American Mineralogist, Volume 58, pages 277-286, 1973

ANALCIME: Free energy from hydrothermal data. Implications for phase equilibria and thermodynamic quantities for phases in $NaAlO_2$-SiO_2-H_2O.

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Abstract

Tabulated values for the standard Gibbs energy of formation (Robie and Waldbaum, 1968) of low albite, analcime, quartz and liquid H_2O suggest that low albite plus liquid H_2O are stable at 298 K, 1 bar. While this does not violate any field observation to date, there is experimental evidence to suggest that analcime plus quartz should be the stable assemblage. Calculations of $G^\circ_f(298, 1)$ [Anc] from equilibrium studies involving albite or nepheline introduce uncertainties as to amount of disorder or non-stoichiometry of composition. The calculations are presented in terms of difference functions which should only need revision if more precise experimental data become available, and not each time a tabulated standard Gibbs energy changes. Examination of evaluated G°_f values indicate that the tabulated Gibbs energy values for analcime may be up to 2.5 kcal mol^{-1} too positive and the tabulated value for low albite may be some 1.8 to 4.1 kcal mol^{-1} too negative.

Introduction

The feldspathoid-zeolite analcime is remarkable in that it occurs as phenocrysts in alkaline undersaturated igneous rocks (possibly pseudomorphing leucite) and also in diagenetic environments (probably as a solid-solution variant or even polymorph).

Recent reversed experimental investigations in the subsolidus region for the reactions

$$\text{analcime} = \tfrac{1}{2}\text{albite} + \tfrac{1}{2}\text{nepheline} + H_2O \qquad \langle 1 \rangle$$

$$\text{analcime} + \text{quartz} = \text{albite} + H_2O \qquad \langle 2 \rangle$$

$$\text{analcime} = \text{jadeite} + H_2O \qquad \langle 3 \rangle$$

$$\text{albite} = \text{jadeite} + \text{quartz} \qquad \langle 4 \rangle$$

have been used in this study to examine the G°_f (298,1)[Anc].

The problem of possible stable analcime solid-solutions has received much attention. Available data suggests that the analcime in equilibrium with albite and nepheline (plus excess H_2O) is silica *and H_2O* deficient relative to "stoichiometric $NaAlSi_2O_6 \cdot H_2O$" (or 1:2:1 analcime). At lower temperatures (and possibly coexisting with low albite, quartz and excess H_2O), the stable analcime appears to be silica and H_2O enriched over 1:2:1 analcime. These relationships are shown by Thompson (1971, Fig. 1, p. 81).

It is the purpose of this study to examine thermodynamic parameters from reversed hydrothermal equilibrium investigations, compare them with tabulated values for the above phases in the recent compilation by Robie and Waldbaum (1968), and examine the consequences for field relations of assemblages containing analcime.

Sources of Data

Entropies. The calorimetric entropies of analcime, low albite, jadeite and nepheline, determined by heat capacity measurements by Kelley *et al.* (1953), King (1955), King and Weller (1961), as summarized by Robie and Waldbaum (1968) are shown in Table 1 under the column $S^\circ(298,1)$.

In order to use the tabulated $H^\circ_f(298,1,\text{elements})$ and $G^\circ_f(298,1,\text{elements})$ values tabulated by Robie and Waldbaum (1968), or conversely to calculate the $G^\circ_f(298,1,\text{elements})$ from measured $H^\circ_f(298,1,\text{elements})$ and measured entropy, the $S^\circ_f(298,1,\text{elements})$ is needed. $S^\circ_f(298,1,\text{elements})$ can be calculated directly from the calorimetric entropy for the mineral and the entropies of the constituent elements, which are the reference states in Robie and Waldbaum (1968).

It is generally assumed that a calorimetric entropy is a "Third Law Entropy" but it may in fact only represent non-quenchable contributions to the total Third Law Entropy. Small configurational entropy contributions may still be present at the lowest temperature of the heat capacity determination (usually 51 K). The effect of "residual" configurational entropy at absolute zero increases the assigned entropy values. As pointed out by Waldbaum

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TABLE 1. Tabulated Thermodynamic Data*

Phase	$S^\circ(298,1)$ (cal K^{-1} mol^{-1})	$S^\circ_f(298,1)$ (cal K^{-1} mol^{-1})	$H^\circ_f(298,1)$ (kcal mol^{-1})	$G^\circ_f(298,1)$ (kcal mol^{-1})	V/mol (cal bar^{-1})
Analcime Anc	56.03 ± 0.60	-174.673	-786.341 ± 0.86	-734.262 ± 0.88	2.33006
Albite (low) Ab	50.20 ± 0.40	-178.294	-937.146 ± 0.74	-883.988 ± 0.76	2.3917
Analbite Anl	54.67 ± 0.45	-173.825	-934.513 ± 0.77	-882.687 ± 0.79	2.4003
Nepheline Ne	29.72 ± 0.30	- 91.782	-497.029 ± 1.0	-469.664 ± 1.01	1.2944
Jadeite Jd	31.90 ± 0.30	-143.099	-719.871 ± 1.0	-677.206 ± 1.01	1.4435
Quartz Q	9.88 ± 0.02	- 43.616	-217.650 ± 0.4	-204.646 ± 0.41	0.54226

*$S^\circ_f(298,1)$ values calculated from $H^\circ_f(298,1)$ and $G^\circ_f(298,1)$. All other values from Robie and Waldbaum (1968).

