

Gibbs Free Energies of Formation Calculated from Dissolution Data Using Specific Mineral Analyses. II. Plagioclase Feldspars

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Abstract

Gibbs free energies of formation (ΔG°_f) for plagioclase feldspars, albite, oligoclase, labradorite, bytownite, and anorthite were calculated from the dissolution in aqueous solutions, using (a) the actual mineral formulas derived from the chemical analyses of the specific mineral samples, and (b) the ideal structural formulas of the minerals. Results with ΔG°_f in kcal/mole were: albite, $Ab_{95}An_5Or_4$, -897.1 ; albite, $Ab_{99}An_1$, -894.7 ; oligoclase, $Ab_{76}An_{24}Or_7$, -910.3 ; oligoclase, $Ab_{80}An_{20}$, -906.8 ; labradorite, $Ab_{50}An_{50}Or_{11}$, -930.9 ; labradorite, $Ab_{52}An_{48}$, -928.5 ; bytownite, $Ab_{30}An_{70}Or_3$, -948.5 ; bytownite, $Ab_{31}An_{69}$, -942.7 ; anorthite, $Ab_{12}An_{88}Or_2$, -959.4 , and anorthite, $Ab_{12}An_{88}$, -957.7 .

The Gibbs free energy of formation for a high K-plagioclase ($Ab_{14}Or_{86}$) was also calculated to be -896.4 kcal/mole.

Introduction

Supplementing the calculation of Gibbs free energies of formation (ΔG°_f) for primary rock-forming silicate minerals (Huang and Keller, 1972), this paper presents the calculation of ΔG°_f for a series of plagioclase minerals from aqueous dissolution data.

Laboratory Work

Three grams (3.00 gm) each of freshly fractured albite, oligoclase, labradorite, bytownite, anorthite, and a high-K variety of plagioclase in particle size between 44 μm and 150 μm were equilibrated at room temperature in deionized water for periods up to 24 days. The detailed experimental procedure and analytical results have been published in a paper by Huang and Kiang (1972). The results of the laboratory dissolution show that the dissolution of major cations (Si, Al, Ca, and Na) from the plagioclase minerals increased very rapidly within the first 24 hours, slowed down between the period of one day and six days, and then reached near saturation after 24 days. Although complete equilibrium cannot be established, the cation concentrations at 24 days dissolution may be taken as "apparently" equilibrated concentrations, and the solubilities (K_s) calculated from these concentrations then represent "apparent" solubilities.

Methods of Calculation

The detailed steps and assumptions for the calculation of ΔG°_f from the laboratory dissolution data were given in a paper by Huang and Keller (1972). These include the following:

(1) *Species in the Equilibrium Solution.* It is possible to calculate, if chemical equilibrium is assumed, the proportion of each dissolved species of a specific element in the system, where certain species are assumed more likely to be present in the system. The equilibrium concentration (Huang and Keller, 1972) of each species in the systems was calculated (1) from the pH of the solution; (2) from the concentration of each cation in the solution in which Si, Al, Fe, Mg, Ca, K, and Na were determined and reported as moles/liter as in an earlier paper (Huang and Kiang, 1972); and (3) using the constants of hydrolysis and dissociation obtained from Sillén and Martell (1964). The validity of the calculation is based on the law of mass action (Butler, 1964). The results of the calculation of each Al, Fe, Mg, Ca species from the dissolution of plagioclase are shown in Table 2.

(2) *Activities.* Using the Debye-Hückel method, ions in the solution were computed on an IBM 360/65 electronic computer.

(3) *Mineral formulas.* The actual mineral for-

mulas, as determined for each plagioclase feldspar from bulk analyses published earlier (Table 1, Huang and Kiang, 1972), were used in calculation of ΔG°_f . For comparison, ideal structural formulas were also used in calculation of ΔG°_f .

(4) *Solubility constants (K_s) and Gibbs free energies of formation (ΔG°_f)*. Assuming "apparent" equilibrium in the systems, the solubility constants (K_s) from aqueous dissolution of plagioclase minerals could be calculated from the most probable chemical reactions of the minerals in water. Then, Gibbs free energies of formation for the minerals (ΔG°_f) can be calculated from the following two relationships: (1) ΔG°_r (Gibbs free energies of reaction) = $-1.364 \log K_s$ (Nernst equation), and (2) $\Delta G^\circ_r = \sum \Delta G^\circ_f$ (products) - $\sum \Delta G^\circ_f$ (reactants), using known Gibbs free energies of formation for other species in equation (2) (Table 1).

