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ASSESSMENT OF FELDSPAR SOLUBILITY CONSTANTS IN WATER IN THE RANGE 0° TO 350°C AT VAPOR SATURATION PRESSURES

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ABSTRACT. The equilibrium constants for endmember feldspar hydrolysis for the following reactions

\[
\begin{align*}
\text{NaAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} & = \text{Na}^+ + \text{Al(OH)}_4^- + 3\text{H}_2\text{SiO}_4^0 \\
\text{KAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} & = \text{K}^+ + \text{Al(OH)}_4^- + 3\text{H}_2\text{SiO}_4^0 \\
\text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{H}_2\text{O} & = \text{Ca}^{+2} + 2\text{Al(OH)}_4^- + 2\text{H}_2\text{SiO}_4^0
\end{align*}
\]

are accurately described by

\[
\begin{align*}
\log K_{\text{low-albite}} & = 96.267 + 305,542/T^2 - 3985.54/T - 28.588 \cdot 10^{-6} \cdot T^2 + 35.790 \cdot \log T \\
\log K_{\text{high-albite}} & = 97.275 + 306,065/T^2 - 3313.51/T - 28.622 \cdot 10^{-6} \cdot T^2 + 35.851 \cdot \log T \\
\log K_{\text{microcline}} & = 78.594 + 311,970/T^2 - 6068.38/T - 27.776 \cdot 10^{-6} \cdot T^2 + 30.308 \cdot \log T \\
\log K_{\text{sanidine}} & = 77.837 + 316,431/T^2 - 5719.10/T - 27.712 \cdot 10^{-6} \cdot T^2 + 29.738 \cdot \log T \\
\log K_{\text{anorthite}} & = 88.591 + 326,546/T^2 - 2720.61/T - 40.100 \cdot 10^{-6} \cdot T^2 + 31.168 \cdot \log T
\end{align*}
\]

where T is in K. They are valid in the range 0° to 350°C, at 1 bar below 100°C and at vapor saturation pressures \( P_{\text{sat}} \) at higher temperatures. The equations for low-albite and microcline are valid for Amelia albite and for microcline with the same degree of Al-Si order \( Z = 0.95 \), respectively. The same kind of log K-temperature equations have also been retrieved for alkali-feldspar and plagioclase solid solutions (tables 4 and 6).

The calculated feldspar equilibrium constants of this study indicate much higher solubility under weathering conditions than generally accepted to date, the difference being more than one and a half orders of magnitude at 0°C for both high- and low-albite, but somewhat less for microcline, sanidine, and anorthite. This higher solubility is largely a consequence of new data for the thermodynamic properties of \( \text{H}_2\text{SiO}_4^0 \). The present results have a particularly important bearing on the stability of feldspars under weathering conditions and the study of interaction between water and rock/soil in this environment. They are, however, also important for the study of equilibrium/dis-equilibrium conditions in active geothermal systems.

INTRODUCTION

Knowledge of the thermodynamic properties of feldspars and of the aqueous species that form when they dissolve in water is essential for quantitative interpretation of interactions between these minerals and natural waters. Studies of mineral saturation in aqueous solutions involve essentially two steps: (1) derivation of equilibrium constants (K) for mineral hydrolysis from thermodynamic data taking into account the effects of variable composition of the minerals and ordering, as appropriate, and (2) calculation of individual aqueous species activities from analytical data on the waters to retrieve values for the respective activity products (Q). The Gibbs energy of any reaction, \( \Delta G_r \), is defined
where $Q$ is the activity product (reaction quotient) for the reaction; $R$, the gas constant; $T$, temperature in Kelvin; and $\Delta G_r^0$, the standard Gibbs energy of the reaction, which is equal to $-RT \ln K$ where $K$ represents the equilibrium constant. For the following general reaction:

$$aA + bB \rightarrow cC + dD$$

the activity product is defined as

$$Q = \frac{a_c \cdot a_d}{a_a \cdot a_b}$$

$a$ denotes the activity of the subscribed species. At equilibrium $\Delta G_r = 0$ so $K = Q$ at equilibrium.

In this contribution calorimetric and other thermodynamic data on the feldspars have been compiled and assessed with the purpose of deriving temperature equations describing their solubility constants ($K$) in the range 0° to 350°C at 1 bar below 100°C and at vapor saturation pressures ($P_{sat}$) at higher temperatures. Solubility constants are presented for both fully ordered and fully disordered alkali-feldspars with respect to Al and Si (low-albite high-albite, microcline, sanidine) and anorthite as well as solid solutions of low-albite/microcline, high-albite/sanidine, and of the “low” and “high” plagioclase series. The specified temperature and pressure ranges cover the P-T environment of almost all natural waters assessable for sampling: surface waters, springs, wellheads, and downhole. Comparison between the values taken by these solubility constants ($K$) and activity products ($Q$) calculated with the aid of aqueous speciation programs such as WATCH (Arnorsson, Sigurdsson, and Svavarsson, 1982), EQ-3 (Wolery, 1992), WATEQ (Ball and Nordstrom, 1991), SOLMNEQ (Kharaka and others, 1988) and pH-CALC (Spycher and Reed, 1989) allows evaluation of saturation states of waters with respect to feldspars as a function of their composition and Al-Si ordering.

In igneous and high grade metamorphic rocks, feldspars form plagioclase and alkali feldspar solid solutions that are, at least, partly disordered with respect to Al and Si. In the greenschist and lower temperature metamorphic facies, as well as in hydrothermally altered rocks, the feldspars are essentially pure sodium and potassium feldspars (Miyashiro, 1994). Due to their low formation temperatures one would expect them to be largely ordered unless the phase that initially precipitates is disordered. Field data in this respect are lacking.

The thermodynamic stability of feldspars is much affected by their Al-Si ordering (Waldbaum and Robie, 1971; Hovis and Waldbaum, 1977; Helgeson and others, 1978; Carpenter, McConnell, and Navrotsky, 1985; Salje, 1985; Salje and others, 1985; Berman, 1988; Hovis, 1988; Holland and Powell, 1992; Navrotsky, 1989) making disordered feldspars more soluble in water than ordered ones at low temperatures (less than 300°C). As a result natural waters may be simultaneously dissolving disordered feldspars of igneous or metamorphic origin and precipitating ordered ones under hydrothermal conditions.

been carried out to obtain data on the absolute entropy of these feldspars and heat capacity-temperature relationships (Openshaw and others, 1976; Krupka, Robie, and Hemingway, 1979; Hemingway, Krupka, and Robie, 1981).

When feldspars dissolve in natural waters many aqueous species form. Their relative abundance depends largely on the water pH, salinity, and temperature. In relatively dilute waters with alkaline pH Na\(^+\), K\(^+\), Ca\(^{2+}\), H\(_4\)SiO\(_4\)\(^0\), and Al(OH)\(_4\)\(^-\) are the dominant feldspar-derived species in the temperature range 0\(^\circ\) to 350\(^\circ\)C and, according to recent experiments, also the alumina-silica complex \((\text{OH})_3\text{Al} - \text{O} - \text{Si(\text{OH})}_3\)^-\(^1\) (Pokrovski and others [1998]. The thermodynamic properties of the first listed species have been established accurately in the range 0\(^\circ\) to 350\(^\circ\)C (Apps, Neil, and Jun, 1989; Pokrovskii and Helgeson, 1995; Diakonov and others, 1996; Rimstidt, 1997; Arnorsson and Andredottir, 1999; Shock and Helgeson, 1988; Gunnarsson and Arnorsson, 1999).

Thus, if the thermodynamic properties of the feldspars themselves are also accurately known, so are their equilibrium constants, when expressed in terms of these aqueous species.

In most natural waters silica exists largely as H\(_4\)SiO\(_4\)\(^0\). However in alkaline waters (pH > 9.5) an appreciable fraction of the dissolved silica occurs as H\(_3\)SiO\(_4\)\(^-\). The first ionization constant of silicic acid is quite accurately known over a large temperature range (Seward, 1974; Busey and Mesmer, 1977) allowing the concentration of the H\(_4\)SiO\(_4\)\(^0\) species to be calculated with good precision from analytical data on total dissolved silica.

Some disagreement still exists on the dissociation constants of Al(OH)\(_4\)\(^-\) and Al(OH)\(_3\)\(^0\). The aluminate ion [Al(OH)\(_4\)]\(^-\) tends to dominate in geothermal waters although the neutral Al-hydroxy species is sometimes important. In many surface waters and non-thermal groundwaters Al(OH)\(_3\)\(^0\) and Al(OH)\(_2\)\(^-\) are apparently the most abundant Al-hydroxy species. Therefore, the largest uncertainty involved in retrieving activity products (\(Q\)) for feldspar-water reactions lies in the calculation of the activities of individual aluminium species except where one can be certain that the dominant aqueous Al-hydroxy species is the aluminate ion.

Assessment of the state of saturation of a wide variety of natural waters with respect to endmember and solid solution feldspars will be the subject of another contribution (Stefansson and Arnorsson, 1999).

**EXPERIMENTAL THERMODYNAMIC DATA**

Various techniques have been used to obtain data on the thermodynamic properties of minerals. For obtaining such data at relatively low temperatures the most important ones are heat capacity and heat of solution measurements and solubility experiments. However, low temperature thermodynamic data have also been retrieved by extrapolation of high temperature phase equilibrium experimental results (Helgeson and others, 1978; Berman, 1988; Holland and Powell, 1990, 1998; Gottschalk, 1997). In the case of the feldspars calorimetric measurements are considered to be the most useful in assessing their thermodynamic properties at low temperatures. The results of these measurements are reviewed below.

In publications on the results of thermodynamic experiments the error of measurement is sometimes reported, but sometimes it is not. In the major compilations on thermodynamic data on minerals this has been done by Robie, Hemingway, and Fisher (1979), Holland and Powell (1990, 1998), Robie and Hemingway (1995), and Gottschalk (1997) but not by Helgeson and others (1978) and Berman (1988). In the present contribution no attempt has been made to assess and report measurement errors.

**Enthalpy of Formation at 25\(^\circ\)C and 1 Bar**

**Albite.**—Calorimetric measurements of the standard enthalpy of formation of low-albite from the elements have been carried out by Kracek and Neuvonen (1952),
Waldbaum (1966, 1968), Waldbaum and Robie (1971), Hemingway and Robie (1977), Hovis (1982), and Kiseleva and others (1990). The low-albite samples used in these studies are from three localities: Amelia, Virginia; Floras Creek, Oregon; and Varuträsk, Sweden.

The data presented by Hovis (1982) are based on experiments carried out by him at Harvard and Princeton Universities and at Lafayette College. Experiments carried out since 1978 are, according to Hovis (1982), in excellent agreement with data from the thermochemistry laboratory at the United States Geological Survey. However, older data are not, as a result of design error in the circuit of the calorimeter used for the experiments. In the data presented by Hovis (1982) this error has been corrected.

Hemingway and Robie (1977) determined the enthalpy of formation of low-albite \((NaAlSi_3O_8)\) from Amelia and Floras Creek by hydrofluoric acid calorimetry from measurements of the heats of solution of these low-albites, NaAlO\(_2\), \(\alpha\)-quartz (SiO\(_2\)), gibbsite [Al(OH)\(_3\)], Al, H\(_2\)O, NaCl, and HCl in 20.1 wt percent hydrofluoric acid at 50\(^\circ\)C to 66\(^\circ\)C. Using a value of \(-910,700\) J mol\(^{-1}\) for the standard enthalpy of formation of \(\alpha\)-quartz from the elements (CODATA, 1976) Hemingway and Robie (1977) obtained a value for the standard enthalpy of formation of low-albite from the elements of \(-3,935,115 \pm 3415\) J mol\(^{-1}\) at 25\(^\circ\)C and 1 bar.

Waldbaum (1968), Waldbaum and Robie (1971), and Hovis (1982) also measured the heat of solution of Amelia albite but used different thermochemical cycles. Their results give the following values for its standard enthalpy of formation from the elements at 25\(^\circ\)C and 1 bar: \(-3,921,019, -3,936,511, \) and \(-3,936,931\) J mol\(^{-1}\), respectively.

Earlier experiments by Kracek and Neuvonen (1952) yielded \(-3,933,500\) J mol\(^{-1}\). Hovis (1988) obtained the same values for the heat of solution of low-albite as Hovis (1982), the difference being only 60 J mol\(^{-1}\).