(1968), the tabulated entropy of analbite should be regarded as a *minimum* value. Calculated values of S°_f(298,1,elements) are shown in Table 1.

Enthalpy of formation. The tabulated values for H°_f(298,1,elements) from Robie and Waldbaum (1968) are shown in Table 1. These are determined from calorimetric heat of solution measurement of the mineral corrected by measurement of heat of solution of constituent oxides (and related substances) and knowledge of their heat of formation.

Gibbs energy of formation. The values of G°_f(298,1,elements) from Robie and Waldbaum (1968) are shown in Table 1. In the calculation of $G^\circ_f(298,1)$ for any particular phase from reversed equilibrium studies, it is necessary to assume that the tabulated values actually lie within their stated limits of accuracy.

Values of $\mu^\circ_{T,P}[H_2O] = G^\circ_{T,P}[H_2O]$. These values are interpolated from the tabulation by Fisher and Zen (1971) of the Burnham, Holloway and Davis (1969) calculations of $\Delta G^\circ_{f,T,P}[H_2O]$. Values used for the individual temperatures and pressures of the calculations for the various equilibria in this study are indicated in Tables 2, 3, and 4.

Molar volumes of minerals. These values are tabulated by Robie and Waldbaum (1968) and by Robie, Bethke, and Beardsley (1967) and are shown in units of cal bar^{-1} in Table 1.

Calculation of $G^\circ_f(298,1)$. The calculation of Gibbs energy of formation and difference functions from reversed experimental data follows the procedure outlined by Apps (1968) and Zen (1969, 1972). The approximations include the assumptions that

TABLE 2. Calculated Thermodynamic Parameters for the Reaction ⟨1⟩, Anc = 1/2Ab + 1/2Ne + H_2O

T, (°C)	P total = P H_2O, (bars)	$\mu_w = G^*_{T,P}[H_2O]$, (cal mol^{-1})	F[low albite][a], (kcal mol^{-1})	F[analbite][b], (kcal mol^{-1})	Reference[c]
492 ± 5	500 ± 30	-40446	+59.199 ± 0.6[d]	+60.240 ± 0.6	L
538 ± 5	1000 ± 30	-38386	+59.206 ± 0.6	+60.347 ± 0.6	L
578 ± 5	2000 ± 30	-36271	+59.163 ± 0.6	+60.390 ± 0.6	L
598 ± 5	3000 ± 30	-34965	+59.137 ± 0.6	+60.040 ± 0.6	L
	Average		+59.176 ± 0.9[e]	+60.345 ± 0.9	
487 ± 5	500 ± ?	-40476	+59.030 ± 0.6	+60.060 ± 0.6	G
502 ± ?	700	-39800	+59.046 ± ?	+60.109 ± ?	G
521 ± 5	1000	-38941	+59.007 ± 0.6	+60.107 ± 0.6	G
548 ± 11	1500	-37658	+59.117 ± 1.1	+60.286 ± 1.1	G
570 ± 4	2000	-36592	+59.167 ± 0.6	+60.376 ± 0.6	G
	Average		+59.073 ± 1.2	+60.187 ± 1.2	
600 ± 16	2000	-35630	+59.404 ± 1.2	+60.645 ± 1.2	K
650 ± 5	4800	-32237	+59.397 ± 0.6	+60.722 ± 0.6	K
	Average		+59.400 ± 1.3	+60.682 ± 1.3	

[a] calculated using ΔV_s ⟨1⟩ = -0.48701 (cal bar^{-1}), $S^\circ_{f,s}(298)$ ⟨1⟩ = +39.636 (cal K^{-1} mol^{-1}).

[b] calculated using ΔV_s ⟨1⟩ = -0.48271 (cal bar^{-1}), $S^\circ_{f,s}(298)$ ⟨1⟩ = +41.870 (cal K^{-1} mol^{-1}).

[c] sources: L--Liou (1971), G--Greenwood (1961), K--Kim and Burley (1971).

[d] uncertainty from experimental bracket.

[e] experimental uncertainty plus average range.

TABLE 3. Calculated Thermodynamic Parameters for the Reaction ⟨2⟩Anc + Q = albite + H_2O

T, (°C)	P total = P H_2O (bars)	$\mu_w = G^*_{T,P}$ H_2O (cal mol^{-1})	D[low albite][a] (kcal mol^{-1})	D[analbite][b] (kcal mol^{-1})	Reference[c]
190 + 10 - 20	12 × 1.013	-51946[d]	-145.499 ± 1.1		CF
190 ± 10	2000	-49564	-146.925 ± 0.5		T
170 ± 10	4000	-49494	-146.906 ± 0.5		T
150	4750 50	-49939	-146.973 ± 0.5		T
	5250	-49739	-146.931 ± 0.5		T
	Average		-146.933 ± 0.55		
200 ±	2000	-49245	-146.807 ± 0.5	-146.973 ± 0.5	L
196 ± 5	3000	-49174	-146.746 ± 0.5	-147.218 ± 0.5	L
190 ± 5	4000	-48753	-146.505 ± 0.5	-146.679 ± 0.5	L
183 ± 5	5000	-48713	-146.702 ± 0.5	-146.879 ± 0.5	L
	Average		-146.690 ± 0.6	-146.937 ± 0.6	

[a] calculated using ΔV_s ⟨2⟩ = -0.48062 (cal bar^{-1}), $S^\circ_{f,s}(298)$ ⟨2⟩ = +43.616 (cal K^{-1} mol^{-1}).