Results

(A) ΔG°_f based on aqueous solubility data

The analytical data and calculated activities for the dissolution of the plagioclase minerals are listed in Table 2. Table 3 summarizes the reactants and the assumed products of dissolution calculated for both specific and ideal mineral formulas. Points worthy of note are as follows:

TABLE 1. Gibbs Free Energies of Formation Used in Calculation of ΔG°_f

Species	G°_f kcal/mole	Source
H ₄ SiO ₄	-312.8	Reesman and Keller (1965)
Al ³⁺	-115.0	Rossini et al (1952)
Al(OH) ²⁺	-164.9	Raupach (1963)
Al(OH) ₂ ⁺	-216.1	Reesman et al (1969)
Al(OH) ₄ ⁻	-311.3	Reesman et al (1952)
Fe ²⁺	-20.30	Rossini et al (1952)
Fe(OH) ⁺	-52.58	Huang and Keller (1972)
Fe(OH) ₂ ²⁺	-55.91	Rossini et al (1952)
Fe(OH) ₂ ⁺	-106.2	Rossini et al (1952)
Mg ²⁺	-108.76	Langmuir (1968)
Mg(OH) ⁺	-149.76	Berner (1971)
Ca ²⁺	-132.35	Langmuir (1968)
Na ⁺	-62.59	Rossini et al (1952)
K ⁺	-67.47	Rossini et al (1952)
OH ⁻	-37.63	Reesman and Keller (1965)
H ₂ O	-56.72	Wicks and Block (1963)

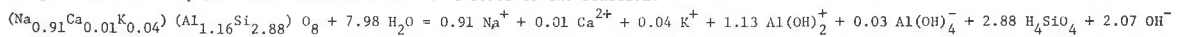
TABLE 2. Analytical Data and Activities of Dissolved Species in the Dissolution of Plagioclase Minerals

Species	Moles/liter	Activity	Log act.
(I) ALBITE			
pH = 5.81; ionic strength = 1.25 x 10 ⁻⁴			
Na ⁺	0.231 x 10 ⁻⁴	0.228 x 10 ⁻⁴	-4.64
K ⁺	0.332 x 10 ⁻⁶	0.328 x 10 ⁻⁶	-6.48
Ca ²⁺	0.548 x 10 ⁻⁴	0.521 x 10 ⁻⁴	-4.28
Al(OH) ₂ ⁺	0.518 x 10 ⁻⁵	0.511 x 10 ⁻⁵	-5.29
Al(OH) ₄ ⁻	0.121 x 10 ⁻⁶	0.119 x 10 ⁻⁶	-6.92
H ₄ SiO ₄	0.166 x 10 ⁻⁴	0.166 x 10 ⁻⁴	-4.78
OH ⁻		10 ^{-8.19}	-8.19
(II) OLIGOCLASE			
pH = 5.83; ionic strength = 1.73 x 10 ⁻⁴			
Na ⁺	0.199 x 10 ⁻⁴	0.196 x 10 ⁻⁴	-4.71
K ⁺	0.703 x 10 ⁻⁵	0.693 x 10 ⁻⁵	-5.16
Ca ²⁺	0.758 x 10 ⁻⁴	0.714 x 10 ⁻⁴	-4.15
Al(OH) ₂ ⁺	0.385 x 10 ⁻⁵	0.379 x 10 ⁻⁵	-5.42
Al(OH) ₄ ⁻	0.126 x 10 ⁻⁶	0.124 x 10 ⁻⁶	-6.91
H ₄ SiO ₄	0.436 x 10 ⁻⁴	0.436 x 10 ⁻⁴	-4.36
OH ⁻		10 ^{-8.17}	-8.17
(III) LABRADORITE			
pH = 6.05; ionic strength = 2.86 x 10 ⁻⁵			
Na ⁺	0.892 x 10 ⁻⁵	0.886 x 10 ⁻⁵	-5.05
K ⁺	0.271 x 10 ⁻⁵	0.269 x 10 ⁻⁵	-5.57
Ca ²⁺	0.103 x 10 ⁻⁴	0.101 x 10 ⁻⁴	-4.99
Al(OH) ₂ ⁺	0.116 x 10 ⁻⁵	0.115 x 10 ⁻⁵	-5.94
Al(OH) ₄ ⁻	0.208 x 10 ⁻⁶	0.207 x 10 ⁻⁶	-6.68
H ₄ SiO ₄	0.229 x 10 ⁻⁴	0.229 x 10 ⁻⁴	-4.64
OH ⁻		10 ^{-7.95}	-7.95
(IV) BYTOWNITE			
pH = 5.95; ionic strength = 5.74 x 10 ⁻⁵			
Na ⁺	0.163 x 10 ⁻⁴	0.161 x 10 ⁻⁴	-4.79
K ⁺	0.332 x 10 ⁻⁶	0.330 x 10 ⁻⁶	-6.48
Ca ²⁺	0.169 x 10 ⁻⁴	0.163 x 10 ⁻⁴	-4.79
Al(OH) ₂ ⁺	0.168 x 10 ⁻⁵	0.167 x 10 ⁻⁵	-5.78
Al(OH) ₄ ⁻	0.163 x 10 ⁻⁶	0.162 x 10 ⁻⁶	-6.79
H ₄ SiO ₄	0.393 x 10 ⁻⁴	0.393 x 10 ⁻⁴	-4.41
OH ⁻		10 ^{-8.05}	-8.05
(V) ANORTHITE			
pH = 5.91; ionic strength = 3.71 x 10 ⁻⁵			
Na ⁺	0.196 x 10 ⁻⁵	0.194 x 10 ⁻⁵	-5.71
K ⁺	0.102 x 10 ⁻⁶	0.102 x 10 ⁻⁶	-6.99
Ca ²⁺	0.116 x 10 ⁻⁴	0.162 x 10 ⁻⁴	-4.79
Al(OH) ₂ ⁺	0.885 x 10 ⁻⁶	0.887 x 10 ⁻⁶	-6.06
Al(OH) ₄ ⁻	0.149 x 10 ⁻⁶	0.148 x 10 ⁻⁶	-6.83
H ₄ SiO ₄	0.280 x 10 ⁻⁴	0.280 x 10 ⁻⁴	-4.55
OH ⁻		10 ^{-8.09}	-8.09
(VI) HIGH-K PLAGIOCLASE			
pH = 5.97; ionic strength = 3.05 x 10 ⁻⁵			
Na ⁺	0.124 x 10 ⁻⁴	0.123 x 10 ⁻⁴	-4.91
K ⁺	0.187 x 10 ⁻⁴	0.186 x 10 ⁻⁴	-4.73
Ca ²⁺	0.474 x 10 ⁻⁵	0.462 x 10 ⁻⁵	-5.34
Al(OH) ₂ ⁺	0.229 x 10 ⁻⁵	0.214 x 10 ⁻⁵	-5.67
Al(OH) ₄ ⁻	0.171 x 10 ⁻⁶	0.170 x 10 ⁻⁶	-6.77
H ₄ SiO ₄	0.180 x 10 ⁻⁴	0.180 x 10 ⁻⁴	-4.74
OH ⁻		10 ^{-8.03}	-8.03

