On the thermodynamic data of kaolinite

ALEY EL-DIN K. EL-SHAZLY

Department of Earth Sciences, Sultan Qaboos University, P.O. Box 36, Al-Khod, Sultanate of Oman

ABSTRACT

Phase equilibria in the system NASH calculated using Berman's (1988) data base are inconsistent with field and petrological data on the stability of paragonite and the assemblage albite + kaolinite. This inconsistency appears to result from erroneous values for entropy and enthalpy for kaolinite. Although the entropy value of 203.7 J/(mol·K) in Berman's (1988) data base is based on some calorimetric measurements, it is ~15 J/(mol·K) greater than values derived by various summation methods. Using a set of experimental and empirical constraints, it is possible to derive by mathematical programming an entropy of 187.46 J/(mol·K) and a corresponding enthalpy of 4129.92 kJ/mol, values that are very close to estimates obtained by oxide summation methods. These values are therefore consistent with most available experimental data involving kaolinite and produce phase diagrams that are also consistent with geological observations. The discrepancy between most calorimetrically based entropies and values derived by oxide summation methods is attributed to impurities of amorphous $Al(OH)_3$ in the samples used for calorimetry.

INTRODUCTION

Kaolinite is an important clay mineral that is common in the weathering, diagenetic, hydrothermal, and very low-grade metamorphic environments. Despite its economic importance, the stability relations and thermodynamic properties of this mineral are not well understood. Because only a few equilibria involving kaolinite have been investigated experimentally, thermodynamic data for this mineral included in well-accepted and widely used data bases (e.g., Robie et al., 1978; Helgeson et al., 1978; Berman, 1988) are mainly based on available calorimetric measurements. However, calculation of phase relations in the system Na_2O-Al_2O_3-SiO_2-H_2O (NASH) using such data bases suggests that the assemblage kaolinite + albite is unstable relative to paragonite at P and T as low as 1 bar and 25 °C. Because the assemblage kaolinite + albite is common in diagenetically altered rocks, whereas paragonite is a metamorphic mineral known to be stable at P-T conditions above those of the low anchizone (e.g., Kisch, 1983), thermodynamic data for kaolinite are herein reevaluated.

PREVIOUS WORK

Barany and Kelley (1961) determined the heat of formation of kaolinite by solution calorimetry on two samples from New Mexico and Arkansas. They also measured ΔH_f^0 of dickite and halloysite by the same technique. On the basis of low-temperature calorimetry (50–300 K), which included heat capacity measurements for a kaolinite sample from Georgia, King and Weller (1961) calculated S^0 for kaolinite, dickite, and halloysite at 202.924 ± 1.2, 197.066 ± 1.2, and 203.342 ± 1.2 J/(mol·K), respectively. By combining these entropy values with the

solution-calorimetry results, Barany and Kelley (1961) calculated ΔG_f^0 for all three phases and concluded that such values for kaolinite and dickite were identical within error!

On the basis of differential scanning calorimetric measurements on well-crystallized Georgia kaolinite (KGa-1) between 110 and 300 K, Lipsicas et al. (1986) presented heat capacity data that yield an S_{Kln}^0 value of 183.15 J/(mol·K). On the other hand, by performing a new set of low-temperature (7–380 K) calorimetric measurements on KGa-1, Robie and Hemingway (1991) reproduced, within error, the heat capacity values reported by King and Weller (1961). Accordingly, Robie and Hemingway (1991) questioned the validity of the results of Lipsicas et al. (1986) and concluded that $S_{Kln}^0 = 200.9 ± 0.5$ J/(mol·K).

