})_4^-$; K^+ , H_2O

Case 2) KH_2AlO_3 , KOH , H_2O

[Examination of tables 4-20 to 4-26 shows that other species are actually present in significant amounts in both cases. This complicating factor is discussed later in the chapter. For the sake of simplicity, it will be ignored at this stage.]

For aqueous solutions in the system $\text{Al}_2\text{O}_3\text{-H}_2\text{O-KOH}$, these species (three in each case) can be taken to be the components of the system. Because these species are so dominant in each solution model, then as a first approximation, the activity models of the aqueous species can be equated to the activity models of the components.

Consequently, the activity coefficients of the components in Case 2) are all close to unity, as shown earlier; whilst in Case 1) the activity coefficients of the charged components are inversely proportional to $\gamma^{-0.5}$. Although the behaviour for Case 1) is reasonable for a system involving charged ions, it is not ideal. Therefore Case 2) is preferable, for empirical reasons. This argument gives us an objective criterion for preferring Case 2) over Case 1). This criterion is not reliant on theoretical speculation regarding the actual structure of the solution.

One should always bear in mind that neither model is consistent with theoretical considerations. Even though one or

the other model may fit the experimental data, this does not prove that the proposed species actually exist.

Much of the data in tables 4-14 and 4-15 extend to temperatures and pressures beyond the range of validity of HK's (1974a) expression for ϵ . Therefore, Pitzer's (1983) equation was used. This equation is based on the same experimental data, but has a simpler form and is based on the theoretical Kirkwood equation. It gives more reasonable values of ϵ at pressures and temperatures beyond the limit of the experimental data. It allows the properties of aqueous species to be calculated to higher temperatures and pressures than HKF's limit of 600°C and 5 kbar.

One further modification was the development of a new procedure for calculating α in the Debye-Huckel equation. This is summarised in Appendix F. It led to unique values of activity coefficients for each charged aqueous species.

Before going on to detailed consideration of the two principal alternative models, we must first obtain thermodynamic data for the aqueous species $\text{Al}(\text{OH})_3$ and $\text{Si}(\text{OH})_4$, which are present in both models.

Step 11. Thermodynamic data for $\text{Al}(\text{OH})_3(\text{aq})$

Let us assume that the solubility of corundum in pure water at supercritical temperatures and pressures can be modelled by:

as suggested by theoretical considerations (Baes and Mesmer, 1981, figure 7).

As a general observation on the solubility of minerals in supercritical water, one can note that solubility increases as temperature increases and as density increases. But at constant pressure, as temperature increases, density decreases. Hence the two effects oppose one another. The data of Ragnarsdottir and Walther (1983) suggest that at 2 kbar, in the range 400 to 700°C, the two effects almost cancel one another, giving a corundum solubility that is essentially constant as temperature rises.

If the equation given earlier (p138; based on Becker et al.'s (1983) experimental data) for corundum solubility at 670°C,

$$\log_{10} m_{\text{Al}} = -2.72504 + 4.81282 \log_{10} \rho_{\text{H}_2\text{O}}$$

is used to predict solubilities at lower pressures than the experiments on which the equation is based, we obtain

at 1 kbar, corundum solubility = 0.17 ppm Al

at 2 kbar, corundum solubility = 2.23 ppm Al

Let us assume that at 2 kbar, corundum solubility is constant at this value in the region 400 to 700°C. Using values of corundum solubility at 2 kbar from 400 to 700°C in 50°C increments, and the preferred 670°C data set discussed earlier (summarised in

table 4-16), regression analysis gives the following equation for corundum solubility as a function of T and ρ :

$$\log_{10} m_{Al} = -5.86428 + 0.00329 T + 4.53137 \log_{10} \rho_{H_2O}$$

T in Kelvin

ρ in $g\ cm^{-3}$

correlation coefficient, $R = 0.99739$

This equation is empirical. The density of water, ρ , is used as a parameter, rather than pressure, because many studies have shown it to lead to simpler empirical fits to experimental data (e.g. Marshall and Mesmer, 1981; Fournier and Potter, 1982; figures 3-6 to 3-9 in this thesis).

Assuming that in pure water, the dominant Al species is $Al(OH)_3$, we can write:

$$2 \Delta G_{Al(OH)_3} = \Delta G_{Crm} + 3 \Delta G_{H_2O}$$

$$\Delta G^{\circ}_{Al(OH)_3} = 0.5 (\Delta G_{Crm} + 3 \Delta G_{H_2O}) - R T \ln a_{Al(OH)_3}$$

Assuming corundum to be pure, neglecting activity coefficients for H_2O and assuming the activity coefficient of $Al(OH)_3$ equals unity, we can obtain values of $\Delta G^{\circ}_{Al(OH)_3}$ as a function of P and T .

Table 4-17 lists predictions of corundum solubility as a function of P and T , consistent with the above model and equations. Figure 4-8 shows the phase relations in the system Al_2O_3 - H_2O as a function of P and T , predicted using the thermodynamic database compiled in step 4. Note that corundum is predicted to be unstable in this system with respect to both diascore and boehmite below 350 - 400°C.

Table 4-16 Observed vs. predicted corundum solubilities in pure water

T (°C)	P (kbar)	Observed	ppm Al Hypothesised	Predicted
670	2.5	1.43	-	4.15
670	3.0	5.66	5.66	6.02
670	3.5	7.67	7.67	7.98
670	4.0	10.32	10.32	9.97
670	4.5	8.78	-	11.95
670	5.0	13.71	13.71	13.90
670	5.0	12.44	12.44	13.90
670	5.0	15.66	15.66	13.90
670	5.0	12.59	12.59	13.90
670	5.0	13.81	13.81	13.90
670	5.0	16.09	16.09	13.90
670	5.0	13.92	13.92	13.90
670	5.0	14.18	14.18	13.90
670	5.0	14.18	14.18	13.90
670	5.0	14.50	14.50	13.90
670	6.0	17.62	17.62	17.80
400	2.0	2.52	2.23	2.08
450	2.0	3.03	2.23	2.27
500	2.0	2.70	2.23	2.39
550	2.0	2.52	2.23	2.45
600	2.0	2.00	2.23	2.47
650	2.0	-	2.23	2.46
700	2.0	2.52	2.23	2.47
500	1.04	0.95	-	0.79

The observed values are taken from table 4-4.

The hypothesised values are those used to generate the equation for corundum solubility as a $f(T, \rho)$.

The predicted values are those obtained from the equation for corundum solubility:

$$\log_{10} m_{Al} = -5.864 + 0.00329 T + 4.531 \log_{10} \rho_{H_2O}$$

T in Kelvin, ρ in $g\ cm^{-3}$

Table 4-17 Predicted corundum solubility in pure water in the range 750 to 9000 bar and 400 to 900°C

Solubility in ppm Al

	400.0	450.0	500.0	550.0	600.0	650.0	700.0	750.0	800.0	850.0	900.0
750.0	.8550	.5733	.2902	.1356	.0774	.0549	.0454	.0417	.0412	.0429	.0465
1000.0	1.1578	.9728	.7193	.4807	.3202	.2330	.1891	.1687	.1620	.1645	.1745
1250.0	1.4176	1.3363	1.1642	.9457	.7505	.6074	.5156	.4646	.4437	.4445	.4617
1500.0	1.6575	1.6647	1.5828	1.4419	1.2779	1.1328	1.0251	.9606	.9380	.9507	.9927
1750.0	1.8751	1.9742	1.9925	1.9427	1.8538	1.7585	1.6827	1.6437	1.6551	1.7127	1.8174
2000.0	2.0829	2.2680	2.3899	2.4496	2.4650	2.4626	2.4693	2.5008	2.5963	2.7497	2.9811
2250.0	2.2870	2.5538	2.7793	2.9586	3.1013	3.2273	3.3607	3.5259	3.7456	4.0420	4.4388
2500.0	2.4900	2.8361	3.1645	3.4689	3.7544	4.0360	4.3344	4.6732	5.0777	5.5774	6.2101
2750.0	2.6924	3.1165	3.5474	3.9802	4.4193	4.8772	5.3723	5.9274	6.5700	7.3373	8.2913
3000.0	2.8934	3.3949	3.9281	4.4917	5.0919	5.7417	6.4596	7.2688	8.2046	9.3060	10.6597
3250.0	3.0922	3.6706	4.3059	5.0018	5.7684	6.6220	7.5879	8.6842	9.9511	11.4499	13.2965
3500.0	3.2877	3.9426	4.6796	5.5084	6.4449	7.5109	8.7377	10.1479	11.7910	13.7467	16.1727
3750.0	3.4792	4.2099	5.0481	6.0098	7.1111	8.4075	9.9029	11.6488	13.7031	16.1690	19.2535
4000.0	3.6665	4.4721	5.4104	6.5047	7.7904	9.2980	11.0751	13.1739	15.6685	18.6899	22.5014
4250.0	3.8496	4.7288	5.7663	6.9922	8.4513	10.1835	12.2486	14.7134	17.6712	21.2853	25.8799
4500.0	4.0286	4.9805	6.1158	7.4722	9.1042	11.0622	13.4198	16.2602	19.6994	23.9356	29.3563
4750.0	4.2040	5.2274	6.4594	7.9499	9.7497	11.9340	14.5871	17.8107	21.7455	26.6266	32.9046
5000.0	4.3763	5.4702	6.7979	8.4173	10.3886	12.7998	15.7510	19.3641	23.8062	29.3501	36.5069
5250.0	4.5461	5.7096	7.1322	8.8799	11.0225	13.6613	16.9133	20.9218	25.8816	32.1034	40.1535
5500.0	4.7137	5.9462	7.4632	9.3389	11.6530	14.5207	18.0767	22.4867	27.9745	34.8880	43.8423
5750.0	4.8795	6.1805	7.7959	9.7953	12.2817	15.3803	19.2440	24.0626	30.0895	37.7089	47.5773
6000.0	5.0436	6.4127	8.1224	10.2501	12.9100	16.2419	20.4181	25.1632	32.2314	40.5725	51.3663
6250.0	5.2062	6.6432	8.4472	10.7038	13.5388	17.1071	21.6011	27.2617	34.4051	43.4858	55.2194
6500.0	5.3673	6.8720	8.7704	11.1568	14.1687	17.9768	22.7946	28.8905	36.6142	46.4548	59.1469
6750.0	5.5268	7.0990	9.0923	11.6093	14.8001	18.8516	23.9993	30.5408	38.8610	49.4842	63.1583
7000.0	5.6848	7.3245	9.4128	12.0615	15.4332	19.7316	25.2156	32.2130	41.1466	52.5767	67.2991
7250.0	5.8415	7.5486	9.7322	12.5135	16.0681	20.6171	26.4432	33.9069	43.4705	55.7334	71.5022
7500.0	5.9971	7.7760	10.0508	12.9659	16.7053	21.5082	27.6823	35.6217	45.8318	58.9539	75.8052
7750.0	6.1520	7.9985	10.3695	13.4194	17.3458	22.4060	28.9333	37.3575	48.2297	62.2376	80.2117
8000.0	6.3068	8.2211	10.6890	13.8752	17.9910	23.3120	30.1977	39.1151	50.6643	65.6220	84.7249
8250.0	6.4619	8.4447	11.0107	14.3352	18.6431	24.2287	31.4782	40.8969	53.1373	69.0363	89.3499
8500.0	6.6181	8.6703	11.3359	14.8012	19.3048	25.1597	32.7787	42.7071	55.6527	72.5200	94.0950
8750.0	6.7754	8.8986	11.6600	15.2754	19.9792	26.1040	34.1045	44.5515	58.2169	76.0404	98.9754
9000.0	6.9354	9.1303	12.0020	15.7595	20.6691	27.0808	35.4611	46.4370	60.8378	79.7276	103.9978

Figure 4-8 Phase equilibria in the system Al_2O_3 - H_2O

as $f(P, T)$

Step 12 Thermodynamic data for $\text{Si(OH)}_4(\text{aq})$

W+H's thermodynamic data for $\text{SiO}_2(\text{aq})$ are valid only up to 600°C and 5 kbar. The data cannot be safely extrapolated to higher temperatures and pressures. (See McKenzie and Helgeson (1984) for an attempt to do so.)

Fournier and Potter (1982) developed an equation which accurately describes quartz solubility up to 900°C and 10 kbar. Table 4-18 lists quartz solubilities as $f(\text{P}, \text{T})$ obtained using their equation.

Let us assume that quartz solubility in pure water at supercritical conditions can be modelled by:

Values of $\log K$ for this equilibrium were obtained using Fournier and Potter's equation for quartz solubility. The activity coefficient of Si(OH)_4 was assumed to equal unity.

Table 4-18 Quartz solubility in pure water in the range 750 to 9000 bar and 400 to 900°C.

Solubility in ppm Si, calculated from Fournier and Potter's (1982) equation.

	400.0	450.0	500.0	550.0	600.0	650.0	700.0	750.0	800.0	850.0	900.0
750.0	749.8969	833.5904	803.9650	744.0951	743.4087	802.7685	911.3686	1066.6602	1272.2162	1535.7915	1868.6751
1000.0	860.5823	1053.5141	1186.9028	1257.5955	1315.0305	1413.0222	1573.2272	1803.4725	2111.9795	2510.9914	3017.5832
1250.0	944.1655	1214.1874	1465.3506	1680.3606	1878.4554	2092.6439	2355.4950	2694.9184	3134.1275	3692.2913	4388.4023
1500.0	1014.5292	1340.7073	1679.0373	2018.9362	2359.1833	2721.6122	3134.8048	3633.5015	4252.0430	5020.9951	5969.1924
1750.0	1073.9533	1448.4853	1860.9189	2302.3355	2773.7662	3288.4802	3871.3166	4557.0996	5393.4648	6419.8774	7676.0498
2000.0	1127.4544	1542.9250	2019.3551	2552.1965	3144.2464	3808.8008	4570.5986	5465.5620	6544.2290	7857.8613	9477.9531
2250.0	1177.4121	1628.9284	2161.7959	2777.0279	3481.4914	4291.0356	5232.1553	6342.7129	7677.2266	9291.4995	11269.3076
2500.0	1224.8930	1709.1011	2292.8220	2982.9847	3791.8284	4739.6445	5856.5938	7188.2046	8781.6377	10711.3706	13072.5972
2750.0	1270.2835	1784.7492	2415.0932	3174.1219	4080.0939	5159.0254	6450.0542	7993.5352	9892.8940	12109.1899	14876.6450
3000.0	1313.6886	1856.4900	2530.1002	3352.9816	4349.6636	5552.6929	7008.2173	8762.8799	10888.6455	13479.1108	16671.7314
3250.0	1355.1131	1924.6141	2638.5841	3521.1495	4602.8262	5923.2534	7536.5283	9497.0606	11887.3125	14816.0825	18447.9751
3500.0	1394.5603	1989.2912	2741.3702	3679.6770	4841.1943	6272.6660	8036.7798	10196.8970	12847.6763	16115.4551	20195.2070
3750.0	1432.0750	2050.6788	2838.5669	3829.3665	5066.0308	6606.3228	8510.5855	10863.3311	13768.9839	17373.2397	21903.6675
4000.0	1467.7535	2108.9702	2930.6704	3970.9413	5278.4702	6918.4102	8959.5986	11497.6357	14651.2080	18586.5762	23564.9722
4250.0	1501.7361	2164.4047	3018.1077	4105.1284	5479.6382	7214.0190	9385.6597	12101.5635	15495.2534	19754.1367	25172.9834
4500.0	1534.1913	2217.2575	3101.3399	4232.6826	5670.6943	7494.7842	9790.8418	12677.3872	16303.0273	20876.3262	26724.3613
4750.0	1565.2975	2267.8197	3180.8455	4354.3740	5852.8237	7762.4116	10177.4121	13227.8340	17077.3545	21955.2388	28218.7202
5000.0	1595.2269	2316.3772	3257.0943	4470.9595	6027.1948	8018.6187	10547.7378	13755.9351	17821.7666	22994.4038	29658.4082
5250.0	1624.1333	2363.1914	3330.5220	4583.1445	6194.9136	8265.0591	10904.1655	14264.8359	18540.2134	23998.3857	31047.9995
5500.0	1652.1440	2408.4871	3401.5102	4691.5581	6356.9761	8503.2481	11248.8994	14757.5977	19236.7544	24972.3135	32393.6138
5750.0	1679.3578	2452.4453	3470.3746	4796.7285	6517.9448	8734.5049	11583.8989	15237.0215	19915.2651	25921.4141	33702.1865
6000.0	1705.8465	2495.2041	3537.3626	4899.0786	6671.1982	8959.9165	11910.8086	15705.5176	20579.2007	26850.6045	34980.7788
6250.0	1731.6598	2536.8641	3602.6599	4998.9307	6820.8696	9180.3306	12230.9268	16165.0259	21231.4331	27764.1777	36236.0142
6500.0	1756.8336	2577.4988	3666.4030	5096.5225	6967.3545	9396.3721	12545.2139	16616.9980	21874.1699	28665.6069	37473.6631
6750.0	1781.3981	2617.1677	3728.6981	5192.0332	7110.9399	9608.4863	12854.3379	17062.4331	22508.9600	29557.4756	38698.4194
7000.0	1805.3866	2655.9289	3789.6417	5285.6143	7251.8530	9816.9966	13158.7480	17501.9644	23136.7773	30441.5225	39913.8467
7250.0	1828.8428	2693.8527	3849.3407	5377.5209	7390.3057	10022.1753	13458.7734	17935.9854	23758.1680	31318.7935	41122.4932
7500.0	1851.8251	2731.0299	3907.9294	5467.6406	7526.5440	10224.3164	13754.7285	18364.7974	24373.4443	32189.8765	42326.1392
7750.0	1874.4087	2767.5773	3965.5809	5556.5161	7660.8848	10423.8003	14047.0156	18788.7632	24982.9004	33055.1821	43526.1426
8000.0	1896.6828	2803.6363	4022.5089	5644.3540	7793.7427	10621.1411	14336.2104	19208.4438	25587.0190	33915.2402	44723.8262
8250.0	1918.7441	2839.3651	4078.9606	5731.5220	7925.6314	10817.0078	14623.1099	19624.6948	26186.6421	34770.9600	45920.8516
8500.0	1944.6862	2874.9236	4135.1963	5818.4224	8057.1401	11012.2065	14908.7334	20038.7012	26783.0542	35623.8022	47119.4980
8750.0	1962.5851	2910.4505	4191.4570	5905.4512	8188.8789	11207.6147	15194.2549	20451.9189	27377.9595	36475.8047	48322.7744
9000.0	1984.4821	2946.0343	4247.9185	5992.9287	8321.3867	11404.0635	15430.8555	20865.9038	27973.2954	37329.4053	49534.2695