TABLE 3. The Subscripts* (and/or Coefficients) and Calculated ΔG_f° and $\log K_s$ Values for Laboratory Dissolutions of Several Plagioclase Minerals

	Reactants Mineral Formula							Products Assumed for Dissolution							ΔG_f° (kcal/mole)	$\log K_s^{**}$	
	(Na	Ca	K)	(Al	Si)	O+H ₂ O	↔	Na ⁺	Ca ²⁺	K ⁺	+ Al(OH) ₂ ⁺	+ Al(OH) ₄ ⁻	+ H ₄ SiO ₄	+ OH ⁻			
Albite																	
Specific, Ab ₉₅ An ₁ Or ₄	0.91	0.01	0.04	1.16	2.88	8	7.98	±	0.91	0.01	0.04	1.13	0.03	2.88	2.07	-897.1	-41.43
Ideal, Ab ₉₉ An ₁	0.99	0.01	--	1.01	2.99	8	8	±	0.99	0.01	--	0.98	0.03	2.99	1.96	-894.7	-40.36
Oligoclase																	
Specific, Ab ₇₅ An ₁₈ Or ₇	0.70	0.17	0.06	1.44	2.64	8	7.99	±	0.70	0.17	0.06	1.39	0.05	2.64	2.44	-910.3	-43.64
Ideal, Ab ₈₀ An ₂₀	0.80	0.20	--	1.20	2.80	8	8	±	0.80	0.20	--	1.15	0.05	2.80	2.30	-906.8	-42.18
Labradorite																	
Specific, Ab ₅₀ An ₄₆ Or ₄	0.47	0.43	0.04	1.74	2.34	8	7.97	±	0.47	0.43	0.04	1.48	0.26	2.34	2.59	-930.9	-46.72
Ideal, Ab ₅₂ An ₄₈	0.52	0.48	--	1.48	2.52	8	8	±	0.52	0.48	--	1.26	0.22	2.52	2.52	-928.5	-45.70
Bytownite																	
Specific, Ab ₃₀ An ₆₇ Or ₃	0.31	0.70	0.03	1.87	2.15	8	7.97	±	0.31	0.70	0.03	1.70	0.17	2.15	3.27	-948.5	-51.80
Ideal, Ab ₃₁ An ₆₉	0.31	0.69	--	1.69	2.31	8	8	±	0.31	0.69	--	1.54	0.15	2.31	3.08	-942.7	-49.69
Anorthite																	
Specific, Ab ₁₂ An ₈₆ Or ₂	0.12	0.85	0.02	2.07	1.97	8	7.96	±	0.12	0.85	0.02	1.76	0.31	1.97	3.29	-959.4	-53.27
Ideal, Ab ₁₂ An ₈₈	0.12	0.88	--	1.88	2.12	8	8	±	0.12	0.88	--	1.60	0.28	2.12	3.20	-957.7	-52.06
High-K plagioclase ***																	
Specific, Ab ₄₄ Or ₅₆	0.42	--	0.53	1.11	2.92	8	7.98	±	0.42	--	0.53	1.03	0.08	2.92	1.90	-896.4	-40.05
Ideal, Ab ₄₄ Or ₅₆	0.44	--	0.56	1	3	8	8	±	0.44	--	0.56	0.93	0.07	3	1.86	-896.9	-39.71