[b] calculated using ΔV_s ⟨2⟩ = -0.47202 (cal bar^{-1}), $S^\circ_{f,s}(298)$ ⟨2⟩ = +42.768 (cal K^{-1} mol^{-1}).

[c] sources: CF--Crawford and Fyfe (1965), T--Thompson (1971), L--Liou (1971).

[d] estimated from Sharp (1962).

$\int_{P_o}^{P} \Delta\bar{V}_s dP = \Delta V_s(P - P_o)$, that $a_{H_2O} = 1$ and that $\Delta\bar{C}_{p,r} = 0$.

Since ($H^\circ_T - H^\circ_{298}$) and ($S^\circ_T - S^\circ_{298}$) are not available for analcime it is not possible to use the more rigorous method of calculation of Robie (1965). Robie demonstrated that more consistent values for G°_f could be obtained by using $\Delta\bar{C}_{p,r}$ as a function of temperature, through the Gibbs function.

Errors. The treatment of errors is discussed by Zen (1972, p. 531).

The Equilibrium Analcime-Albite-Nepheline-H_2O

The reaction

$$\underset{\text{analcime}}{NaAlSi_2O_6 \cdot H_2O} = \tfrac{1}{2}\underset{\substack{\text{low albite}\\ \text{or analbite}}}{NaAlSi_3O_8} + \tfrac{1}{2}\underset{\text{nepheline}}{NaAlSiO_4} + H_2O \qquad \langle 1 \rangle$$

has been investigated by many workers using mainly gels and oxide mixes, and when reversed by using the recrystallized oxide mixes at lower temperatures. The most recent study by Kim and Burley (1971) suggests equilibrium at significantly higher temperatures than the previous investigations (Yoder, 1954; Sand, Roy, and Osborn, 1957; Saha, 1961; Greenwood, 1961; Peters, Luth, and Tuttle, 1966). The recent study by Liou (1971)—who used oxide mixes, crystallized oxide mixes, synthetic albite and nepheline with natural analcime—produced very similar results to those of Greenwood (1961). Liou's study had the added advantage of longer run times which may diminish the possibility of metastability in experiments using reactive oxide mixes.

TABLE 4. Calculated Thermodynamic Parameters for the Reaction ⟨3⟩Anc = Jd + H_2O

T[a], (°C)	P total = P H_2O[a], (bars)	$\mu_w = G^*_{T,P}[H_2O]$ (cal mol^{-1})	C[b] (kcal mol^{-1})	C (mean value) (kcal mol^{-1})
350	6400	-41893	+57.858	+57.995 ± 0.4
	7000	-41637	+58.134	
450	7500	-37827	+57.933	+58.045 ± 0.4
	8000	-37608	+58.157	
500	8000	-35827	+57.959	+58.069 ± 0.4
	8500	-35604	+58.179	
575	9000	-32734	+58.128	+58.347 ± 0.4
	10000	-32287	+58.567	
	Average			+58.114 ± 0.6

[a] calculated from results of Manghnani (1970).

[b] calculated using ΔV_s ⟨3⟩ = -0.88656 (cal bar^{-1}), $\Delta S^\circ_{f,s}(298)$ ⟨3⟩ = +31.664 (cal K^{-1} mol^{-1}).

Manghnani (1970) used natural materials and his data certainly bracket the values of the above workers, but his data are considered to be too widely spaced to give limiting equilibrium temperatures with any precision.

From all of the above data the univariant brackets from Liou (1971), Greenwood (1961), and Kim and Burley (1971) are considered to represent the best approaches to equilibrium.

In addition to the problems regarding analcime solid solutions, several important points should be mentioned with regard to the other phases in the above reaction. An examination of the phase diagram for the Ab-Ne join (see Kim and Burley, 1971; Bell and Roseboom, 1969) and/or determination of the coexisting phase compositions indicates appreciable mutual solid solution between albite and nepheline.

At these temperatures albite (and nepheline, analcime) may be disordered to some extent. Until precise data on the ΔG increments of disorder in albites become available, we can only compare the values using those for low albite and analbite.

The results of the calculations using the above reversed equilibrium data are shown in Table 2. They are tabulated as a difference function[1]

$$F \equiv \tfrac{1}{2}G^{\circ}_{f}(298,\ 1)[\mathrm{Ab}] + \tfrac{1}{2}G^{\circ}_{f}(298,\ 1)[\mathrm{Ne}] - G^{\circ}_{f}(298,\ 1)[\mathrm{Anc}]$$

$$= -\Delta V_{s}\,\Delta P + \Delta S^{\circ}_{f,s}\,\Delta T - G_{T,P}{}^{*}[\mathrm{H_2O}] \qquad (1)$$

where ΔV_s is the volume change of the solids in cal bar^{-1} (compressibility neglected); $\Delta S^{\circ}_{f,s}$ is the entropy change (of formation) of the solids in cal $\mathrm{K}^{-1}\ \mathrm{mol}^{-1}$ (assumed to be independent of temperature); $G_{T,P}{}^{*}[\mathrm{H_2O}]$ is the Gibbs free energy of water from Fisher and Zen (1971).

