

The system albite–H₂O–CO₂: a model for melting and activities of water at high pressures¹

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Abstract

The melting of albite in the presence of H₂O–CO₂ vapor has been determined in piston-cylinder apparatus from 5 to 25 kbar for mole fractions of H₂O in the vapor ($X_{\text{H}_2\text{O}}^{\text{V}}$) from 1.0 to 0.0. Albite in the presence of CO₂-rich vapor melts as much as 150–300°C lower than indicated by previous theoretical and experimental studies. The albite–CO₂ melting curve is indistinguishable from the vapor-absent melting curve up to 15 kbar, but it is significantly lower above 15 kbar as a result of a substantial increase in the solubility of CO₂ in the liquid. Calculated activity coefficients (γ) for water in H₂O–CO₂ vapor in the range 700–1000°C, 5–15 kbar are everywhere greater than unity and increase isobarically and isothermally toward CO₂-rich compositions. For $X_{\text{H}_2\text{O}}^{\text{V}} < 0.3$ calculated $\gamma_{\text{H}_2\text{O}}^{\text{V}}$ are significantly greater than those predicted by the modified Redlich-Kwong equation.

Introduction

The thermodynamic properties of silicate melts and H₂O–CO₂ vapors are of great interest to petrologists attempting to unravel the evolutionary history of the upper mantle and lower crust. In this regard the melting of albite in the presence of a vapor has been used as a model for melting, for solubilities of volatile components in silicate liquids, and for physical and thermodynamic properties of vapors and silicate liquids.

The first such study (Goranson, 1938) was designed to determine the maximum solubility of H₂O in liquid of albite composition and to infer thermodynamic data from the phase relationships. Subse-

quent studies established the solubility of H₂O in albite liquid at high pressures and located the H₂O-saturated solidus (Tuttle and Bowen, 1958; Yoder, 1958; Burnham and Jahns, 1962; Orlova, 1962; Luth *et al.*, 1964; Boettcher and Wyllie, 1969; Morse, 1970). Recently, Burnham and Davis (1971; 1974) determined the *P*–*V*–*T* relations of albite–H₂O, developed a quantitative model for the dissolution of H₂O in albite liquid, and calculated the *P*–*T*–*a*_{H₂O} relations of albite–H₂O. Burnham (1974; 1975; 1979) has since demonstrated how the results for albite–H₂O can model the behavior of H₂O in hydrous felsic and mafic magmas.

In addition to H₂O, CO₂ is also recognized as an important volatile component in the lower crust and upper mantle. As a consequence, several workers have investigated the melting of albite in the system albite–H₂O–CO₂, not only to evaluate melting in

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multi-component vapor, but also to understand solubility mechanisms for CO₂ in silicate melts and to infer the mixing properties of CO₂-H₂O solutions. Millhollen *et al.* (1971) determined the melting of albite coexisting with a CO₂-H₂O vapor ($X_{\text{H}_2\text{O}}^{\text{V}} = 0.5$) to 20 kbar. Kesson and Holloway (1974) located the vapor-saturated albite solidus ($X_{\text{H}_2\text{O}}^{\text{V}} = 0.25$) at 4.4 kbar. In the most comprehensive work to date, Eggler and Kadik (1979) investigated the melting of albite coexisting with vapor spanning the range $X_{\text{H}_2\text{O}}^{\text{V}} = 0.8-0.05$, and at $X_{\text{CO}_2}^{\text{V}} = 1.0$, at pressures to 30 kbar. The results of these studies are all discordant with the calculated data of Burnham and Davis (1974) and Burnham (1979). For some compositions the disagreement is as great as 150°C.

Boettcher *et al.* (1980; 1982) experimentally determined the vapor-absent melting of albite to be at lower temperatures with a steeper slope than previously determined experimentally (Boyd and England, 1963) or calculated (Burnham and Davis, 1974). These new data require significant revision of the thermodynamic data for liquids of albite composition at high pressure (Boettcher *et al.*, 1982), resulting in changes in the calculated albite-H₂O data of Burnham and Davis (1974) and in CO₂-H₂O mixing parameters previously inferred from experiments on albite-H₂O-CO₂. Therefore, to obtain accurate data for H₂O-CO₂ solutions and the melting of albite, we have reinvestigated melting relationships in the system albite-H₂O-CO₂.