* Example: The subscript/coefficient numbers of line 1 refer to the reaction:



** Example of calculation: for albite (Ab₉₅An₁Or₄) $K_s = [\text{Na}^+]^{0.91} [\text{Ca}^{2+}]^{0.01} [\text{K}^+]^{0.04} [\text{Al}(\text{OH})_2^+]^{1.13} [\text{Al}(\text{OH})_4^-]^{0.03} [\text{H}_4\text{SiO}_4]^{2.88} [\text{OH}^-]^{2.07}$

Then, $\log K_s = -41.43$ ΔG_f° (products) - $\Sigma \Delta G_f^\circ$ (reactants) = $-840.63 - \Delta G_f^\circ$ (albite)

$\Delta G_f^\circ = -1.364 \log K_s$ ΔG_f° (albite, Ab₉₅An₁Or₄) = $-840.63 + 1.364 \log K_s = -897.1$ kcal/mole

*** A specimen purchased as and labelled "andesine" proved to be a high-K variety of plagioclase by bulk chemical analyses. Laboratory dissolution data (Huang and Keller, 1972) are in accord with this composition.

(1) The difference in ΔG_f° for albite by the two calculations (Table 3) is 2.4 kcal/mole. The ΔG_f° (-894.7 kcal/mole) for albite (Ab₉₉An₁) in terms of the ideal structural formula, however, is smaller than the value obtained by Waldbaum (1966) for low albite (Ab₁₀₀) ($\Delta G_f^\circ = -884.0$ kcal/mole). The presence of one mole percent of CaAl₂Si₂O₈ in our albite sample could significantly affect the ΔG_f° .

(2) Our data on ΔG_f° for labradorite in terms of the specific mineral formula or the ideal structural formula (Table 3) lie just between the values for oligoclase and the labradorite (Ab₄₀An₅₉Or₁ = -932.4 kcal/mole, or Ab₄₀An₆₀ = -932.1 kcal/mole) reported by Huang and Keller (1972). This adds confidence to the validity of the dissolution method used for the calculation of ΔG_f° .

(3) The difference in ΔG_f° for the two bytownite calculations is 5.8 kcal/mole, which might become

significant in determining stabilities of minerals in some geologic systems.

(4) Our data on ΔG_f° for anorthite is lower than the reported data of -955.6 kcal/mole for anorthite (An₁₀₀) by Barany (1962).

(5) The value for high-K plagioclase (-896.4 or -896.9 kcal/mole) lies just between the value for albite (Ab₉₅An₁Or₄, or -887.3 kcal/mole, this study) and that for microcline (Ab₂₅Or₆₈An₇, -887.3 kcal/mole, or Or₁₀₀, ideal, -892.6 kcal/mole, Huang and Keller, 1972). Our ΔG_f° for this "high-K plagioclase" specimen indicates that the mineral is not andesine; if the sample were andesine, its ΔG_f° should lie between -910.3 for oligoclase and -930.9 kcal/mole for labradorite.