Step 13 Development of a charged, mononuclear model

Let us try to explain the experimental data in terms of the two equilibria

$$\log K_3 = \log a_{\text{Al(OH)}_3} + \log a_{\text{OH}^-} - \log a_{\text{Al(OH)}_4^-}$$

$$\log K_4 = \log a_{\text{Si(OH)}_4} + \log a_{\text{OH}^-} - \log a_{\text{Si(OH)}_5^-}$$

Assuming $a_{\text{H}_2\text{O}} = 1$ and substituting

$$\log K_{\text{Crn}} = 2 \log a_{\text{Al(OH)}_3}$$

$$\log K_{\text{Qtz}} = \log a_{\text{Si(OH)}_4}$$

we obtain

$$\log K_3 = 0.5 \log K_{\text{Crn}} + \log a_{\text{OH}^-} - \log a_{\text{Al(OH)}_4^-}$$

$$\log K_4 = \log K_{\text{Qtz}} + \log a_{\text{OH}^-} - \log a_{\text{Si(OH)}_5^-}$$

Let us consider the experimental data on corundum and quartz solubilities in KOH solutions. Adding KOH to the initial experimental solution leads to identical increases in quartz and corundum solubilities, as linear functions of the electrolyte concentration. Let us assume that this relationship remains valid as $\bar{I}$ tends to zero. Figure 4-7 supports this assumption over the range of experimental compositions.

The molalities of Al(OH)_3 and Si(OH)_4 are fixed (assuming $\gamma_{\text{Al(OH)}} = \gamma_{\text{Si(OH)}} = 1$) because of equilibrium with respect to corundum and quartz respectively. Hence, the increase in solubilities must be wholly accounted for by increases in $m_{\text{Al(OH)}_4^-}$ and $m_{\text{Si(OH)}_5^-}$. At a given concentration of KOH, the molalities of Al(OH)_4^- and Si(OH)_5^- will be equal in equivalent

corundum and quartz solubility experiments.

In the interpretation of the experiments, the aqueous solution is modelled in terms of two very similar sets of mass action and mass balance equations. These are for both sets of experiments:-

$$\log K_{H_2O} = \log a_{H^+} + \log a_{OH^-}$$

$$\log K_{KOH} = \log a_{K^+} + \log a_{OH^-} - \log K_{KOH}$$

$$K_{total} = m_{K^+} + m_{KOH}$$

for the corundum experiments:-

$$\log K_3 = \log a_{Al(OH)_3} + \log a_{OH^-} - \log a_{Al(OH)_4^-}$$

$$\log K_{Crm} = \log a_{Al(OH)_3}$$

$$Al_{total} = m_{Al(OH)_3} + m_{Al(OH)_4^-}$$

$$m_{K^+} + m_{H^+} = m_{Al(OH)_4^-} + m_{OH^-}$$

for the quartz experiments:-

$$\log K_4 = \log a_{Si(OH)_4} + \log a_{OH^-} - \log a_{Si(OH)_5^-}$$

$$\log K_{Qtz} = \log a_{Si(OH)_4}$$

$$Si_{total} = m_{Si(OH)_4} + m_{Si(OH)_5^-}$$

$$m_{K^+} + m_{H^+} = m_{Si(OH)_5^-} + m_{OH^-}$$

For the corundum experiments, the seven unknown quantities, determined by solving the set of seven equations, are

$$\log K_3 \quad m_{Al(OH)_3} \quad m_{Al(OH)_4^-} \quad m_{OH^-} \quad m_{K^+} \quad m_{H^+} \quad m_{KOH}$$

For the quartz experiments, the seven unknowns are

$$\log K_4 \quad m_{Si(OH)_4} \quad m_{Si(OH)_5^-} \quad m_{OH^-} \quad m_{K^+} \quad m_{H^+} \quad m_{KOH}$$

These sets of equations can be simplified by noting that $m_{Al(OH)_3}$ and $m_{Si(OH)_4}$ are easily obtained from $\log K_{Crm}$ and $\log K_{Qtz}$ (assuming $\gamma = 1$ for neutral species). This then makes it easy to

determine $m_{\text{Al}(\text{OH})_4^-}$ and $m_{\text{Si}(\text{OH})_5^-}$ from Al_{total} and Si_{total} . Hence, we can easily reduce the problem to five equations in five unknowns. One of these unknowns occurs in only one of the five equations: $\log K_3$ for the corundum experiments and $\log K_4$ for the quartz experiments.

Hence, we can further reduce the problem to solving initially for four unknowns in four equations. These four equations are identical in both the quartz and corundum experiments. Hence, at fixed P , T and K_{total} , they will lead to identical values for m_{OH^-} , m_{K^+} , m_{H^+} and m_{KOH} . The fifth unknown can then be solved for by substitution into the fifth equation. The ionic strengths of the quartz and corundum solutions will be identical. Using any model for activity coefficients in which γ_{OH^-} is a function only of I , γ_{OH^-} in the corundum experiments will equal γ_{OH^-} in the equivalent quartz experiments. Similarly for γ_{K^+} and γ_{H^+} . Using the modified Debye-Hückel equation, these values will vary slightly from one another because of variation in the B parameter. Similarly, $\gamma_{\text{Al}(\text{OH})_4^-}$ and $\gamma_{\text{Si}(\text{OH})_5^-}$ will be slightly different from one another. This difference will be very slight in dilute solutions. Hence, we can write, for equivalent experiments

$$a_{\text{Si}(\text{OH})_5^-} \approx a_{\text{Al}(\text{OH})_4^-}$$

Hence

$$\log K_3 - \log K_4 \approx 0.5 \log K_{\text{Crn}} - \log K_{\text{Qtz}}$$

At 600°C and 2 kbar, we obtain

$$\log K_3 - \log K_4 \approx -3.083$$

Note that this result is dependent not on the actual slope of m_{Al} vs. $m_{K,total}$ ($= 0.89$ at $600^{\circ}C$, 2 kbar), but only on the slope being identical for Qtz-KOH and Crn-KOH experiments.

Let us consider the albite dissolution data at $600^{\circ}C$ and 2 kbar, summarised in table 4-19. For these experiments, we can describe the solution in terms of twelve equations involving twelve unknowns:

$$\begin{aligned}
 \log K_{Ab} &= \log a_{Na^+} + \log a_{OH^-} + \log a_{Al(OH)_3} + 3 \log a_{Si(OH)_4} \\
 \log K_{H_2O} &= \log a_{H^+} + \log a_{OH^-} \\
 \log K_{KOH} &= \log a_{K^+} + \log a_{OH^-} - \log K_{KOH} \\
 \log K_{NaOH} &= \log a_{Na^+} + \log a_{OH^-} - \log K_{NaOH} \\
 \log K_3 &= \log a_{Al(OH)_3} + \log a_{OH^-} - \log a_{Al(OH)_4^-} \\
 \log K_4 &= \log a_{Si(OH)_4} + \log a_{OH^-} - \log a_{Si(OH)_5^-} \\
 -3.083 &= \log K_3 - \log K_4 \\
 K_{total} &= m_{K^+} + m_{KOH} \\
 Na_{total} &= m_{Na^+} + m_{NaOH} \\
 Al_{total} &= m_{Al(OH)_3} + m_{Al(OH)_4^-} \\
 Si_{total} &= m_{Si(OH)_4} + m_{Si(OH)_5^-} \\
 m_{K^+} + m_{Na^+} + m_{H^+} &= m_{Al(OH)_4^-} + m_{Si(OH)_5^-} + m_{OH^-}
 \end{aligned}$$

Table 4-19 Albite dissolution - experimental solubilities at
600°C and 2 kbar

Run no.	Si (ppm)	Al (ppm)	Na (ppm)	K (ppm)
PP21K	1020	248	250	5
PP21M	953	231	245	4
PP43E	1019	295	270	5
46N	1043	292	281	20
PA62	965	149	230	5

Table 4-20 Extraction of values of $\log K_3$ and $\log K_4$ from albite
dissolution experiments at 600°C, 2 kbar

Run no.	PP21K	PP21M	PP43E	PA62	66N	Ab0010
$\log K_3$	-4.549	-4.420	-4.653	-4.199	-4.576	-4.500
$\log K_4$	-1.466	-1.337	-1.570	-1.116	-1.493	-1.467
$\gamma_{\text{Al}(\text{OH})_3}$	0.299E-03	0.279E-03	0.467E-03	0.133E-03	0.327E-03	0.233E-03
$\gamma_{\text{Si}(\text{OH})_4}$	0.354E-01	0.331E-01	0.356E-01	0.303E-01	0.362E-01	0.268E-01
γ_{Na^+}	0.105E-01	0.101E-01	0.115E-01	0.890E-02	0.118E-01	0.119E-01
γ_{H^+}	0.125E-03	0.921E-04	0.130E-03	0.108E-03	0.480E-03	
γ_{H^-}	0.831E-03	0.112E-02	0.492E-03	0.252E-02	0.842E-03	0.218E-02
$\gamma_{\text{H}_2\text{O}}$	0.490E-07	0.360E-07	0.853E-07	0.153E-07	0.555E-07	0.176E-07
$\gamma_{\text{Al}(\text{OH})_4^-}$	0.889E-02	0.828E-02	0.105E-01	0.538E-02	0.105E-01	0.731E-02
$\gamma_{\text{Si}(\text{OH})_5^-}$	0.872E-03	0.815E-03	0.660E-03	0.111E-02	0.962E-03	0.239E-02
γ_{NaOH}	0.405E-03	0.533E-03	0.255E-03	0.110E-02	0.424E-03	0.116E-02
$\gamma_{\text{H}_2\text{O}}$	0.102E-04	0.102E-04	0.604E-05	0.279E-04	0.367E-04	
$\gamma_{\text{Al}(\text{OH})_3}$	1.0	1.0	1.0	1.0	1.0	1.0
$\gamma_{\text{Si}(\text{OH})_4}$	1.0	1.0	1.0	1.0	1.0	1.0
γ_{Na^+}	0.696	0.700	0.685	0.713	0.681	0.683
γ_{K^+}	0.698	0.702	0.688	0.716	0.684	
γ_{OH^-}	0.695	0.699	0.685	0.713	0.681	0.682
γ_{H^+}	0.695	0.699	0.685	0.713	0.681	0.682
$\gamma_{\text{Al}(\text{OH})_4^-}$	0.688	0.692	0.677	0.706	0.673	0.675
$\gamma_{\text{Si}(\text{OH})_5^-}$	0.687	0.691	0.676	0.705	0.672	0.673
γ_{NaOH}	1.0	1.0	1.0	1.0	1.0	1.0
γ_{KOH}	1.0	1.0	1.0	1.0	1.0	
γ_{T}	0.106E-01	0.102E-01	0.116E-01	0.901E-02	0.123E-01	0.119E-01

Constraints

$$\log_{10} K_{\text{H}_2\text{O}} = -16.706$$

$$\log_{10} K_{\text{KOH}} = -2.303$$

$$\log_{10} K_{\text{NaOH}} = -1.983$$

$$\log_{10} K_{\text{Ab}} = -13.251$$

$$V_{\text{H}_2\text{O}} = 1.695 \text{ cm}^3 \text{ g}^{-1}$$

$$\epsilon = 9.87$$

$$A_\gamma = 1.75 \text{ kg}^{0.5} \text{ mole}^{-0.5}$$

$$B_\gamma = 41.6 \times 10^6 \text{ kg}^{0.5} \text{ mole}^{-0.5} \text{ cm}^{-1}$$

In these calculations, the solution composition is predicted to be supersaturated with respect to corundum ($K_{\text{Crn}} = 0.871\text{E-}08$). We can use the values obtained for $\log K_3$ and $\log K_4$ to predict the solution composition in equilibrium with albite and corundum. Average values for $\log K_3$ and $\log K_4$, excluding the anomalous values obtained from run no. PA62, are -4.550 and -1.467. Using these values, the predicted solution composition is shown in the final column of table 4-20. The species molalities are consistent with

$$\text{Na} = 300 \text{ ppm} \quad \text{Al} = 200 \text{ ppm} \quad \text{Si} = 1099 \text{ ppm}$$

Let us now consider the Crn-KOH and Qtz-KOH experiments. As described earlier, these experiments can be modelled by seven equations in seven unknowns. Because the solution models will have high ionic strengths, the Debye-Huckel activity model will give unreliable values for γ . Hence, the values obtained for $\log K_3$ and $\log K_4$ will be less reliable than for the albite experiments. The derived values may vary as functions of composition, in contradiction of their thermodynamic definitions.

Let us term these predicted values $\log K_{3,p}$ and $\log K_{4,p}$.

The activity coefficient model can be modified to make $\log K_{3,p}$ and $\log K_{4,p}$ independent of composition. Four activity coefficient models were tried:

- 1) Debye-Huckel model
- 2) $\gamma = 1$ for all aqueous species
- 3) $\gamma = A \bar{I}^{-0.5}$ for all charged aqueous species, where A is an empirical constant

4) $\gamma = A [(m_{K^+} m_{Al(OH)_4^-}) / (m_{KOH})]^{-0.5}$ for all charged aqueous species, where A is an empirical constant

The forms of the last two models were suggested by considerations detailed in step 10. The results are given in tables 4-21 and 4-22, for $m_{K, total} = 0.1$ or 1.0. Table 4-21 shows the results for all four models, with empirically determined "best" values for A in the last two models. Table 4-22 shows the effect of varying A in the last two models.

Table 4-21 Calculation of $\log K_{j,p}$ for different activity models

	$\gamma = \text{Debye-Huckel}$		$\gamma = 1$		$\gamma = -0.01 \bar{I}^{-0.5}$		$\gamma = 0.13 \left[\frac{m_{K^+} m_{Al(OH)_3}}{m_{KOH}} \right]^{-0.5}$	
$m_{K, \text{total}}$	0.1	1.0	0.1	1.0	0.1	1.0	0.1	1.0
$\log K_{j,p}$	-5.551	-5.759	-6.217	-7.193	-4.947	-4.947	-4.561	-4.561
$m_{Al(OH)_3}$	0.933E-04	0.933E-04	0.933E-04	0.933E-04	0.933E-04	0.933E-04	0.933E-04	0.933E-04
$m_{Al(OH)_4^-}$	0.890E-01	0.890E+00	0.890E-01	0.890E+00	0.890E-01	0.890E+00	0.890E-01	0.890E+00
m_{K^+}	0.915E-01	0.903E+00	0.896E-01	0.891E+00	0.998E-01	0.998E+00	0.100E+00	0.100E+01
m_{OH^-}	0.252E-02	0.131E-01	0.579E-03	0.611E-03	0.108E-01	0.108E+00	0.262E-01	0.262E+00
m_{H^+}	0.438E-07	0.404E-07	0.340E-07	0.322E-07	0.182E-05	0.182E-05	0.152E-01	0.152E+00
m_{KOH}	0.848E-02	0.970E-01	0.104E-01	0.109E+00	0.217E-03	0.217E-02	0.460E-07	0.260E-07
$\gamma_{Al(OH)_3}$	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
$\gamma_{Al(OH)_4^-}$	0.397	0.152	1.0	1.0	0.032	0.010	0.005222	0.005222
γ_{K^+}	0.433	0.212	1.0	1.0	0.032	0.010	0.005222	0.005222
γ_{OH^-}	0.422	0.193	1.0	1.0	0.032	0.010	0.005222	0.005222
γ_{H^+}	0.422	0.193	1.0	1.0	0.032	0.010	0.005222	0.005222
γ_{KOH}	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
I	0.915E-01	0.903E+00	0.998E-01	0.994E+00	0.115E-01	0.115E+00	0.115E-01	0.115E+00

Table 4-22 A comparison of calculated values of $\log K_{3,p}$ for different activity models

	$\log K_{3,p}$	
$m_{K, \text{total}}$	0.1	1.0
Debye-Huckel model	-5.551	-5.759
$\gamma = 1$	-6.217	-7.193
$\gamma = A \cdot I^{-0.5}$		
$A = 1.0$	-7.24334	-7.24334
$= 0.1$	-5.41658	-5.41659
$= 0.01$	-4.94666	-4.93747
$= 0.001$	-4.93126	-4.93747
$= 0.0001$	-4.65268	-4.87951
$= 0.00001$	-3.54462	-4.20195
$\gamma = A \left[\frac{m_{K^+} m_{Al(OH)_4^-}}{m_{KOH}} \right]^{-0.5}$		
$A = 1.0$	-6.33318	-6.33318
$= 0.15$	-4.68537	-4.68537
$= 0.13$	-4.56108	-4.56108
$= 0.10$	-4.33319	-4.33321
$= 0.01$	-2.33345	-2.33469

Tables 4-21 and 4-22 show that only the fourth model leads to values of $\log K_{3,p}$ which are constant as $m_{K,total}$ increases, and also in agreement with the value of $\log K_3$ determined from the albite dissolution experiments.