The Equilibrium Analcime-Quartz-Albite-H_2O

Use of the $G^{\circ}_{f}(298,1)$ values in Table 1 for the reaction

$$\underset{\text{analcime}}{\mathrm{NaAlSi_2O_6\cdot H_2O}} + \underset{\text{quartz}}{\mathrm{SiO_2}} = \underset{\text{low albite}}{\mathrm{NaAlSi_3O_8}} + \mathrm{H_2O}\ 802\rangle$$

suggest a $\Delta G^{\circ}(298,1)$ of -1768 cal (with a maximum range of ± 2050 cal). This figure implies that low albite + liquid H_2O is more stable than analcime + quartz.

Field evidence, however, does not give a clear answer to the problem. The associations analcime, analcime + albite, and albite + quartz are commonly found in diagenetic to low grade metamorphic environments. Although the transition of analcime to albite has been observed in some low grade progressive metamorphic sequences, either the analcime *does not* coexist with quartz or the isogradic reaction cannot be precisely defined. If the silica saturation level in diagenetic fluids is at a higher level than at equilibrium with quartz (*i.e.*, the presence of amorphous silica, opal or chalcedony) albite will be favored at the expense of analcime + SiO_2. However, analcime (in the absence of quartz) is often found in saline-lake deposits. With the $a_{\mathrm{H_2O}}$ reduced in saturated brines ($\mu_{\mathrm{H_2O}} < G^{\circ}_{\mathrm{H_2O}}$), albite again would be favored from reaction ⟨2⟩.

It is possible that the difficulty in locating reaction ⟨2⟩ in nature is due to chemical controls and kinetic difficulties. Since analcime shows extensive solid solution with respect to SiO_2 and H_2O, the composition of diagenetic fluids can influence its stability. Analcime grows very readily from compositions in $NaAlO_2$-SiO_2-H_2O and even if low albite were stable at 25°C, 1 atm, the chemically equivalent assemblage analcime plus quartz would be favored by growth kinetics.

Reaction ⟨2⟩ has been investigated by several workers (see Table 3), and reversibility of the boundary has been demonstrated. The data suggest that analcime plus quartz is stable relative to low (albite) up to about 190°C at low pressures.

Liou (1971) used natural analcime, synthetic high albite, and synthetic quartz, and on the basis of paired-capsule increase or decrease of phases limited the boundary between analcime plus quartz and *disordered* albite plus H_2O. Liou's univariant curve lies at slightly higher temperatures than that determined by this writer using a solubility weight-change method (Thompson, 1971). The natural analcime used by the writer was of similar composition to that used by Liou, but the albite was *natural low* (Amelia) albite. The boundary was determined on the basis of weight gain/loss of quartz crystals in the presence of powdered analcime plus albite and by weight *loss* of low albite in the presence of powdered analcime plus quartz. The boundary so determined is believed to reflect the reaction

analcime + quartz → *low* albite + H_2O

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[1] The use of difference functions was suggested by D. R. Waldbaum (personal communication), since they should not need revision each time the tabulated $G^{\circ}_{f}(298,1)$ values for the crystalline phases involved in the reaction are changed (see also Robie, 1965).

The analcime sample used by Thompson was slightly SiO_2 and H_2O enriched over 1:2:1 analcime. The fact that 0.05 g of the powdered analcime produced negligible weight loss ($< -10\mu g$) of a quartz crystal at 190°C, 2 kbar, was taken to indicate that the analcime used in the experiments was near to the stable analcime solid-solution composition in equilibrium with low albite and quartz. Since no other phases were observed in microscopic examination of the run powder, it was assumed that the analcime composition is ternary in $NaAlO_2$-SiO_2-H_2O.

In the presence of disordered albite the stability field of analcime plus quartz is enlarged (Liou, 1971) relative to that with low albite (Thompson, 1971) by about 20°C at 2 kbar and 10–15°C at 4 kbar. If the measurement of $2\theta_{131-\bar{1}31}$ is sufficient to characterize the disorder in albite at these temperatures, the ΔG associated with disorder in albite may be estimated from the ΔT between the curves for low albite and partly disordered albite.

Campbell and Fyfe (1965) used a similar technique to that described by Thompson (1971) and located an equilibrium point near 190°C at 12 atm. (probably +10 to −20°C).

The results of the calculations using the above reversed equilibrium data are given in Table 3 as the difference function

$$\begin{aligned} D \equiv {} & G^\circ_f(298,\,1)[\mathrm{Ab}] - G^\circ_f(298,\,1)[\mathrm{Anc}] \\ = {} & G^\circ_f(298,\,1)[\mathrm{Q}] \\ & - \Delta V_s\,\Delta P + \Delta S^\circ_{f,s}\,\Delta T - G_{T,P}{}^*[\mathrm{H_2O}] \qquad (2) \end{aligned}$$

The Equilibrium Analcime-Jadeite-H_2O

A value of $G^\circ_f(298,1)$ analcime obtained from experimental data on the reaction

$$\underset{\text{analcime}}{NaAlSi_2O_6 \cdot H_2O} = \underset{\text{jadeite}}{NaAlSi_2O_6} + H_2O \qquad \langle 3 \rangle$$

avoids the uncertainties in the structural state of the coexisting albite in reaction ⟨2⟩ or non-stoichiometry of albite and nepheline in reaction ⟨1⟩. The problem of non-stoichiometry and order/disorder in analcime, however, remains.