Experimental studies on the synthesis and stability relations of kaolinite or kaolinite-bearing assemblages have been impeded by the relatively impure and very fine-grained nature of this mineral and its stability over a temperature range at which reaction rates are too slow for lab observations. Nevertheless, Thompson (1970) presented data for the equilibrium

$$Kln + 2Qtz = Prl + H_2O \qquad (1)$$
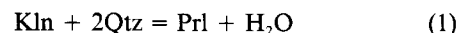
which he derived by monitoring weight changes in quartz crystals in a set of hydrothermal experiments using natural minerals. Chatterjee (1973) was unable to reverse the reaction

$$Kln + Ab = Pg + 2Qtz + H_2O \qquad (2)$$
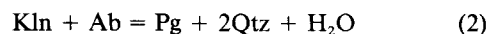
which is believed to be responsible for the first appearance of paragonite in low-grade metamorphic rocks (e.g., Zen, 1960). However, on the basis of unreversed exper-

iments, Chatterjee (1973) attributed the first appearance of paragonite in metamorphic rocks to the fluid-absent reaction

$$3Na\text{-}Mnt + 2Ab = 3Pg + 8Qtz \qquad (3)$$
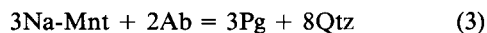
and concluded that this reaction has a steep negative slope in $P\text{-}T$ space and takes place at $T \approx 335\ °C$ at $P = 2$ kbar. By applying Schreinemakers' principles to Equilibria 2 and 3, Chatterjee (1973) constructed a petrogenetic grid for the system NASH in which Reaction 2 has a positive slope in $P\text{-}T$ space and is stable only at pressures higher than those of the stability field of sodium montmorillonite + albite. Hemley et al. (1980) performed several mineral solubility experiments that showed that Reaction 1 takes place at $273 \pm 10\ °C$ at 1 kbar. Using the calorimetric data of Barany and Kelley (1961) and King and Weller (1961), Hemley et al. (1980) derived a thermodynamic data set for kaolinite, which they used to calculate Reaction 1 at higher P and T.

In his compilation of the thermodynamic data of rock-forming minerals, Berman (1988) optimized ΔH_f^0 and S^0 of kaolinite by mathematical programming using as constraints one bracket for Reaction 1 at 5 kbar reported by McPhail (see Berman, 1988) and the calorimetric data of King and Weller (1961). Heat capacity coefficients were derived by the algorithm of Berman and Brown (1985). The results of this optimization are consistent with the data of Hemley et al. (1980) but inconsistent with those of Thompson (1970). On the other hand, Holland and Powell (1990), who derived enthalpy values of rock-forming minerals by least-squares regression analysis of available experimental data after estimating their entropies by the volume-corrected oxide sum method of Holland (1989), did not include data for kaolinite in their data base. Holland and Powell's (1990) decision to exclude kaolinite from their data base was probably influenced by the large difference [14 J/(mol·K)] between the entropy estimated using the oxide sum method of Holland (1989) and the calorimetric values of King and Weller (1961).

From this brief review, it is clear that the thermodynamic data for kaolinite are not very well determined. In particular, several points lead this author to question the validity of the currently accepted, calorimetrically based entropy value included in Berman's (1988) data base.

First, phase equilibria among albite, kaolinite, paragonite, quartz, and H_2O in the system NASH, calculated using the data base of Berman (1988) and program GeO-Calc (Perkins et al., 1986), indicate that paragonite is stable at P and T as low as 1 bar and 25 °C, whereas the assemblage albite + kaolinite, common in the diagenetic environment (e.g., Coombs, 1954; Pittman, 1979; Hoffman and Hower, 1979; Surdam et al., 1989; Tilley and Longstaffe, 1989), is unstable at all $P\text{-}T$ conditions. Because the thermodynamic data for albite and paragonite in Berman's (1988) data base are well constrained by numerous experimental reversals (see Berman, 1988, for

references), the data for kaolinite appear to be the most likely source of this discrepancy.

Second, there are discrepancies between the low-temperature calorimetric measurements of King and Weller (1961) and Robie and Hemingway (1991) on the one hand, and the differential scanning calorimetry measurements of Lipsicas et al. (1986) on the other. Both Lipsicas et al. (1986) and Robie and Hemingway (1991) conducted their measurements on samples of Georgia kaolinite (KGa-1), but neither laboratory characterized the samples used by wet chemical or microprobe analysis, even though variations in the composition of Georgia kaolinite are reported in the literature (e.g., Hinkley, 1961; Weaver and Pollard, 1973).