Experimental methods

Starting materials

Synthetic albite was prepared by hydrothermally crystallizing albite gel (Luth and Ingamells, 1965) in cold-seal vessels at 1 kbar and 800°C for at least 20 days. The albite was then dried at 1100°C for 24 hours and inspected optically to ensure that no uncrystallized gel remained. Boiled, doubly distilled, deionized H₂O and anhydrous silver oxalate (Ag₂C₂O₄) were used to generate appropriate fluid compositions. The silver oxalate was dried under a soft vacuum at 40°C for 48 hours and stored in a vacuum desiccator; it was checked for purity and absorbed H₂O by loading carefully weighed amounts into Pt capsules, sealing and heating the capsule to 400°C to dissociate the oxalate. After freezing the capsule, it was punctured, weighed, heated to 200°C and reweighed. Such analyses, repeated several times, confirm that the heated silver oxalate liberated a mass equal to that of CO₂.

For each run, 1–2 mg of albite and appropriate amounts of H₂O and silver oxalate were loaded into 1.6-mm diameter Pt capsules so that the amount of CO₂-H₂O vapor generated was between 20 and 30 wt%. We used 15 wt% H₂O for albite-H₂O and 10 wt% CO₂ for albite-CO₂. In all experiments in the systems albite-H₂O-CO₂ and albite-CO₂, sealed 1.6-mm capsules were loaded into 3-mm diameter Pt capsules with approximately 100 mg of hematite to maintain a high ambient f_{O_2} ; this prevented the precipitation of graphite and maintained a low f_{CO} and f_{H_2} .

Apparatus and run procedure

Most experiments were conducted in a piston-cylinder apparatus with 25.4-mm diameter furnace assemblies and pistons. Several experiments were carried out in an internally heated gas apparatus by Professor James Blencoe at The Pennsylvania State University. Furnace assemblies for the piston-cylinder experiments differ from those used previously (Boettcher *in* Johannes *et al.*, 1971) in that the talc bushing is replaced by KBr (Boettcher *et al.*, 1981). Temperature was measured with Pt₁₀₀-Pt₉₀Rh₁₀ thermocouples for all albite-H₂O and albite-H₂O-CO₂ experiments. WRe₃-WRe₂₅ thermocouples were used for albite-CO₂ experiments so that the results could be compared directly with those of vapor-absent melting of albite (Boettcher *et al.*, 1982). We used the piston-in technique by bringing the pressure to 10% below that of the final run pressure, increasing the temperature to the final value, and increasing the pressure to the final value.

Each of the melting curves for albite-H₂O and albite-H₂O-CO₂ have been reversed at 10 kbar by making two-stage runs in which the initial conditions were those that were known from previous runs to yield significant amounts of liquid. The temperature was then lowered and held for 24 hours at conditions inferred to be about 10°C below the solidus. The absence of glass in these runs demonstrates reversibility. The solidus for albite-CO₂ was similarly reversed at 20 and 25 kbar.

Furnace assemblies have been calibrated against the reactions fayalite + quartz $\rightleftharpoons$ ferrosilite (Bohlen *et al.*, 1980a) and quartz $\rightleftharpoons$ coesite (Boettcher and Wyllie, 1968). The results relative to those obtained in a talc assembly with a -6% pressure correction indicate that the KBr assembly requires no pressure correction. We have also calibrated our assemblies against the melting of LiCl, CsCl and NaCl. To be certain of the calibrations of our apparatus at low

pressure, we determined the melting points of LiCl, CsCl, KCl and NaCl at 5 kbar. Experiments were carried out in our piston-cylinder apparatus and in internally heated gas-pressure apparatus kindly performed for us by Dr. James Blencoe at The Pennsylvania State University, and in a similar gas apparatus performed by one of us (SRB) in the laboratory of Dr. John Holloway at Arizona State University and at Stanford University by R. W. Luth of UCLA with the help of Dr. Michael Apted of Stanford University. The results indicate that Clark's (1959) temperatures for melting of these salts are systematically 10–15°C too low (at 5 kbar) and that our furnace assembly requires no friction correction for pressures as low as 5 kbar. Other workers (Mirwald *et al.*, 1975; Johannes, 1978; Holland, 1980) have also noted that salt assemblies require little or no pressure correction. Hence, pressures in Tables 1 and 2 are uncorrected values.