In retrieving the value for the standard enthalpy of formation of low-albite at 25\(^\circ\)C and 1 bar, Waldbaum (1968) used his data on the heat of solution of low-albite and combined them with heat capacity data from Kelley and others (1953) and their heat of solution data for NaCl, SiO\(_2\), AlCl\(_3\) · 6H\(_2\)O, HCl · nH\(_2\)O, and H\(_2\)O in 20.1 percent hydrofluoric acid. Using the data of Hayman (1974) on the heat of solution of AlCl\(_3\) · 6H\(_2\)O, as reported by Chatterjee and Johannes (1974), instead of those by Coughlin (1958), as done by Waldbaum (1968), and the standard enthalpy data on gibbsite from Hemingway and Robie (1977) leads to a correction of the value given by Waldbaum (1968) by \(-11,234\) J mol\(^{-1}\), yielding \(-3,932,253\) J mol\(^{-1}\) for the standard enthalpy of formation of low-albite from the elements at 25\(^\circ\)C and 1 bar (table 1). Thus, all the heat of solution experiments compare rather well, and they are within the limit of error given by the authors. The average of the latest acid colorimetry measurements, those of Waldbaum and Robie (1971), Hemingway and Robie (1977) and Hovis (1982, 1988) gives \(-3,936,185\) J mol\(^{-1}\) for the standard enthalpy of formation of low-albite from the elements at 25\(^\circ\)C and 1 bar (table 1).

Kiseleva and others (1990) use a value for the heat of dissolution of quartz at 333 K of \(-139,200\) J mol\(^{-1}\) instead of the value of Hemingway and Robie (1977), which is \(-137,737\) J mol\(^{-1}\). They also used a value from Senderov (1980) for the enthalpy of formation of NaAlO\(_2\) \((-1,133,200\) J mol\(^{-1}\)) instead of the value determined by Hemingway and Robie (1977), \(-1,135,990\) J mol\(^{-1}\). Using the values selected by Kiseleva and others (1990) and the calorimetric results for low-albite dissolution from Waldbaum and Robie (1971), Hemingway and Robie (1977), and Hovis (1982) to retrieve the enthalpy of formation of low-albite from the reaction

\[
3\text{SiO}_2 + \text{NaAlO}_2 \rightleftharpoons \text{NaAlSi}_3\text{O}_8
\]  

yields an average value which is 1599 J mol\(^{-1}\) more negative or \(-3,937,784\) J mol\(^{-1}\). Hemingway and Robie (1977) carefully assessed available experimental data on the heat of solution of quartz. Their selected value is considered more reliable than that used by
Kiseleva and others (1990). Accordingly, the less negative average acid calorimetric
value for the enthalpy of formation of low-albite is preferred \( (-3,936,185 \text{ J mol}^{-1}) \).

The measurements of Kracek and Neuvonen (1952) indicate considerable differ-
ences in the standard enthalpies of formation of the Amelia and Varuträsk albites. They
obtained more negative values for the heat of solution of Amelia albite than Hemingway
and Robie (1977), Waldbaum (1968), Waldbaum and Robie (1971), and Hovis (1982,
1988) whereas their value for the Varuträsk albite is similar. The results of Hemingway
and Robie (1977) indicate no significant difference between the heat of solution of
Amelia and Floras Creek albites. It, therefore, seems likely that the observed difference
in the heat of solution of the two albites obtained by Kracek and Neuvonen (1952) is due
to measurement imprecision.

Kiseleva and others (1990) determined the enthalpy of formation of low-albite
calorimetrically by measuring the heat of dissolution in molten \( 2\text{PbO} \cdot \text{B}_2\text{O}_3 \) at 700°C.
They obtained an average value of \( -3,936,150 \text{ J mol}^{-1} \), which is experimentally
identical to the average of the acid calorimetry measurements.

Holland and Powell (1990) used phase equilibrium experiments between quartz,
jadeite, and low-albite to retrieve a value for the enthalpy of formation of the last listed
mineral obtaining \( -3,937,860 \text{ J mol}^{-1} \), which is 1675 J mol\(^{-1}\) more negative than the
average value obtained from acid calorimetry. In deriving their value for the standard
enthalpy of formation of low-albite from the elements Holland and Powell (1990) used
enthalpy data for quartz and jadeite as given by Robie, Hemingway, and Fisher (1979).

Holland and Powell (1998) selected a value which is 3,260 J mol\(^{-1}\) less negative than
their earlier value and only 400 J mol\(^{-1}\) less negative than the value \( ( -3,935,000 \text{ J mol}^{-1}) \)
recommended by Robie and Hemingway (1995).

Helgeson and others (1978) used high temperature/pressure phase equilibrium data
and field data to retrieve thermodynamic values for both low-albite and microcline.

The field data consisted of Na/K ratios in interstitial waters from sandstone at Kettleman
North Dome, California that were considered to be in equilibrium with albite and
K-feldspar found in the rock [Merino, ms]. The enthalpy data selected by Helgeson and
others (1978) are consistent with their kaolinite data, which were based on the assump-
tion of chemical equilibrium between mineral assemblages, which included kaolinite,
and coexisting interstitial waters in Jamaican bauxite deposits and weathered Hawaiian
basalts. The assumption of chemical equilibrium under such geological conditions is
questionable. Hemingway, Haas, and Robinson (1982) proposed a correction involving
the addition of \( -6500 \text{ J mol}^{-1} \) per mole of aluminium to the data of Helgeson and others
(1978) for all aluminium silicates because they considered the enthalpy value selected by
Helgeson and others (1978) for kaolinite to be in error by this amount. The value for the
standard enthalpy of formation of low-albite from the elements recommended by
Helgeson and others (1978), corrected as proposed by Hemingway, Haas, and Robinson
(1982), yields \( -3,938,121 \text{ J mol}^{-1} \) which is more negative than the average value from
acid calorimetric measurements (see table 1) by 1,936 J mol\(^{-1}\).

Berman (1988) selected the value of Hemingway and Robie (1977) for the standard
enthalpy of formation of low-albite from the elements. Sverjensky, Hemley, and
D’Angelo (1991) suggest a correction to this value involving addition of \( -6803 \text{ J mol}^{-1} \) to
make it consistent with measured high temperature solubilities in the system \( \text{Na}_2\text{O}–\text{Al}_2\text{O}_3–\text{SiO}_2–\text{H}_2\text{O}–\text{HCl} \), yielding \( -3,941,918 \text{ J mol}^{-1} \) for the standard enthalpy of formation of
low-albite from the elements at 25°C and 1 bar. This value is significantly more negative
than those obtained from calorimetric experiments and also more negative than the
results of phase equilibrium studies. The value proposed by Gottachalk (1997), on the
other hand, is significantly less negative than all calorimetric values or by 5000 to 8000 J
mol\(^{-1}\) (table 1).

Hemingway and Haselton (1994) conducted a review of aqueous hydrofluoric acid
and molten \( \text{PbO} \cdot \text{B}_2\text{O}_3 \) calorimetric data for albite and some other minerals in order to
evaluate the suggested correction to these data by Sverjensky, Hemley, and D’Angelo (1991). The results of Hemingway’s and Haselton’s examination did not support the suggestion of Sverjensky, Hemley, and D’Angelo (1991). The values derived by Hemingway and Haselton (1994) for the enthalpy of formation of low-albite from the experimental results of Kracek and Neuvonen (1952), Hemingway and Robie (1977), Navrotsky and others (1980), and Hovis (1988) form a remarkably tight cluster ranging from \(-3,933,960\) to \(-3,935,060\) J mol\(^{-1}\) despite the fact that these values are based on different reaction schemes. Hemingway and Haselton (1994) recommended a value of \(-3,935,000\) J mol\(^{-1}\) for the enthalpy of formation of low-albite from the elements. It is valid for the natural low-albites from Amelia and Varutrask. Hemingway and Haselton (1994) argued that the value of Navrotsky and others (1980) represents a minimum value because the low-albite sample they used might have been slightly disordered. The same may also apply to the sample used by Kracek and Neuvonen (1952) which was very finely ground producing an excess enthalpy of solution from surface energy contribution.

Heat of solution experiments have revealed the enthalpy of ordering between high- and low-albite. Determinations carried out at 700°C yield values in the range 9800 to 14226 J mol\(^{-1}\) (12887 J mol\(^{-1}\), Carpenter, McConnell, and Navrotsky, 1985; 11715 J mol\(^{-1}\), Blinova and Kiseleva, 1982; 9,800 J mol\(^{-1}\), Navrotsky and others, 1980; 11966 J mol\(^{-1}\), Newton, Charlu, and Kleppa, 1980; 14226 J mol\(^{-1}\), Holm and Kleppa, 1968). Hemingway and Haselton (1994) considered that the value of Navrotsky and others (1980) is low because the low-albite they used in their experiments was somewhat disordered. Eliminating this value yields an average value of 12698 J mol\(^{-1}\). At 25°C this average becomes 9350 J mol\(^{-1}\). According to Waldbaum and Robie (1971) the enthalpy difference between high- and low-albite at 50°C is 10878 J mol\(^{-1}\) whereas the value of Thompson, Waldbaum, and Hovis (1974), corrected as suggested by Hovis (1982), is 10,883 J mol\(^{-1}\) and that of Hovis (1988) 11966 J mol\(^{-1}\). Hemingway and Haselton (1994) and Robie and Hemingway (1995) selected a value of 11400 J mol\(^{-1}\) and 12000 J mol\(^{-1}\), respectively.

From phase equilibrium studies between albite (high and low), jadeite, and quartz by Newton and Smith (1967) and Holland (1980), Holland and Powell (1990) retrieved values for the enthalpy difference between high- and low-albite at 25°C as 8730 J mol\(^{-1}\), a value slightly lower than those derived from heat of solution experiments. On the other hand, Holland and Powell (1998) report a difference of 9760 J mol\(^{-1}\).

The theoretical advancement of Salje (1985) and Salje and others (1985) indicates that the Gibbs energy, enthalpy, and entropy differences between low-albite (fully ordered) and high-albite (fully disordered) is 8,422 J mol\(^{-1}\), 13,481 J mol\(^{-1}\), and 16.97 J mol\(^{-1}\) K\(^{-1}\), respectively. The enthalpy difference is somewhat larger than that obtained from calorimetric experiments. On the other hand, the entropy difference is slightly less (by 1.73 J mol\(^{-1}\) K\(^{-1}\)) than that obtained from simple configurational consideration. The enthalpy values for high- and low-albite selected by Gottschalk (1997) yield a difference, which is very close to that of Salje and others (1985), or 13,419 J mol\(^{-1}\).

Holm and Kleppa (1968) have concluded that the Amelia albite is somewhat disordered with respect to Al and Si. According to Bragg and Claringbull (1965) the Z ordering parameter [Z = 1 for full ordering and Z = 0 for full disordering] for Amelia albite is 0.89. From the cell constants in Amelia albite, reported by Waldbaum (1968) and Openshaw and others (1976), and the equation relating cell parameters to the degree of ordering (Thompson, Waldbaum, and Hovis, 1974), a Z value of 0.81 is obtained. Neutron diffraction studies indicate, on the other hand, a higher degree of order or Z = 0.95 (Harlow, Brown, and Hamilton, 1973). Hemingway and Robie (1977) used albites from Amelia and Floras Creek for their experiments, and they did not observe any
difference in the heat of solution of the two albites suggesting that their degree of Si-Al
ordering is about the same.

Taking the enthalpy difference between fully ordered and fully disordered albite to
be 13,481 J mol\(^{-1}\) (Salje and others, 1985) and the Z ordering parameter in Amelia albite
to be 0.95 suggests that the enthalpy of formation from the elements of fully ordered
low-albite should be more negative by 674 J mol\(^{-1}\) and that of fully disordered
high-albite 12,807 J mol\(^{-1}\) less negative. In the present study we have selected the
average acid calorimetry value for the low-albites from Amelia, Varuträsk, and Floras
Creek (–3,936,185 J mol\(^{-1}\)). Accordingly the standard enthalpy of formation from the
elements of fully ordered low-albite and fully disordered high-albite are –3,936,859 and
–3,923,378 J mol\(^{-1}\), respectively (table 1).