Third, according to King and Weller (1961) and Barany and Kelley (1961), the entropies and enthalpies of kaolinite and halloysite are almost identical, whereas dickite has a lower entropy but almost the same enthalpy. This is highly unlikely if not impossible because kaolinite and dickite are polymorphs with different stability fields. Because kaolinite forms by weathering and authigenically (e.g., Curtis, 1983; Bjorkum and Gjelsvik, 1988), whereas dickite occurs mostly in hydrothermally altered rocks (e.g., Murray, 1988), dickite is therefore the higher-temperature (i.e., higher-entropy) polymorph.

Fourth, oxide summation methods for entropy estimation, which are reported to yield values within 5% or better (usually 0–2%) of the well-constrained calorimetric entropies, give values that are 7–8% lower than the calorimetric entropies of King and Weller (1961) and Robie and Hemingway (1991) (Table 1). Because these estimation techniques work best for minerals with simple structures or a small number of oxide components, and because they all yield entropy estimates for other aluminosilicates that are within experimental errors of calorimetric values (Table 1), they are expected to give reliable values for kaolinite.

RETRIEVAL OF AN ALTERNATE SET OF THERMODYNAMIC DATA FOR KAOLINITE

From the above discussion, it is clear that a new set of calorimetric measurements on kaolinite samples characterized by wet chemical and electron microprobe analyses is necessary to resolve some of the discrepancies. However, because such measurements are beyond the scope of this communication, I present an alternate set of entropy and enthalpy data for kaolinite that is consistent with available experimental data, is close to the theoretical and empirical estimates, and yields phase diagrams consistent with geological observations.

The new data set was obtained by retrieving values of S^0 and ΔH_f^0 for kaolinite by mathematical programming from a set of experimental and empirical constraints following the method of Gordon (1977) and using the data base of Berman (1988). Because Equilibrium 1 is the only reaction involving kaolinite for which experimental reversals have been reported, the problem was expanded

TABLE 1. Entropy estimates for selected aluminosilicates

	Structural analogues*	Simple analogues**	Oxide sums†	Oxide sums‡	Calorimetric entropies§	Berman (1988)
Pyrophyllite	239.3		242.75	239.4	239.4 (1)	239.28
Andalusite			93.78	—	91.39 ± 0.5 (2)	91.43
Kyanite			85.28	84.13	82.8 ± 0.5 (2)	82.43
Sillimanite			96.65	93.22	95.4 ± 0.5 (2)	95.93
Kaolinite	185.95	179.22	185.91	188.44	202.51 (3)	203.3
	2Prl − 6Qtz − Cor	2Prl − 6Qtz − Cor			183.15 (4)	
	200.54				200.9 (5)	
	Prl + H₂O − 2Qtz					

Note: all values are expressed in joules per mole kelvin.
* Structural analogue method of Helgeson et al. (1978).
** Simple summation and subtraction of entropies of oxides.
† Oxide sum method of Robinson and Haas (1983).
‡ Volume-corrected oxide sum method of Holland (1989).
§ References are as follows: 1 = Robie et al. (1978), 2 = Hemingway et al. (1991), 3 = King and Weller (1961), 4 = Lipsicas et al. (1986), and 5 = Robie and Hemingway (1991).

to include optimizing S^o and ΔH_f^o for pyrophyllite using the same experimental constraints that Berman (1988) used in his global optimization. Heat capacity, thermal expansion, and compressibility coefficients for kaolinite and pyrophyllite given in Berman (1988) were used in this optimization to ensure that the new data set is consistent with Berman's (1988) data base.