In a recent experimental study, Manghnani (1970) used natural analcime ($NaAl_{1.02}Si_{2.16}O_6$:1.05 H_2O) and natural jadeite (98.4% Jd) to bracket the equilibrium boundary. His results have been used to obtain the function

$$\begin{aligned} C \equiv {} & G^\circ_f(298,\,1)[\mathrm{Jd}] - G^\circ_f(298,\,1)[\mathrm{Anc}] \\ = {} & -\Delta V_s\,\Delta P + \Delta S^\circ_{f,s}\,\Delta T - \Delta G_{T,P}{}^*[\mathrm{H_2O}] \qquad (3) \end{aligned}$$

and are shown in Table 4.

The results of Manghnani (1970) for reaction ⟨3⟩ fall about 2 kbar lower than those of Newton and Kennedy (1968). These workers used natural materials in a mixture of Ab + Ne + Jd, at the jadeite composition. The presence of albite and nepheline in addition to jadeite may significantly influence the regions of analcime synthesis. The higher pressures obtained by Newton and Kennedy (1968) compared with Manghnani (1970) probably result from a coupling of the reactions ⟨3⟩ and ⟨1⟩. Although both of these studies used "reasonable" friction corrections (averaging the in-stroke and out-stroke displacements of piston compared with ram-pressure), they cannot be exactly compared to hydrothermal pressures.

The fact that the analcime which is synthesized near the univariant boundary for reaction ⟨1⟩ is known to be silica- and H_2O-deficient relative to 1:2:1 analcime, and the fact that albite was recorded in high pressure-temperature investigations of reaction ⟨3⟩, mean that the analcime-jadeite relation at these conditions should be

$$\mathrm{analcime_I} + \mathrm{albite} = \mathrm{jadeite} + H_2O$$

(analcime nomenclature from Thompson, 1971). This may be the actual reaction pertaining in the higher pressure-temperature runs of Manghnani (1970; see Table 2, p. 459, run #25).

In the lower temperature-pressure runs of Manghnani, reaction ⟨3⟩ appears to be occurring as written. The data for the runs at 350° and 450°C are considered to give the closest values for $G^\circ_f(298,1)$ [Jd] − $G^\circ_f(298,1)$[Anc]. The data for run #48 is assumed to read "jadeite grew" as indicated in his Figure 4 (p. 459).

Difference Functions and Analcime Free-Energy

The difference functions obtained thus far have been obtained from bracketed univariant equilibria. Further values for these functions may be obtained from the shapes and P-T locations of the univariant curves themselves.

The univariant curve for the analcime-quartz-albite-H_2O equilibrium.

The experimental studies by Thompson (1971) for reaction ⟨2⟩ indicate that this slope has negative P_{H_2O}-T curvature. The data indicate that the curve passes through 298 K (25°C) between 6 and 8 kbar. A value of $\Delta G^\circ_r(298,\,1)$ ⟨2⟩ may be obtained using the relation

$$\Delta G^\circ_r(298,\ 1) \simeq \Delta V_r\ \Delta P \qquad (4)$$

The ΔV_r term must include compressibility data to obtain accurate information. Yoder and Weir (1960) demonstrated an anomalously high compressibility for samples of natural analcime, possibly indicating that H_2O may be squeezed out of analcime at elevated pressure or that polymorph(s) exist at high pressure. They present an expression for ΔV (in cm^3) of reaction ⟨2⟩ based on their compressibility measurements

$$\Delta V = -0.04649 - (0.125 \times 10^{-4})P + (1.047 \times 10^{-9})P^2. \qquad (5)$$

Using the Gibbs energy relation (4) and the volume-compressibility equation (5) above, the ΔG°_r (298,1) for reaction ⟨2⟩ may be calculated, at $\Delta P = 6$ kbar (= +502 cal) and 8 kbar (= +659 cal). The value of $\Delta G^\circ_r(298,1)$ ⟨2⟩ = 659 cal is double that estimated by Campbell and Fyfe (1965) using available data at that time. Using the currently available $G^\circ_f(298,1)$ values (shown in Table 1), a value of $\Delta G^\circ_r(298,1)$ ⟨2⟩ = −1768 cal is obtained. Since data for quartz and H_2O are certainly reliable, the difference of 2427 to 2270 cals probably relates to the function $G^\circ_f(298,1)$ [Ab] − $G^\circ_f(298,1)$[Anc]. It should be noted that while low albite was believed to be the form of $NaAlSi_3O_8$ at the equilibrium for reaction ⟨2⟩, the calculation of $\Delta G^\circ_r(298,1)$ ⟨2⟩ using the value tabulated in Table 1 for analbite gives a value of −467 cal. This observation lessens the discrepancy in the data but finds little support in the natural association of *low* albite-analcime ± quartz. Similar treatment (using volume-compressibility relations) for reaction ⟨3⟩ was not attempted, since extrapolation of the univariant curve from Manghnani (1970, Fig. 4, p. 459) implies that jadeite plus H_2O is stable relative to analcime at 298 K, 1 bar.