\textit{K-feldspar.}—Waldbaum (1968) and Waldbaum and Robie (1971) report solution
calorimetric data for alkali-feldspars dissolved in 20.1 percent hydrofluoric acid. Combin-
ing the results with heat capacity data and heat of solution measurements for \(\text{AlCl}_3 \cdot 6\text{H}_2\text{O}\),
\(\text{HCl} \cdot n\text{H}_2\text{O}\) and \(\text{H}_2\text{O}\) in 20.1 percent hydrofluoric acid, Waldbaum (1968) retrieved
enthalpy, entropy, and Gibbs energy values for microcline and high-sanidine over a
range of temperatures. His enthalpy values for the standard enthalpies of formation from
the elements of microcline and high-sanidine at 25°C and 1 bar are –3,959,173 and
–3,951,278 J mol\(^{-1}\), respectively (table 1). These data have been revised in the light of
better data on the heat of solution of \(\text{AlCl}_3 \cdot 6\text{H}_2\text{O}\) and improved data on the standard
enthalpy of formation of gibbsite from the elements (Chatterjee and Johannes, 1974;
Hemingway and Robie, 1977) indicating that both values should be more negative by
11895 J mol\(^{-1}\) (2.843 kcal mol\(^{-1}\)), if the gibbsite data of Hayman (1974), as quoted by
Chatterjee and Johannes (1974), are chosen and by 11234 J mol\(^{-1}\) for the gibbsite data of
Hemingway and Robie (1977) (table 1).

The microcline and sanidine used for the experiments by Waldbaum (1968) and
Waldbaum and Robie (1971) were prepared from Amelia albite and high-albite by ion
exchange in fused KCl. Waldbaum and Robie (1971) concluded that no exchange in the
Al-Si distribution occurred during the alkali metal exchange. Thus, their prepared
microcline is taken to be equally disordered with respect to Al and Si as Amelia albite,
that is, \(Z = 0.95\). Later studies have shown that the sanidine Waldbaum and Robie (1971)
prepared is slightly ordered, the value of the ordering parameter being 0.098 (Helgeson
and others, 1978).

Hovis (1974) reported results on the heat of solution on monoclinic K-feldspars. For
adularia and sanidine the values, as corrected by Hovis (1982), are –606,402 and
–615,090 J mol\(^{-1}\), respectively at 49.7°C. Heat of solution experiments carried out on
adularia at Lafayette College yield identical results (Hovis, 1982). To explain the
difference between Hovis’s (1974) data, as originally presented, Chatterjee and Johannes
(1974) concluded that the data of Waldbaum and Robie (1971) on sanidine was in error
by 1.700 kcal mol\(^{-1}\) (7.113 J mol\(^{-1}\)). Hemingway and Robie (1977) did not see any
evidence that supported this. As discussed above for albite, Hovis’s original data were
faulty due to design error in the circuit of the calorimeter used for the experiments
(Hovis, 1982).

The corrected value of Hovis (1974) for sanidine is more negative by 1,306 J mol\(^{-1}\)
than that of Waldbaum and Robie (1971) indicating that its standard enthalpy of
formation from the elements at 25°C and 1 bar is less negative by this amount. The
difference between the heat of solution of fully ordered monoclinic K-feldspar and
microcline is, according to the data of Hovis (1974, 1982) and Waldbaum and Robie
(1971) 2080 J mol\(^{-1}\) suggesting that the enthalpy of transformation from monoclinic to
triclinic (microcline) K-feldspar is small.

Following their calorimetric experiments to retrieve standard enthalpy data on
low-albite and other minerals, Hemingway and Robie (1977) revised thermodynamic
### Table 1
Thermodynamic data on feldspars, both experimental data and data selected in published compilations of such data

<table>
<thead>
<tr>
<th>Source</th>
<th>( \Delta G^\circ )</th>
<th>( \Delta H^\circ )</th>
<th>( \Delta S^\circ )</th>
<th>( \Delta V^\circ )</th>
<th>( C_p = a + b \cdot T + c \cdot T^{-1} + f \cdot T^{-2} + g \cdot T^{-3} )</th>
<th>( \text{Source} )</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Low-albite</strong></td>
<td>-3,933,500</td>
<td>-3,921,019</td>
<td>210.04</td>
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<td>208.20 - 10.043 - 55.839 - 100.393</td>
<td>This study (Amelia albite)</td>
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<tr>
<td><strong>Adularia</strong></td>
<td>-3,936,859</td>
<td>-3,936,859</td>
<td>207.40</td>
<td>-3,936,859</td>
<td>207.40 - 10.043 - 55.839 - 100.393</td>
<td>This study (Amelia albite)</td>
</tr>
</tbody>
</table>

Note: The table represents thermodynamic data on feldspars, with sources and calculated values for various properties such as free energy, enthalpy, entropy, and volume changes. The values are given with their respective units, and the study of each source is indicated. The data includes both experimental results and selected compilations from various studies.
## TABLE 1

(continued)

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<td>-4.254,910</td>
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</table>

*Consistent with the heat of solution experiments of Hemingway and Robie (1977). Recalculated value by Hemingway and Haselton (1994) is 3.935,000 J mol⁻¹. *Corrected using ΔH₂ₙa₁ for AC₁₃, H₂O from Hayma (1974) as reported by Chuterje and Johannes (1974) instead of Coughlin (1958) and the standard enthalpy of formation for gibbsite from Hemingway and Robie (1977). *The heat capacity data selected by Helgeson (1969) are from Kelley’s (1960) compilation and based on the measurements of White (1909, 1919). Other data are from Waldbaum (1968) and Robie and Waldbaum (1968). *As reported by Kieselver and others (1990). *The Gibbs free energy and enthalpy values have been corrected as proposed by Hemingway, Haas, and Robinson (2002). *As reported by Hemingway and Haselton (1988). *Based on heat of solution measurements for quartz and low-albite of Hovis (1982) and on Na₂O of Hemingway and Robie (1977). *Berman (1988) presents constants for a heat capacity polynomial of the form Cᵥ = k₀ + k₁ T⁻¹ + k₂ T⁻² + k₃ T⁻³. His heat capacity polynomials yields results numerically very similar to those of Krupa, Robie, and Hemingway (1979) for anorthite and Hemingway, Krupa, and Robie (1981) for the alkalai feldspars. *The higher enthalpy value (less negative) is based on heat of solution experiments in molten ZrPO₄ · B₂O₃, whereas the lower value (more negative) is based on published acid calorimetry results. The heat capacity polynom is based on the eat capacity measurements of Krupa, Robie, and Hemingway, 1979) and Hemingway, Krupa, and Robie (1981) for the alkalai feldspars. *The lower (more negative) value is based on natural anorthite whereas the other value is based on a synthetic one. *The enthalpy value is based on calorimetric measurements of Kracke (1953). *The reported heat capacity polynomial does not match the heat capacity data of Krupa, Robie and Hemingway (1979). *As reported by Holland and Powell (1990). *These heat capacity constants are valid in the range 0-350°C.
data for many aluminium silicates, including microcline and recommended a value of $-3,967,690 \text{ J mol}^{-1}$ for its standard enthalpy of formation from the elements at 25°C and 1 bar. Later Hemingway and Haselton (1994) analyzed HF solution calorimetric data on microcline and recommended a value of $-3,974,600 \pm 3900 \text{ J mol}^{-1}$ for its standard enthalpy of formation from the elements at 25°C and 1 bar. They concluded that the value selected by Hemingway and Robie (1977) was in error due to an erroneous value they adopted for the enthalpy of solution of aluminium chloride hexahydrate in aqueous HF. Kiseleva and others (1990) determined the standard enthalpy of formation of microcline from the elements as $-3,979,260 \text{ J mol}^{-1}$ at 25°C and 1 bar by dissolution in molten lead borate (table 1).

As discussed above for albite, Helgeson and others (1978) combined phase equilibrium studies and field data to retrieve thermodynamic data on the alkali feldspars. Their value for the standard enthalpy of formation for K-feldspar (microcline) from the elements at 25°C and 1 bar, corrected as proposed by Hemingway, Haas, and Robinson (1982), yields $-3,977,903 \text{ J mol}^{-1}$. This value is significantly more negative than other calorimetric values reported except for that of Kiseleva and others (1990) whereas the original value of Helgeson and his coworkers is similar to many enthalpy values previously and subsequently reported (table 1).

Apps and Chang (1992) used field data to retrieve a value for the Gibbs energy of formation from the elements for K-feldspar (microcline) assuming simultaneous equilibrium between albite, K-feldspar and solution, and using the data of Hemingway and Robie (1977) on low-albite. They retrieved a value of $-3,748,600 \pm 3700 \text{ J mol}^{-1}$ (table 1). By selecting our enthalpy value for low-albite (table 1) the estimated value by Apps and Chang (1992) for the standard Gibbs energy of formation from the elements at 25°C and 1 bar for K-feldspar (microcline) becomes $-3,749,908 \text{ J mol}^{-1}$.

Sverjensky, Hemley, and D’Angelo (1991) proposed a correction to the microcline enthalpy values recommended by Helgeson and others (1978) and Berman (1988) in order to make them consistent with measured high temperature solubilities in the system Na$_2$O–K$_2$O–Al$_2$O$_3$–SiO$_2$–H$_2$O–HCl. The corrected values for the standard enthalpy of formation from the elements are $-3,977,469$ and $-3,972,379 \text{ J mol}^{-1}$, respectively, at 25°C and 1 bar. The former value is similar to the corrected value of Helgeson and others (1978), according to Hemingway, Haas, and Robinson (1982), whereas the latter is some 5,000 J mol$^{-1}$ less negative.

Berman (1988) derived a value for the standard enthalpy of formation of microcline from the elements from phase equilibrium data on sanidine and consideration of order-disorder effects based on heat of solution experiments by Hovis (1974). Their value for the standard enthalpy of formation of microcline from the elements so derived is $-3,970,791 \text{ J mol}^{-1}$ at 25°C and 1 bar (table 1).

Garrels (1957), Reesman, and Keller (1965), and Huang and Keller (1972) have determined the Gibbs energy of formation of microcline from the elements (Garrels used unspecified K-feldspar) from solubility experiments. The results indicate much higher solubility than the calorimetric measurements. Experimentally it is difficult to demonstrate mineral-solution equilibrium for relatively complex minerals as the feldspars by approaching equilibrium from under- and supersaturation due to slow kinetics and possibly also because of the formation of unwanted phases. For this reason the results of the mentioned solubility experiments are suspect.

Waldbaum (1968) determined the standard enthalpy of formation of sanidine from the elements by acid calorimetry as $-3,951,278 \text{ J mol}^{-1}$ at 25°C and 1 bar (table 1). Chatterjee and Johannes (1974) proposed a correction to this value by using the results of Hayman (1974), for the heat of solution of AlCl$_3$·6H$_2$O instead of Coughlin (1958). Using Waldbaum’s results and the standard enthalpy of formation for gibbsite from the
elements, as determined by Hemingway and Robie (1977), yields a value of $-3,962,512$ J mol$^{-1}$ for the standard enthalpy of formation of sanidine from the elements at 25°C and 1 bar (table 1). From phase equilibrium studies Chatterjee and Johannes (1974) obtained a value of $-3,956,750$ J mol$^{-1}$. Following their hydrofluoric acid dissolution experiments on low-albite, α-quartz, and NaAlO$_2$, Hemingway and Robie (1977) revised enthalpy values for many aluminium silicates, including sanidine, and recommended a value of $-3,959,530$ J mol$^{-1}$ for its standard enthalpy of formation from the elements at 25°C and 1 bar.

The difference between the standard enthalpy of formation of low-albite and microcline from the elements corresponds to the difference in the heat of solution of these minerals and those of NaCl and KCl as can be seen from the following reaction:

$$\text{KAlSi}_3\text{O}_8 + \text{NaCl} \rightleftharpoons \text{NaAlSi}_3\text{O}_8 + \text{KCl}$$

The heats of solution of the chloride salts are small and similar (Waldbaum and Robie, 1971; Barany and Kelley, 1961), so the error in their measurement contributes little to the overall enthalpy of the above reaction. Because of this it is reasonable to take the difference between the heat of solution of the two alkali-feldspars to be an accurate measure of the differences in their standard enthalpy of formation. The only experiments that involved heat of solution experiments of both low-albite and microcline are those of Waldbaum and Robie (1971) and Hovis (1988). The precision in their measurements is expected to be better than their accuracy. In view of this and in order to make the enthalpy data on low-albite and microcline internally consistent with calorimetric measurements, it is concluded that the value for the standard enthalpy of formation of microcline from the elements at 25°C and 1 bar, reported by Waldbaum and Robie (1971), should be corrected by the difference between their value for low-albite ($-3,932,253$ J mol$^{-1}$) and that selected in the present study ($-3,936,185$ J mol$^{-1}$), which is $-3,932$ J mol$^{-1}$. Thus, the value for the standard enthalpy of formation of microcline from the elements at 25°C and 1 bar becomes $-3,974,339$ J mol$^{-1}$ (table 1). As already stated this is valid for a microcline with the same Al-Si disorder as Amelia albite ($Z = 0.95$). The data of Hovis (1988) yield practically the same number for the heat of solution of microcline, the difference being 60 J mol$^{-1}$ whereas his value for the heat of solution of low-albite is 580 J mol$^{-1}$ more negative than that of Waldbaum and Robie (1971). Using Hovis’s (1988) data would give a value for the standard enthalpy of formation of microcline from the elements that is more negative by only 520 J mol$^{-1}$ than the value retrieved from the experiments of Waldbaum and Robie (1971). This difference is not significant in view of experimental error.