(B) ΔG_f° based on equilibrium with secondary phase

The results of analyses in Table 2 show that the concentration of Al in the solution is less than that

TABLE 4. Summary of ΔG°_f Calculated on the Basis of Equilibrium with Secondary Phase

	Reactants Mineral Formula							Products Assumed for Dissolution							ΔG°_f ** (kcal/mole)		
	(Na)	Ca	K)	(Al	Si)	O + H ₂ O	↔	Na ⁺	Ca ²⁺	K ⁺	+ Al(OH) ₂ ⁺	+ Al(OH) ₄ ⁻	+ H ₄ SiO ₄	+ OH ⁻		+ Al(OH) ₃	
Albite																	
Specific, Ab ₉₅ An ₁ Or ₄	0.91	0.01	0.04	1.16	2.88	8	7.98	↔	0.91	0.01	0.04	0.89	0.02	2.88	1.84	0.25	-897.0*
Ideal, Ab ₉₉ An ₁	0.99	0.01	--	1.01	2.99	8	8	↔	0.99	0.01	--	0.91	0.03	2.99	1.89	0.07	-894.7
Oligoclase																	
Specific, Ab ₇₅ An ₁₈ Or ₇	0.70	0.17	0.06	1.44	2.64	8	7.99	↔	0.70	0.17	0.06	0.23	0.01	2.64	1.32	1.20	-909.1
Ideal, Ab ₈₀ An ₂₀	0.80	0.20	--	1.20	2.80	8	8	↔	0.80	0.20	--	0.24	0.01	2.80	1.43	0.95	-905.9
Labradorite																	
Specific, Ab ₅₀ An ₄₆ Or ₄	0.47	0.43	0.04	1.74	2.34	8	7.97	↔	0.47	0.43	0.04	0.12	0.02	2.34	1.47	1.60	-928.9
Ideal, Ab ₅₂ An ₄₈	0.52	0.48	--	1.48	2.52	8	8	↔	0.52	0.48	--	0.13	0.02	2.52	1.59	1.33	-926.8
Bytownite																	
Specific, Ab ₃₀ An ₆₇ Or ₃	0.31	0.70	0.03	1.87	2.15	8	7.97	↔	0.31	0.70	0.03	0.09	0.01	2.15	1.82	1.77	-946.4
Ideal, Ab ₃₁ An ₆₉	0.31	0.69	--	1.69	2.31	8	8	↔	0.31	0.69	--	0.10	0.01	2.31	1.78	1.58	-940.8
Anorthite																	
Specific, Ab ₁₂ An ₈₆ Or ₂	0.12	0.85	0.02	2.07	1.97	8	7.96	↔	0.12	0.85	0.02	0.06	0.01	1.97	1.89	2.00	-956.2
Ideal, Ab ₁₂ An ₈₈	0.12	0.88	--	1.88	2.12	8	8	↔	0.12	0.88	--	0.07	0.01	2.12	1.94	1.80	-956.6
High-K plagioclase																	
Specific, Ab ₄₄ Or ₅₆	0.42	--	0.53	1.11	2.92	8	7.98	↔	0.42	--	0.53	0.34	0.03	2.92	1.26	0.74	-895.6
Ideal, Ab ₄₄ Or ₅₆	0.44	--	0.56	1	3	8	8	↔	0.44	--	0.56	0.35	0.03	3	1.32	0.62	-896.2

* Example of calculation: for albite (Ab₉₅An₁Or₄) $K_s = [Na^+]^{0.91} [Ca^{2+}]^{0.01} [K^+]^{0.04} [Al(OH)_2^+]^{0.89} [Al(OH)_4^-]^{0.02} [H_4SiO_4]^{2.88} [OH^-]^{1.84}$
 Then, $\log K_s = -38.21$ ΔG°_f (products) - ΔG°_f (reactants) = $-844.84 - \Delta G^\circ_f$ (albite)
 $\Delta G^\circ_f = -1.364 \log K_s$ ΔG°_f (albite, Ab₉₅An₁Or₄) = $-844.84 + 1.364 \log K_s = -897.0$ kcal/mole.

** ΔG°_f calculated on the basis of equilibrium with secondary amorphous aluminum hydroxide ($\Delta G^\circ_f = -271.3$ kcal/mole).

TABLE 5. Comparison of ΔG°_f Obtained from Different Calculations

	ΔG°_f based on aqueous solubility data		ΔG°_f based on equilibrium with secondary phase*			
	A	B	C	D	E	F
Albite						
Specific, Ab ₉₅ An ₁ Or ₄	-897.1	-897.0	-897.2	-897.6	-897.9	
Ideal, Ab ₉₉ An ₁	-894.7	-894.7	-894.7	-894.8	-894.9	
Oligoclase						
Specific, Ab ₇₅ An ₁₈ Or ₆	-910.3	-909.1	-910.3	-912.2	-913.9	
Ideal, Ab ₈₀ An ₂₀	-906.8	-905.9	-906.8	-908.3	-909.7	
Labradorite						
Specific, Ab ₅₀ An ₄₆ Or ₄	-930.9	-928.9	-930.5	-933.0	-935.3	
Ideal, Ab ₅₂ An ₄₈	-928.5	-926.8	-928.2	-930.3	-932.1	
Bytownite						
Specific, Ab ₃₀ An ₆₇ Or ₃	-948.5	-946.4	-948.1	-951.0	-953.4	
Ideal, Ab ₃₁ An ₆₉	-942.7	-940.8	-942.3	-944.9	-947.1	
Anorthite						
Specific, Ab ₁₂ An ₈₆ Or ₆	-959.4	-956.2	-958.2	-961.4	-964.2	
Ideal, Ab ₁₂ An ₈₈	-957.7	-956.6	-958.4	-961.3	-963.8	
High-K plagioclase						
Specific, Ab ₄₄ Or ₅₆	-896.4	-895.6	-896.4	-897.5	-898.6	
Ideal, Ab ₄₄ Or ₅₆	-896.9	-896.2	-896.8	-897.8	-898.7	