The univariant curve for the albite-jadeite-quartz equilibrium.

Experimental brackets for the equilibrium

$$\underset{\text{low albite or analbite}}{NaAlSi_3O_8} = \underset{\text{jadeite}}{NaAlSi_2O_6} + \underset{\text{quartz}}{SiO_2} \qquad \langle 4\rangle$$

from various studies have been used to calculate a difference function

$$B \equiv G^\circ_f(298,\ 1)[\mathrm{Jd}] - G^\circ_f(298,\ 1)[\mathrm{Ab}]$$
$$= -G^\circ_f\ (298,\ 1)[\mathrm{Q}] - \Delta V_s\ \Delta P + \Delta S^\circ_{f,s}\ \Delta T \quad (6)$$

The results of the calculations are shown in Table 5. In addition values of $\Delta G_r(298,1)$ ⟨4⟩ are shown.

TABLE 5. Calculated Thermodynamic Parameters for the Reaction ⟨4⟩Ab = Jd + Q

T, (°C)	P total, (kbar)	ΔG°_r(298,1)[low albite][a] (kcal mol^{-1})	B[low albite][b] (kcal mol^{-1})	B[analbite][c] (kcal mol^{-1})	Reference[d]
500	14.60 ± 0.3	+1.926	+202.720 ± 0.5	+204.715 ± 0.5	NS
550	15.30 ± 0.5	+1.789	+202.857 ± 0.7	+205.070 ± 0.7	NS
600	16.70 ± 0.5	+1.936	+202.710 ± 0.7	+205.134 ± 0.7	NS
600	16.00 - 17.00	+1.855	+202.791 ± 0.7	+205.218 ± 0.7	BW
800	20.00 ± 0.5	+1.591	+203.055 ± 0.7	+206.345 ± 0.7	BW
800	20.75 ± 0.25	+1.895	+202.751 ± 0.7	+206.033 ± 0.7	EBF
1200	30.50 ± 0.5	+2.484	+202.162 ± 0.7	+207.148 ± 0.7	EBF
500	15.75 ± 0.05	+2.392	+202.254 ± 0.7	+204.239 ± 0.7	NK
600	17.50 ± 0.5	+2.261	+202.385 ± 0.7	+204.803 ± 0.7	NK
800	21.40 ± 0.5	+2.159	+202.487 ± 0.7	+205.764 ± 0.7	NK
600	16.30 ± 0.5	+1.774	+202.872 ± 0.7	+205.300 ± 0.7	J
	Average	+2.005 ± 0.7	+202.640 ± 0.7	+205.433 ± 2.3	

[a] calculated directly from experimental bracket as outlined in text.

[b] calculated using ΔV_s ⟨4⟩ = −0.40594 (cal bar^{-1}), $\Delta S^\circ_{f,s}(298)$ ⟨4⟩ = −8.423 (cal k^{-1} mol^{-1})

[c] calculated using ΔV_s ⟨4⟩ = −0.41454 (cal bar^{-1}), $\Delta S^\circ_{f,s}(298)$ ⟨4⟩ = −12.890 (cal k^{-1} mol^{-1})

[d] sources: NS--R.C. Newton and Smith (1967), BW--Boettcher and Wyllie (1969), EBF--Essene, Boettcher and Furst (1972), NK--M.S. Newton and Kennedy (1968), J--Johannes and others (1971).

The slightly different values for these quantities (using *low* albite volume-entropies in Table 5) may result from the use of recrystallized gels as starting materials (Boettcher and Wyllie, 1969), synthetic high albite (Johannes *et al.,* 1971) or sluggish kinetics and impurities in addition to disorder problems with natural materials (Newton and Kennedy, 1968; Newton and Smith, 1967; Essene, Boettcher and Furst, 1972). The average value for $\Delta G_r(298,1)$ ⟨4⟩ from the calculations (using *low* albite) is $+2.005 \pm 0.7$ kcal. The value from the data in Table 1 is 2.136 ± 0.75 kcal.

Hlabse and Kleppa (1968) measured $\Delta H^\circ_r(964,1)$ for the reaction of Amelia albite to jadeite plus quartz, by comparison of $\Delta H_{\mathrm{soln}}(964,1)$ in a $2PbO{:}B_2O_3$ melt. They obtained a value of $\Delta H^\circ_r(964,1) = +0.27 \pm 0.5$ kcal, which they extrapolated to 298 K giving $\Delta H^\circ_r(298,1) = -0.66 \pm 0.50$ kcal. Using $T\Delta S^\circ_{298} = -2.51$, they estimate $\Delta G^\circ_r(298,1)$ as $+1.850$ (± 0.50 ?) kcal. Thus the three values for $\Delta G^\circ_r(298,1)$ ⟨4⟩ are compatible well within quoted limits of error.