Run products

After the completion of most runs, the inner capsule was cleaned and placed in a freezer for 10–15 minutes. It was then punctured, weighed, placed in a drying oven (112°C) for 15 minutes and reweighed. With the exception of runs in which extensive melting had occurred the CO₂/H₂O ratio was always within 2 mole % of the intended value and usually within 1 mole %. After this process, the run products were examined optically.

Location of the albite-H₂O-CO₂ solidi requires a determination of the temperature at which the first trace of albite glass (quenched liquid) is formed. The glass has an index of refraction > 1.50, whereas the quenched vapor has an index of < 1.49. There was no evidence that liquid quenched to crystalline albite. Occasionally, inclusions of vapor trapped in glass were sufficiently large to observe two phases, an H₂O-rich liquid and a CO₂-rich gas. No carbonate phase was detected in any of the run products, including those in the system albite-CO₂.

Results and discussion

All pertinent experimental data and results are listed in Tables 1 and 2. Figure 1 shows the results for albite-H₂O, albite-H₂O-CO₂ and albite-CO₂. The results of experiments in the gas-pressure apparatus are consistent with those in piston-cylinder apparatus, and they provide tight brackets for $X_{\text{H}_2\text{O}}^V = 0.2$ at 7 kbar and constrain the locations of the curves for $X_{\text{H}_2\text{O}}^V = 0.7$ at 5 and 8 kbar and $X_{\text{H}_2\text{O}}^V = 1.0$ at 5 kbar.

Table 1. Experimental results for albite-H₂O and albite-H₂O-CO₂

Run #	$X_{\text{H}_2\text{O}}^V$	T(°C)	P(kbar)	Duration (hrs)	Products
454	1.0	710	5.0	7.5	Ab+V
453	1.0	720	5.0	8	Ab+L
654	1.0	725	5.0	7	Ab+V
450	1.0	730	5.0	8	Ab+L
589*	1.0	737	5.0	1	Ab+L
422	1.0	690	7.0	24	Ab+V
447	1.0	700	7.0	7.5	Ab+L
435	1.0	720	7.0	7.5	Ab+L
448	1.0	660	10.0	7.5	Ab+V
656	1.0	670	10.0	8.3	Ab+V
655	1.0	680	10.0	9	Ab+L
417	1.0	690	10.0	8	Ab+L
476	1.0	680	10.0	8	(see run #425)
		650	10.0	24	Ab+V
449	1.0	630	15.0	7.5	Ab+V
662	1.0	635	15.0	7	Ab+V
663	1.0	645	15.0	7	Ab+L
423	1.0	650	15.0	8	Ab+L
416	1.0	660	15.0	8	Ab+L
473	0.8	760	5.0	8	Ab+V
657	0.8	770	5.0	7	Ab+V
658	0.8	780	5.0	7.5	Ab+V
659	0.8	790	5.0	7.5	Ab+L+V
394*	0.8	833	5.0	7.5	Ab+L+V
458	0.8	750	7.0	7.5	Ab+V
445	0.8	760	7.0	8	Ab+L+V
432	0.8	700	10.0	7.5	Ab+V
436	0.8	720	10.0	8	Ab+V
437	0.8	730	10.0	8.5	Ab+L+V
424	0.8	740	10.0	8.5	Ab+L+V
469	0.8	740	10.0	8	(see run #424)
		710	10.0	24	Ab+V
446	0.8	690	15.0	8	Ab+V
451	0.8	710	15.0	7.5	Ab+V
452	0.8	720	15.0	8.5	Ab+L+V
395*	0.7	833	5.0	7.5	Ab+L+V
397*	0.7	775	8.0	8	Ab+V
396*	0.6	833	5.0	7.5	Ab+V
398*	0.6	775	8.0	8	Ab+V
399*	0.55	775	8.0	8	Ab+V
459	0.5	860	5.0	8	Ab+V
475	0.5	870	5.0	10.5	Ab+L+V
458	0.5	880	5.0	8	Ab+L+V
317	0.5	840	7.0	8	Ab+V
325	0.5	850	7.0	9	Ab+L+V
321	0.5	860	7.0	8	Ab+L+V
382	0.5	790	10.0	8	Ab+V
390	0.5	800	10.0	8.5	Ab+L+V
381	0.5	810	10.0	8	Ab+L+V
354	0.5	830	10.0	8.1	Ab+L+V
455	0.5	820	10.0	8	(see run #381)
		780	10.0	24	Ab+V
380	0.5	790	15.0	8	Ab+V
414	0.5	800	15.0	8	Ab+L+V
316	0.5	810	15.0	8	Ab+L+V
324	0.5	820	15.0	9	Ab+L+V
315	0.5	830	15.0	8	Ab+L+V
383	0.5	780	20.0	8	Ab+L+V(?)
363	0.5	810	20.0	8	Ab+L+V
456	0.5	780	19.0	8	Ab+V
391	0.5	790	19.0	9.1	Ab+L+V
460	0.3	900	5.0	12	Ab+V
461	0.3	910	5.0	13	Ab+V
479	0.3	920	5.0	10.5	Ab+L+V
377	0.3	860	7.0	8	Ab+V
388	0.3	870	7.0	8	Ab+V
415	0.3	880	7.0	8	Ab+L+V
410	0.3	890	7.0	9.3	Ab+L+V
376	0.3	840	10.0	8	Ab+V
444	0.3	850	10.0	7.3	Ab+V
365	0.3	860	10.0	8.5	Ab+L+V
462	0.3	870	10.0	8	(see run #365)
		840	10.0	24	Ab+V
371	0.3	830	15.0	8	Ab+V
413	0.3	840	15.0	8	Ab+V
370	0.3	850	15.0	8	Ab+L+V
361	0.3	860	15.0	8	Ab+L+V
389	0.3	840	20.0	8	Ab+V
443	0.3	850	20.0	7.5	Ab+V
411	0.3	860	20.0	9.5	Ab+L+V
481*	0.25	915	7.0	7.5	Ab+L+V