Hovis (1988) determined the enthalpy difference between microcline and sanidine (fully ordered and fully disordered K-feldspars with respect to Al and Si, respectively) by solution calorimetric measurements to be 9163 J mol$^{-1}$ at 25°C and 1 bar. This difference is smaller than the value of Hovis (1974), as corrected by Hovis (1982), by almost 2000 J mol$^{-1}$. Using the more recent value and the selected enthalpy value for microcline (table 1), a value of $-3,965,730$ J mol$^{-1}$ is obtained for the standard enthalpy of formation of sanidine from the elements at 25°C and 1 bar. This value, which has been accepted in the present study, is considerably more negative than most values selected to date. It is, on the other hand, very similar to the value of Helgeson and others (1978) corrected, as proposed by Hemingway, Haas, and Robinson (1982), and also the value Sverjensky, Hemley, and D’Angelo (1991) and practically identical to the enthalpy value recommended by Hemingway and Haselton (1994) which is based on review of acid calorimetry measurements and the values selected by Robie and Hemingway (1995) and Holland and Powell (1998).
Anorthite.—The standard enthalpy of formation of anorthite from the elements has been determined by acid calorimetry (Barany, 1962; Kracek, 1953) and by heat of solution measurements in lead borate melt at 970 K (Charlu, Newton, and Kleppa, 1978; Newton, Charlu, and Kleppa, 1980; Carpenter, McConnell, and Navrotsky, 1985; Zhu, Newton, and Kleppa, 1994). The results are shown in table 1. Charlu, Newton, and Kleppa (1978) used both natural and synthetic samples whereas Newton, Charlu, and Kleppa (1980) used only synthetic ones. The results on both types of samples are quite similar indicating about the same degree of ordering with respect to Si and Al in both natural and synthetic anorthites, which is not consistent with the later heat of solution experiments of Carpenter, McConnell, and Navrotsky (1985).

Robie and Waldbaum (1968) recommended a value of $-4,222,911$ J mol$^{-1}$ which is based on the results of Kay and Taylor (1960) and Barany (1962). Robie, Hemingway, and Fisher (1979) selected a value of $-4,229,100$ J mol$^{-1}$, which is based on recalculation of the calorimetric experiments of Kracek (1953). Further refinement of Kracek’s data (Haas, Robinson, and Hemingway, 1979, 1980, 1981) yield $-4,227,830$ J mol$^{-1}$ for the standard enthalpy of formation from the elements of anorthite at 25°C and 1 bar. This value was selected by Hemingway, Haas, and Robinson (1982) and Kiseleva and others (1990). It corresponds very well to the values of Charlu, Newton, and Kleppa (1978) and Newton, Charlu, and Kleppa (1980), which are based on lead borate melt calorimetry, the difference only being 353 and $-187$ J mol$^{-1}$, respectively. Later heat of solution experiments in lead borate melt by Carpenter, McConnell, and Navrotsky (1985) and Zhu, Charlu, and Kleppa (1994) yielded, on the other hand, more negative values, by 3880 and 4270 J mol$^{-1}$, respectively. Gottschalk (1997) retrieved a value intermediate, or $-4,230,290$ J mol$^{-1}$.

Holland and Powell (1990) derived a value for the standard enthalpy of formation from the element for anorthite of $-4,232,740$ J mol$^{-1}$ (table 1), which was based on the results of the calorimetric experiments of Carpenter, McConnell, and Navrotsky (1985) and phase equilibrium studies of Newton (1966), Boettcher (1970), Allen and Fawcett (1982), and Chatterjee, Johannes, and Leostner (1984). This value is about 5000 J mol$^{-1}$ more negative than the revised acid calorimetry value of Kracek (1953) and the experimental values of Charlu, Newton, and Kleppa (1978) and Newton, Charlu, and Kleppa (1980). On the other hand, enthalpy values refined by Berman (1988), who also takes into consideration results of phase equilibria, are only about 1 kJ more negative than most earlier calorimetric results or $-4,228,730$ J mol$^{-1}$. Robie and Hemingway (1995) and Holland and Powell (1998) both selected very similar values for the standard enthalpy of formation of anorthite from the elements, or $-4,234,000$ and $-4,233,480$ J mol$^{-1}$, respectively.

There are essentially two populations with respect to the values for the standard enthalpy of formation of anorthite from the elements at 25°C and 1 bar as determined by lead borate melt calorimetry, at about $-4228$ and $-4232$ kJ mol$^{-1}$ (table 1). The acid calorimetry measurements of Kracek (1953), as revised by Haas, Robinson, and Hemingway (1979), yield enthalpy values almost identical to the first population ($-4228$ kJ mol$^{-1}$). Previous assessments of calorimetric and phase equilibrium data show about equal discrepancy (Berman, 1988; Holland and Powell, 1990, 1998; Robie and Hemingway, 1995; Gottschalk, 1997). The difference of 4 kJ between these two populations corresponds to a difference of about 0.7 in the value for the logarithm of the anorthite solubility constant at 25°C. There exists, thus, considerable discrepancy between experimental enthalpy data published during the last two decades.

In the present study the value recommended by Haas, Hemingway, and Robinson (1979) has been selected. Inspection of data (not yet published) on the composition of >200°C geothermal waters discharged from drillholes in Iceland suggests these waters tend to be somewhat supersaturated with respect to anortite, if the more negative
enthalpy values, which yield lower solubility, are selected. This seems unlikely as observations show that the primary plagioclase (labradorite) in the basaltic rocks in contact with these waters is being altered and secondary anorthite has not been reported.

**Entropy and Gibbs Energy of Formation at 25°C and 1 Bar**

Openshaw and others (1976) determined the standard absolute entropy values of albite and K-feldspar at 298.15°C and 1 bar from low temperature heat capacity measurements as 207.4 ± 0.4 and 214.2 ± 0.4 J mol⁻¹ K⁻¹ (table 1). From configurational entropy considerations they calculated the entropy of high-albite and sanidine as 18.7 J mol⁻¹ K⁻¹ more positive than that of their fully ordered counterparts as 226.4 and 232.9 J mol⁻¹ K⁻¹. Heat capacity measurements at low temperatures by Krupka, Robie, and Hemingway (1979) constrain the absolute entropy of anorthite as 199.30 J mol⁻¹ K⁻¹ at 25°C and 1 bar (table 1).

Salje and others (1985) evaluated the entropy difference between low-albite (fully ordered) and high-albite (fully disordered) to be 16.97 J mol⁻¹ K⁻¹. Simple configurational considerations indicate this difference should be a little larger or 18.7 J mol⁻¹ K⁻¹. Accepting the entropy value measurement of Openshaw and others (1976) of 207.4 J mol⁻¹ K⁻¹ for low-albite and the results of Salje and others (1985) yields a standard absolute entropy value of 224.37 J mol⁻¹ K⁻¹ for fully disordered albite (high-albite) at 25°C and 1 bar.

As already discussed measurements indicate that Amelia albite is not fully ordered. Accordingly, there will be a configurational contribution to its entropy. Taking the ordering parameter, Z, to be 0.95 a configurational entropy contribution value of 0.8 J mol⁻¹ K⁻¹ is obtained, yielding a standard absolute entropy value of 207.4 + 0.8 = 208.2 J mol⁻¹ K⁻¹ for this albite and 215.0 J mol⁻¹ K⁻¹ for equally ordered microcline at 25°C and 1 bar (table 1).

In the present study, the entropy measurements of Openshaw and others (1976) on the ordered alkali-feldspars (low-albite and microcline) have been accepted. The entropy difference selected here between fully ordered and fully disordered albite is that given by Salje and others (1985). On the other hand, simple configurational entropy considerations were used to obtain the entropy difference between fully ordered (microcline) and fully disordered (sanidine) K-feldspar (table 1).

The standard entropies of formation from the elements (ΔSᵢ⁰) at 25°C and 1 bar of the endmember feldspars have been calculated from their selected standard absolute entropy values (table 1) and the standard absolute entropies of the elements as given by Cox, Wagman, and Medvedev (1989). From these values and the respective selected values for the standard enthalpy of formation from the elements (ΔHᵢ⁰) (table 1) the standard Gibbs energy of formation of the feldspars from the elements (ΔGᵢ⁰) at 25°C (Tᵢ) and 1 bar (Pᵢ) were obtained from

$$ΔG_i^{0}_{T_i,P_i,i} = ΔH_i^{0}_{T_i,P_i,i} - T_i · ΔS_i^{0}_{T_i,P_i,i} \tag{6}$$

where the subscript i stands for the i-th endmember feldspar.

**Heat Capacity-Temperature Equations**

Hemingway, Krupka, and Robie (1981) determined the heat capacity of low- and high-albite, microcline, and sanidine between 350 and 1000 K by differential scanning calorimetry. Using these measurements and the heat capacity measurements of Openshaw and others (1976) at low temperatures, Hemingway, Krupka, and Robie (1981) retrieved heat capacity-temperature polynomials for all these feldspars considered to be valid in the range 298 to 1400 K at 1 bar. Krupka, Robie, and Hemingway (1979) measured heat capacity for anorthite in the same temperature range and by the same technique. They combined their data with the low-temperature heat capacity measure-
ments of Robie, Hemingway, and Wilson (1978) to derive a heat capacity-temperature polynomial for anorthite at 1 bar considered to be valid in the range 298 to 1800 K (table 1). The heat capacity data for the endmember feldspars are satisfactorily described in the range 0° to 350°C by a heat capacity polynomial of the form $C_P = a + c \cdot T^{-2} + f \cdot T^2$ where $a$, $c$, and $f$ are constants independent of temperature (table 1).

**EXPRESSION OF FELDSPAR-SOLUTION REACTIONS**

Calculation of the state of saturation of minerals in natural waters requires knowledge of their solubility constants ($K$) and computation of the species distribution in the water to obtain a value for the activity product ($Q$). The accuracy of such calculations depends on the quality of the thermodynamic data used to calculate the aqueous species distribution and the equilibrium constant for the respective mineral-solution reaction. It also depends on the quality of the chemical analysis of the water and the accuracy by which its temperature is evaluated. Further, chemical reactions occurring as the fluid flows from the aquifer to the wellhead or surface discharge can affect the results. If the thermodynamic properties of the aqueous species considered are not equally well known, which is always the case, the accuracy by which the activity product is calculated depends on the relative concentrations of the species which in turn is dictated by the composition of the water and its temperature.

Many natural waters have somewhat alkaline pH. In these waters the chemical components of feldspars, Na, K, Ca, Al, and Si, occur largely as $Na^+$, $K^+$, $Ca^{2+}$, $Al(OH)_4^-$ and $H_4SiO_4^0$. The thermodynamic properties of these species have been well established (Shock and Helgeson, 1988; Gunnarsson and Arnórsson, 1999; Arnórsson and Andrésdóttir, 1999). For mildly alkaline waters it is, therefore, best to express feldspar-aqueous solution reactions in terms of these species, that is

$$\text{NaAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} \rightleftharpoons \text{Na}^+ + \text{Al(OH)}_4^- + 3\text{H}_4\text{SiO}_4^0$$ (7)

$$\text{KAlSi}_3\text{O}_8 + 8\text{H}_2\text{O} \rightleftharpoons \text{K}^+ + \text{Al(OH)}_4^- + 3\text{H}_4\text{SiO}_4^0$$ (8)

and

$$\text{CaAl}_2\text{Si}_2\text{O}_8 + 8\text{H}_2\text{O} \rightleftharpoons \text{Ca}^{2+} + 2\text{Al(OH)}_4^- + 2\text{H}_4\text{SiO}_4^0$$ (9)

as for such waters the activity product ($Q$) can be accurately calculated according to these reactions, as well as the solubility constant.