The activity coefficients obtained using model 4) are very small. When activity coefficients drop well below unity, some kind of interaction, or complex formation, is usually inferred to be occurring.

Perhaps the tetrahedral $Al(OH)_4^-$ ion is being surrounded by K^+ ions attracted to the OH^- ligands; to give a time-averaged, three dimensional structure; something like:

When the model is described in these terms, it becomes physically very similar to the polynuclear, uncharged model.

The mononuclear, charged model is not developed further here, for three reasons:

- 1) The predicted activity coefficients are very small for

corundum dissolution in KOH solutions.

2) The activity model for Crn-KOH solutions

[$\gamma = 0.13 [(m_{K^+} m_{Al(OH)_4^-}) / m_{KOH}]^{-0.5}$ for charged species]

has no theoretical basis and cannot easily be made consistent with the Debye-Huckel model as $\bar{T}$ tends to zero.

3) The value of $\log K_3 = -4.550$ is consistent with $a_{Al(OH)_3} = a_{Al(OH)_4^-}$ when $a_{OH^-} = -4.550$ (i.e. pH = 6.156 at 600°C, 2 kbar). This is very close to neutral pH (5.353), in contradiction of theoretical predictions (discussed in step 10).

Step 14 Development of an uncharged, polynuclear model

Let us try to explain the experimental data in terms of the four equilibria

According to Pascal's (1984) data, corundum solubility in KOH solutions at 600°C and 2 kbar can be represented by

$$m_{\text{Al},\text{total}} = m_{\text{CW}} + 0.89 m_{\text{K},\text{total}}$$

where $m_{\text{Al},\text{total}}$ = measured molality of Al

m_{CW} = solubility of Crn in pure water

Let us assume for quartz solubility in KOH solutions

$$m_{\text{Si},\text{total}} = m_{\text{QW}} + 0.89 m_{\text{K},\text{total}}$$

where $m_{\text{Si},\text{total}}$ = measured molality of Si

m_{QW} = solubility of Qtz in pure water

For corundum solubility in NaOH solutions at 600°C, 2 kbar, Pascal's data give

$$m_{\text{Al},\text{total}} = m_{\text{CW}} + 0.86 m_{\text{Na},\text{total}}$$

Let us then assume for quartz solubility in NaOH solutions

$$m_{\text{Si},\text{total}} = m_{\text{QW}} + 0.86 m_{\text{Na},\text{total}}$$

Using these four relationships, values of $\log K_{4,p}$, $\log K_{5,p}$, $\log K_{6,p}$ and $\log K_{7,p}$ were obtained. The results are given in

tables 4-23 and 4-24 for $m_{X,\text{total}} = 0.1m$ or $1.0m$ (where $X = \text{Na}$ or K).

$\log K_{4,p}$, $\log K_{5,p}$, $\log K_{6,p}$ and $\log K_{7,p}$ are predicted equilibrium constants. They may vary as functions of composition, in contradiction of the definition of thermodynamic equilibrium constants. Any variations must be ascribed to either experimental error or failure of the model.

Table 4-23 Calculation of $\log K_{4,p}$, $\log K_{5,p}$, $\log K_{6,p}$ and $\log K_{7,p}$ at 600°C and 2 kbar γ = Debye-Huckel term for charged species $\gamma = 1$ for neutral species

	Crn-KOH		Crn-NaOH		Qtz-KOH		Qtz-NaOH	
$\mu_{K, total}$	0.1	1.0	0.1	1.0	0.1	1.0	0.1	1.0
$\log K_{4,p}$	27.619	-2.404						
$\log K_{5,p}$			-2.303	-2.022				
$\log K_{6,p}$					-4.234	-4.320		
$\log K_{7,p}$							4.213	3.908
$\mu_{Al(OH)_3}$	0.933E-04	0.933E-04	0.933E-04	0.933E-04				
$\mu_{KH_2AlO_3}$	0.890E-01	0.890E+00						
$\mu_{NaH_2AlO_3}$			0.860E-01	0.860E+00				
$\mu_{Si(OH)_4}$					0.113E+00	0.113E+00	0.113E+00	0.113E+00
$\mu_{FH_3SiO_4}$					0.890E-01	0.890E+00		
$\mu_{NaH_3SiO_4}$							0.860E-01	0.860E+00
μ_{OH^-}	0.639E-02	0.344E-01	0.958E-02	0.594E-01	0.638E-02	0.344E-01	0.957E-02	0.593E-01
μ_{H^+}	0.549E-08	0.182E-08	0.411E-08	0.140E-08	0.548E-08	0.182E-08	0.410E-08	0.140E-08
μ_{FeOH}	0.461E-02	0.756E-01			0.462E-02	0.756E-01		
μ_{NaOH}			0.442E-02	0.806E-01			0.443E-02	0.807E-01
μ_{K^+}	0.639E-02	0.344E-01			0.638E-02	0.344E-01		
μ_{Na^+}			0.958E-02	0.594E-01			0.957E-02	0.593E-01
γ_{OH^-}	0.749	0.560	0.707	0.486	0.751	0.561	0.708	0.488
γ_{H^+}	0.749	0.560	0.707	0.486	0.751	0.561	0.708	0.488
γ_{K^+}	0.751	0.567			0.753	0.568		
γ_{Na^+}			0.707	0.488			0.709	0.489
γ	0.639E-02	0.344E-01	0.958E-02	0.594E-01	0.638E-02	0.344E-01	0.957E-02	0.593E-01

Table 4-24. Calculation of $\log K_{1,p}$, $\log K_{2,p}$, $\log K_{3,p}$ and $\log K_{7,p}$ at 600°C and 2 kbar $\gamma = 1$ for all aqueous species

	Cen-KOH		Cen-H ₂ O/H		Qtz-KOH		Qtz-NaOH	
$\log K_{1,p}$	0.1	1.0	0.1	1.0	0.1	1.0	0.1	1.0
$\log K_{2,p}$	7.528	-7.339						
$\log K_{3,p}$			-7.166	-6.929				
$\log K_{7,p}$					-6.445	-6.250		
$\log K_{4,p}$							-4.052	-3.837
$a_{\text{H}_2\text{O}}$	0.933E-04	0.933E-04	0.933E-04	0.933E-04				
$a_{\text{H}_2\text{AlO}_3}$	0.590E-01	0.590E-01						
$a_{\text{H}_2\text{AlO}_3}$			0.860E-01	0.860E-01				
$a_{\text{H}_2\text{O}}$					0.113E+00	0.113E+00	0.113E+00	0.113E+00
$a_{\text{H}_2\text{O}}$					0.890E-01	0.890E-01		
$a_{\text{H}_2\text{O}}$							0.860E-01	0.860E+00
a_{OH^-}	0.532E-02	0.210E-01	0.794E-02	0.333E-01	0.532E-02	0.210E-01	0.794E-02	0.333E-01
a_{H^+}	0.370E-08	0.935E-09	0.248E-08	0.591E-09	0.370E-08	0.935E-09	0.248E-08	0.591E-09
a_{KOH}	0.568E-02	0.890E-01			0.568E-02	0.890E-01		
a_{NaOH}			0.606E-02	0.107E+00			0.606E-02	0.107E+00
a_{H^+}	0.532E-02	0.210E-01			0.532E-02	0.210E-01		
a_{H^+}			0.794E-02	0.333E-01			0.794E-02	0.333E-01
γ_{OH^-}	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
γ_{H^+}	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
γ_{K^+}	1.0	1.0			1.0	1.0		
γ_{Na^+}			1.0	1.0			1.0	1.0
T	0.532E-02	0.210E-01	0.794E-02	0.333E-01	0.532E-02	0.210E-01	0.794E-02	0.333E-01

The results in table 4-23 were obtained using the Debye-Huckel model for activity coefficients of charged aqueous species, whilst the results in table 4-24 were obtained by assuming $\gamma = 1$ for all aqueous species. The alternative assumptions had little effect on the value of $\log K_p$. In both cases, $\log K_p$ varied as a $f(m_{K, total})$. This contradicts the theoretical prediction in step 10. The prediction fails because the assumption that $m_{KOH} \gg m_{K^+}$ is invalid, as seen in table 4-23.

By direct analogy with the procedure followed in step 13, we can obtain

$$\log K_5 - \log K_7 \approx -3.083$$

and hence use the albite dissolution data to directly obtain values of $\log K_{5,p}$ and $\log K_{7,p}$. The K species were ignored in this calculation. The results are presented in tables 4-25 and 4-26. The mean values of $\log K_{6,p}$ and $\log K_{7,p}$ (excluding the anomalous results from run PA62) are

Table 4-25	$\log K_{5,p} = -6.836$	$\log K_{7,p} = -3.753$
Table 4-26	$\log K_{5,p} = -6.838$	$\log K_{7,p} = -3.755$

Table 4-25 Calculation of $\log K_{5,P}$ and $\log K_{7,P}$ at 600°C and 2 kbar, using albite dissolution data

γ = Debye-Huckel term for charged species

$\gamma = 1$ for neutral species

	46N	PP21K	PP21M	PP43E	PA62
$\log K_{5,P}$	-6.844	-6.850	-6.731	-6.919	-6.557
$\log K_{7,P}$	-3.761	-3.767	-3.648	-3.836	-3.474
$m_{\text{Al(OH)}_3}$	0.758E-03	0.599E-03	0.541E-03	0.935E-03	0.207E-03
$m_{\text{NaH}_2\text{AlO}_3}$	0.101E-01	0.859E-02	0.802E-02	0.100E-01	0.530E-02
$m_{\text{Si(OH)}_4}$	0.367E-01	0.359E-01	0.335E-01	0.360E-01	0.337E-01
$m_{\text{NaH}_3\text{SiO}_4}$	0.403E-03	0.425E-03	0.410E-03	0.318E-03	0.713E-03
m_{OH^-}	0.160E-02	0.166E-02	0.196E-02	0.130E-02	0.330E-02
m_{H^+}	0.183E-07	0.162E-07	0.140E-07	0.199E-07	0.915E-08
m_{NaOH}	0.174E-03	0.195E-03	0.265E-03	0.124E-03	0.684E-03
m_{Na^+}	0.160E-02	0.166E-02	0.196E-02	0.130E-02	0.330E-02
γ_{OH^-}	0.860	0.856	0.846	0.871	0.807
γ_{H^+}	0.860	0.856	0.846	0.871	0.807
γ_{Na^+}	0.860	0.857	0.846	0.871	0.807
I	0.160E-02	0.166E-02	0.196E-02	0.130E-02	0.330E-02

Table 4-26 Calculation of $\log K_{5,P}$ and $\log K_{7,P}$ at 600°C and 2 kbar, using albite dissolution data

$\gamma = 1$ for all aqueous species

	46N	PP21K	PP21M	PP43E	PA62
$\log K_{5,P}$	-6.846	-6.852	-6.733	-6.921	-6.554
$\log K_{7,P}$	-3.763	-3.769	-3.650	-3.838	-3.471
$m_{\text{Al(OH)}_3}$	0.681E-03	0.532E-03	0.470E-03	0.858E-03	0.170E-03
$m_{\text{NaH}_2\text{AlO}_3}$	0.101E-01	0.866E-02	0.809E-02	0.101E-01	0.534E-02
$m_{\text{Si(OH)}_4}$	0.367E-01	0.358E-01	0.335E-01	0.359E-01	0.335E-01
$m_{\text{NaH}_3\text{SiO}_4}$	0.451E-03	0.482E-03	0.475E-03	0.348E-03	0.866E-03
m_{OH^-}	0.146E-02	0.151E-02	0.178E-02	0.119E-02	0.296E-02
m_{H^+}	0.149E-07	0.130E-07	0.110E-07	0.166E-07	0.666E-08
m_{NaOH}	0.195E-03	0.220E-03	0.306E-03	0.135E-03	0.841E-03
m_{Na^+}	0.146E-02	0.151E-02	0.178E-02	0.119E-02	0.296E-02
γ_{OH^-}	1.0	1.0	1.0	1.0	1.0
γ_{H^+}	1.0	1.0	1.0	1.0	1.0
γ_{Na^+}	1.0	1.0	1.0	1.0	1.0
I	0.146E-02	0.151E-02	0.178E-02	0.119E-02	0.296E-02

The variation of $\log K_{5,p}$ from -6.838 to -7.166 to -6.920 as the solute concentration increases is difficult to explain.

The variation may be an artefact of any combination of the following:

- a) experimental error,
- b) errors in the thermodynamic database,
- c) errors in the activity models.

But the variation of $\log K_{5,p}$ from -7.166 to -6.920 as $m_{\text{Na},\text{total}}$ increases from 0.1m to 1.0m is a flat in the model which cannot reasonably be ascribed to experimental or database errors. It suggests an error in the activity/speciation model. The theoretical prediction in step 10 was invalid because m_{NaOH} is not greatly dominant over m_{Na^+} in tables 4-23 to 4-26. One could modify the activity model and force this condition to be satisfied. Table 4-27 lists a number of predicted values of $\log K_{5,p}$ for alternative activity models.

Table 4-27 Variation of $\log K_{5,p}$ as a function of alternative activity models

Unless noted otherwise, $\gamma = 1.0$ for all aqueous species, and $a_{H_2O} = 1.0$

$\log K_{5,p}$	Special conditions
$m_{K,total} = 0.1$	$m_{K,total} = 1.0$
-7.166	-6.920 none
-7.303	-7.042 charged species $\gamma = D.H.$
-8.906	-7.977 charged species $\gamma = 0.1$
-6.964	-6.935 " " = 10.0
-6.926	-6.923 " " = 100.0
-6.92167	-6.92164 " " = 10000.0
-7.014	-6.960 neutral species $\gamma = 0.1$
-7.984	-7.329 " " = 10.0
-7.914	-7.324 all species $\gamma = 0.1$
-7.059	-6.965 " " = 10.0
-7.055	-6.964 $\gamma_{Na^+} = 0.1$
-6.964	-6.935 " = 10.0
-8.055	-7.964 $\gamma_{NaOH} = 0.1$
-8.964	-8.935 " = 10.0
-6.673	-6.541 $a_{H_2O} = 0.1$
-6.768	-6.772 charged species $\gamma = 100.0$
	$a_{H_2O} = 0.5$
-6.876	-6.874 charged species $\gamma = 100.0$
	$a_{H_2O} = 0.8$
-6.806	-6.784 charged species $\gamma = 10.0$
	$a_{H_2O} = 0.5$
-6.914	-6.887 charged species $\gamma = 10.0$
	$a_{H_2O} = 0.8$

A reasonable activity model can be derived by allowing γ for charged species to increase above unity to a value in the range 10.0 to 100.0 and allowing a_{H_2O} to decrease to a value in the range 0.5 to 0.8. Both a_{H_2O} and γ must approach unity as the solution becomes more dilute.

One can calculate $\log K_{5,p}$ and $\log K_{7,p}$ for various activity models, using the albite dissolution data. Run 46N gives

$$\log K_{5,p} = -6.846 \quad \text{with } \gamma = 1 \text{ for all aqueous species}$$

$$= -6.841 \quad \text{with } \gamma = 10 \text{ for charged species}$$

$$= -6.137 \quad \text{with } a_{H_2O} = 0.8 \quad \gamma = 1 \text{ for all aqueous species}$$

The value of $\log K_{5,p}$, obtained using the albite data, is insensitive to the value of γ for charged species, but quite sensitive to the value of a_{H_2O} .

Given the small range in $\log K_{5,p}$ and the lack of a theoretical basis for activity model modifications, none were developed. For example, the equilibria

are all equivalent when a_{H_2O} is equal to unity, but not when a_{H_2O} departs from unity.

A "preferred" set of values for $\log K_4$, $\log K_5$, $\log K_6$ and $\log K_7$ were obtained:

$$\log K_4 = -7.252$$

$$\log K_5 = -6.838$$

$$\log K_6 = -4.168$$

$$\log K_7 = -3.755$$

The values of $\log K_5$ and $\log K_7$ were taken from the albite dissolution experiments, because these solutions were the most dilute (i.e. closest to ideal). Values of $\log K_4$ and $\log K_6$ were obtained by assuming that $\log K_{4,p}$ and $\log K_{6,p}$ varied analogously to $\log K_{5,p}$ and $\log K_{7,p}$ as functions of solute concentrations.