For this optimization, upper and lower limits were set on S_{Kln}^o at 185 and 202.45 J/(mol·K) and on S_{Prl}^o at 239 and 239.8 J/(mol·K), respectively, so that the retrieved values would not lie outside these limits. Similar limits on ΔH_f^o of pyrophyllite and kaolinite were also set and were selected at ±1% of ΔH_f^o estimates obtained using Chermak and Rimstidt's (1989) polyhedral sum method, calorimetric values reported by Barany and Kelley (1961) and Krupka et al. (1979), or both. The remaining constraints included all the experimental brackets of Hemley et al. (1980) and McPhail (see Berman, 1988) for Reaction 1, as well as three empirical constraints for Reaction 2 (Table 2).[1] The latter are based on geological observations and P-T estimates pertaining to the stability of the assemblage albite + kaolinite in the diagenetic environment (e.g., Pittman, 1979; Hoffman and Hower, 1979; Surdam et al., 1989; Tilley and Longstaffe, 1989; Coombs, 1954; Kisch, 1968) and the stability of paragonite in anchizonal rocks estimated to have been metamorphosed at temperatures ≥200 °C (Kisch, 1983).

Feasible solutions for S_{Kln}^o and $\Delta H_{f,Kln}^o$ were obtained in the ranges 188.33–197.41 J/(mol·K) and from −4127.51 to −4124.22 kJ/mol, respectively, whereas corresponding values for pyrophyllite were, as expected, almost identical to those given in Berman (1988). By tightening one of the empirical constraints for Reaction 2 and relaxing one of the half brackets of McPhail by 0.3 kbar (Table 2), a unique solution of S_{Kln}^o = 187.46 J/(mol·K)

[1] A copy of Table 2 may be ordered as Document AM-95-594 from the Business Office, Mineralogical Society of America, 1015 Eighteenth Street NW, Suite 601, Washington, DC 20036, U.S.A. Please remit $5.00 in advance for the microfiche.

and ΔH_f^o = −4129.92 kJ/mol is obtained. This result is very close to entropies and enthalpies estimated by oxide summation methods (Table 1).

DISCUSSION

Accepting a value of S^o = 187.4 J/(mol·K) and ΔH_f^o = −4129.92 kJ/mol for kaolinite suggests that the calorimetric entropies of King and Weller (1961) and Robie and Hemingway (1991) are in error. However, given that the low-temperature calorimeters used by these authors have always been well calibrated (as indicated by the numerous reliable data these laboratories have produced over the years, and which have been shown to be consistent with phase equilibrium studies), the source of discrepancy in the case of kaolinite merits a more detailed discussion.

Both King and Weller (1961) and Robie and Hemingway (1991) reported S_{Kln}^o values that are at least 12 J/(mol·K) higher than the calorimetric entropy of Lipsicas et al. (1986), the values estimated by structural analogue or oxide summation methods (Table 1), or the value obtained in the last section by mathematical programming. For any mineral, a calorimetric entropy substantially higher than that estimated by the different methods used in Table 1 could be explained by the configurational entropy of the mineral (i.e., $S_0^o \neq 0$) or by the occurrence of impurities in the sample used for calorimetric measurements. A configurational contribution to S_{Kln}^o is highly unlikely because no Al-Si disorder is known to exist in the kaolinite structure (e.g., Giese, 1988). On the other hand, kaolinite is known to contain numerous impurities, and although the Georgia kaolinite is considered relatively pure, it is characterized by significant variations in the Al_2O_3:SiO_2 ratios (Hinkley, 1961), which led Weaver and Pollard (1973) to conclude that it contains variable amounts of amorphous SiO_2 and $Al(OH)_3$ as impurities.