In waters with a very high pH (>9.5 when measured at 25°C) a substantial fraction of the aqueous silica may be ionized. As the dissociation constant of $H_4SiO_4^0$ is well known (Seward, 1974; Busey and Mesmer, 1977) the concentration of the uncharged silica species can be accurately derived for such strongly alkaline waters. The saturation state of feldspars in such waters can, therefore, be accurately assessed when writing the mineral-solution reaction according to eqs (7) through (9).

In near neutral and weakly acidic waters the dissolved aluminium occurs dominantly as $Al(OH)_3^0$ or $Al(OH)^+$. When this is the case the error in the calculated activity product for the feldspar-water reactions becomes larger. The situation is not improved by writing the feldspar-solution reaction in terms of $Al(OH)_3^0$ or $Al(OH)^+$, because the thermodynamic properties of these species have not been very well established and neither is the feldspar solubility constant when written in terms of either of these species.

In very acid waters, such as acid mine waters, $Al^{3+}$ tends to be the dominant aluminium species. In such waters, it would be appropriate to express feldspar-water reactions in terms of $Al^{3+}$. For albite, the reaction would be

$$\text{NaAlSi}_3\text{O}_8 + 4\text{H}^+ \rightleftharpoons \text{Na}^+ + \text{Al}^{3+} + 3\text{H}_4\text{SiO}_4^0$$ (10)
It is, however, to be realized that the thermodynamic properties of Al\(^{3+}\) are not as accurately known as those of Al(OH)\(_4^-\). For that reason it is not possible to assess the state of feldspar saturation as accurately in acid waters as in alkaline waters.

**THE EFFECTS OF TEMPERATURE AND PRESSURE ON MINERAL SOLUBILITY**

Temperatures and pressures measured in wells drilled into groundwater systems range with few exceptions from about 0\(^\circ\)C to about 350\(^\circ\)C and from 1 bar to some 300 bars. The exceptions include deep basinal systems and some submarine geothermal systems where pressure and temperature may exceed 300 bars and 350\(^\circ\)C, respectively. For the mentioned ranges of P and T, pressure has a very small effect on the thermodynamic properties of minerals and aqueous species compared to temperature and, therefore, also on mineral-solution equilibrium constants. It is, therefore, acceptable and convenient to eliminate pressure as an independent variable in the study of most mineral-natural water reactions. However, in order to make data from thermodynamic experiments on minerals and aqueous species consistent and closest to the actual conditions most often met in such systems, we have chosen to express the temperature dependence of the thermodynamic properties of aqueous species and minerals at 1 bar below 100\(^\circ\)C and at vapor saturation pressures \(P_{\text{sat}}\) at higher temperatures (see tables 2 and 3).

To demonstrate variations in the apparent standard Gibbs energy \(\Delta G^0\) of minerals with temperature and pressure, consider low-albite. In going from 0\(^\circ\)C to 350\(^\circ\)C at 1 bar the apparent standard molal Gibbs energy of low-albite becomes more negative by a little more than 100,000 J mol\(^{-1}\) (fig. 1). On the other hand, the change in \(\Delta G^0\) in going from 1 to 165 bars (vapor saturation pressure at 350\(^\circ\)C), and taking the standard molal volume of low-albite to be both temperature and pressure independent in this range is only 1,650 J mol\(^{-1}\). Around 350\(^\circ\)C a temperature change of 4\(^\circ\)C produces about the same

### Table 2

**Thermodynamic properties at 25\(^\circ\)C and 1 bar of endmember feldspars, liquid water and the most important aqueous species which form when feldspars dissolve in water. Also shown are constants in a temperature equation describing the standard apparent Gibbs energy of the feldspars and the respective species which is valid in the range 0 to 350\(^\circ\)C at 1 bar below 100\(^\circ\)C and at \(P_{\text{sat}}\) at higher temperatures.**

<table>
<thead>
<tr>
<th>Mineral Species</th>
<th>(\Delta G^0) J mol(^{-1})</th>
<th>(\Delta H^0) J mol(^{-1})</th>
<th>(S^0) J mol(^{-1}) K(^{-1})</th>
<th>(\Delta G^0 = k_1 \cdot T + k_2 / T + k_3 + k_4 \cdot T^3 + k_5 \cdot T \cdot \log T)</th>
<th>(k_1 \cdot 10^8)</th>
<th>(k_2)</th>
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<tbody>
<tr>
<td>NaAlSi(_3)O(_8) (low)</td>
<td>-3,713,038</td>
<td>-3,936,185</td>
<td>208.20</td>
<td>2305.69</td>
<td>5,849,500</td>
<td>-3,796,532</td>
</tr>
<tr>
<td>NaAlSi(_3)O(_8) (high)</td>
<td>-3,705,061</td>
<td>-3,923,378</td>
<td>224.40</td>
<td>2286.34</td>
<td>5,855,450</td>
<td>-3,783,639</td>
</tr>
<tr>
<td>KAlSi(_3)O(_8) (mic)</td>
<td>-3,749,546</td>
<td>-3,974,893</td>
<td>214.20</td>
<td>2315.01</td>
<td>5,972,550</td>
<td>-3,831,971</td>
</tr>
<tr>
<td>KAlSi(_3)O(_8) (san)</td>
<td>-3,745,958</td>
<td>-3,965,730</td>
<td>232.90</td>
<td>2329.50</td>
<td>6,057,950</td>
<td>-3,825,284</td>
</tr>
<tr>
<td>CaAl(_2)Si(_2)O(_8)</td>
<td>-4,002,095</td>
<td>-4,227,830</td>
<td>199.30</td>
<td>2437.05</td>
<td>6,251,600</td>
<td>-4,095,996</td>
</tr>
<tr>
<td>H(_2)O</td>
<td>-237,140*</td>
<td>-285,830*</td>
<td>69.95*</td>
<td>436.13</td>
<td>-238,788</td>
<td>0.596</td>
</tr>
<tr>
<td>H(_2)SiO(_4)</td>
<td>-1,309,181*</td>
<td>-1,460,238*</td>
<td>178.85*</td>
<td>1790.03*</td>
<td>-1,338,980*</td>
<td>109,877</td>
</tr>
<tr>
<td>Al(OH)(_3)</td>
<td>-1,305,575**</td>
<td>-1,500.690**</td>
<td>111.12**</td>
<td>1832.20**</td>
<td>-1,348,645**</td>
<td>250,592</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>-261,881***</td>
<td>-240,300***</td>
<td>58.41***</td>
<td>435.43</td>
<td>-264,950***</td>
<td>36,454</td>
</tr>
<tr>
<td>K(^+)</td>
<td>-282,462***</td>
<td>-252,170***</td>
<td>101.04***</td>
<td>106.41</td>
<td>-260,513***</td>
<td>25,732</td>
</tr>
<tr>
<td>Ca(^2+)</td>
<td>-552,790***</td>
<td>-543,083***</td>
<td>-56.48***</td>
<td>377.68</td>
<td>-578,965***</td>
<td>120,620</td>
</tr>
</tbody>
</table>

*Cox, Wagman, and Medvedev (1989); **Arnórsson and Andreásdóttir (1999); *Gunnarsson and Arnórsson (1999); ***Shock and Helgeson (1988).
change in the apparent standard molal Gibbs energy of low-albite as 165 bars change in pressure, that is the change produced in going from surface conditions to vapor saturation pressure at 350°C. In terms of the equilibrium constant for low-albite solubility this pressure variation amounts to 0.11 log K units.

**Table 3**

The standard Gibbs energy, enthalpy and entropy of endmember feldspar hydrolyses reactions (see eqns 12 to 14 in text) at 25°C and 1 bar. Also shown are values for constants in a temperature equation describing endmember feldspar solubility in waters. The constants are valid in the range 0-350°C at 1 bar below 100°C and at $P_{\text{sat}}$ at higher temperatures. The equations for low-albite and microcline are valid for the same ordering ($Z = 0.95$) as Amelia albite.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>$\Delta G^\circ_m$</th>
<th>$\Delta H^\circ_m$</th>
<th>$\Delta S^\circ_m$</th>
<th>log $K = k_1 + k_2/T + k_3/T + k_4 \cdot 10^{-8} \cdot T^2 + k_5 \cdot \log T$</th>
</tr>
</thead>
<tbody>
<tr>
<td>low-albite</td>
<td>115,159</td>
<td>96,757</td>
<td>-61.72</td>
<td>$-96.267 + 305.542 - 3985.50 - 28.588 + 35.790$</td>
</tr>
<tr>
<td>high-albite</td>
<td>107,182</td>
<td>83,950</td>
<td>-77.92</td>
<td>$-97.275 + 306.065 - 3313.51 - 28.622 + 35.851$</td>
</tr>
<tr>
<td>microcline</td>
<td>130,770</td>
<td>123,289</td>
<td>-25.89</td>
<td>$-78.594 + 311,970 - 6068.38 - 27.776 + 30.308$</td>
</tr>
<tr>
<td>sanidine</td>
<td>127,498</td>
<td>114,442</td>
<td>-43.79</td>
<td>$-77.837 + 316,431 - 5719.10 - 27.712 + 29.738$</td>
</tr>
<tr>
<td>anorthite</td>
<td>116,913</td>
<td>46,717</td>
<td>-235.55</td>
<td>$-88.591 + 326,546 - 2720.61 - 40.100 + 31.168$</td>
</tr>
</tbody>
</table>

![Fig. 1. Effect of temperature and pressure on changes in the apparent standard Gibbs energy of low-albite.](image)

1. Effect of temperature for $P = 1$ bar. 2. Effect of pressure for temperatures corresponding to $P_{\text{sat}}$. 3. Effect of pressure for $P = 300$ bars. 4. Effect of pressure corresponding to a geothermal gradient of 60°C/km and surface temperature of 20°C.
For geothermal wells there is always an uncertainty involved in estimating the aquifer temperature for the fluid discharged and, therefore, in selecting the appropriate temperature values for equilibrium constants and speciation calculations. This uncertainty tends to increase with rising aquifer temperature. In the example above on the apparent standard molal Gibbs energy of low-albite it is evident that the effect of pressure is less than the generally anticipated error involved in specifying the aquifer temperature of a particular geothermal water that enters a well and is sampled at the surface.

The effect of temperature and pressure variations on changes in the apparent standard Gibbs energy of many aqueous species can be assessed from Helgeson, Kirkham, and Flowers (1981), Shock and Helgeson (1988), Shock, Helgeson, and Sverjensky (1989), Shock and others (1997), and Sverjensky, Shock, and Helgeson (1997). In general the effects of pressure variations are trivial compared to those of temperature when dealing with geothermal systems.

Various heat capacity polynomials have been adopted to describe changes in the standard heat capacity \( C_{pi}^0 \) of solids and aqueous species with temperature (Maier and Kelley, 1932; Naumov, Ryzhenko, and Khodakovsky, 1971; Haas and Fisher, 1976; Helgeson, Kirkham, and Flowers, 1981, Arnórsson, Sigurðsson, and Svaravárson, 1982; Berman, 1988; Holland and Powell, 1990, 1998). The most widely used are probably those of Helgeson, Kirkham, and Flowers (1981) and Haas and Fisher (1976). For the \( i \)-th aqueous species Haas and Fisher (1976) used:

\[
C_{pi}^0 = a + 2bT + cT^{-2} + fT^2 \tag{11}
\]

and

\[
C_{pi}^0 = a + 2bT + cT^{-2} + gT^{-0.5} \tag{12}
\]

for the \( i \)-th mineral where \( a, b, c, f, \) and \( g \) are temperature and pressure independent constants characteristic for a particular species.