These values of $\log K$ were used, in conjunction with the assumption that $\gamma = 1$ for all aqueous species and $a_{H_2O} = 1$, to predict solution compositions in equilibrium with mineral assemblages. Some results are given in table 4-28.

Table 4-28 Predicted equilibrium solution compositions, and
comparison with experimental data

Experimental values are given in brackets beneath the
predicted values

Phases present	Solvent	Si ppm	Al ppm	Na ppm	K ppm	Notes
Qtz	pure water	3172				a
Qtz	0.1m KOH	5505 (5672)			3910	b
Qtz	1.0m KOH	27663 (28168)			39098	b
Qtz	1.0m KCl	3224			39098	
Qtz	1.0m NaOH	26724 (27326)		22990		b
Crn	pure water		2.5			a
Crn	0.1m KOH		2241 (2404)		3910	b
Crn	1.0m KOH		23531 (24016)		39098	b
Crn	1.0m KCl		49		39098	
Crn	1.0m NaOH		22622 (23207)	22990		b
Ab	pure water	954 (1043)	306 (292)	260 (281)		c
Ab Crn	pure water	1140	188	311		
Ab Qtz	pure water	3174	18	15		

Phases present	Solvent	Si ppm	Al ppm	Na ppm	K ppm	Notes
Kfs	pure water	839	269		389	
		(1070)	(251)	(182)	(178)	d
Kfs Qtz	pure water	3174	11		16	
Kfs Ab	pure water	1071	343	186	180	
Kfs Ab Ms	pure water	1337	200	243	207	
Lct	pure water	656	315		457	
		(623)	(557)	(213)	(659)	e
Lct Kfs	pure water	1156	111		161	
Lct Ne	pure water	777	530	267	314	
Lct Crn Ms	pure water	722	279		629	
		(854) (463)	(237) (598)	(12)	(392)	f f
Lct Crn Ms	0.0435m KCl	723	279		2249	
		(354)	(337)			g
Qtz And Ms	pure water	3178	6.3		30	
Qtz And Ms	0.043272m KCl	3182	6.3		1689	
		(2612)	(25)			h
Qtz And Ms	0.40823m KCl	3182	6.3		15743	
		(3623)	(51)			i

Phases present	Solvent	Si ppm	Al ppm	Na ppm	K ppm	Notes
Qtz Kfs Ms	pure water	3178	6.3		30	
		(2528)	(27)	(7)	(31)	j
		(3005)	(40)	(10)	(49)	j
		(3005)	(36)			j
Qtz Kfs Ms	0.1m KCl	3182	6.3		3876	
		(3134)	(14)	(17)		k
Qtz Kfs Ms	0.5m KCl	3182	6.3		19275	
		(2087)	(20)			l
Qtz Kfs Ms	1.0m KCl	3182	6.3		38514	
		(2613)	(19)	(34)		m
Qtz Kfs Ms Ab	pure water	3188	13	31	22	
		(3692)	(296)	(126)	(108)	n
Qtz Kfs Ms Ab	0.06m HCl	3192	13	1011	662	
		(3365)	(35)	(816)	(913)	o
Qtz Kfs Ms Ab	0.6m HCl	3192	13	9502	7230	
		(3132)	(291)	(6455)	(5977)	p
Qtz Kfs Ms Ab	1.0m NaCl	3192	13	15730	12196	
		(2576)	(26)	(20674)	(70)	q
		(2350)	(20)			q

Table 4-28 notes

- a) The quartz and corundum solubilities in pure water differ from those given in tables 4-17 and 4-18. The values in table 4-28 were calculated using Haar et al.'s expression for V_{H_2O} , whilst the values in tables 4-17 and 4-18 were calculated using H+K's (1974a) expression. Strictly speaking, H+K's expression should be used to calculate quartz and corundum

solubility, because this expression was the one used in the regression of the experimental data as $f(T, V_{H_2O})$. However, the differences in predicted solubilities are minor, and well within the limits of experimental error.

- b) These values were obtained from the expressions given at the beginning of step 14 (empirical correlations of corundum and quartz solubilities with $m_{K, total}$ and $m_{Na, total}$, based on the experimental results of Pascal).
- c) Run 46N, table 3-18
- d) Run AM8, table 3-7
- e) Run AC41, table 3-10
- f) Runs JR-11 and JR-3, table 4-15
- g) Run MLP-68, table 4-15
- h) Run MLP-51, table 4-15
- i) Run MLP-60, table 4-15
- j) Runs MLP-103, MLP-106 and JR-1, table 4-15
- k) Run JR-7, table 4-15
- l) Run JR-6, table 4-15
- m) Run JR-8, table 4-15
- n) Run SPP-2, table 4-15
- o) Run SPP-19, table 4-15
- p) Run SPP-11, table 4-15
- q) Runs JR-9 and JR-2, table 4-15

Abbreviations

MLP Marie-Lola Pascal
 JR Jilong Rao
 SPP Spruce Pine Pegmatite

Table 4-28 shows two notable predictions:

- 1) The solution compositions in equilibrium with Qtz-And-Ms and Qtz-Kfs-Ms, with pure water as the solvent, are almost identical, differing only in the third or more significant figure (measured in ppm):

e.g. Qtz-And-Ms Si = 3178.324 Al = 6.275 K = 29.63

Qtz-Kfs-Ms Si = 3178.339 Al = 6.281 K = 29.68

These predicted differences are much too small to be detectable experimentally. The compositions are very similar because the P-T condition is very close to the muscovite breakdown curve:

The curve passes through 600°C and 1988 bars (calculated using data given in Appendix B). At this P-T point, the solution compositions would be identical.

- 2) Adding Cl to the solvent has very little effect on the equilibrium solution concentrations of Si and Al:

e.g. for Qtz-Kfs-Ms

$m_{\text{Cl, total}} = 0.1m \text{ KCl}$ Si = 3181.8437 ppm Al = 6.2824 ppm

$= 0.5m \text{ KCl}$ Si = 3181.8438 ppm Al = 6.2824 ppm

Again, this effect is much too small to be observable experimentally.

Another notable predicted effect concerns the dissolution of Qtz-Kfs-Ms-Ab in a 1.0m NaCl solvent. The model predicts approximately equal amounts of Na and K in the equilibrium solution, which result from precipitation of a large amount of

albite and dissolution of a large amount of K-feldspar. The experimental result of Rao (run JR-9 in table 4-28) is not consistent with this prediction. In Rao's experiments with 1.0m NaCl, all the K-feldspar present initially was dissolved during the experiment (Anderson, pers. comm., 1985).

One final note concerns the interpretation of the albite, K-feldspar and leucite single phase dissolution data. The final equilibrium phase assemblages in these experiments are unknown. Predictions using a variety of possible phase assemblages, summarised in table 4-29, give an indication of what the equilibrium phase assemblages may have been.

The anomalously low predicted Al concentrations in table 4-28 cannot be easily explained. Invoking additional aqueous species would raise $m_{Al, total}$ in all the predictions, making it too high in some cases. A careful choice of additional species may lead to higher predictions of Al concentrations in Si-rich solutions, whilst having little effect on the predictions at lower Si concentrations. This option is difficult to constrain, given the present experimental database. It is discussed qualitatively later in this chapter. Alternatively, one can modify the activity model arbitrarily to improve the agreement. Table 4-29 lists some results, showing to what degree the activity coefficients must be changed to get a good fit to the data.

Table 4-29 Variation of the activity model to improve the fit to the experimental data

Consider Qtz-Kfs-Ms dissolution in pure water at 600°C, 2 kbar

Unless noted otherwise, $\gamma = 1.0$ for all aqueous species and $a_{\text{H}_2\text{O}} = 1.0$

Experimental equilibrium solution composition (in ppm)

Si = 2528	Al = 27	K = 31	Na = 7
3005	40	49	10
3005	36		

Predicted equilibrium solution composition (in ppm)

Special constraints on the activity model

Si = 3178	Al = 6.3	K = 30	none
3178	6.3	17	charged species $\gamma = 10.0$
3178	6.3	16	charged species $\gamma = 100.0$
3559	564	1633	$a_{\text{H}_2\text{O}} = 0.5$
3195	23	97	$a_{\text{H}_2\text{O}} = 0.8$
3195	23	70	charged species $\gamma = 10.0$ $a_{\text{H}_2\text{O}} = 0.8$
3223	56	165	charged species $\gamma = 10.0$ $a_{\text{H}_2\text{O}} = 0.7$
3223	56	161	charged species $\gamma = 100.0$ $a_{\text{H}_2\text{O}} = 0.7$
3206	35	102	charged species $\gamma = 100.0$ $a_{\text{H}_2\text{O}} = 0.75$
3173	35	56	charged species $\gamma = 100.0$ $a_{\text{H}_2\text{O}} = 0.75$ $\gamma_{\text{KH}_3\text{SiO}_4} = 100.0$

The final activity model given in table 4-29 is in very good agreement with the experimental results. The predicted K concentration is slightly higher than the experimental concentration, but the discrepancy is eliminated if the Na in solution is assumed to behave identically to the K (i.e. treat the Na as if it were K, such that 23 ppm Na are equivalent to 39 ppm K, to give adjusted experimental K concentrations of 43 ppm and 66 ppm).

Table 4-29 reinforces some of the conclusions derived from table 4-27, namely that to get a better fit to the experimental data with the present aqueous speciation model, it is necessary to

- a) let γ for charged species increase to about 10.0 to 100.0;
- b) let a_{H_2O} decrease to about 0.75.

In addition it is necessary to let $\gamma_{KH_3SiO_4}$ increase by about the same magnitude as γ for charged species.

However, these variations must be quite complex functions of solution composition. For example, $\gamma_{KH_3SiO_4}$ (or $\gamma_{NaH_3SiO_4}$) must increase only when KH_2AlO_3 (or NaH_2AlO_3) is present.

The effect of increasing γ is to decrease the abundance of the associated species in the model. For example, increasing γ for charged species in the system Al_2O_3 - H_2O - KOH makes KH_3SiO_4 , KOH and H_2O the dominant species in the solution (m_{K^+} and m_{OH^-} become insignificant). These three species can be taken to be thermodynamic components of the system. The solution model thus has components which mix ideally ($\gamma = 1.0$), giving the model an

appealing simplicity, as discussed in step 10. Increasing $\gamma_{\text{charged species}}$ also makes it easy to reconcile the linearity of $\log m_{\text{Al}}$ vs. $\log m_{(\text{Na}+\text{K})}$ (figure 4-7) with theoretical models.

Detailed calculations of how γ must vary as a function of solution composition would require a large amount of very accurate experimental data and are not practical with the present database.

Solution compositions in equilibrium with three solid phases in the system K-Al-Si-O-H could be modelled in terms of the thermodynamic components Si(OH)_4 , KH_2AlO_3 , KOH and H_2O ($m_{\text{KH}_3\text{SiO}_4}$ is insignificant relative to $m_{\text{Si(OH)}_4}$ in such solutions (see table 4-28)).

Interpreting the data in terms of carefully chosen thermodynamic components, rather than aqueous species, would simplify the interpretation. The choice of components would be controlled by the empirical constraint that γ for each component be as close as possible to unity. However, such an approach would be impossible to reconcile with other data. For example, data for $\log K_{\text{KOH}}$ derived from conductivity data, and HKF's data for $\Delta G^\circ_{\text{K}^+}$, require K^+ to exist in solution with other K-bearing species. But K^+ cannot be chosen as a component without invoking complex activity models.

The only major failure of the present model at 600°C and 2 kbar concerns the low predictions of Al concentrations in Si-rich

solutions, clearly shown in table 4-28. Could this problem be resolved by allowing the formation of additional aqueous species? There are many hypothetical aqueous dissociation equilibria one could experiment with, to try and improve the predictions. Some examples are:

In step 13 and this step, it was shown that there is good evidence for strong Na-Al, Na-Si, K-Al and K-Si interaction, possibly via OH^- ligands. This interaction can be simply described thermodynamically in terms of neutral polynuclear species such as NaH_2AlO_3 . Perhaps there is also significant Al-Si interaction, which may be described by a species such as

Again, a lack of precise experimental data prevent this possibility from being quantitatively assessed.

Future work - suggestions for additional experiments

The polynuclear, uncharged model gives a reasonable fit to the available data. A better fit could be obtained by allowing $a_{\text{H}_2\text{O}}$ and activity coefficients for some aqueous species to depart from unity. The departures should be expressed analytically as functions of solution composition. This is impractical with the present database. More complex speciation schemes may also yield better fits to the data. These are also difficult to constrain with the present database. Additional experiments are necessary.

More experiments are needed on simple systems - most notably, the binaries $\text{H}_2\text{O}-\text{NaOH}$ and $\text{H}_2\text{O}-\text{KOH}$ up to high solute concentrations. A knowledge of how activities vary in these simple systems would help to place constraints on activities in more complex systems.

The computer code used to make the predictions in step 14 can be used to predict solution compositions for any phase assemblage in the system Na-K-Al-Si-O-H-Cl . Experiments can be planned according to their predicted results. Alternative predictions can be made by varying γ and $a_{\text{H}_2\text{O}}$ as suggested in step 14. More accurate experiments would lead to much tighter constraints on the allowable variation of γ and $a_{\text{H}_2\text{O}}$. Discrepancies outside the range of experimental error can be interpreted in terms of variations in γ and $a_{\text{H}_2\text{O}}$. New predictions can then be made and tested by experiment. Ultimately, a reliable activity model may emerge.

The present study has shown that some experiments are more

useful than others for constraining proposed models. Experiments which produce the widest possible range in $m_{\text{Si,total}}$ and $m_{\text{Al,total}}$ should be performed. Table 4-29 gives an indication of which experiments yield the most useful data.

For example, Qtz-And-Ms and Qtz-Kfs-Ms predictions are very similar near the muscovite breakdown curve. Only one of the two assemblages need be investigated in detail, initially. Interpretation of experiments in which new, unknown, phases are produced is more difficult than experiments which start with an isobaric, isothermal invariant phase assemblage. The new phases should be identified, if possible. The data in tables 4-15 and 4-28 indicate that variation in $m_{\text{Cl,total}}$ leads to a negligible change in $m_{\text{Si,total}}$ and $m_{\text{Al,total}}$ in experiments involving Na- and K-bearing solids (though this may not be true under different P-T-X conditions).

Solubility experiments should use thermodynamically well characterised starting materials. If quartz is present, then $m_{\text{Si,total}}$ must be determined very accurately. Si(OH)_4 will be the dominant Si species. A small error in $m_{\text{Si,total}}$ (measured) may lead to a very large error in $m_{\text{NaH}_3\text{SiO}_4}$ or $m_{\text{KH}_3\text{SiO}_4}$ (calculated).

Because Na dissolves preferentially relative to K, trace amounts of Na in the starting material may lead to relatively large Na concentrations in solution. The system Na-Al-Si-O-H may be better to study initially than the system K-Al-Si-O-H, unless synthetic, high purity materials are used.

For example, one useful series of experiments, which could easily be carried out using the dynamic flow apparatus (assuming that sufficient quantities of the starting materials are available), would be to determine the solubility of albite + corundum + andalusite and albite + quartz + andalusite in pure water at 600°C and 2 kbar. Several values of $\log K_{5,p}$ and $\log K_{7,p}$ could be obtained from these experiments. Alternative activity coefficient models could be fitted to the data in order to obtain a consistent set of values of $\log K_5$ and $\log K_7$.