* A: equilibrium with amorphous Al(OH)₃
 B: equilibrium with microcrystalline gibbsite
 C: equilibrium with gibbsite ($\Delta G^\circ_f = -273.9$ kcal/mole)
 D: equilibrium with gibbsite ($\Delta G^\circ_f = -275.3$ kcal/mole)

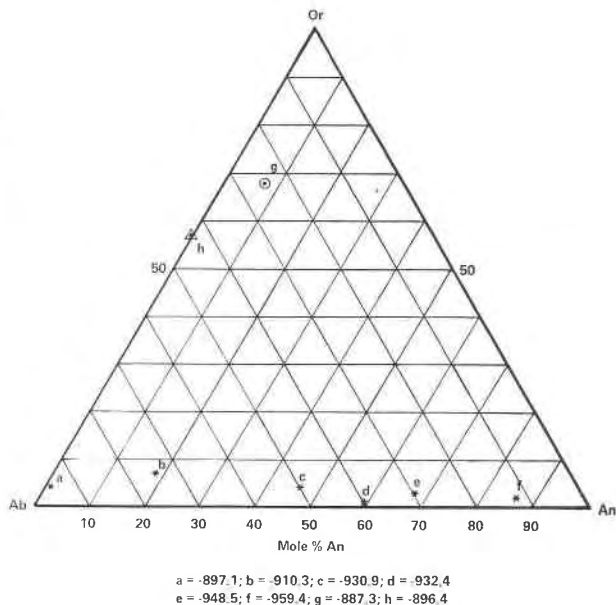


FIG. 1. Triangular diagram showing the ΔG°_f (kcal/mole) for the plagioclases and K-feldspars. The value, -887.3 kcal/mole, for microcline (g) is obtained from Huang and Keller (1972).

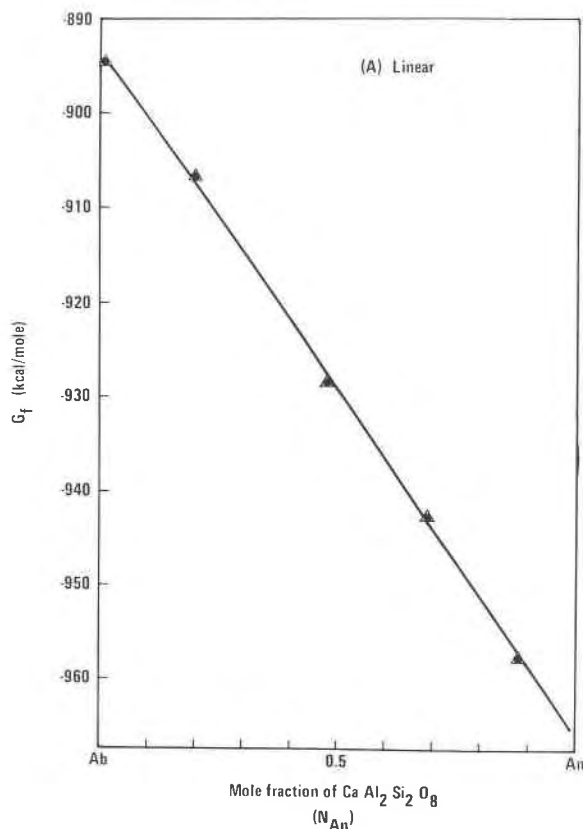


FIG. 2a. The best linear curve for five experimentally determined ΔG°_f as a function of mole fraction (N_{An}) of $CaAl_2Si_2O_8$. The linear equation is $\Delta G^\circ_f = -893.24 - 0.726 N_{An}$.

of Si with respect to its mineral formula, suggesting that secondary Al-phase could be formed during the dissolution of plagioclase feldspar. Thus, secondary phase, such as amorphous aluminum hydroxide ($\Delta G^\circ_f = -271.3$ kcal/mole, Feitknecht and Schindler, 1963), microcrystalline gibbsite ($\Delta G^\circ_f = -272.3$ kcal/mole, Hem and Roberson, 1967), or gibbsite ($\Delta G^\circ_f = -273.9$ kcal/mole, Latimer, 1952; $\Delta G^\circ_f = -275.9$ kcal/mole, Parks, 1972), may be assumed in the equilibrium equation from which ΔG°_f for plagioclase is calculated. The results of ΔG°_f from such calculations are shown in Table 4.