The apparent standard Gibbs energy of compound \( i \) at temperature \( T \) and pressure \( P \) \( \Delta G_{T,P,i}^0 \) is given by

\[
\Delta G_{T,P,i}^0 = \Delta G_{T,i}^0 + S_{T,P,i}^0(T - T_i) + \int_{T_i}^T C_{P,i}^0 \, dT - T \int_{T_i}^T \frac{C_{P,i}^0}{T} \, dT + \int_P^{P_i} V_i^0 \, dP \tag{13}
\]

where \( \Delta G_{T,i}^0 \) stands for that standard Gibbs energy of formation from the elements of the \( i \)-th mineral or species at 25°C \( (T_i) \) and 1 bar \( (P_i) \), and \( S_{T,P,i}^0 \) is the standard absolute entropy of the \( i \)-th compound under these conditions; that is, we use the standard state chosen by Helgeson, Kirkham, and Flowers (1981). \( V_i^0 \) is the standard molal volume of compound \( i \). \( C_{P,i}^0 \) is defined by eqs (11) and (12). Combining the two heat capacity polynomials of Haas and Fisher (1976) (eqs 11 and 12) yields:

\[
C_{pi}^0 = a + 2bT + cT^{-2} + fT^2 + gT^{-0.5} \tag{14}
\]

leading upon integration of eq (13) to the following expression for the temperature dependence of \( \Delta G^0 \)

\[
\Delta G_{T,j}^0 = \Delta G_{T,i}^0 + S_{T,P,i}^0(T - T_i) + a(T - T_i + T(\ln T_i - \ln T)) + b(T - T_i)(T_i - T)
\]

\[
+ c \left( \frac{1}{T_i} - \frac{1}{T} - \frac{T}{2T_i^2} \right) + f \left( \frac{TT_i^2}{2} - \frac{T_i^3}{3} - \frac{T^3}{6} \right) + g \left( 4T_i^{0.5} - 2T_i^{0.5} - \frac{2T_i}{T_i^{0.5}} \right) \tag{13A}
\]

The approach taken in the present study to describe the temperature dependence of \( \Delta G^0 \) for the feldspars in the range 0°C to 350°C was to select a heat capacity polynomial.
with the fewest number of constants that described accurately the experimental heat capacity data. It was observed that these data could be described adequately by heat capacity polynomials of the form $C_p = a + bT + cT^{-2} + dT^2$ in the temperature range of interest (0°-350°C). Numerically both forms yielded practically the same results. The latter form was selected, that is $b$ and $d$ in eq. (14) were taken to be zero. This reduces eq (13A) to

$$\Delta G_{T,j}^0 = \Delta G_{T,j}^0(T - T_r) + a(T - T_r + T(ln T_r - ln T))$$

$$+ c\left(\frac{1}{T_r} - \frac{1}{2T} - \frac{T}{2T_r^2}\right) + f\left(\frac{TT_r^2}{2} - \frac{T_r^3}{3} - \frac{T^3}{6}\right)$$

(13B)

The heat capacity constant values for the endmember feldspars consistent with eq (13B) are shown in table 1.

Table 2 summarizes the basic thermodynamic data at 25°C and 1 bar selected in the present study for the endmember feldspars. It also gives equations that describe the temperature dependence of the apparent standard Gibbs energy of these feldspars which are valid in the range 0° to 350°C, at 1 bar below 100°C and at vapor saturation pressures at higher temperatures. These $\Delta G^0$-temperature equations were retrieved from the heat capacity constants selected in this study (table 1) and the molal volume data given by Robie, Hemingway, and Fisher (1979) taking the molal volume to be independent of both temperature and pressure. The differences between the standard apparent Gibbs energy values as given by the respective temperature equations in table 2 and those calculated from the molal volumes given by Robie, Hemingway and Fisher (1979) and the heat capacity polynomials given by Hemingway, Krupka, and Robie (1981) for low- and high-albite, microcline and sanidine and those of Krupka, Robie, and Hemingway (1979) for anorthite (see table 1) are shown in figure 2. It is seen from this figure that the

![Figure 2](image.png)

**Fig. 2.** Difference between the apparent standard Gibbs energy of endmember feldspars as calculated from the molal volume and heat capacity data of Robie, Hemingway, and Fisher (1979), Hemingway, Krupka, and Robie (1981) and Krupka, Robie, and Hemingway (1979) on one hand and the temperature equations given in table 2 on the other.
difference is generally within about 50 J mol$^{-1}$ and always within 80 J mol$^{-1}$. Thus, the equations presented in table 2 yield quite acceptable values for $\Delta G^0$ of the endmember feldspars up to 350°C at $P_{sat}$.

The temperature dependence of the apparent standard partial molal Gibbs energy ($\Delta G^0$) of the aqueous species that form when feldspars dissolve in water according to eqs (7) to (9) and under the pressure conditions selected above for the feldspars is given in table 2. Below 300°C the apparent standard Gibbs energy values calculated from the respective equations in table 2 are similar to those of the HKF-model according to the data presented by Shock and Helgeson (1988) and Shock, Helgeson, and Sverjensky (1989). However, above this temperature discrepancy increases and particularly so above 325°C for the aluminate ion. This should be born in mind when calculating standard apparent partial molal Gibbs energies of aqueous species and feldspar solubilities above 325°C from the data given on the aqueous species in table 2. By summing up in appropriate proportions the standard apparent Gibbs energies of the feldspars and the aqueous species and dividing by $-RT \cdot \ln (10)$ a log K expression is obtained for the solubility constants of the endmember feldspars (table 3).

**ALKALI-FELDSPAR AND PLAGIOCLASE SOLID SOLUTIONS**

Gislason and Arnórsson (1990, 1993) expressed the standard state of mineral solid solutions as an ideal solution of fixed composition at the temperature and pressure of interest. A definition of this kind, whether the solution is ideal or not, is considered convenient for studying the state of saturation of feldspar solid solutions in natural waters. It requires assessment of the non-ideal behavior of the solid solution of a given composition at 25°C and 1 bar as well as a heat capacity polynomial for that solution.

The Gibbs energy and conventional absolute entropy of solid solutions, $G_{\text{real}}$ and $S_{\text{real}}$, are given by

$$G_{\text{real}} = \sum_i X_i G_i^0 + RT \sum_j n_j \sum_i X_{ij} \ln a_{ij}$$  \hspace{1cm} (15)

and

$$S_{\text{real}} = \sum_i X_i S_i^0 + R \sum_j n_j \sum_i X_{ij} \ln a_{ij}$$  \hspace{1cm} (16)

where $G_i^0$ represents the standard partial molal Gibbs energy of endmember $i$ in the solid solution, $S_i^0$ the standard partial molal absolute entropy of endmember $i$, and $X_i$ its mole fraction. $n_j$ is the total number of sites of type $j$ per formula unit on which mixing takes places, and $a_i$ stands for the activity of component $i$ in the solid solution. Activity is related to mole fraction by

$$a_i = X_i \gamma_i$$  \hspace{1cm} (17)

Inserting eq (17) into (15) and (16), respectively, yields

$$G_{\text{real}} = \sum_i X_i G_i^0 + RT \sum_j n_j \sum_i X_{ij} \ln X_{ij} + RT \sum_j n_j \sum_i X_{ij} \ln \gamma_{ij}$$  \hspace{1cm} (18)

and

$$S_{\text{real}} = \sum_i X_i S_i^0 + R \sum_j n_j \sum_i X_{ij} \ln X_{ij} - R \sum_j n_j \sum_i X_{ij} \ln \gamma_{ij}$$  \hspace{1cm} (19)

The last term on the right hand side of eqs (18) and (19) represents the excess Gibbs energy and entropy of mixing, respectively, $G_{\text{excess}}$ and $S_{\text{excess}}$, whereas the second term in these equations is the ideal Gibbs energy and entropy of mixing, respectively, $G_{\text{ideal mix}}$. 

---

*constants in water in the range 0° to 350°C at vapor saturation pressures*
and $S_{\text{ideal mix}}$. Together these two terms in both equations, that is the second term on the right side of eqs (15) and (16), are the Gibbs energy and entropy of mixing, $G_{\text{mix}}$ and $S_{\text{mix}}$. From eqs (18) and (19) it is seen that

$$G_{\text{ideal mix}} = -T \cdot S_{\text{ideal mix}} \quad (20)$$

The excess Gibbs energy of mixing can be resolved into contributions from excess enthalpy and excess entropy, or

$$G_{\text{excess}} = H_{\text{excess}} - TS_{\text{excess}} \quad (21)$$

The above equations form the basis for estimating the respective thermodynamic parameters for feldspar solid solutions as described below.

**Alkali-feldspars**

Low-albite and microcline do not form an ideal solution. Waldbaum and Robie (1971) determined the excess enthalpy of mixing of these feldspars by acid calorimetry as

$$H_{\text{excess}} = 24803X_{\text{low alb}}^2 + 35384X_{\text{low alb}}X_{\text{micr}} \quad (22)$$

where $X_{\text{low alb}}$ and $X_{\text{micr}}$ represent the mole fraction of low-albite and microcline in the alkali-feldspar solid solution, respectively. Hovis and Waldbaum (1977) expressed the results of Waldbaum and Robie (1971) by a simpler symmetrical equation, or

$$H_{\text{excess}} = 29600X_{\text{low alb}}X_{\text{micr}} \quad (22A)$$

for low-albite/microcline and for high-albite/sanidine they give

$$H_{\text{excess}} = 23800X_{\text{high alb}}X_{\text{san}} \quad (23)$$

Hovis (1988) investigated by acid solution calorimetric measurements the enthalpy of mixing of alkali feldspars as a function of composition and Al-Si ordering. He derived the following relationship:

$$H_{\text{excess}} = (12.97 + 65.10Z - 30.92Z^2)X_{\text{K-feld}}^2 + (20.71 - 9.75Z)X_{\text{alb}}X_{\text{K-feld}} \quad (24)$$

Here $Z$ represents the Al-Si ordering parameter.

Heat capacity measurements carried out by Haselton and others (1983) in the range 5 to 380 K revealed an excess entropy for intermediate compositions of highly disordered alkali feldspars. For practical calculations they concluded that the entropy of mixing could be regarded as being temperature independent above room temperature. The excess entropy is rather small, reaching a maximum of 2.6 J mol$^{-1}$ K$^{-1}$ at 50 percent albite. Only a small change in Al-Si order/disorder is required to change the configurational entropy by this amount. In the present contribution we have, therefore, chosen to treat the alkali feldspars as a regular solution, that is $S_{\text{excess}} = 0$. Ignoring also the small volume change associated with the mixing leads to $G_{\text{excess}} = H_{\text{excess}}$, and

$$S_{\text{alb feld}}^0 = S_{\text{alb}}^0X_{\text{alb}} + S_{\text{K-feld}}^0X_{\text{K-feld}} - R[X_{\text{alb}} \ln X_{\text{alb}} + X_{\text{K-feld}} \ln X_{\text{K-feld}}] \quad (25)$$

as mixing takes place on one crystallographic site. Further, from eq (18) we have at 25°C ($T_r$) and 1 bar

$$\Delta G_{\text{alk feld}}^0 = X_{\text{alb}}\Delta G_{\text{alb}}^0 + X_{\text{K-feld}}\Delta G_{\text{K-feld}}^0 \quad (26)$$

Figure 3 depicts values for $G_{\text{mix}}$ of fully ordered (low-albite/microcline) and fully disordered (high-albite/sanidine) alkali-feldspars according to eqs (24) and (26), respec-
tively. It is seen that $G_{\text{mix}}$ is considerably positive and reaches a maximum of about 2.6 and 6.2 kJ mol$^{-1}$ at 40 and 60 percent microcline and sanidine, respectively, indicating that both ordered and disordered alkali-feldspar solid solutions are more soluble than their respective endmembers. It should be noted here that the high series alkali-feldspars, high-albite/sanidine, form a complete solid solution. There is, on the other hand, very limited solid solution in the low series, low-albite/microcline. Treating the low series as a solid solution, assumes its existence in a metastable state due to relatively rapid cooling after its formation that has prevented exsolution (unmixing) but not ordering.

By assuming the excess enthalpy of mixing of the alkali-feldspars to be temperature independent implies that their heat capacity of mixing is zero. Accordingly, their heat capacity can be obtained by summing up in appropriate proportions the standard molal heat capacities of their constituent endmembers. This gives

$$C_{p,\text{alk feld}}^0 = [a_{\text{alb}} + c_{\text{alb}}T^{-2} + f_{\text{alb}}T^2]X_{\text{alb}} + [a_{\text{K-feld}} + c_{\text{K-feld}}T^{-2} + f_{\text{K-feld}}T^2]X_{\text{K-feld}}$$

(27)

where $X_{\text{alb}}$ and $X_{\text{K-feld}}$ represent the mole fraction of albite and K-feldspar in the solid solution and $a$, $c$, and $f$ are constants independent of temperature and pressure (see eq (14)).

The temperature dependence of the apparent standard Gibbs energy of alkali-feldspar solid solutions of any composition at 1 bar can be obtained by calculating $S_{\text{alk-feld}}^0$ at 25°C ($T_i$) from eq (25), combining eqs (24) and (26) to obtain a value for $\Delta G_{\text{alk-feld}}^0$ also at 25°C and insert the Gibbs energy and entropy values so obtained into eq (13B) together with eq (27).