Summary of the final activity/speciation model at 600°C, 2 kbar

a) Species present:-

b) Activity model

$$\gamma = 1.0 \quad \text{for all aqueous species}$$

$$a_{\text{H}_2\text{O}} = 1.0$$

c) Values of log K

$$\begin{aligned} \log K_{\text{H}_2\text{O}} &= \log a_{\text{H}^+} + \log a_{\text{OH}^-} - \log a_{\text{H}_2\text{O}} \\ &= -10.706 \end{aligned}$$

$$\begin{aligned} \log K_{\text{KOH}} &= \log a_{\text{K}^+} + \log a_{\text{OH}^-} - \log K_{\text{KOH}} \\ &= -2.303 \end{aligned}$$

$$\begin{aligned} \log K_{\text{NaOH}} &= \log a_{\text{Na}^+} + \log a_{\text{OH}^-} - \log K_{\text{NaOH}} \\ &= -1.983 \end{aligned}$$

The above values were calculated using the expressions given in Appendix E, with $V_{\text{H}_2\text{O}} = 1.695 \text{ cm}^3 \text{ g}^{-1}$ at 600°C and 2 kbar. They are derived from conductance data obtained from very dilute solutions.

$$\begin{aligned} \log K_{\text{Crn}} &= 2 \log a_{\text{Al(OH)}_3} - 3 \log a_{\text{H}_2\text{O}} \\ &= -8.060 \end{aligned}$$

$$\begin{aligned} \log K_{\text{Qtz}} &= \log a_{\text{Si(OH)}_4} - 2 \log a_{\text{H}_2\text{O}} \\ &= -0.947 \end{aligned}$$

$$\begin{aligned} \log K_{\text{Ab}} &= \log a_{\text{Na}^+} + \log a_{\text{OH}^-} + \log a_{\text{Al(OH)}_3} + 3 \log a_{\text{Si(OH)}_4} \\ &\quad - 8 \log a_{\text{H}_2\text{O}} \end{aligned}$$

$$\log K_{Ab} = -13.251$$

$$\begin{aligned} \log K_4 &= \log a_{K^+} + \log a_{OH^-} + \log a_{Al(OH)_3} \\ &\quad - \log a_{KH_2AlO_3} - \log a_{H_2O} \\ &= -7.252 \end{aligned}$$

$$\begin{aligned} \log K_5 &= \log a_{Na^+} + \log a_{OH^-} + \log a_{Al(OH)_3} \\ &\quad - \log a_{NaH_2AlO_3} - \log a_{H_2O} \\ &= -6.838 \end{aligned}$$

$$\begin{aligned} \log K_6 &= \log a_{K^+} + \log a_{OH^-} + \log a_{Si(OH)_4} \\ &\quad - \log a_{KH_3SiO_4} - \log a_{H_2O} \\ &= -4.168 \end{aligned}$$

$$\begin{aligned} \log K_7 &= \log a_{Na^+} + \log a_{OH^-} + \log a_{Si(OH)_4} \\ &\quad - \log a_{NaH_3SiO_4} - \log a_{H_2O} \\ &= -3.755 \end{aligned}$$

The model has been developed only at 600°C and 2 kbar. Only at this condition are sufficient experimental data available to adequately constrain and test it. $\log K_{H_2O}$, $\log K_{NaOH}$, $\log K_{KOH}$, V_{H_2O} and $\log K$ for mineral dissolution equilibria can all be easily obtained at other P-T conditions, but the experimental data required to obtain values of $\log K_{4,p}$, $\log K_{5,p}$, $\log K_{6,p}$ and $\log K_{7,p}$ are very sparse.

Shortcomings in the model can be explained by a combination of

- increase in $\gamma_{\text{charged species}}$ to about 10 to 100 as the equilibrium solution composition departs from pure water,
- decrease in a_{H_2O} to about 0.5 to 0.8 as the equilibrium solution composition departs from pure water,

c) increase in $\gamma_{\text{KH}_3\text{SiO}_4}$ and $\gamma_{\text{NaH}_3\text{SiO}_4}$ to about 10 to 100 in the presence of KH_2AlO_3 and NaH_2AlO_3 .

Exact functional forms for these variations cannot be obtained without overfitting the present database.

Alternatively, additional species may be involved. This possibility has not been quantitatively assessed.

Finally, one can speculate about what the actual structure of the solution might be. Perhaps the OH^- ion acts as a "structure-maker", stabilising networks of K--OH--Al bonds. The Cl^- ion may act as a "structure-breaker". Hence, hydroxyl solutions lead to an increase in corundum and quartz solubilities, whilst chloride solutions have little effect.

Ideally, any proposed species should conform to what is theoretically reasonable. The decrease in ϵ as temperature increases will favour attraction of oppositely charged species to one another (Moore, 1972, p429). Polynuclear species at room temperature and pressure are generally symmetrical and held together by OH^- or O^{2-} bridges. The following three quotes from Baes and Mesmer (1976) emphasise the unique character of the OH^- ligand.

"Hydrolysis is favored for cations of high charge and small size. This is consistent with the classification of OH^- as a "hard" ligand, one that forms its more stable complexes with the less polarizable pre-transition metal cations (the "hard" cations) through the formation of predominantly ionic bonds. But

it is also true that quite stable hydrolysis products are formed by the so-called "soft" cations of the post-transition metals, suggesting that hydroxide ion can also act as a "soft" ligand that forms bonds with appreciable covalent character." [Baes and Mesmer, 1976, p397]

"The "hard-soft" character of the OH^- ligand, the three kinds of ligands (O^{2-} , OH^- , and OH_2) that can be bound, their interconversion by the loss or gain of a proton, and the formation of OH^- -bridged and O^{2-} -bridged polynuclear species are characteristics that serve to distinguish hydrolysis products from other complex ions both in variety and stability. All of these attributes stem from the peculiar properties of the oxygen atom of the ligands. It can have a co-ordination number from 2 to 4, including bonds to one or two H atoms, which are largely covalent, and bonds to M atoms, which can be largely ionic to largely covalent." [Baes and Mesmer, 1976, p397]

"The strong tendency of OH^- to co-ordinate to more than one cation in solution to form bridges is almost unique among the simple ligands. It is probably caused by the relatively large negative charge that can reside on the oxygen atom in the electric field of two or more neighbouring cations. The F^- ion, a ligand of similar size and net charge, forms mononuclear complexes with "hard" cations not greatly different in stability from the corresponding hydroxide species, but F^- has virtually no tendency to form bridges." [Baes and Mesmer, 1976, p421]

A quote from Pitzer (1981, p271) helps to clarify the

physical interpretation of activity coefficient variations:

"BARNES [in discussion of Pitzer's paper]:

Are you bothered by activity coefficients for an aqueous ion that fall below 0.01? In other words, how do you look at an activity coefficient of say 10^{-3} ?

PITZER:

Well, some forces are pretty strong, and cause large departures from an ideal solution. On the other hand, e.g. $\text{La}(\text{ClO}_4)_3$ at high concentration has an activity coefficient that exceeds 1000! Its enormous! You can't explain large activity coefficients with ion pairing. Instead, it is very strong ion hydration, if you wish, that leads to a large repulsive diameter."

Note that Pitzer is referring to $\gamma_{\text{La}(\text{ClO}_4)_3}$, where $\text{La}(\text{ClO}_4)_3$ is a thermodynamic component in the system $\text{La}(\text{ClO}_4)_3\text{-H}_2\text{O}$. Interpretation of activity coefficient variations of individual aqueous species is much more speculative, because of the inherent non-uniqueness of the variations (see Appendix F).

The following quote from Seward (1981, p129) illustrates some theoretical aspects of ion solvation (synonymous with ion hydration when the solvent is water):

"HELGESON [in discussion of Seward's paper]:

You dangled before us a provocative statement that contradicts what I would expect. You said you think the silver ion increases its degree of solvation with increasing temperature. Would you enlarge on that please?

SEWARD:

We don't know anything in much detail about ion-solvent interaction at high temperatures. But my interpretation of those quite large entropies of complex formation is that the silver ion becomes relatively more solvated. This is very qualitative, but the silver ion becomes relatively more solvated at high temperatures, because the water dipoles have less competition amongst each other with regard to bulk solvent water. In other words, the interaction between water molecules is less strong than between ion-water as the temperature increases. And in that respect the ions become more solvated.

HELGESON:

So your opinion is based solely on conceptual reasoning?

SEWARD:

Yes. There's nothing quantitative about it.

HELGESON:

It seems to me that a decreasing dissociation constant with increasing temperature would be consistent with replacement of coordinate H_2O dipoles by other ligands. Ion solvation would then decrease.

SEWARD:

I was referring to the free silver ion. In addition, there is a positive contribution to the entropy of complex formation arising from the greater tendency to form inner sphere complexes with increasing temperature."

Hydration of aqueous complexes may lead to a large reduction

in the amount of "free" H_2O , and hence a lowering of a_{H_2O} .

Chapter 5 Uses of the data

Introduction

The model developed in Chapter 4 can be put to two closely related predictive uses:-

- a) calculation of activities of species in aqueous solutions,
- b) calculation of molalities of species in aqueous solutions.

Activities of aqueous species, not molalities, determine whether or not a fluid phase is saturated with respect to a mineral and hence whether or not that mineral will tend to dissolve or precipitate. For example, increasing the $a_{K^+}:a_{Na^+}$ ratio in an aqueous phase in equilibrium with alkali feldspar will stabilise the Kfs component relative to the Ab component.

Activity diagrams can be constructed which show how the stable mineral assemblage changes as the activities of aqueous species change. These diagrams help to place constraints on what conditions must be satisfied for specific phase assemblages to form during water-rock interaction. See, for example, the compilations of Helgeson et al. (1969) and Bowers et al. (1985). The diagrams indicate how activities must vary to produce the observed phase assemblages, but not why the activities vary.

The activity of an aqueous species is dependent on the composition of the fluid. If the composition is known, activities can be calculated using aqueous solution models. To fully understand how changes in activities of aqueous species occur, one must understand how the composition of the aqueous phase changes in response to P-T-X (pressure - temperature -

composition) changes.

Aqueous fluids in the Earth's crust are always complex multi-component phases which have undergone continuous evolution. Activities of species within such fluids change in response to

- a) changes in pressure or temperature which in turn are brought about by fluid migration e.g. in a convective cell in a cooling pluton;
- b) changes in fluid composition, brought about by diffusion of individual aqueous species, in response to chemical potential gradients;
- c) changes in the mineral assemblage adjacent to the fluid, as a result of minerals dissolving or precipitating or fluid migrating.

How can the chemical evolution of an aqueous fluid be modelled? For example, assume that we have a system containing alkali feldspar in equilibrium with an aqueous solution. At constant temperature and pressure, the aqueous $a_{K^+} : a_{Na^+}$ ratio can only be changed by mass transfer. This can occur by

- a) fluid flow, bringing an entirely new "packet" of solution into contact with the alkali feldspar,
- or by
- b) diffusion, whereby the various components of the aqueous solution migrate down chemical potential gradients.

In either case, one cannot consider the alkali feldspar - aqueous solution to be a "closed system". Instead, one can consider the alkali feldspar - aqueous solution to be a "sub-

system", surrounded by other sub-systems, each at a unique P-T-X condition and each one assumed to be close to thermodynamic equilibrium. A whole grid of sub-systems can be arranged to model a hypothetical section through the Earth's crust. Fluid flow and diffusion will occur between adjacent sub-systems. The solutions may re-equilibrate; minerals may dissolve or precipitate.

A complex system can be approximated by a large number of simple sub-systems, each at a constant temperature and pressure. Mineral dissolution and precipitation between adjacent sub-systems can be predicted, assuming each sub-system remains at thermodynamic equilibrium. An assumption must also be made regarding the fluid composition, prior to its initial equilibration with the mineral assemblage e.g. what is its Cl molality? The future evolution of the system is critically dependent on this initial choice.

The computer code developed in Chapter 4 allows one to predict effects between adjacent sub-systems, and, subject to a set of initial assumptions, allows one to explain observed geological phenomena. Computer codes which permit simultaneous evaluation of mass transfer over a grid of sub-systems, using reasonable thermodynamic models, are feasible but not yet developed.

A fully realistic model of water-rock interaction in the Earth's crust, such as the one summarised in figure 1-2, involves a multitude of additional processes. There are very little data

relating to many of these, and many simplifying assumptions must be made. For example, the pore structure of a granite is very different to the pore structure of a sandstone. This will affect fluid^o flow rates and paths. Heat transfer will occur by convection (fluid flow) and conduction. The redistribution of heat will lead to chemical reactions. Fluid flow will be primarily convective, and will change as the pluton cools and the country rock heats up. As the pluton cools, fractures will develop i.e. its pore structure will change. Clearly, all these effects are inter-related.

As the simplifying assumptions are removed, the model will become more complex, and will rapidly exceed the capacities of the most powerful modern computers. Rather than merely await the development of more powerful computers, some useful insights can be gained by developing simplistic models. The necessary approximations may have little effect on the predictions.

Metasomatic processes have often been modelled in terms of mass balance constraints. One starts with an observed metasomatic rock, of known bulk composition. One decides, from geological evidence, what the bulk composition was before metasomatism e.g. the metasomatic rock may grade into an unaltered sedimentary rock. Then, subject to certain constraints (commonly an assumption of constant volume, or constant mass of a specific element), one can calculate which elements have been gained and which have been lost. The method takes no account of thermodynamic constraints. The assumptions are obviously

approximations. The system is, by definition, an open one, and since every element dissolves in water to some extent, the mass of every element must vary. Minerals, with different densities, will dissolve and precipitate. If the chosen assumption is approximately valid, then the method describes what happens, but offers no insight into how or why.

An alternative approach would be based on thermodynamic calculations. Let us suppose that fluid flow is rapid and pervasive, such that diffusion is not a major process. The experimental data given in Chapter 3 indicate that thermodynamic equilibrium is approximately maintained at high flow rates. Suppose that the metasomatic driving force is a cooling pluton, from which fluids are convecting away. By splitting the system into a series of equilibrium sub-systems, the metasomatic effects of the fluid could be modelled. The initial fluid composition and the P-T path of the fluid could be varied to maximise the agreement between the model and the observed alteration.

The applications given in this chapter all stress the importance of aqueous Al in rock-water interaction.

Thermodynamic data for aqueous Al are essential for predicting the course of such interaction. The data presented in this thesis allow, for the first time, a quantitative assessment of the importance of aqueous Al at supercritical temperatures and pressures. Prior to this work, thermodynamic modelling at high pressures and temperatures, in closed systems, necessitated the assumption that whenever an aluminosilicate dissolved, a more

Al-rich phase precipitated (see, for example, Frantz et al., 1981). The data presented in Chapter 4 remove the need for this assumption.

If one assumes that Al is insoluble, then one cannot explain the common occurrence of Al-bearing minerals in veins. Al must dissolve into the fluid; and the fluid must reach saturation with respect to the vein mineral, for the mineral to precipitate out.

All the calculations reported in this chapter use the thermodynamic data listed in Appendices B and E, plus the expressions obtained in Chapter 4. The computer programme used to carry out the calculations is described briefly in Appendix A. The dissociation constants for KH_2AlO_3 , KH_3SiO_4 , NaH_2AlO_3 and NaH_3SiO_4 were evaluated at 600°C , 2 kbar over a range of "apparent" ionic strengths up to about 1.0 molal. It is unsafe to apply the model at greatly different conditions. All the calculations in this chapter were performed at or near 600°C , 2 kbar, with $m_{\text{Cl},T} < 1.0$ molal. For the sake of simplicity, the calculations consider only Na-, K-, Al-, Si-bearing minerals. The model could be applied to Ca- and Mg-bearing minerals using the data of HKF and Frantz and Marshall (1982). There is no provision for solid solutions in the present computer code.

1. Calculation of the aqueous solution composition in equilibrium with a granite

Consider a hypothetical granite consisting only of the pure phases K-feldspar, albite, muscovite and quartz. The phase assemblage contains only K, Na, Al, Si, O and H. When it reacts with water at a specific temperature and pressure, a specific aqueous solution composition will result. Fluid inclusion evidence indicates that Cl^- is often the dominant anion in supercritical aqueous solutions, sometimes reaching concentrations of several molal. How would the fluid composition vary as a function of chloride concentration? This would be important during subsequent rock-water interaction, as diffusion and fluid flow occurred.

Table 5-1 shows the predicted solution composition resulting from reaction of Qtz-Ab-Kfs-Ms with Cl^- -bearing water. Whilst albite and K-feldspar are predicted to dissolve and muscovite to precipitate at all Cl molalities, the behaviour of quartz changes from dissolution at low Cl molalities to precipitation at high Cl molalities. This has some relevance to the origin of quartz veins in granites. However, caution is required in applying the data, because of the very simple initial solution composition.

The equilibrium solution compositions given in table 5-1 are essential starting points for mass transfer calculations of the type pioneered by Helgeson et al. (1970). With an expanded database (including data for KAl_2SiO_5 , KAl_3SiO_8 , $\text{KNa}_2\text{Al}_2\text{Si}_2\text{O}_{10}$ and $\text{KNa}_3\text{Si}_3\text{O}_{10}$ as $f(P,T)$), one could predict alteration patterns

involving Na-K-Al-Si minerals within and adjacent to a cooling pluton.

Table 5-1 Predicted solution compositions in equilibrium with a hypothetical granite.

T = 600°C. P = 2 kbar

Phase assemblage Ab-Kfs-Ms-Qtz-aq

mCl,T	Si ppm	Al ppm	Na ppm	K ppm	Qtz
0.0	3188.237	13.485	30.8	21.8	d
0.02	3191.745	13.488	359.5	212.9	d
0.04	3191.745	13.488	687.1	433.9	p
0.06	3191.745	13.488	1010.5	662.3	p
1.0	3191.745	13.488	15729.9	12195.6	p

d - quartz dissolves en route to equilibrium

p - quartz precipitates en route to equilibrium

The dissolution or precipitation of quartz is controlled by the composition of the initial solvent. For the calculations given above, the initial solvent was assumed to be H₂O + HCl. If Na or K had been present in the initial solvent, then the amounts of minerals dissolving or precipitating would have changed, but not the final equilibrium solution composition.

2. Alteration of microcline perthite

If one assumes that Al is insoluble (as one is forced to, in the absence of reliable thermodynamic data for aqueous Al at supercritical conditions), then one is forced to assume that an Al-enriched phase (or phases) precipitates when feldspar dissolves in pure water. If one assumes that Al is soluble, then no assumptions need be made about any precipitated phases. Feldspar may dissolve congruently (i.e. no phases precipitate); any phase within the system Na-K-Al-Si-O-H may precipitate.

Feldspars in plutonic igneous rocks often show some alteration to sericite (Deer, Howie and Zussman, 1966). Does the model developed in Chapter 4 predict such alteration at 600°C and 2 kbar when the starting aqueous solution is pure water or 1.0m chloride?