Table 1. (continued)

Run #	X _{H₂O}	T(°C)	P(kbar)	Duration (hrs)	Products
465	0.2	950	5.0	8	Ab+V
464	0.2	960	5.0	8	Ab+V
480	0.2	970	5.0	14	Ab+L+V
327	0.2	890	7.0	8	Ab+V
345	0.2	900	7.0	7.5	Ab+V
322	0.2	910	7.0	8	Ab+V
482*	0.2	915	7.0	7.5	Ab+V
318	0.2	920	7.0	8	Ab+L+V
366	0.2	890	10.0	8	Ab+V
358	0.2	900	10.0	8	Ab+L+V
367	0.2	910	10.0	8	Ab+L+V
463	0.2	920	10.0	8	(see run #367)
		880	10.0	24	Ab+V
331	0.2	900	15.0	9	Ab+V
346	0.2	910	15.0	7	Ab+L+V
338	0.2	920	15.0	8.5	Ab+L+V
333	0.2	940	15.0	9	Ab+L+V
357	0.2	900	20.0	8.5	Ab+V
373	0.2	910	20.0	8.3	Ab+V
344	0.2	920	20.0	9.3	Ab+L+V
343	0.2	940	20.0	8	Ab+L+V
339	0.2	960	20.0	9	Ab+L+V
400*	0.15	915	7.0	8	Ab+V
467	0.1	1020	5.0	9	Ab+V
468	0.1	1030	5.0	8	Ab+V
483	0.1	1040	5.0	4	Ab+L+V
401*	0.1	915	7.0	8	Ab+V
393	0.1	970	7.0	8	Ab+V
408	0.1	980	7.0	8.8	Ab+V
412	0.1	990	7.0	8.5	Ab+V
409	0.1	1000	7.0	7.5	Ab+L+V
384	0.1	940	10.0	8	Ab+V
374	0.1	950	10.0	8	Ab+V
440	0.1	960	10.0	7.8	Ab+V
368	0.1	970	10.0	8	Ab+L+V
466	0.1	980	10.0	8	(see run #368)
		950	10.0	24	Ab+V
375	0.1	950	15.0	6.8	Ab+V
369	0.1	960	15.0	8	Ab+V
439	0.1	970	15.0	7.5	Ab+V
360	0.1	980	15.0	8	Ab+L+V
359	0.1	1000	15.0	8.8	Ab+L+V
385	0.1	980	20.0	8	Ab+V
438	0.1	990	20.0	8	Ab+V
392	0.1	1000	20.0	8	Ab+L+V

* Experiment in internally heated gas apparatus; Ab = albite, Jd = jadeite, L = liquid, V = vapor.