The volume of mixing of the alkali-feldspars can be taken to be zero. Accordingly, the effect of pressure on the apparent standard Gibbs energy of alkali-feldspar of any composition, that is on $\Sigma X_i \bar{G}_i^0$ (see eq 15), is taken to be equal to

$$[V_{\text{alb}}^0 \cdot X_{\text{alb}} + V_{\text{K-feld}}^0(1 - X_{\text{alb}})](P - 1)$$

(28)
where \( V_{Alb}^0 \) and \( V_{K-feld}^0 \) represent the standard molal volume of albite (low or high) and K-feldspar (microcline or sanidine), respectively, and \( X_{Alb} \) is the mole fraction of albite in the alkali-feldspar solid solution. \( P \) is pressure in bars.

With the aid of the expressions given by eq (13B) and eqs (24) through (28) \( G_{real} \) for alkali-feldspars of any composition can be calculated over a range of temperatures and pressures and subsequently log \( K \)-temperature equations for alkali-feldspar hydrolysis for the following reaction

\[
\text{Na}_2\text{K}_{1-x}\text{AlSi}_3\text{O}_8 + 8\text{H}_2\text{O} = X\text{Na}^+ + (1 - X)\text{K}^+ + \text{Al(OH)}_4^- + 3\text{H}_2\text{SiO}_4^0
\]  

(29)

where \( X \) denotes the mole fraction of albite in the alkali-feldspar solid solution. Constants in such equations for selected values of \( X \) are given in Table 4. These constants are valid in the range \( 0^\circ \text{C} \) to \( 350^\circ \text{C} \) at 1 bar below \( 100^\circ \text{C} \) and at \( P_{sat} \) at higher temperatures.

**Plagioclase Feldspars**

The thermodynamic properties of the plagioclase feldspars are not well understood due to their diverse subsolidus ordering and unmixing behavior. At low temperatures the solid solution contains three different ordered structures, low-albite, an intermediate \( \varepsilon \) structure, and anorthite. Both low- and high-albite possess \( \text{C}_1 \) symmetry. Between An\(_{20}\) and An\(_{51}\) the \( \varepsilon \) plagioclase structure is converted to the \( \text{C}_1 \) albite structure by heating. For An\(_{65}\) the transformation temperature is around \( 1000^\circ \text{C} \) (Carpenter and McConnell, 1984), and it is probably similar for other compositions (Carpenter, McConnell, and Navrotsky, 1985). In the range An\(_{65}\) to An\(_{71}\) the \( \varepsilon \) plagioclases are first converted to the \( \text{I}_1 \) symmetry and subsequently to the \( \text{C}_1 \) symmetry. At An\(_{71}\) the \( \varepsilon \) structure no longer exists. Here \( \text{P}_1 \) symmetry is the stable structure at low temperatures being replaced by \( \text{I}_1 \) symmetry upon heating. Melting occurs before conversion to the \( \text{C}_1 \) symmetry. At low temperatures the plagioclases tend to exsolve. The position of the solvus is, however, poorly known (Carpenter, 1985).

Newton, Charlu, and Kleppa (1980) determined the heat of solution of heated plagioclase feldspars (\( \text{C}_1 \) and \( \text{I}_1 \) symmetry) of variable composition in molten \( 2\text{PbO} \cdot \text{B}_2\text{O}_3 \) at \( 700^\circ \text{C} \). Carpenter, McConnell, and Navrotsky (1985) determined the enthalpy of ordering between the different structural states and concluded that their results were consistent with an interpretation of the plagioclase as being two ideal solid solutions corresponding with “low-” and “high-temperature” varieties, respectively. The former constitutes the \( \varepsilon \) and “low-” \( \text{I}_1 \) symmetry plagioclases whereas the latter incorporates \( \text{C}_1 \) symmetry and “high-” \( \text{I}_1 \) symmetry (fig. 4).

The heat of solution experiments of Newton, Charlu, and Kleppa (1980) and Carpenter, McConnell, and Navrotsky (1985) indicate that the low- and high-temperature plagioclases form two segments each, one from An\(_0\) to about An\(_{70}\) and the other from about An\(_{70}\) to An\(_{100}\). This observation can be used to estimate the standard enthalpy of formation from the elements at 25\(^\circ \text{C} \) and 1 bar of the “endmember” albites and anorthites in both the “low-“ and “high-temperature” series. Extrapolation of the low-temperature (\( \varepsilon \) plagioclase) segment to An\(_0\) and An\(_{100}\) allows estimation of the enthalpy of formation of hypothetical albite and anorthite in the series, termed “\( \varepsilon \) albite” and “\( \varepsilon \) anorthite” here. The heat of solution in \( 2\text{PbO} \cdot \text{B}_2\text{O}_3 \) at \( 700^\circ \text{C} \) for “\( \varepsilon \) albite” is 80,530 \( \text{J mol}^{-1} \). The corresponding number for “\( \varepsilon \) anorthite” is 67,560 \( \text{J mol}^{-1} \). According to the results of Carpenter, McConnell, and Navrotsky (1985) the difference between the heat of solution of low-albite and “\( \varepsilon \) albite” on one hand and anorthite and “\( \varepsilon \) anorthite” on the other is 4240 and 6060 \( \text{J mol}^{-1} \) at \( 700^\circ \text{C} \), respectively, the “\( \varepsilon \)” endmembers having lower heat of solution values, making the enthalpy of formation of the “\( \varepsilon \)” members less negative than their fully ordered counterparts by this amount. Taking the heat capacity-temperature polynomials of both albites and anorthites, respectively, to be the same, “\( \varepsilon \)” albite has a standard enthalpy of formation from the
elements of $-3,931,945 \text{ J mol}^{-1}$ at 25°C and 1 bar. For “e” anorthite the corresponding enthalpy value is $-4,221,770 \text{ J mol}^{-1}$ (table 5).

If the results for the solution for high-albite, according to figure 4 had been selected to retrieve the enthalpy value for “e albite” instead of the results of Carpenter, McConnell, and Navrotsky (1985) for low-albite, a value of $-3,934,040 \text{ J mol}^{-1}$ is obtained for the enthalpy of formation of “e albite.” This value is 2095 J mol$^{-1}$ more negative than the previous one suggesting considerable uncertainty in this value for the “e albite.”

### Table 4

Constants in temperature equation describing alkali-feldspar (low-albite-microcline and high-albite-sanidine) solubility in water as a function of temperature at 1 bar below 100°C and at $P_{sat}$ at higher temperatures. Valid in the range 0 to 350°C. The low series correspond with Al-Si ordering equal to that of Amelia albite (Z = 0.95).

\[
\log K = k_1 + k_2/T^2 + k_3/T + k_4 \cdot 10^{-6} \cdot T^2 + k_5 \cdot \log T. \quad T \text{ in K}
\]

<table>
<thead>
<tr>
<th>Percent microcline</th>
<th>k_1</th>
<th>k_2</th>
<th>k_3</th>
<th>k_4</th>
<th>k_5</th>
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<td>10</td>
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<td>-3988.35</td>
<td>-28.507</td>
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The enthalpies of formation of "low" and "high" I albites have been estimated in the same way as those for the "e albite" and "e anorthite" as well as that of "high" I I anorthite and CI anorthite. The results are shown in table 5.

The configurational entropy of e plagioclases is not known. However, Carpenter, McConnell, and Navrotsky (1985) have estimated this entropy from the enthalpy of ordering and the transformation temperatures as 2 cal mol⁻¹ K⁻¹ (8.4 J mol⁻¹ K⁻¹). Thus, the standard absolute entropy of "e albite" is 215.8 J mol⁻¹ K⁻¹ at 25°C and 1 bar (table 5). The standard absolute entropy of the "low" I I series albite and anorthite are taken to be the same as those of "e albite" and fully ordered anorthite, respectively, and that of the "high" series albite the same as that of completely disordered albite, 224.4 J mol⁻¹ K⁻¹ (table 5).

From extrapolated values for I T ↔ CT transformation temperatures for anorthite and the enthalpy of ordering, Carpenter, McConnell, and Navrotsky (1985) estimated the configurational entropy in "high" I I anorthite as 0.4 to 0.8 cal mol⁻¹ K⁻¹ (1.7–3.3 J mol⁻¹ K⁻¹). Helgeson and others (1978) observed that the third law entropy of anorthite, as determined by Robie, Hemingway, and Wilson (1978), was in good agreement with phase equilibrium data if a configurational entropy of about 1 cal mol⁻¹ K⁻¹ (4.2 J mol⁻¹ K⁻¹) was added to it. In line with this we have assigned an entropy value of 199.3 + 4.2 =
203.5 J mol\(^{-1}\) K\(^{-1}\) to “high” II series anorthite. For “CT anorthite” the entropy was taken to be 206.6 J mol\(^{-1}\) K\(^{-1}\) which is based on the average value for the enthalpy of ordering for the transformation of the ordered II state to the extrapolated disordered CT state as given by Carpenter, McConnell, and Navrotsky (1985) and a transformation temperature of 2125 K.

Having estimated both the enthalpies and entropies of the endmember albites and anorthites in the various plagioclase solid solution series their standard Gibbs energies of formation from the elements at 25°C and 1 bar were calculated from data on the entropy of formation from the respective elements, as given by Cox, Wagman, and Medvedev (1989) and eq (6) (table 5).

From the estimated entropy values for the “endmember” albites and anorthites the standard absolute entropy of “low” and “high” plagioclase of any composition can be obtained at 25°C and 1 bar from eq (16). The entropy of mixing [the second term on the right hand side of eq 16] has been calculated applying the statistical thermodynamic model of Kerrick and Darken (1975) assuming Al-avoidance. For the “low” series plagioclases, it was assumed that the anorthite endmember is ordered whereas the albite endmember is disordered. This leads to

\[
\Delta S_{\text{mix}} = R \left[ X_{\text{alb}} \ln \left( X_{\text{alb}}^2 (2 - X_{\text{alb}}) \right) + X_{\text{an}} \ln \left( \frac{X_{\text{an}} (1 + X_{\text{an}})}{4} \right) \right] \]  

so

\[
a_{\text{alb}} = X_{\text{alb}}^2 (2 - X_{\text{alb}}) \]  

and

\[
a_{\text{an}} = \frac{X_{\text{an}} (1 + X_{\text{an}})^2}{4} \]  

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<th>(\Delta H_f^0)</th>
<th>(S^0)</th>
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<td>-4,226,694 J/mol</td>
<td>203.5 J/K</td>
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### Table 6

Constants in temperature equations describing plagioclase solubility in water as a function of temperature at 1 bar below 100°C and at $P_{sas}$ at higher temperatures. For explanation of “low” (partly ordered) and “high” (maximum disordered) series see Fig. 4. Two sets of constants are given for An$_{70}$. The upper one in each series corresponds with $e$ and “low” $\Pi$ plagioclase whereas the lower one corresponds to $\tilde{C}$ and “high” $\Pi$ plagioclase. $\log K = k_1 + k_2/T^2 + k_3/T + k_4 \cdot 10^{-d} \cdot T^2 + k_5 \cdot \log T$. $T$ in $K$

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For the “high” series Al-avoidance was not assumed in which case Ca-Na and Al-Si mixing is random and independent, that is the endmembers are disordered anorthite and disordered albite, respectively. We have

\[
a_{\text{alb}} = \frac{X_{\text{alb}}(4 - X_{\text{alb}}^2)(2 + X_{\text{alb}})^2}{27}
\]

\[
a_{\text{an}} = \frac{X_{\text{an}}(1 + X_{\text{an}})^2(3 - X_{\text{an}})^2}{16}
\]

and

\[
S_{\text{mix}}^{\text{“high” plag}} = -R \left( X_{\text{alb}} \ln \left( \frac{X_{\text{alb}}(4 - X_{\text{alb}}^2)(2 + X_{\text{alb}})^2}{27} \right) + X_{\text{an}} \ln \left( \frac{X_{\text{an}}(1 + X_{\text{an}})^2(3 - X_{\text{an}})^2}{16} \right) \right)
\]

Inserting the entropy mixing terms of eqs (32) and (35) into eqs (16) and (17) allows calculation of the standard Gibbs energy of formation from the elements and the standard absolute entropy at 25°C and 1 bar of plagioclase of any composition, or

\[
S_{\text{plag}}^0 = S_{\text{alb}}^0 X_{\text{alb}} + S_{\text{an}}^0 X_{\text{an}} - R S_{\text{mix, plag}}^{\text{“high”}}
\]

and

\[
\Delta G_{f, \text{plag}}^0 = X_{\text{alb}} \Delta G_{f, \text{alb}}^0 + X_{\text{an}} \Delta G_{f, \text{an}}^0 + R T S_{\text{mix, plag}}^{\text{“high”}}
\]

Finally, the heat capacity of plagioclase solid solution can be obtained from an equation of the form of (27):

\[
C_{\text{p, plag}}^0 = [a_{\text{alb}} + c_{\text{alb}}T^{-2} + f_{\text{alb}}T^2]X_{\text{alb}} + [a_{\text{an}} + c_{\text{an}}T^{-2} + f_{\text{an}}T^2]X_{\text{an}}
\]

As for the alkali-feldapars the volume of mixing of albite and anorthite can be taken to be zero. On that basis (see eq 28) and by combining eq (13B) and eqs (30) through (38) the apparent Gibbs energy of plagioclase of any composition can be retrieved over a range of temperatures and pressures as well as log K-temperature equations for plagioclase hydrolysis according to

\[
\text{Ca}_{1-x}\text{Na}_x\text{Al}_{2-x}\text{Si}_{2+x}\text{O}_{8} + 8\text{H}_2\text{O} = (1 - X)\text{Ca}^{+2} + \text{XNa}^{+} + \text{(2 - X)}\text{Al(OH)}_4^- + (2 + X)\text{H}_4\text{SiO}_4^0
\]

where X denotes the mole fraction of the albite component in the plagioclase solid solution. Constants in such equations for selected “low” and “high” plagioclase compositions are given in table 6. They are valid in the range 0° to 350°C at 1 bar below 100°C and at P_{sat} at higher temperatures. The Gibbs energy of mixing of “low” and “high” series plagioclases, respectively, is shown in figure 5.