Table 5-2 gives predicted solution compositions resulting from dissolution of albite and K-feldspar and precipitation of either muscovite, paragonite, corundum or quartz at 600°C and 2 kbar.

The final column of table 5-2 shows which phases (out of muscovite, paragonite, corundum and quartz) the solution is supersaturated with respect to. The results are consistent with alteration of feldspar to muscovite i.e. an Al-enriched phase precipitates. The model predicts what is observed geologically.

Quartz is predicted to precipitate when $m_{Cl,T} = 1.0$, but not when $m_{Cl,T} = 0.0$. As in table 5-1, the predictions of which minerals dissolve or precipitate is dependent on the composition

of the initial solvent. Reaction with an initial solvent rich in NaCl, but poor in KCl, would lead to precipitation of albite and dissolution of K-feldspar.

Table 5-2 Dissolution of microcline perthite - predicted
solution compositions and alteration products

T = 600°C P = 2 kbar

Initial solution	Precipitated phase	Solution composition				Supersaturated phases		
		Si ppm	Al ppm	Na ppm	K ppm			
pure water	none	1071	343	186	180	Ms	Pg	Crn
	Ms	1337	200	243	207	none		
	Pg	1231	238	222	194	Ms	Crn	
	Crn	1282	218	232	200	Ms		
mCl,T = 1.0	none	5294	1695	1041	687	Ms	Pg	Crn
	Ms	25386	1.9	4835	3557	Qtz		
	Pg	22230	3.5	4243	3099	Ms	Crn	Qtz
	Crn	23877	2.5	4552	3338	Ms	Qtz	
	Ms Qtz	3192	13.5	15730	12196	none		

3. The origin of Qtz-And segregations

This application of the data gives a simple illustration of how the sub-system approach to metasomatism, discussed in the introduction to this chapter, can be applied to observed phenomena.

Segregations consisting mainly of quartz and andalusite, kyanite and/or sillimanite occur in many metamorphic terranes. They are found in pelitic schist, quartzite, and quartzofeldspathic gneisses. They may be lensoid, nodular or vein-like in shape, and range in size from a few centimetres to several metres. Many segregations contain minor amounts of minerals present in the adjacent rocks (e.g. feldspar, tourmaline, mica, hematite). The Al-silicate polymorph in a segregation is not necessarily the same as that in the surrounding rocks.

Based on the field evidence, it is reasonable to assume that the segregations result from transport of material in an intergranular fluid phase. Two possible driving forces for this process are evaluated here:-

- 1) chemical potential gradients resulting from the sillimanite-andalusite transition (proposed by Fisher, 1973);
- 2) chemical potential gradients resulting from muscovite breakdown.

Mechanism 1) can only be considered for rocks which contain sillimanite whilst in the P-T field of andalusite stability. At some degree of metastability, the sillimanite will invert to andalusite. Assume that the other phases present are Qtz-Ab-Kfs-

aq. The equilibrium composition of the aqueous phase can be calculated at 600°C and 2 kbar (within the stability field of andalusite). Some results are given in table 5-3.

Table 5-3 Qtz-And segregations - predicted solution compositions
(in ppm)

And-Sil transition control

phase assemblage Ab-Qtz-Kfs-Als-aq

T = 600°C P = 2 kbar

Initial solution	Al-silicate polymorph	Solution composition			
		Si ppm	Al ppm	Na ppm	K ppm
pure water	And	3188.224	13.487	30.755	21.771
	Sil	3188.149	13.496	30.675	21.713
$m_{\text{Cl},T} = 1.0$	And	3191.731	13.490	15729.84	12195.50
	Sil	3191.657	13.499	15729.43	12195.17

From table 5-3, it is clear that chemical potential gradients within the aqueous phase will result. In the simple system being modelled here, it is safe to assume that the chemical potential of an element is proportional to its concentration. Al will migrate towards andalusite, whilst Na and K will migrate away from andalusite i.e. the thermodynamic data obtained in Chapter 4 are consistent with Fisher's model.

With mechanism 2), some method of obtaining a solution supersaturated with respect to Al-silicate must be devised, when the phases present in the adjacent rock do not necessarily include any Al-silicate. Let us assume an initial phase assemblage Qtz-Ab-Kfs-Ms-aq. Note that for the reaction

$\Delta G_{\text{reaction}} = 0.0$ at 600°C and 1988.1 bars (calculated using data given in Appendix B). At greater pressures, the left hand side of the reaction is stable. The solution compositions in equilibrium with the phase assemblages Qtz-Ab-Kfs-Ms and Qtz-Ab-Kfs-Als at pressures in the range 1980 to 1990 bars and with $m_{\text{Cl},T} = 0.0$ or 1.0 are given in table 5-4 (calculated using the values for $K_{\text{KH}_2\text{AlO}_3}$, $K_{\text{KH}_3\text{SiO}_4}$, $K_{\text{NaH}_2\text{AlO}_3}$ and $K_{\text{NaH}_3\text{SiO}_4}$ at 2000 bars).

Consider the data for $m_{\text{Cl},T} = 1.0$ and $P = 1980$ bars. Assume that andalusite forms at the expense of muscovite in one region. The rock could be represented as two sub-systems - one containing Ab-Kfs-Qtz-Ms-aq, the other containing Ab-Kfs-Qtz-And-aq, both sub-systems being at the same pressure and temperature.

Each sub-system would have a specific aqueous solution composition, as shown in table 5-4. Diffusion gradients would result. Na, K and Si would migrate to the muscovite-bearing sub-system, whilst Al would migrate to the andalusite-bearing sub-system.

One further refinement which can be introduced into this model is to consider the effect of a small pressure drop from, for example, 1980.05 bars to 1980 bars. Assuming that a 3 km depth of rock exerts a pressure of about 1 kbar, then a pressure drop of 0.05 bars is equivalent to about a 150 mm decrease in depth.

If the muscovite-bearing sub-system is at a pressure of 1980.05 bars, and the andalusite-bearing sub-system is at a pressure of 1980 bars, then the model predicts that Al and Si will migrate to the low pressure area and Na and K will migrate to the high pressure area. This is consistent with the formation of Qtz-And segregations. The presence of "tension gashes" may facilitate this process by allowing increased fluid flow.

A larger pressure drop would not necessarily enhance the process, because K would then tend to migrate to the lower pressure sub-system, where it would precipitate, together with some of the Al and Si, as K-feldspar.

The concentrations in table 5-4 change only very slightly, but the direction of change is more important than the magnitude. If a mass transfer process operates over a long period, the cumulative effect of very small changes may become significant.

Mass transfer by diffusion and/or fluid flow can thus lead to the development of Qtz-And segregations. In the Cl-rich solutions, Al is by far the least abundant element. However, it cannot be assumed to be insoluble; otherwise a solution supersaturated with respect to andalusite could never develop.

4 OF/DE 4

MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS
STANDARD REFERENCE MATERIAL 1010a
(ANSI and ISO TEST CHART No. 2)

Table 5-4 Qtz-And segregations - predicted solution compositions (in ppm)

Muscovite breakdown control						
T = 600°C						
Solid phases	Initial solution	Pressure bars	Si ppm	Solution composition Al ppm	Na ppm	K ppm
Ab-Kfs-Qtz-Ms	pure water	1990	3173.135	12.947	29.827	21.053
Ab-Kfs-Qtz-Ms	pure water	1985	3165.569	12.685	29.366	20.697
Ab-Kfs-Qtz-Ms	pure water	1980	3157.993	12.427	28.911	20.345
Ab-Kfs-Qtz-Als	pure water	1990	3173.122	12.948	29.813	21.043
Ab-Kfs-Qtz-Als	pure water	1985	3165.570	12.685	29.367	20.698
Ab-Kfs-Qtz-Als	pure water	1980	3158.007	12.426	28.927	20.357
Ab-Kfs-Qtz-Ms	m _{Cl,T} = 1.0	1990	3176.622	12.950	15732.218	12186.274
Ab-Kfs-Qtz-Ms	m _{Cl,T} = 1.0	1985	3169.047	12.687	15733.391	12181.579
Ab-Kfs-Qtz-Ms	m _{Cl,T} = 1.0	1980	3161.460	12.430	15734.579	12176.848
Ab-Kfs-Qtz-Als	m _{Cl,T} = 1.0	1990	3176.609	12.951	15732.144	12186.214
Ab-Kfs-Qtz-Als	m _{Cl,T} = 1.0	1985	3169.047	12.687	15733.399	12181.585
Ab-Kfs-Qtz-Als	m _{Cl,T} = 1.0	1980	3161.474	12.428	15734.669	12176.921
Ab-Kfs-Qtz-Ms	m _{Cl,T} = 1.0	1980.05	3161.536	12.433	15734.567	12176.896
Ab-Kfs-Qtz-Als	m _{Cl,T} = 1.0	1980	3161.474	12.428	15734.669	12176.921

Concluding remarks

The subject matter in this thesis is very obviously not a closed topic. All of the interpretation needs to be repeated, with more, and better experimental data. This is an ongoing process - every time the database is improved, the data should be re-analysed. There may never be a perfect solution, but one can hope for a solution within the error limits of the data.

The principal conclusions of this thesis are that the experimental data of Chapter 3 are as good as any other available data, and that they can be interpreted satisfactorily in terms of simple solution models. The data analysis techniques developed in Chapter 4 can be extended to more sophisticated solution models, as more experimental data become available. The derived thermodynamic data can be used to provide quantitative explanations for observations of metasomatic phenomena.

Appendix A Details of computer programs

All the calculations for this thesis (with the exception of the non-linear least squares regression) were performed on a Honeywell computer, CP6 operating system, using Fortran 77 (double precision). Statistical Package for the Social Sciences (SPSS, release 9.1) was used to perform the linear regression analyses.

A.1 Non-linear least squares regression

This regression analysis was done using a CDC Cyber computer, at the Geological Survey of Canada. A library subroutine was used (EMRLIB routines DFS001 and DFS002, documented by D. K. Dawson, Computer Science Center, E.M.R., June, 1971), based on an algorithm developed by Powell (1964, 1965).

It was noted that if θ was allowed to vary, the programme invariably attempted to increase it to greater than 298.15 K. This resulted in the programme attempting to calculate the logarithm of a negative number (see Chapter 4, step 7), and hence aborting. Therefore, θ was fixed at 229.6 (the same value as θ_{A13+}).

Initial estimates for the nine adjustable parameters were all set to 1.0. The regression was arbitrarily truncated after 10 000 iterations. Some of the parameters were still changing in the first or second significant figure, but convergence had become very slow.

If different initial estimates had been used, a different

set of values for the parameters would have been obtained.

The data are "overfitted" by HKF eq 276. There are minor undulations in $\Delta G_{\text{AlO}_{1.5}(\text{aq})}^{\circ}$ (as calculated using the equation and the regression coefficients) as a f(P,T). These are not large enough to appear in figures 4-6 and 4-7.

A.2 S12

S12 is the programme used in Chapters 4 and 5 for the thermodynamic calculations. S12 solves the mass balance and mass action equations given in Chapter 4 by using a method based on the computer programme presented by Frantz et al. (1981). The equations are first solved by assuming $\gamma = 1$ for all aqueous species. A solution composition is obtained, for which a value of γ for each aqueous species can be calculated. The mass action equations are then modified, with the $\ln K$ and $\ln \gamma$ terms on the L.H.S. (known quantities) and the $\ln m$ terms on the R.H.S. (unknown quantities), and the set of simultaneous equations again solved. New values of γ are obtained, and the process is repeated until successive values of γ agree to within a specified level ($1.0\text{E-}10$ in the calculations reported here). An average of thirty iterations was needed to solve the problem.

The method appears to work for virtually any initial estimates. For the calculations reported here, the initial estimates for all aqueous species were set to $10.0\text{E-}10$. The activity-composition component of the calculation is confined to one subroutine, and could be very easily modified to work for any a-X model.

The matrix inversion subroutine given by Frantz et al. (1981) is specifically designed for a matrix consisting of mass action and mass balance equations, where the terms in the mass balance equations may have absolute values which are much smaller than the terms in the mass action equations. IMSL (International Mathematical and Statistical Library) matrix inversion subroutines failed with dilute solutions (the matrix became "algorithmically singular").

S12 is capable of reproducing all the figures in HDNB. It can reproduce all the numbers generated by SUPCRT. In order to precisely reproduce the quartz data, it was found necessary to modify $\Delta V_{tr,Qtz}^o$ from $0.372 \text{ cm}^3 \text{ mole}^{-1}$ to $0.3732 \text{ cm}^3 \text{ mole}^{-1}$. This discrepancy between SUPCRT and HDNB is being investigated (Helgeson, pers. comm., 1984; Flowers, pers. comm., 1984).

The computer code is not reproduced here, because of its length (over 3000 lines). It is included on a 5.25" double sided, double density floppy disc at the rear of the thesis. This disc is readable by an IBM PC micro-computer. The disc contains a short user manual for the computer code (file name MANUAL.TXT).

Computer code verification

For the purpose of verification, S12 can be thought of as comprising four distinct sections:

- 1) calculation of values of $\log K$ for mineral dissolution reactions;
- 2) calculation of values of $\log K$ for aqueous speciation

reactions;

- 3) calculation of activity coefficients of aqueous species;
- 4) solution of the set of non-linear simultaneous equations.

The operation of the first section was verified directly against SUPCRT. Subsequent modifications to S12 (the use of Pitzer's expression for ϵ ; the database modification of Hemingway et al.; the use of quartz and corundum solubility data to obtain $\Delta G^\circ \text{Si(OH)}_4(\text{aq})$ and $\Delta G^\circ \text{Al(OH)}_3(\text{aq})$; the use of Haar et al.'s equation of state for water) prevent a direct comparison of the present version with SUPCRT. As each modification was implemented, checks were performed e.g. Pitzer's values of ϵ agree closely with those of H+K (1974a).

Calculation of $\log K$ values for aqueous speciation reactions was verified using published data (e.g. Frantz and Marshall, 1984).

The activity coefficient calculation cannot be directly checked against any published data. Individual components were checked (e.g. values of A_γ and B_γ agree with H+K's (1974b) values when using H+K's (1974a) expression for ϵ). The calculated values are reasonable, behave as expected, and agree with hand-calculated values.

The final section can be easily verified by back-calculation. Having solved for the aqueous solution composition, it is easy to check that the calculated aqueous species molalities and activity coefficients satisfy the mass action and mass balance equations. This can be done using some of the

tables in the latter part of Chapter 4.

I am confident that S12 accurately performs the calculations exactly as described in Chapters 4 and 5. There is a possibility, however, that it will fail on a specific problem for numerical reasons, e.g. the iterative process may fail to converge. S12 has been programmed to provide diagnostic information in the event of such a failure. This feature facilitates easy correction of such numerical problems as they arise. This same feature also picks out improperly formatted input equations (e.g. more unknowns than equations).

A major feature of the programme is its ability to run either interactively or in batch mode. When "standard" problems are being input, it is more efficient to submit batch jobs. Interactive operation is recommended for debugging.

Appendix B Thermodynamic database

The thermodynamic data in tables B-1 and B-2 are taken from HDNB (table 8, p120ff) and HKF (table 18, p1434ff), with modifications and the addition of leucite as noted in Chapter 4, step 4. The only modification not noted in Chapter 4 is $\Delta V_{tr,Qtz}^0$, which was modified to $0.3732 \text{ cm}^3 \text{ mole}^{-1}$ in order to maintain consistency with SUPCRT (see note in Appendix A).

In order to simplify the notation, the bars signifying partial molal properties of aqueous species have been omitted. Also, the following multiplication factors should be applied to the parameters for the aqueous species:

$$a_2 \times 10^{-5} \quad \text{e.g. Na}^+ \quad a_2 = -0.000047852$$

$$a_3 \times 10^{-2} \quad \text{e.g. Na}^+ \quad a_3 = -0.056282$$

$$\omega \times 10^5 \quad \text{e.g. Na}^+ \quad \omega = 33060.0$$

Units are identical to HDNB and HKF except for ΔG_f^0 , ΔH_f^0 and ΔH_{tr}^0 which are all given in kcal mole^{-1} .

Data in tables B-3 and B-4 were calculated using data summarised in Chapter 4, steps 4, 11 and 12, appendices E and G, and tables B-1 and B-2. Additional physical constants at 600°C and 2 kbar are given in table 4-20.