If the entropy of pure kaolinite is taken as 187.4 J/(mol·K), then a simple manipulation of the volume-corrected oxide sum method of Holland (1989) for the estimation of entropy [in which the volumes of gibbsite and quartz

were used for amorphous $Al(OH)_3$ and SiO_2, respectively] shows that an entropy of 202.5 J/(mol·K) requires 0.22 moles of $Al(OH)_3$ as an impurity in each mole of kaolinite. Such an amount of $Al(OH)_3$ results in an Al_2O_3:SiO_2 ratio of ~1.8 and an analysis with 43.55% SiO_2, 41.17% Al_2O_3, and 15.27% H_2O. These ratios and oxide weight percentages are within the range of analyses reported for Georgia kaolinite (e.g., Hinkley, 1961; Weaver and Pollard, 1973), even though no provision was made in this calculation for other impurities such as TiO_2 and Fe_2O_3, which are also known to occur in Georgia kaolinite (van Olphen and Fripiat, 1979). On the other hand, 0.37 moles of excess SiO_2 are required to account for the same entropy value of 202.5 J/(mol·K) for kaolinite. Such an amount results in an Al_2O_3:SiO_2 ratio of 1:2.37 and a total SiO_2 weight percent of 54.02, values that are beyond the ranges reported for kaolinite. Therefore, although impurities of amorphous $Al(OH)_3$ likely account for the difference between the calorimetric and estimated entropy values of kaolinite, impurities of amorphous SiO_2 alone cannot account for such a discrepancy.

PHASE RELATIONS IN THE SYSTEM KNASH

Although equilibrium is not always attained between phases in the near-surface environment, with many mineral assemblages controlled by open-system behavior and irreversible reactions, many diagenetic and low-grade metamorphic changes occur under closed-system conditions (e.g., Coombs, 1954; Bjorkum and Gjelsvik, 1988). Therefore, the validity of the thermodynamic data for kaolinite proposed in this work can to some extent be assessed by comparing petrogenetic grids for several systems calculated using this data set with field observations on the stability of specific mineral assemblages. Figure 1 is a petrogenetic grid for the system KNASH projected from quartz and calculated for $P_{H_2O} = P_{tot}$ using program GeO-Calc (Perkins et al., 1986) and the new data for kaolinite. Such a grid is therefore useful for understanding the diagenesis of sandstones and very low-grade metamorphism of sandstones and granitic rocks.

Figure 1 shows that the assemblage albite + kaolinite is stable at T up to 90 °C and is replaced by paragonite at higher temperatures. These relations are consistent with the results of petrological, stable isotopic, and fluid inclusion studies of diagenesis in sandstones, which suggest that albite + kaolinite is stable up to T of 120 °C at $P \leq$ 1.2 kbar (e.g., Tilley and Longstaffe, 1989; Surdam et al., 1989). Studies on sandstone diagenesis have also shown that although albitization may persist at $T > 120$ °C, kaolinite may be replaced by illite (e.g., Bjorkum and Gjelsvik, 1988; Surdam et al., 1989). Although illite was not considered in the calculation of Figure 1 because of the lack of reliable thermodynamic data for this phase, this petrogenetic grid is still consistent with the results of Bjorkum and Gjelsvik (1988), Tilley and Longstaffe (1989), and Surdam et al. (1989) because it shows that the assemblage kaolinite + potassium feldspar is stable at $T < 100$ °C, beyond which it is replaced by muscovite

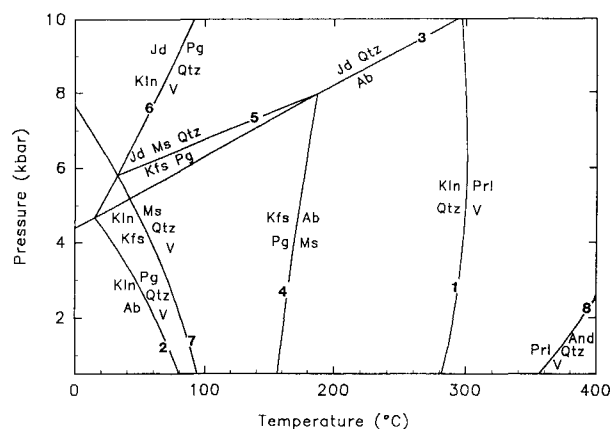Fig. 1. Petrogenetic grid for the system KNASH projected from quartz and calculated at $P_{H_2O} = P_{tot}$ using the program GeO-Calc, the thermodynamic data base of Berman (1988), the newly retrieved values of $S^0_{Kln} = 187.46$ J/(mol·K) and $\Delta H^0_{f,Kln} = -4129.92$ kJ/mol, and the corresponding values of $S^0_{Prl} = 239$ J/(mol·K) and $\Delta H^0_{f,Prl} = -5641.577$ kJ/mol. Reactions: (1) Kln + 2Qtz = Prl + H_2O, (2) Kln + Ab = Pg + 2Qtz + H_2O, (3) Jd + Qtz = Ab, (4) Kfs + Pg = Ab + Ms, (5) Jd + Ms + Qtz = Kfs + Pg, (6) Jd + Kln = Qtz + Pg + H_2O, (7) Kln + Kfs = 2Qtz + Ms + H_2O, (8) Prl = And + 3Qtz + H_2O.