As shown in Table 5, ΔG°_f calculated on the basis of equilibrium with secondary phase (amorphous $Al(OH)_3$, microcrystalline gibbsite, or gibbsite) are somewhat different from ΔG°_f calculated from aqueous solubility data.

Discussion and Conclusions

1) In Figure 1 are plotted the Gibbs free energies of formation for plagioclase minerals of specific mineral formulas (data taken from Table 3) in terms of Ab (albite), An (anorthite), and Or (microcline). There is a consistent decrease of ΔG°_f from Na-rich (albite) to Ca-rich (anorthite) plagioclase minerals. Specific values in the trend are subject to solid-solution and other compositional effects.

2) The Gibbs free energies of formation (ΔG°_f) of ideal mineral formulas (data taken from Table 3) are also plotted against mole fraction of $CaAl_2Si_2O_8$ (N_{An}) in linear, quadratic, and cubic equations in Figures 2 (a), (b), and (c) respectively. Statistical analyses of polynomial regression of ΔG°_f , Table 6, shows that at the 1 percent level, the linear or quadratic relationship between ΔG°_f and N_{An} is highly significant. The cubic relationship, however, is not significant at the 1 percent level, but is significant at the 5 percent level.

3) The Gibbs free energy of formation for a

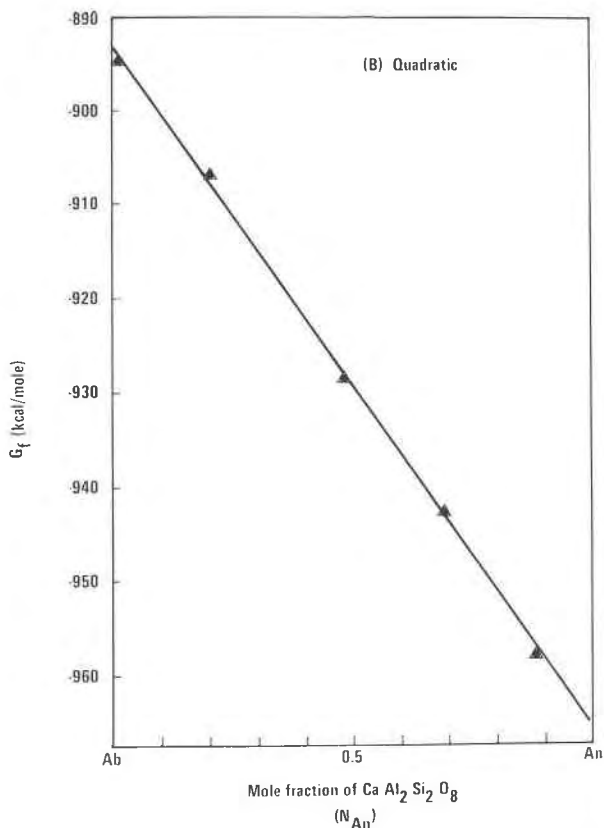


FIG. 2b. The best quadratic curve for five experimentally determined ΔG°_f as a function of mole fraction (N_{An}) of $CaAl_2Si_2O_8$. The quadratic equation is $\Delta G^\circ_f = -893.70 - 0.683 N_{An} - 0.00048 (N_{An})^2$.