Table B-1 Thermodynamic data for solid phases

	ΔG_f°	ΔH_f°	S°	V°	C_p° coefficients			T_{tr}	ΔS_{tr}°	ΔH_{tr}°	ΔV_{tr}°
					a	b	c				
Corundum	-377.931	-400.262	12.18	25.575	27.49	2.82E-03	8.38E+05	1800.0			
Quartz	-204.646	-217.650	9.88	22.688	11.22	8.20E-03	2.70E+05	848.0	0.342	0.290	0.3732
					14.41	1.94E-03	0.00E+05	2000.0			
Boehmite	-218.804	-236.632	11.58	19.535	14.35	4.20E-03	0.00E+05	500.0			
Diaspore	-219.956	-238.724	8.43	17.760	14.435	4.20E-03	0.00E+05	500.0			
Gibbsite	-276.168	-309.065	16.75	31.956	8.65	4.56E-02	0.00E+05	425.0			
Analcime	-739.652	-791.747	56.0	97.1	53.49	2.414E-02	8.88E+05	1000.0			
Dehydrated analcime	-676.543	-716.232	41.9	89.1	42.09	2.414E-02	8.88E+05	1000.0			
Albite	-887.862	-941.234	49.51	100.07	61.70	1.390E-02	1.501E+06	473.0			
					81.88	3.554E-03	5.0154E+06	1200.0			
Low albite	-887.862	-941.234	49.51	100.07	61.70	1.390E-02	1.501E+06	1400.0			
High albite	-886.063	-938.604	52.30	100.43	61.70	1.390E-02	1.501E+06	623.0			
					64.17	1.390E-02	1.501E+06	1400.0			
K-feldspar	-890.428	-950.742	51.13	108.741	76.617	4.311E-03	2.9945E+06	1400.0			

Maximum microcline	-896.928	-950.742	51.13	108.741	63.83	1.290E-02	1.705E+06	1400.0		
High sanidine	-895.292	-948.092	54.53	109.008	63.83	1.290E-02	1.705E+06	1400.0		
Nepheline	-474.426	-501.795	29.72	54.16	35.908	6.458E-03	7.328E+05	1500.0		
Kalsilite	-483.304	-510.962	31.85	59.89	29.43	1.736E-02	5.32E+05	810.0	0.198	0.160
					42.5	0.00E-03	0.00E+05	1800.0		
Kaolinite	-908.721	-985.328	48.53	99.52	72.77	2.920E-02	2.152E+06	1000.0		
Pyrophyllite	-1259.104	-1348.420	57.2	126.6	79.432	3.9214E-02	1.7282E+06	800.0		
Muscovite	-1340.962	-1432.069	68.8	140.71	97.56	2.638E-02	2.544E+06	1000.0		
Paragonite	-1330.673	-1421.624	66.4	132.53	97.43	2.450E-02	2.644E+06	1000.0		
Al-silicate	-584.063	-620.004	20.00	44.09	41.3931	6.8165E-03	1.28821E+06	466.0	2.238	1.043
					41.3108	6.2926E-03	1.23921E+06	1043.0	0.507	0.529
					40.0240	7.3905E-03	1.16741E+06	1200.0		-1.63
Leucite	-687.354	-726.255	47.85	88.39	35.47	3.2086E-02	5.1730E+05	955.0		
					46.96	6.6123E-03	2.93044E+06	1800.0		
Kyanite	-584.063	-620.004	20.00	44.09	41.3931	6.8165E-03	1.28821E+06	466.0	2.238	1.043
Andalusite	-583.694	-618.973	22.20	51.53	41.3108	6.2926E-03	1.23921E+06	1043.0	0.507	0.529
Sillimanite	-583.198	-618.206	23.13	49.90	40.0240	7.3905E-03	1.16741E+06	1200.0		-1.63

Table B-2 Thermodynamic data for aqueous species

	ΔG_f°	ΔH_f°	S	C_p°	V°	c_1	c_2	a_1	a_2	a_3	a_4	θ	ω
H^+	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Na^+	-62.622	-57.433	14.0	10.0	-1.3	35.7153	-6.2856	0.1914	-4.7852	-5.6282	3.6560	215.17	0.3306
K^+	-67.576	-60.270	24.2	3.0	8.7	18.4682	-2.9265	0.3107	0.7452	-1.9460	1.4504	234.19	0.1927
Al^{3+}	-116.969	-127.008	-73.6	3.9	-42.4	65.27	-7.89	-0.703	-0.9	-3.2	2.17	229.6	2.8711
OH^-	-37.604	-54.977	-2.6	-33.0	-7.7	24.7208	-6.2074	0.0515	-0.0994	-1.9845	1.0832	253.52	1.7246
$SiO_2(aq)$	-199.190	-210.726	14.8	-25.0	13.6	48.5169	-15.7891	0.0214	4.9341	6.8259	0.2979	233.00	0.1291
Cl^-	-31.380	-39.933	13.6	-30.2	17.9	-4.8384	-2.0410	0.5761	-6.9590	-1.0698	1.0365	246.02	1.4560

Table B-3 Standard state Gibbs free energies of pure phases and aqueous species at 600°C and 2 kbar (in kcal mole⁻¹)

Crn	-392.379	Low Ab	-933.060	Pr1*	-1 317.598
Qtz	-214.067	High Ab	-932.958	Ms	-1 408.176
Bhm*	-230.466	Kfs	-943.295	Pg	-1 396.327
Dsp*	-229.892	Max Mc	-942.817	Als	-607.396
Gbs*	-294.952	High San	-943.123	Lct	-727.470
Anl	-788.740	Ne	-501.476	Ky*	-606.874
Dehyd Anl	-713.765	Kls	-511.194	And	-607.402
Ab	-933.518	Kln	-958.545	Sil	-607.386
H ₂ O	-71.543				
Si(OH) ₄ (aq)	-353.371	H ⁺	0.0	Al ³⁺	-74.335
Al(OH) ₃ (aq)	-287.402	Na ⁺	-76.634	OH ⁻	-28.770
SiO ₂ (aq)	-206.316	K ⁺	-83.891	Cl ⁻	-26.378

* Heat capacity coefficients assumed to be valid up to 600°C, in contradiction of the upper temperature limit given in table B-1.

Table B-4 Values of log₁₀K for aqueous dissociation equilibria at 600°C, 2 kbar

Molal concentration scale

H ₂ O	-10.706	NaOH	-1.983	KOH	-2.303
HCl	-4.160	NaCl	-1.795	KCl	-2.115

Appendix C An introduction to the theory of electrolyte solutions

The major part of this thesis is concerned with the thermodynamic properties of cations in aqueous solution. Hence, it is appropriate to give a brief review of the theory of electrolyte solutions.

Pure water can be thought of as an extremely dilute solution of H^+ and OH^- ions in a solvent of H_2O molecules.

The water molecule is bent, with $H-O-H = 104.523^\circ$. The oxygen - hydrogen distances are 0.9571 angstroms, and the dipole moment of water is 1.84 D. The O-H bond energy is estimated to be 110 kcal mole⁻¹, while the angle subtended by the two lone pairs at the oxygen atom has been calculated to be close to 120° . In liquid water there is extensive hydrogen bonding between adjacent molecules. It is generally assumed that the $O-H \cdots O$ arrangement is linear in normal circumstances, with an oxygen - oxygen distance of between 2.5 and 3.0 angstroms. The energy of dimerisation of water is about -4 kcal mole⁻¹. A unique property of water is that it can hydrogen bond from two points, the two hydrogen atoms, in each molecule. Further, each molecule can bond to one of two points, the two lone pairs, in another molecule. This balance permits uniformity of growth of hydrogen-bonded aggregates in three dimensions; the growth of aggregates is energetically favourable. A popular description of liquid water is in terms of a mixture of low density hydrogen-bonded clusters with non-hydrogen-bonded molecules, in the ratio of

about 4 to 1. Rearrangements within the system are very rapid; the half life for a water molecule in a particular environment is thought to be only about 10^{-11} s. X-ray studies of liquid water suggest that the number of nearest neighbours to a given water molecule is 4.4 rather than 4.0, and are consistent with such a picture of open hydrogen-bonded frameworks with non-hydrogen-bonded molecules in cavities. The interpretation of infrared and Raman spectra of liquid water should provide support for, and information on, this model but it remains a matter of controversy. [Account taken from Burgess, 1978, p16-17.]

If solid KCl is allowed to come into contact with the water, then K^+ and Cl^- ions will dissolve. The solutions could be described in terms of particle-particle pair correlation functions, $g_{\alpha\beta}(r)$, with $\alpha, \beta = K, Cl, O$ and H . Statistically, certain elements will tend to be closer to some elements than other elements, and for varying lengths of time. For example, if K and Cl tended to spend a lot of time in very close proximity to one another, then they could be thought of as forming an ion-pair. Neilson and Enderby (1983) obtained correlation functions for a 4.35 molal solution of $NiCl_2$ in D_2O . Their results indicated strong ion pairing between Ni^{2+} and Cl^- , but with a very short lifetime ($\approx 5 \times 10^{-12}$ s) for individual pairs.

Since there is no adequate theory of water at present, any statistical mechanical models of electrolyte solutions must start with a model for the interionic potentials of mean force. The interionic radial distribution functions, $g(r)$ can be calculated

from this model. A departure from unity in $g(r)$ expresses a departure from randomness in the particle distribution. If there is a repulsive core, $g(r)$ drops to zero at point a in figures C-1 and C-2 (Pitzer, 1981, p269-270). The ion distribution can be treated as a single distribution, or split at some convenient point; i.e. the distribution may be represented by a single equation (Pitzer's approach) or by two or more simpler equations involving "ion-association equilibria" (the more common geochemical approach). The choice is purely one of convenience.

Figure C-1 The radial distribution function for unlike
ions for a Debye-Hückel distribution and for a
Bjerrum distribution
(figure taken from Pitzer, 1981)

Figure C-2 The population distribution for unlike ions according to Debye-Huckel and Bjerrum and the Bjerrum assignment of a radius, r_B , within which ions are said to be paired.
(figure taken from Pitzer, 1981)

Appendix D The design of solubility experiments

Over the past forty years, innumerable aqueous solubility experiments for operation at elevated temperatures and pressures have been designed. This appendix reviews the whole range, noting their various limitations.

Solubility has been determined for minerals, whole rocks and silicate melts in water. The water itself may be made acidic or alkaline by addition of HCl, NaCl, NaOH, CO₂, H₂S etc.

Perhaps the simplest technique available is that involving weight loss of individual crystals. Kennedy (1950) pioneered this method. He used pressure vessels with internal capacities of 11 to 45 ml, in which he placed single quartz plates and a measured mass of water. The vessel was sealed and allowed to come to equilibrium at the desired conditions, then quenched. The quartz plate was removed and reweighed. Hence its solubility could be calculated.

Subsequent experiments by Kennedy et al. (1962) used specifically oriented quartz plates to allow the fastest rate of dissolution. The quartz and water were sealed inside a platinum capsule to avoid problems caused by vessel corrosion. Quench precipitates on the quartz plate were removed using cold HF, and a correction made to allow for dissolution of the quartz plate itself.

Anderson and Burnham (1965) used a more complex version of the weight loss technique. They used a perforated inner capsule containing quartz grains, placed inside a larger (~ 22 x 70 mm)

capsule containing water. The inner capsule was removed after a run, weighed, dried and reweighed. By assuming that all the quartz dissolved in water in the inner capsule was precipitated in the inner capsule, an allowance could be made for it. This involved only a small correction in any case.

The weight loss technique can be used over a very wide range of P-T conditions. Anderson and Burnham reached 900°C and 10 kbar. The main restriction to its use is that it assumes stoichiometric dissolution. This must be the case for SiO_2 , but appears to be very rarely the case for other more complex silicates.

There has been only one published study (Ellis, 1959) using the weight loss technique to determine simple sulphide solubilities, and this gave solubilities which were inconsistent and unreproducible. Ellis suggested that this was due to variable oxidation. Quench reactions provide another possible explanation.

Other techniques all involve analysis of the solution, and can be split into two categories. In one, the solution is collected while the vessel is maintained at high temperature and pressure; in the other, the solution is collected after quenching.

There are three basic designs for extracting solution while maintaining the vessel at high temperature and pressure:-

- a) the dynamic flow apparatus (Morey and Hesselgesser, 1951),
- b) rocking autoclave (Barnes, 1963),

c) collapsible bag (Dickson et al. (1963).

The dynamic flow apparatus is the simplest of the three. A vessel with an internal capacity of 80 ml or more is filled with the material under study, and closed at each end with modified Bridgman seals. Water at pressure is slowly passed into one end of the vessel, allowing it to reach the operating temperature before entering the reaction chamber, and is allowed to slowly drip out of the other end through a capillary cooling tube into a collection bottle. The rate of collection must be very slow to allow the water entering the vessel time to equilibrate with the solid. Pure water is usually used as the solvent, to minimise problems due to vessel corrosion. Currie (1968) reached 600°C and 3.5 kbar with this design.

The rocking autoclave is also a fairly simple design. Barnes' apparatus has a Cr-plated reaction chamber with a capacity of 1100 ml. The whole assembly can be rocked, and the vessel tilted at such an angle as to sample either gas or liquid should two fluid phases be present. Small (~ 5 ml) samples are collected at intervals. Since they are so small relative to the vessel size, collection is nearly isobaric. The large size of the vessel restricts its operation to low temperatures and pressures (up to 300 bars at 400°C and 500 bars at 25°C).

The collapsible bag apparatus is rather more complex. A bag containing the solid and solution is held inside a large vessel (capacity 600 ml). Samples can be withdrawn from this bag at the same time as water is pumped into the vessel, thus maintaining

constant pressure. In the original design (Dickson et al., 1963) the solution could be stirred by means of a bar magnet and external magnetic field. In more recent designs, the solution is agitated by rotating the whole furnace assembly (Bischoff, pers. comm., 1980). Dickson et al. also used a teflon bag. Teflon suffers from two drawbacks:

- a) it degenerates above about 290°C ;
- b) it acts as an osmotic membrane, allowing gases and dissolved molecular species to migrate through the cell walls.

Seyfried et al. (1979) redesigned the whole apparatus, and incorporated a 45 x 180 mm gold bag into it. The apparatus remains restricted to operation at low temperatures and pressures, though (up to 300°C and 1 kbar).

All three "sampling at temperature" techniques appear to be free of quench problems. Precipitation in the exit tubes appears to be virtually non-existent in every case.

Techniques involving collection of the sample after quenching have two main problems:

- a) quench reactions may be very serious,
- b) recovery of the fluid is difficult.

The double capsule technique of Anderson and Burnham (1965) can be used in order to minimise quench reactions. Innumerable techniques have been used to extract the solution after quenching. The fluid may be frozen by allowing it to expand rapidly on quenching, or by immersing the capsule in liquid nitrogen.

Many studies have used a simple single capsule. In several of these studies, the time from beginning the quench to extracting the fluid from the capsule is extremely short. Quenching to room temperature can be achieved in less than one second (Jacobs and Kerrick, 1980).

The main advantages of quench experiments are:

- a) their simplicity,
- b) the high temperatures and pressures that can be attained.

Their main disadvantages are:

- a) the small amount of solution that can be obtained, making accurate analysis difficult,
- b) the possibility of quench reactions.

The varying degrees of success which people have had with the quenching technique may be attributed partly to the sophistication of their experimental technique and partly to the susceptibility of the system under study to quench reactions.

Appendix E. Equilibrium constants for dissociation
equilibria in supercritical aqueous solutions

Abstract

Recently published expressions for the calculation of equilibrium constants have been compiled, and re-cast into a common form:

$$\log_{10} K = A + \frac{B}{T} + C \log_{10} d_{H_2O}$$

where K is based on molality concentration units, T is in Kelvins and d_{H_2O} is the density of pure water, in $g\ cm^{-3}$. The expressions are suitable for use in the region 400 to 600°C and 1 to 2 kbar, but may be extrapolated with some confidence outside this region. Expressions are presented for H_2O , HCl , $NaCl$, KOH , KCl , $CaCl^+$, $CaCl_2$, $MgCl^+$ and $MgCl_2$. In addition, an expression for $NaOH$ is obtained by assuming

$$\frac{K_{NaOH}}{K_{NaCl}} = \frac{K_{KOH}}{K_{KCl}}$$

Introduction

Accurate knowledge of dissociation constants is essential for aqueous speciation calculations. These calculations in turn are essential for predicting water-rock interaction. Data have been available for several years for sub-critical pressure / temperature conditions (e.g. Helgeson, 1969); but are still sparse for supercritical conditions.

Published expressions for the dissociation constants of some geologically important species are summarised in table E-1.

Data for K_{KOH} are presented by Franck (1956, table 4, molar

concentration units) and Barnes et al. (1966, p411, same data, molal concentration units).

Data analysis

Published studies of dissociation equilibria show that in the supercritical region, the dissociation constant can be accurately described by

$$\log_{10} K = A + \frac{B}{T} + C \log_{10} d_{H_2O}$$

The expressions in table E-1 were re-cast into this form (except for K_{H_2O} , where the more complex equation was retained), bearing in mind that

$$K_{\text{molar}} = K_{\text{molal}} d_{H_2O}$$

for 1:1 electrolytes. Franck's data for K_{KOH} were also fitted to an expression of this form. Figure E-1 shows Franck's data and curves of $\log_{10} K_{KOH}$ as a f(P) at constant T, generated using the equation given in table E-2.

Following Montoya and Hemley (1975), it is assumed that

$$\log K_{NaOH} - \log K_{NaCl} = \log K_{KOH} - \log K_{KCl}$$

The resultant expressions for the dissociation constants are given in table E-2.

An application of the data

Montoya and Hemley examined the equilibria

at 500°C and 1 kbar. Total chloride in solution was 1 molal.