+ quartz. Because illite is characterized by an interlayer site occupancy of 0.6–0.8 atoms pre formula unit and a phengitic substitution leading to a Si:Al ratio in excess of 3:1 (Bailey et al., 1984), it is expected to have lower entropy than muscovite (on the basis of an estimate using the oxide sum method of Holland, 1989). Accordingly, the reaction responsible for the illitization of kaolinite + potassium feldspar in a closed system (e.g., Bjorkum and Gjelsvik, 1988) has a steeper negative slope in P-T space than that shown for Reaction 7 (Fig. 1). Therefore, at low pressures, kaolinite + potassium feldspar may be illitized at $T < 100$ °C, as suggested by Bjorkum and Gjelsvik (1988). In contrast, a petrogenetic grid for KNASH calculated with Berman's (1988) data for kaolinite has no stability field for the assemblages kaolinite + albite or kaolinite + potassium feldspar.

Although the new data for kaolinite and the petrogenetic grid of Figure 1 can account for field and petrological observations on the stability of albite + kaolinite and kaolinite + potassium feldspar, this calculated grid appears to contradict empirical observations on the stability and first appearance of paragonite in low-grade metamorphic rocks. According to Figure 1, paragonite forms at temperatures as low as 80–90 °C by Reaction 2. Such temperatures appear to be too low for the formation of this metamorphic mineral, which reportedly first appears in anchizonal rocks formed at temperatures >200 °C (e.g., Kisch, 1983). However, if phases such as rectorite (mixed-layer paragonite-smectite) and sodium illite, which are reportedly stable in the diagenetic environment (e.g., Blokh et al., 1973; Weaver and Pollard, 1973), are considered mechanical mixtures of paragonite with smectite

and illite, respectively, then the first appearance of paragonite at the low temperatures suggested by Figure 1 may be reasonable. The alternative model of considering these phases as solid solutions is not supported by available experimental data, which suggest a very limited substitution of Na for K (or vice versa) in the mica structure at the low temperatures over which sodium illite or rectorite are stable (see Guidotti, 1984, for a review of such experiments). In this context, it is worth noting that Garrels (1984) also showed that a geochemical model, in which mixed-layer illite-smectite is considered a mechanical mixture of illite and smectite, better accounts for the compositions of pore water in equilibrium with these mixed-layer minerals than a solid-solution model.

The petrogenetic grid of Figure 1 and, in particular, the topology and location of Reaction 2 are inconsistent with the experimental results and grids proposed by Chatterjee (1973). Chatterjee's (1973) unreversed experiments suggest that the fluid-absent reaction sodium montmorillonite + albite = paragonite + quartz has a steep negative slope in P-T space, which, according to Schreinemakers' principles, requires that Reaction 2 have a positive slope. For the slope of Reaction 2 to be positive, it must have a negative ΔS_r^0 because it is characterized by a negative ΔV_r^0. However, Reaction 2 has a positive ΔS_r^0 for all values of S_{Kln}^0 between 185 and 203 J/(mol·K) (Table 1), which leads to the conclusion that the experimental results and petrogenetic grid of Chatterjee (1973) are inaccurate.

ACKNOWLEDGMENTS

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