Albite-H₂O

The results for albite-H₂O are in general agreement with those of previous determinations. Tuttle and Bowen (1958) determined the vapor-saturated solidus to about 3.92 kbar in synthesis experiments using synthetic albite. Their results, shown in Figure 1, are consonant with our results extrapolated below 5 kbar. Goranson (1938) investigated this reaction to about 3 kbar using albite glass and synthetic albite. With the exception of ambiguous results at 2.41 kbar and 830°C, his data are in accord with the results of Tuttle and Bowen, although his illustrated curve is at least 20°C higher at 3 kbar, but in agreement at 2 kbar. Our brackets at 10 and 15 kbars at 670–680°C and 635–645°C, respectively, compare with 680–690°C and 650–660°C obtained by Boettcher and Wyllie (1969). We repeated the

experiments at 10 kbar using talc furnace assemblies and chromel–alumel thermocouples similar to those employed by Boettcher and Wyllie, and we obtained brackets of 660–670°C. Examination of the run products of Boettcher and Wyllie substantiates their original interpretation. Thus, if any difference beyond experimental uncertainty occurs between these results, it must be in the measurement of temperature and/or pressure. Burnham and Jahns (1962) report melting at temperatures <690°C at 10.1 kbar, which agrees with our results, but Luth *et al.* (1964) at this same pressure obtained brackets of 697°C (extrapolated by us from 695°C at 10.3 kbar) and 720°C. However, Luth (1976) reported that the temperatures of Luth *et al.* (1964) in the 8–10 kbar range should be corrected by –(10 to 15)°C.

A more serious problem is the temperature of 758±3°C at 5.0 kbar obtained by Morse (1970) in cold-seal apparatus and internally heated, gas-pressure apparatus. These results are dissonant with our data obtained from gas-pressure and piston-cylinder apparatus and with the values of Tuttle and Bowen extrapolated beyond 4 kbar, and we are unable to detect any basis for the differences. Morse standardized his values against the melting of RbCl at 5 kbar, for which he obtained a value of 817°C, compared to 805°C obtained by Clark (1959) (a difference similar to those found by us for other alkali halides; see previous section).

Albite-H₂O-CO₂

Eggler and Kadik (1979) investigated the beginning of melting for Ab-H₂O-CO₂ compositions for values of X_{H₂O}^V from 0.8 to 0.0. They made no determinations for X_{H₂O}^V = 1, apparently using the

Table 2. Experimental results for albite-CO₂

Run #	T(°C)	P(kbar)	Duration (hrs)	Products
487	1220	10.0	18	Ab+L+V
427	1210	15.0	23.5	Ab+V
428	1230	15.0	24	Ab+V
441	1240	15.0	22.5	Ab+L+V
429	1250	15.0	22	L+V
442	1250	15.0	24	L+V
490	1240	20.0	20.5	Ab+V
477	1250	20.0	8	Ab+L+V
491	1260	20.0	8	(see run #447)
	1230	20.0	24	Ab+V
485	1260	25.0	12	Ab+V
486	1270	25.0	5	Ab+L+V
478	1290	25.0	7	L+V
471	1310	25.0	5.3	L+V
492	1280	25.0	4	(see run #486)
	1250	25.0	24	Ab+V

values of Boettcher and Wyllie (1969). Within the H₂O-rich part of the system, there is agreement between our data and those of Eggler and Kadik; our curve for $X_{\text{H}_2\text{O}}^{\text{V}} = 0.8$ is identical with theirs. For $X_{\text{H}_2\text{O}}^{\text{V}} = 0.5$, there is good agreement, especially above 10 kbar (Fig. 2). Millhollen *et al.* (1971) investigated the beginning of melting in the system Ab-H₂O-CO₂ with $X_{\text{H}_2\text{O}}^{\text{V}} = 0.5$. As shown in Figure 2, their temperatures are higher than ours over the entire pressure range. One explanation for this disparity is that they used oxalic acid (dihydrate) as the source of H₂O and CO₂. It is now known that this compound dehydrates very rapidly, such as when stored in a desiccator, and their H₂O/CO₂ ratio likely was less than unity. Also, although they did surround the sample capsule with hematite to prevent H₂ from entering the capsule and reducing the CO and CO₂ to graphite, our experience with a similar arrangement suggests that sufficient proportions of H₂ may diffuse into the capsule and significantly lower $f_{\text{H}_2\text{O}}$. With our double-capsule configuration, at least 50% (~70 mg) of the hematite remained in the outer capsule at the completion of every experiment. Nevertheless, the disparity between our results is less than 35°C at any pressure.