Experimental values of $(m_{K^+} + m_{KCl})/(m_{H^+} + m_{HCl}) = 1.2$ and $(m_{Na^+} + m_{NaCl})/(m_{H^+} + m_{HCl}) = 2.2$ were obtained graphically from Montoya and Hemley's figures 1 and 2. It is assumed that $(m_{K^+} + m_{KCl})/(m_{H^+} + m_{HCl}) = (a_{K^+} + a_{KCl})/(a_{H^+} + a_{HCl})$, and similarly for Na. A modified version of Frantz et al.'s (1981) computer program was then used to calculate a_{K^+}/a_{H^+} and a_{Na^+}/a_{H^+} . The resultant values are 3.2 and 4.3, respectively. These compare favourably with values of 3.29 and 4.39 calculated from thermodynamic data presented by Helgeson et al. (1978, 1981).

Figure E-1 Graph of $\log_{10} K_{\text{KOH}}$ as a f(P) at constant T
(molal concentration units)
(data points taken from Barnes; curves
calculated using equation given in table E-2)

Table E-1 Published expressions for dissociation constants

$K = \frac{[H^+][OH^-]}{[H_2O]}$	$\log_{10} K = -4.098 - 3245.2/T + 2.2362 \times 10^5/T^2 - 3.984 \times 10^7/T^3$	(1)
$K = \frac{[Na^+][Cl^-]}{[NaCl]}$	$+ (13.957 - 1262.3/T + 8.5641 \times 10^5/T^2) \log_{10}^d H_2O$ $\log_{10} K = -26.820 + 29357.0/T - 0.7976 \times 10^7/T^2$	(2)
$K' = \frac{[K^+][Cl^-]}{[KCl]}$	$= -15.870 + 18121.0/T - 0.5124 \times 10^7/T^2$	(2)
$K = \frac{[CaCl^+][Cl^-]}{[CaCl_2]}$	$\log_{10} K = -23.140 + 24274.0/T - 0.6294 \times 10^7/T^2$	(2)
$K = \frac{[Ca^{2+}][Cl^-]}{[CaCl^+]}$	$= -14.550 + 15528.0/T - 0.4130 \times 10^7/T^2$	(2)
$K = \frac{[MgCl^+][Cl^-]}{[MgCl_2]}$	$\log_{10} K = -3.21 + 2407.0/T + 10.6 \log_{10}^d H_2O$	(3)
$K = \frac{[Mg^{2+}][Cl^-]}{[MgCl^+]}$	$\log_{10} K = -5.05 + 3112.0/T + 16.5 \log_{10}^d H_2O$	(3)
$K = \frac{[H^+][Cl^-]}{[HCl]}$	$\log_{10} K = -3.21 + 2407.0/T + 10.6 \log_{10}^d H_2O$	(3)
	$\log_{10} K = -4.80 + 3415.0/T + 19.2 \log_{10}^d H_2O$	(3)
	$\log_{10} K = -5.405 + 3874.9/T + 14.93 \log_{10}^d H_2O$	(4)

(1) Marshall and Franck (1981), molal concentration units

(2) Frantz et al. (1981), molal concentration units

(3) Frantz and Marshall (1982), molar concentration units

(4) Frantz and Marshall (1983, 1984), molar concentration units

Table E-2 Expressions for dissociation constants, all based on molal concentration units

$K = \frac{[H^+][OH^-]}{[H_2O]}$	$\log_{10} K = -4.098 - 3245.2/T + 2.2362 \times 10^5/T^2 - 3.984 \times 10^7/T^3$ $+ (13.957 - 1262.3/T + 8.5641 \times 10^5/T^2) \log_{10}^d H_2O$
$K = \frac{[Na^+][Cl^-]}{[NaCl]}$	$\log_{10} K = -0.45880 + 788.34430/T + 9.77120 \log_{10}^d H_2O$
$K = \frac{[K^+][Cl^-]}{[KCl]}$	$\log_{10} K = -2.27011 + 1686.91562/T + 7.75325 \log_{10}^d H_2O$
$K = \frac{[CaCl^+][Cl^-]}{[CaCl_2]}$	$\log_{10} K = -3.21 + 2407.0/T + 9.6 \log_{10}^d H_2O$
$K = \frac{[Ca^{2+}][Cl^-]}{[CaCl^+]}$	$\log_{10} K = -5.05 + 3112.0/T + 15.5 \log_{10}^d H_2O$
$K = \frac{[MgCl^+][Cl^-]}{[MgCl_2]}$	$\log_{10} K = -3.21 + 2407.0/T + 9.6 \log_{10}^d H_2O$
$K = \frac{[Mg^{2+}][Cl^-]}{[MgCl^+]}$	$\log_{10} K = -4.80 + 3415.0/T + 18.2 \log_{10}^d H_2O$
$K = \frac{[H^+][Cl^-]}{[HCl]}$	$\log_{10} K = -5.405 + 3824.9/T + 13.93 \log_{10}^d H_2O$
$K = \frac{[Na^+][OH^-]}{[NaOH]}$	$\log_{10} K = -0.43736 + 384.45293/T + 8.66724 \log_{10}^d H_2O$
$K = \frac{[K^+][OH^-]}{[KOH]}$	$\log_{10} K = -2.24867 + 1283.02425/T + 6.64929 \log_{10}^d H_2O$

Appendix F Treatment of the a parameter in the Debye-Huckel equation

The a parameter is incorporated into the Debye-Huckel expression to allow for the finite size of the ions in solution (Atkins, 1978). There is no theoretical method for calculating the "true" value of a , and it has generally been treated as a "fit" parameter by chemists. Typical values lie in the range 2.0 to 10.0 Angstroms and are larger than the corresponding crystallographic ionic radii (Whittaker and Muntus, 1970).

H+K (1976) presented a general expression for a , in which a was allowed to vary as a function of solution composition, but was constant for all ions in a given solution. A very similar expression was used in the initial modelling stages of the present study (steps 1 to 8 of Chapter 4). However, this treatment contradicts thermodynamic theory (H+K, 1976; Baes, 1984; Smith, 1977, p16-18).

The usual treatment of a in geochemical calculations is to use unique values for each ion. This avoids the above theoretical problem. The set of values of a in general use at present (e.g. in the aqueous speciation computer codes WATEQ (Truesdell and Jones, 1974) and EQ3NR (Wolery, 1983)) are taken from the work of Kielland (1937).

A more fundamental problem must be introduced at this stage. To quote from Kielland: "the concept of individual activity coefficients cannot be defined accurately, and such coefficients may not even be determined experimentally without some

supplementary definition of non-thermodynamic nature". (See also Grjotheim, 1981.) The most common supplementary definition is the "MacInnes assumption" (Wood et al., 1984):

$$\gamma_{K^+} = \gamma_{Cl^-} = \gamma_{K^+Cl^-}$$

Kielland's values of $\bar{a}$ are consistent with this approach (he set $\bar{a}_{K^+} = \bar{a}_{Cl^-}$). HKF's approach was to define

$$\Delta G_H^{O+} = 0 \quad \text{at all } P, T, X \text{ conditions.}$$

A third method, and the most satisfying theoretically, is that adopted by Pitzer (1981). The equation for a single ion activity coefficient is written with the understanding that it has an unknown constant associated with it, such that, whenever single ion quantities are combined, the constants cancel out, and a meaningful activity coefficient results.

HKF's method is essentially consistent with this third approach. Activity coefficient corrections can be incorporated to ensure a correct accounting procedure.

Pitzer did not explicitly include the $\bar{a}$ parameter in his model. He treated it as an identical constant for all ions, at all P, T, X conditions (e.g. Pitzer et al., 1984). The effects of varying ion size are effectively incorporated into the virial coefficients in his model.

This leaves one with the problem of how to maintain thermodynamic validity and compatibility with HKF. An entirely empirical algorithm was developed, which gives unique values of $\bar{a}$ for each aqueous species and yet gives values similar to those of HKF's table 2. The algorithm is

$$a = r + 0.9571 (1 + |Z|) \text{ Angstroms}$$

where 0.9571 = O-H distance in H₂O

(Burgess, 1978, p16)

Z = charge of the cation or
anion

r = ionic radius

Values of r are taken from Whittaker and Muntus (1970), who give several values depending on the co-ordination number of the ion.

According to Pauling's first rule (Pauling, 1960, p544), the co-ordination number depends on the radius ratio. For aqueous solutions, let us define the radius ratio as (r/0.9571). Table 13-18 from Pauling (1960, p545) gives the minimum radius ratio for various co-ordination polyhedra. Using these values, in conjunction with the values of Whittaker and Muntus, the values of r, and hence $\bar{a}$, shown in table F-1 were obtained.

Table F-1 Values of crystallographic radii and δ for ions

	r (Angstroms)	δ	
Na ⁺	1.40	3.31	
K ⁺	1.68	3.59	
O ²⁻	1.34	----	
Al ³⁺	0.61	4.44	
Si ⁴⁺	0.48	----	
Al(OH) ₄ ⁻	----	2.52	assuming $r_{\text{Al(OH)}_4^-} = r_{\text{Al}^{3+}}$
Si(OH) ₅ ⁻	----	2.39	assuming $r_{\text{Si(OH)}_5^-} = r_{\text{Si}^{4+}}$
OH ⁻	----	3.25	assuming $r_{\text{OH}^-} = r_{\text{O}^{2-}}$
H ⁺	----	3.25	assuming $r_{\text{H}^+} = r_{\text{H}_2\text{O}^+} = r_{\text{OH}^-}$

Appendix G Thermodynamic data for leucite

After modifying HDNB's database according to the recommendation of Hemingway et al. (1982) and using Robie et al.'s (1979) thermodynamic data for leucite, the slope of the leucite breakdown reaction

was calculated to be about 17°C per kbar, with an intercept of 481°C at 1 bar. Scarfe et al.'s (1966) experimental data can be fitted approximately by a straight line with a slope of 30°C per kbar and a value of 490°C at 1 bar. This intercept agrees closely with the predicted one, but the slopes differ considerably. This appendix describes how the discrepancy was resolved.

Leucite undergoes a phase transition at about 682°C and 1 bar from a tetragonal to a cubic form. This transition has a negligible (possibly zero) ΔV_{tr} and ΔS_{tr} , but the trends of the heat capacity and thermal expansion as functions of temperature change drastically (Pankratz, 1968; Taylor and Henderson, 1968; Henderson, 1981).

For Scarfe et al.'s data, the single straight line with slope = 30°C and $T = 490^\circ\text{C}$ at 1 bar is inconsistent with one data point (Kls + Kfs at 675°C, 6000 bars). Their data can be completely fitted by two straight lines, one from 481°C, 1 bar to 682°C, 6240 bars, the second from 682°C, 6240 bars to 750°C, 8960 bars. Values of $(\Delta G_{\text{Kfs}} + \Delta G_{\text{Kls}})/2$ were calculated for a series of points along these lines. These values then became reference

points, towards which ΔG_{Lct} was adjusted.

Initial attempts to adjust ΔG_{Lct} to these values, by changing $\Delta G^{\circ}_{f,Lct}$ and S°_{Lct} away from Robie et al.'s data failed. Manipulation of all of Robie et al.'s data for leucite could have produced a good fit to the data, but it seems unlikely that the heat capacity and entropy data are all inaccurate when one considers the good agreement with the experimental phase equilibrium data at 1 bar. (There would have to be a fortuitous cancelling of errors.)

This suggested that the problem lay in the effect of pressure. Leucite has an anomalously high rate of expansion up to 682°C at 1 bar, after which it becomes relatively inexpandible. The percentage volume increases for leucite, K-feldspar and kalsilite going from 20°C to 700°C are about 5.7%, 1.4% and 2.0% respectively (Taylor and Henderson, 1968; Henderson, 1978; Henderson and Taylor, 1984). By analogy with quartz (HDNB figures 7 and 8) it is likely that leucite also shows anomalous compressibility.

Let us assume that the behaviour of V_{Lct} as a $f(P,T)$ up to 682°C can be approximated by

$$V_{P_r,T} = V^{\circ} (1.0 + a (T - T_{ref})) ,$$

$$\text{where } V^{\circ} = 88.39 \text{ cm}^3 \text{ mole}^{-1}$$

(from Robie et al., 1979)

$$T_{ref} = 298.15 \text{ K}$$

$$V_{P,T} = V_{P_r,T} (1.0 + b (P - P_{ref}))$$

$$P_{ref} = 1 \text{ bar}$$

Assume that the tetragonal - cubic inversion has a slope of $k \text{ K kbar}^{-1}$.

Above 682°C , assume

$$V_{P,T} = V_{P_r,682} \text{ for cubic leucite}$$

$$V_{P,T} = V_{P_r,682} (1.0 + b (P - P_{tr}))$$

for tetragonal leucite

where P_{tr} = tetragonal-cubic transition
pressure at the temperature
of interest

Hence, there are three constants, a , b and k which can be adjusted to obtain a satisfactory fit to the phase equilibrium data. This was done by "trial and error" calculations and gave

$$a = 1.3 \times 10^{-4} \text{ K}^{-1}$$

$$b = -1.2 \times 10^{-5} \text{ bar}^{-1}$$

$$k = 0.07 \text{ K bar}^{-1}$$

Using these three constants, in conjunction with Robie et al.'s data for leucite, the following set of equilibrium conditions for $2 \text{ Lct} = \text{Kfs} + \text{Kls}$ were calculated:

$$P = 1.0 \text{ bars} \quad T = 481^{\circ}\text{C}$$

$$2000 \quad 557$$

$$4000 \quad 625$$

$$6000 \quad 681$$

$$7150 \quad 713$$

$$8000 \quad 735$$

$$10000 \quad 777$$

These four points
are all very tightly
constrained by
Scarfe et al.'s data

These P-T conditions are fully consistent with Scarfe et al.'s

data.

The value of a is consistent with $V_{Pr,682} = 95.94 \text{ cm}^3 \text{ mole}^{-1}$. This value is higher than that obtained by Taylor and Henderson (about $93.4 \text{ cm}^3 \text{ mole}^{-1}$). Possible causes of this discrepancy were investigated by analysing the $\int V dP$ term contributing to ΔG_{Lct} . For leucite assumed to be in equilibrium with kalsilite, and K-feldspar at 600°C and 3695 bars, the $\int V dP$ term equals $8125 \text{ cal mole}^{-1}$. From Taylor and Henderson, we obtain

$$V_{Pr,600} = 91.4 \text{ cm}^3 \text{ mole}^{-1}$$

If this value of $91.4 \text{ cm}^3 \text{ mole}^{-1}$ is assumed to be independent of pressure, then

$$\begin{aligned} \int V dP &= 91.4 (3695 - 1) / 41.84 \\ &= 8070 \text{ cal mole}^{-1} \end{aligned}$$

i.e. a discrepancy of 55 calories. Decreasing V_{Lct} as pressure increases would cause a larger discrepancy. A value of $8125 \text{ cal mole}^{-1}$ is consistent with a constant $V_{Lct} = 92.03 \text{ cm}^3 \text{ mole}^{-1}$.

i.e. using accurate data for V_{Lct} as a $f(T)$ will not lead to a better fit to Scarfe et al.'s data. The small errors involved are within the range of uncertainty of $\Delta G_{f,Lct}^\circ$ ($\pm 680 \text{ cal mole}^{-1}$; Robie et al. 1979).

The equilibrium

remains an unresolved problem. The thermodynamic data predict an equilibrium at 809°C , 1 bar, whilst experimental data (Schairer and Bowen, 1955) show that K-feldspar remains stable up to 1150°C at 1 bar, where it melts incongruently, producing leucite.

Because the discrepancy between phase equilibrium and thermodynamic data occurs at 1 bar, volume effects cannot be invoked to explain it. As seen in figure 4-3, the discrepancy disappears at pressures above about 2-3 kbar. The only "easy" way to account for the discrepancy whilst maintaining consistency with HDNB's database and Scarfe et al.'s data would be to modify the heat capacity equation for leucite at high temperatures. Such a procedure would be hard to justify without additional supporting arguments. It is possible that the problem lies within HDNB's database, or in differences between the behaviour of synthetic leucite (pure KAlSi_2O_6) and natural leucite (containing some Na, Rb etc.).

The possible importance of the last point can be seen by contrasting the thermal expansion of synthetic and natural leucites (Taylor and Henderson, 1968; Henderson, 1981). It is possible that small amounts of impurities could greatly increase the P-T range of stability of leucite. Phase equilibrium studies such as those of Scarfe et al. (1966) and Schairer and Bowen (1955) involve negligible impurities. The calorimetric data for leucite were obtained using natural leucite (Barany and Adami, 1966; Pankratz, 1968). The sample used by Pankratz contained 0.23 wt % of Na_2O (consistent with 98.52 % KAlSi_2O_6 , 1.48 % $\text{NaAlSi}_2\text{O}_6$).

A more detailed study of all the calorimetric and phase equilibrium data for the system $\text{KAlSiO}_4 - \text{SiO}_2$ should be undertaken, to try to resolve the remaining problems. Thermal

expansion data for K-feldspar, kalsilite, leucite and quartz, should be explicitly accounted for. Compressibility data, especially at elevated temperatures, are largely unavailable, but reasonable approximations can be made.

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Epilogue

The three laws of thermodynamics

1. You can never win; the best you can do is break even.
2. You can only break even at absolute zero.
3. You can never reach absolute zero.

quoted from W. J. Moore (1972) p vi.

END

FIN

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