There exists a relation between the difference functions calculated above.

$$\begin{aligned} &G^\circ_f(298,1)[\mathrm{Jd}] - G^\circ_f(298,1)[\mathrm{Anc}] \\ &\quad - G^\circ_f(298,1)[\mathrm{Ab}] - G^\circ_f(298,1)[\mathrm{Anc}] \\ &\quad = G^\circ_f(298,1)[\mathrm{Jd}] - G^\circ_f(298,1)[\mathrm{Ab}] \end{aligned} \tag{7}$$

or

$$C - D = B \tag{7'}$$

With the results in Tables 3, 4, and 5, using values for low albite we have

$$\begin{aligned} C &= +\ 58.114 \pm 0.6 \ \text{kcal} \\ -D &= -146.993 \pm 0.55\ \text{kcal} \\ \hline B &= +205.047 \pm 1.1 \ \text{kcal} \end{aligned}$$

which is about 2.4 kcal more negative than the calculated average values for B (using low albite) of -202.640 ± 0.7 kcal. However, the value so obtained for B using low albite comes very close to the value for B calculated for reaction ⟨4⟩ using analbite as shown in Table 5. The difference to the function D from equilibrium ⟨2⟩ using analbite instead of low albite is only some 250 cals. Since C does not involve albite, it is suggested that this difference results from variation in $G^\circ(T,P)$[Anc], due probably to analcime solid-solutions, Al/Si disorder (or polymorphism) in analcime or loss of H_2O from the analcime structure at elevated pressure. Different structural states of jadeite with analcime in reaction ⟨3⟩ and albite with analcime in reaction ⟨2⟩ may produce discrepancies in the function $G^\circ_f(298,1)$ [Jd] $-$ $G^\circ_f(298,1)$[Ab] as a function of temperature.

It could be suggested that the discrepancy results from an incorrect value of $G^\circ_f(298,1)$[low albite] in Table 1. This cannot be stated with certainty at this point since the values of $G^\circ_f(298,1)$[Jd] and $G^\circ_f(298,1)$[Ab] are tied through the function B.

Analcime free-energy.

Thus far difference functions have been presented since they should need revision only if better reversed experimental data become available. It is of interest to compare values of $G^\circ_f(298,1)$[Anc] calculated from the difference functions using the currently available Gibbs energy values for albite, nepheline, jadeite, quartz, as shown in Table 1.

By *assuming* that nepheline and albite in equilibrium with analcime are pure phases (that is using the values in Table 1) and that the stable analcime at the equilibrium condition has composition and state of order corresponding to the sample on which Barany (1962) measured heat of solution, we may calculate values for $G^\circ_f(298,1)$[Anc] for the cases of low albite and analbite being stable. Using the data in Tables 1 and 2, the values for $G^\circ_f(298,1)$ [Anc] may be calculated (in kcal mol^{-1})

Experimental data	(using low albite)	(using analbite)
Liou (1971)	-736.002 ± 1.5	-736.520 ± 1.5
Greenwood (1961)	-735.899 ± 2.0	-736.362 ± 2.0
Kim and Burley (1971)	-736.226 ± 1.9	-736.857 ± 1.9

Analysis of the (stable?) analcime in equilibrium with albite and nepheline show that it is silica (and H_2O) deficient relative to 1:2:1 analcime. It is certain that $G^\circ_f(298,1)$[Anc] would be expected to vary for the composition of the analcime. At the equilibrium for reaction ⟨1⟩ the silica and H_2O deficient analcime would have a more negative G_f than 1:2:1 analcime at the same conditions. Here the 1:2:1 analcime would be metastable relative to silica-H_2O deficient analcime plus albite.

Similarly for the data for reaction ⟨2⟩ and assumptions as above and in Tables 1 and 3 values for $G^\circ_f(298,1)$[Anc] may be calculated (in kcal mol^{-1})

Experimental data	(using low albite)	(using analbite)
Campbell and Fyfe (1965)	−738.489 ± 1.8	
Thompson (1971)	−737.055 ± 1.2	
Liou (1971)	−737.298 ± 1.2	−735.750 ± 1.2

The values from Campbell and Fyfe's (1965) data is significantly more negative than that from Thompson's (1971) data. The value from Liou's (1971) data probably lies nearer to the more negative (low albite) value, since he estimates 30 percent disorder based on $2\theta_{131-\bar{1}31}$ peak separation.

The use of Manghnani's (1970) data for reaction ⟨3⟩ and the values from Tables 1 and 4 allow further calculation of $G^\circ_f(298,1)$[Anc]. A value of −735.320 ± 1.6 kcal mol^{-1} is obtained from the average value of C. The values for the 400 and 450°C brackets are −735.251 ± 1.5 and −735.20 ± 1.5 respectively.

The values for $G^\circ_f(298,1)$[Anc] calculated from the difference functions and the data in Table 1 are summaried in Table 6.

Discussion

Effects of the calculated Analcime Gibbs Energy on other thermodynamic quantities.