**DISCUSSION AND CONCLUSIONS**

Experimentally determined and selected values for the standard enthalpies of formation from the elements of low-albite and microcline at 25°C and 1 bar have been drawn in figure 6. For low-albite most values lie in the range of −3934 to −3938 kJ mol⁻¹. The only values that lie significantly outside this range are those from Helgeson and others (1978), Sverjensky, Hemley, and D’Angelo (1991), and Gottschalk (1997). In retrieving their value Helgeson and others (1978) took into consideration field data assuming feldspar equilibrium under selected geological conditions and phase equilibria,
respectively. The results of Sverjensky, Hemley, and D’Angelo (1991) are based on correction of calorimetric values to make them consistent with measured high temperature solubilities in the systems K₂O– and Na₂O–Al₂O₃–SiO₂–H₂O–HCl. The abundance of experimental data on low-albite and their general conformity indicate that its standard enthalpy and standard Gibbs energy of formation from the elements are quite well established and apparently within \( \pm 2000 \text{ J mol}^{-1} \) of the value selected here.

Calorimetric and phase equilibrium data on microcline and sanidine are much more meager than those on albite and do not compare well (table 1, fig. 6). The only sets of experiments that include measurements of the standard enthalpy of formation of both low-albite and microcline are those of Waldbaum (1968), Waldbaum and Robie (1971), and Hovis (1988). Precision of calorimetric measurements is expected to be better than their accuracy. For this reason the difference in the calorimetric heat of solution values between low-albite and microcline in the quoted experiments are expected to be the best measure of the difference in the standard enthalpy of formation between low-albite, on one hand, and microcline, on the other. The calorimetric measurements of Waldbaum and Robie (1971) have been chosen here to retrieve a value for the standard enthalpy of formation of microcline from the elements at 25°C and 1 bar. Consequently, the standard enthalpy value selected for microcline differs from the value published by Waldbaum and Robie (1971) by the same amount as that between their value for low-albite and that selected here. The enthalpy value so selected for microcline is roughly half way between the two populations of previously measured or selected values (fig. 6). The difference between the heat of solution of low-albite and microcline obtained by Hovis (1988) is very similar to that of Waldbaum and Robie (1971) or only 520 J mol⁻¹ larger.

Aqueous Na/K ratios in hot spring and shallow well discharges have been used as a geothermometer in geothermal investigations to predict subsurface temperatures in geothermal systems. For deep wells this ratio has been used to determine the temperature of the producing aquifers. It has generally been considered that the Na/K ratio of geothermal waters was fixed in the deep geothermal reservoir by simultaneous equilibrium with Na- and K-felspars invariably found as hydrothermal minerals in active

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Fig. 5. Gibbs energy of mixing of “low” (solid curve) and “high” (dashed curve) series plagioclases.
geothermal systems, at least when temperatures exceed some 100°C. However, the calibration of this geothermometer, that is the relationship between aqueous Na/K ratios and aquifer temperature, has so far been based on selected drillhole data because thermodynamic data on the feldspars and the aqueous species have yielded temperatures that do not satisfactorily match observed reservoir temperatures. Poor thermody-
namic data have been blamed for the discrepancy rather than departure from equilibrium. The enthalpy and entropy values selected here for both low-albite and microcline yield aqueous Na/K ratios at equilibrium that match very well those of the Na-K geothermometry calibrations of Truesdell (1976) and Arnórsson, Gunnlaugsson, and Svavarsson [1983] (fig. 7). The good conformity between temperature and Na/K ratios according to the drillhole data calibrations, on one hand, and the thermodynamic data selected here for low-albite and microcline, on the other, is considered to indicate that the selected values for the difference between the standard Gibbs energies of these feldspars are close to the actual one. These results, however, say nothing about the accuracy of the standard Gibbs energy values of the individual feldspars. The standard heat capacities and standard molal volumes of Na- and K-feldspars vary little with the degree of Al-Si ordering. Therefore, ordering has very little effect on aqueous Na/K ratios at equilibrium, at least, if the ordering is of about the same degree in both feldspars, which is to be expected in any kind of geological environment.

Acid and lead borate melt calorimetry yield values for the standard enthalpy of formation of anorthite from the elements at 25°C and 1 bar within about 6 kJ mol⁻¹ (fig. 8). The acid calorimetry measurements of Kracek (1953), as revised by Haas, Robinson,

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**Fig. 7.** Aqueous Na⁺/K⁺ activity ratios for simultaneous equilibrium between low-albite, microcline, and solution. Also shown are Na/K geothermometry ratios according to the geothermometry functions of [1] Truesdell (1976) and Arnórsson, Gunnlaugsson, and Svavarsson (1983) valid in the range 50 to 250°C [2] and 250 to 350°C [3], respectively.
and Hemingway (1979), yield very similar values as the lead borate melt measurements of Newton, Charlu, and Kleppa (1980), whereas later measurements in lead borate melts give values that are 5–6 kJ mol\(^{-1}\) more negative (Carpenter, McConnell, and Navrotsky, 1985; Zhu, Newton, and Kleppa, 1994). Enthalpy values for anorthite based on phase equilibria show comparable scatter (fig. 8). Thus, there is still considerable discrepancy in the standard enthalpy of formation values for this mineral and a corresponding discrepancy in its standard Gibbs energy values. The value selected in this study is that recommended by Haas, Hemingway, and Robinson (1979) which falls into the population of the less negative enthalpy values (fig. 8). The reason is apparent discrepancy with field data, if the more negative values are selected, as already discussed.

The thermodynamic data, which have been selected in this contribution, yield higher solubility for the endmember feldspars below about 50°C than published to date (fig. 9). For both high- and low-albite the difference is more than one and a half orders of magnitude at 0°C, but it is somewhat less for microcline, sanidine and anorthite. In the range 50 to 200°C earlier studies indicate similar solubility for the alkali-feldspars, but above 200°C our results indicate somewhat lower solubility. For anorthite our results indicate significantly higher solubility below 100°C but lower solubility at higher temperatures (fig. 9).

The cause of the difference in the calculated endmember feldspar solubilities lies only partly in differences in the data selected on their thermodynamic properties. Below 100°C the difference lies most in the data selected for H\(_4\)SiO\(_4\)\(^0\) which in our case were taken from Gunnarsson and Arnórsson (1999). Above 250°C the difference is largely caused by the data selected on Al(OH)\(_4^-\). We selected data on this species given by

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**Fig. 8.** Experimentally determined and selected values for the standard enthalpy of formation of anorthite from the elements. [1] Corrected value as proposed by Hemingway, Haas, and Robinson (1982). [2] The upper value represents results for synthetic anorthite and the lower value results for a natural one. Symbols have the same signature as in figure 6.
Fig. 9. Feldspar solubility curves. The solid and broken curves represent the results of the present study. The dotted curves represent low-albite, microcline, and anorthite solubilities according to data from Berman (1988) for the minerals, for water from Helgeson and Kirkham (1974), and for aqueous species from Shock and Helgeson (1988), (for Na,$^+$, K,$^+$, Ca,$^{2+}$), Shock, Helgeson, and Sverjensky (1989) (for H,$_4$SiO$_4$), and Pokrovskii and Helgeson (1995) (for Al(OH)$_4$).
Arnorsson and Andredottir (1999). Gunnarsson and Arnorsson (1999) used the quartz solubility data of Rimstidt (1997) to retrieve values for the apparent standard partial molal Gibbs energy for H$_4$SiO$_4$. The quartz solubility data of Rimstidt (1997), which cover the range 21$^\circ$ to 90$^\circ$C, yield apparent standard partial molal Gibbs energy values for H$_4$SiO$_4$ similar to those retrieved from amorphous silica solubility according to Gunnarsson and Arnorsson (1999), an observation considered to substantiate the validity of the thermodynamic data used here on aqueous silica. For the aluminate ion the values on the apparent standard partial molal Gibbs energy selected by Arnorsson and Andredottir (1999) are very similar to those of Apps, Neil, and Jun (1989), Castet and others (1993), and Diakonov and others (1996). On the other hand, the apparent standard partial molal Gibbs energy values for this species, as given by Pokrovskii and Helgeson (1995) and Shock and others (1997), are significantly more negative above 50$^\circ$C and less negative above 200$^\circ$C, respectively.

The higher solubility for the feldspars at low temperatures have major implications for studies of their behavior under weathering conditions. It is generally observed that these minerals break down during weathering indicating their instability. In geothermal systems, at least where temperatures exceed some 100$^\circ$C, albite and K-feldspars are often present as hydrothermal minerals and generally at $>$200$^\circ$C. The waters should, thus, be saturated with them, or somewhat supersaturated. The presently retrieved alkali-feldspar solubility data should facilitate the study of the state of equilibration between these feldspars and water in active geothermal systems.

The present contribution is the first attempt to present solubilities for a range of alkali-feldspar and plagioclase solid solutions. This is of value for the study of feldspar-water interaction, both under weathering and hydrothermal conditions. It seems unlikely that more exact modelling of the entropy and enthalpy of mixing of solid solution feldspars will improve significantly the accuracy of their calculated solubilities and, therefore, their state of saturation in natural waters. This is also the case for variations in solubility with temperature and pressure but not with standard enthalpy of formation (or standard Gibbs energy of formation) data at 25$^\circ$C.

The present assessment and selection of thermodynamic data on the feldspars and the most important species that form when they dissolve in water, respectively, has resulted in quite reliable information on their solubility constants. Yet, considerable uncertainty may still exist in evaluating the state of feldspar saturation with respect to water of a given composition. The uncertainty depends essentially on two factors, the degree of Al-Si ordering and exsolution and the calculation of the respective activity products for water of a given composition with the aid of aqueous speciation programs. In the first case data are needed on the state of ordering of natural feldspars from volcanic and relatively rapidly cooled intrusives. In the second case the uncertainty in calculating the activity product is dependent on the water composition being negligible in alkaline waters, small in very acid waters, but largest in waters with an intermediate pH. In alkaline waters it is certain that the dominant aqueous aluminium bearing species is Al(OH)$_4^-$, but in strongly acidic waters it is Al$^{3+}$. The thermodynamics of both these species are quite well known, particularly that of the former. In waters of intermediate pH, on the other hand, Al(OH)$_3$ and Al(OH)$_2^+$ constitute a significant fraction of the dissolved aluminium, and the uncertainty in the calculated activity product (Q) becomes significant because the thermodynamic properties of these species are not accurately known, or to put it differently, there is still disagreement on the values of dissociation constants of these species, as well as that of Al(OH)$_4^-$ (see for example, Shock and others, 1997; Arnorsson and Andredottir, 1999). It would also be desirable to have more experimental data on the aluminium-silica dimer (see Pokrovskii and others, 1998).

The Gibbs energy differences between ordered and disordered feldspars, both endmembers and solid solutions, is quite significant. It is, thus, possible that dissolution
of disordered feldspars and precipitation of ordered ones occurs simultaneously in geothermal systems. When this happens calculations should show that the water was somewhat undersaturated with the disordered feldspar but somewhat supersaturated with the presumed ordered, hydrothermal ones.

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