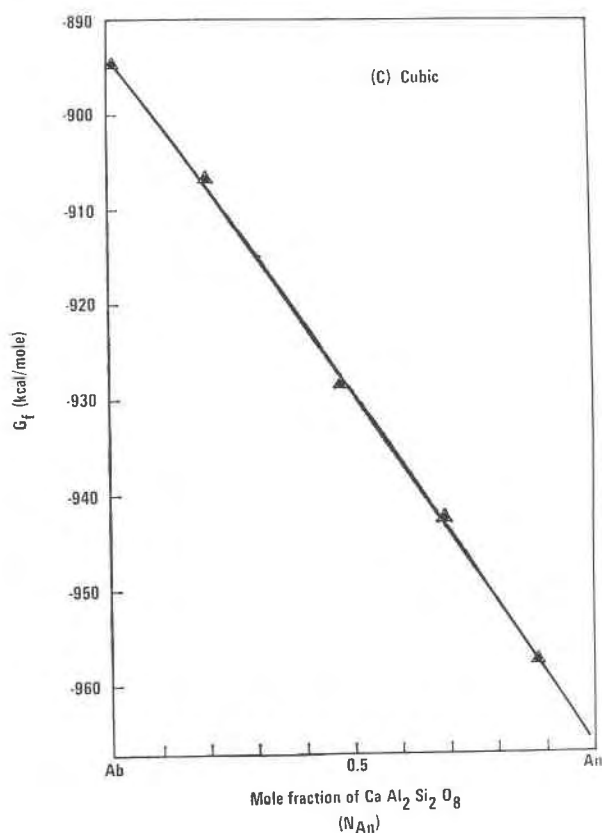


FIG. 2c. The best cubic curve for five experimentally determined ΔG°_f as a function of mole fraction (N_{An}) of $CaAl_2Si_2O_8$. The cubic equation is $\Delta G^\circ_f = -893.88 - 0.640 N_{An} - 0.00179 (N_{An})^2 + 0.00001 (N_{An})^3$.

plagioclase mineral of specific mineral formula is always a smaller negative quantity of ΔG°_f than for that of an ideal structural formula, as shown in Table 7.

4) The values of ΔG°_f calculated from dissolution data of specific mineral samples are subject to *uncertainties* and possible sources of error in (a) bulk chemical analysis of the mineral sample from which the specific mineral formula is calculated; (b) the solution analysis; (c) the ΔG°_f of ions used in the calculation; (d) the computed specific mineral formula used in calculation of ΔG°_f ; and (e) the establishment of complete equilibrium in the laboratory dissolution of minerals (Huang and Keller, 1972). The facts that our ΔG°_f calculated from dissolution data lie between the two end-membered values of albite and anorthite, and that there is a consistent decrease in ΔG°_f from Na-rich to Ca-rich plagioclase, suggest that the possible errors tend to compensate one another, and add confidence to the validity of our calculation.

TABLE 6. Polynomial Regression Analysis of Gibbs Free Energies of Formation (ΔG°_f) for Plagioclase Feldspars

Analysis of Variance			
Degree of freedom	Sum of squares	Mean square	
<u>The best linear equation</u>			
$\Delta G^\circ_f = -893.24 - 0.726 N_{An}$			
Regression	1	2632.27	2632.27
Residual	3	6.04	2.01
F = 1305.67 (1,3)			
F _{1%} (1,3) = 34.12			
F _{5%} (1,3) = 10.13			
<u>The best quadratic equation</u>			
$\Delta G^\circ_f = -893.70 - 0.683 N_{An} - 0.00048 (N_{An})^2$			
Regression	2	2636.64	1318.32
Residual	2	1.67	0.83
F = 1570.85 (2,2)			
F _{1%} (2,2) = 99.00			
F _{5%} (2,2) = 19.00			
<u>The best cubic equation</u>			
$\Delta G^\circ_f = -893.88 - 0.640 N_{An} - 0.00179 (N_{An})^2 + 0.00001 (N_{An})^3$			
Regression	3	2636.79	878.93
Residual	1	1.53	1.53
F = 572.04 (3,1)			
F _{1%} (3,1) = 5403			
F _{5%} (3,1) = 216			

TABLE 7. Comparison of Gibbs Free Energies of Formation for Plagioclase Feldspars (kcal/mole)

Mineral*	Experimental ΔG°_f	Others
Albite		
a ($Ab_{95}An_1Or_4$)	-897.1	-884.0 (Ab_{100})
b ($An_{99}An_1$)	-894.7	(Waldbaum, 1966)
Oligoclase		
a ($Ab_{75}An_{18}Or_7$)	-910.3	
b ($Ab_{80}An_{20}$)	-906.8	
Labradorite		
a ($ab_{50}An_{46}Or_4$)	-930.9	-932.4 ($Ab_{40}An_{59}Or_1$)**
b ($Ab_{52}An_{48}$)	-928.5	-931.1 ($Ab_{40}An_{60}$)**
Bytownite		
a ($Ab_{30}An_{67}Or_3$)	-948.5	
b ($Ab_{31}An_{69}$)	-942.7	
Anorthite		
a ($Ab_{12}An_{86}Or_2$)	-959.4	-955.6 (An_{100})
b ($Ab_{12}An_{88}$)	-957.7	(Barany, 1962)
High-K plagioclase		
a ($Ab_{44}Or_{56}$)	-896.4	
b ($Ab_{44}Or_{56}$)	-896.9	

* a: Specific mineral formula, b: Ideal structural formula
 ** Huang and Keller (1972)

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