As outlined above, the calculated $G^\circ_f(298,1)$ [Anc] are as much as 4.2 kcal more negative than the tabulated value (−734.267 ± 0.88 kcal mole^{-1}). What effect will the calculated values have on the calculated $G^\circ_r(298,1)$ ⟨2⟩? Using the tabulated values for low albite, quartz and liquid H_2O and G°_f[Anc] = −735.201 ± 1.1 (Manghnani's data) and −737.053 ± 0.9 (Thompson's data), we obtain for $\Delta G^\circ_r(298,1)$ ⟨2⟩ values of −0.829 ± 2.0 and +1.023 ± 1.8 kcal, respectively. The latter figure implies analcime plus quartz more stable (as shown experimentally) than low albite plus liquid H_2O.

If the calculated values from phase equilibrium data are reasonable, and we certainly have confidence in the tabulated values for quartz and liquid H_2O, this may imply some error in the tabulated values for G°_f[low Ab]. This statement cannot be made without further qualification since the value of G°_f [Anc] determined for reaction ⟨2⟩ is *tied* to the tabulated value for low albite. Similarly a comparison of G°_f[Anc] from reactions ⟨3⟩ and ⟨1⟩ must acknowledge that G°_f[Jd] and G°_f[Ab] are tied values.

Even if the H°_f[Ab] and H°_f[Anl] values as tabulated are accurate, errors could result from any configurational entropy contribution. An increase in the tabulated entropy from a consideration of configurational contributions would result in *more negative* G°_f[Ab], G°_f[Anl], for the same value of enthalpy of formation.

Internally consistent values for Gibbs energy of low albite, analcime, jadeite.

If we assume that the free energies calculated from the difference functions represent internally consistent sets, we may examine the tabulated values of Gibbs energy of low albite, jadeite, analcime (in kcal mol^{-1})

TABLE 6. Comparison of Calculated G°_f (298,1) [Anc] from the Various Reactions[a]

(using low albite) (kcal mol^{-1})	(using analbite) (kcal mol^{-1})	(using jadeite) (kcal mol^{-1})	Reference[b]
Reaction <1> analcime = ½albite + ½nepheline + H_2O			
-736.002 ± 1.5	-736.520 ± 1.5		L
-735.899 ± 2.0	-736.362 ± 1.5		G
-736.226 ± 2.1	-736.857 ± 2.1		K
Reaction <2> analcime + quartz = albite + H_2O			
-738.489 ± 1.5			CF
-737.055 ± 0.9			T
-737.298 ± 0.9	-735.750 ± 0.9		L
Reaction <3> analcime = jadeite + H_2O			
		-735.320 ± 1.1	M

[a] calculated using tabulated values in Robie and Waldbaum (1968, see Table 1).

[b] sources: L--Liou (1971), G--Greenwood (1961), K--Kim and Burley (1971), CF--Campbell and Fyfe (1965), T--Thompson (1971), M--Manghnani (1970).

a) Use of the tabulated G°_f[Ab] = -883.988 ± 0.76
and using D for reaction ⟨2⟩ = -146.933 ± 0.55
we obtain G°_f[Anc] = -737.055 ± 1.2
and using B for reaction ⟨4⟩ = $+202.640 \pm 0.7$
we obtain G°_f[Jd] = -681.348 ± 1.3

b) Use of the tabulated G°_f[Jd] = -677.206 ± 1.01
and using C for reaction ⟨3⟩ = $+\ 58.114 \pm 0.6$
we obtain G°_f[Anc] = -735.320 ± 1.7
and using B for reaction ⟨4⟩ = -202.640 ± 0.7
we obtain G°_f[Ab] = -879.864 ± 1.7

c) Use of the tabulated G°_f[Anc] = -734.262 ± 0.88
and using C for reaction ⟨3⟩ = $+\ 58.114 \pm 0.6$
we obtain G°_f[Jd] = -676.148 ± 1.3
and using D for reaction ⟨2⟩ = -146.933 ± 0.55
we obtain G°_f[Ab] = -881.195 ± 1.3

Thus definite discrepancies exist between the difference functions and the tabulated values of the phases. Both sets of calculations in a) and b) above indicate that G°_f[Anc] should be more negative by some 1 to 2.5 kcal mol^{-1}. Similarly the calculations in sets b) and c) imply that G°_f[Ab] may be in error by some 1.8 to 4.1 kcal mol^{-1}. However, since the values are *tied* through the difference functions, the individual discrepancies may lie at the lower end of these ranges.

Summary

Recent reversed equilibrium studies for reactions involving analcime, albite, jadeite, nepheline, quartz and H_2O have been used to derive difference functions involving $G^\circ_f(298,1)$[Anc]. These difference functions should need little revision (unless more precise experimental data than used in the calculations become available). If future calorimetric investigations provide more accurate data for *any one of these phases*, the G°_f for the others are calculable from the functions tabulated in this study. When accurate calorimetric data become available for two or more of these phases, the G°_f[Anl] and G°_f[Ne] may be evaluated from the tabulated functions. In addition, the ΔG associated with analcime solid solutions may be evaluated.

No particular significance is attached to the values for Gibbs energy of the phases (related through the difference functions) calculated by evaluation of the functions, but the order of magnitude of possible discrepancies in the tabulated values for G°_f[Ab], G°_f[Anl], G°_f[Jd], G°_f[Anc] are suggested.

Acknowledgments

Thorough and perceptive reviews by David R. Waldbaum and E-an Zen significantly improved the manuscript.

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Manuscript received, June 12, 1972; accepted for publication, October 25, 1972.