With decreasing values of $X_{\text{H}_2\text{O}}^{\text{V}}$, the discrepancies between the experimental studies increase in magnitude, as illustrated in Figure 3. In addition to the differences in the positions of the curves, ours

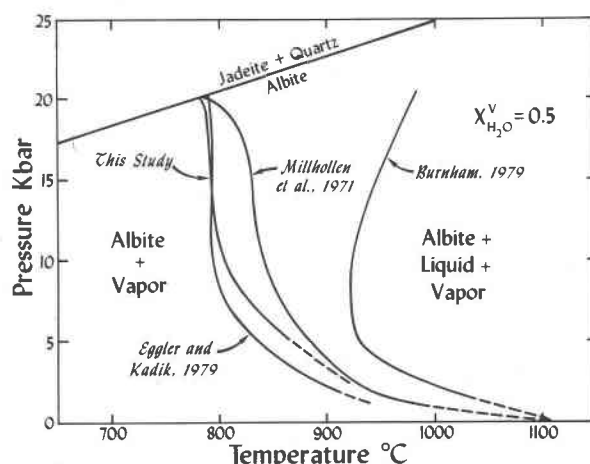


Fig. 2. Pressure-temperature projection comparing the various calculated and experimental determinations of the albite-vapor solidus for a mole fraction of H₂O in the H₂O-CO₂ vapor of 0.5.

lack the pronounced temperature minima of Eggler and Kadik. Conversely, our results at $X_{\text{H}_2\text{O}}^{\text{V}} = 0.2$ and 0.3 are in agreement with the carefully determined point of Kessen and Holloway (1974) at $X_{\text{H}_2\text{O}}^{\text{V}} = 0.25$.

Greater discrepancies between our results and those of others occur at $X_{\text{H}_2\text{O}}^{\text{V}} = 0.1$, as shown in Figure 4. The calculated curve of Burnham (1979) differs from what we believe to be the correct configuration because of a lack of reliable values for molal volume and molal entropy of H₂O-poor albite liquids at high pressures. Our revised melting curves for Ab and Ab-H₂O-CO₂ provide a basis upon which new calculations can be made, following on the pioneering work of Burnham.

It is not apparent why the results of the two experimental studies are so markedly different at low values of $X_{\text{H}_2\text{O}}^{\text{V}}$, but Eggler and Kadik did not reverse their experiments, many of which used corundum, cristobalite, and Na₂CO₃ as starting mixes. Eggler and Kadik inferred the initial melting of albite by determining the location of the reactions albite + vapor = albite + liquid + vapor and albite + liquid + vapor = liquid + vapor, and then projected the liquid compositions from albite through the experimental brackets to the CO₂-H₂O sideline. This permitted indirect determination of the CO₂-H₂O ratio in equilibrium with a small amount of melt for the given *P-T* conditions. Alternatively, we looked carefully for the first trace of melt at a given *P-T-X*. The presence or absence of melt allowed us to directly locate the reaction

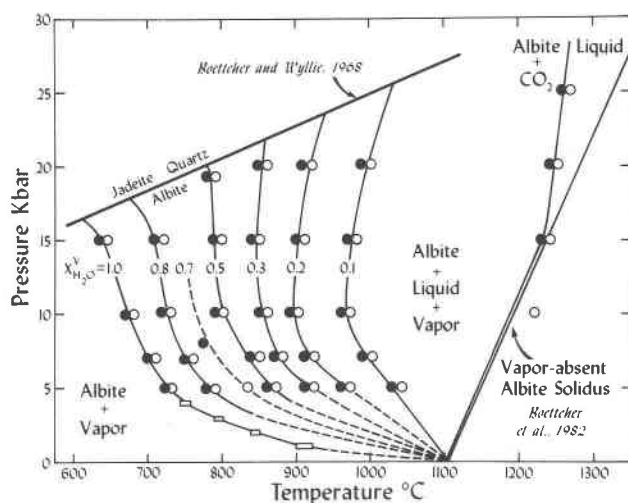


Fig. 1. Pressure-temperature projection of the solidi of albite-vapor for various values of the mole fraction of H₂O ($X_{\text{H}_2\text{O}}^{\text{V}}$) in the H₂O-CO₂ vapor. Definitive experiments are in Table 3. Closed circles indicate absence of liquid; open circles indicate albite + liquid + vapor.

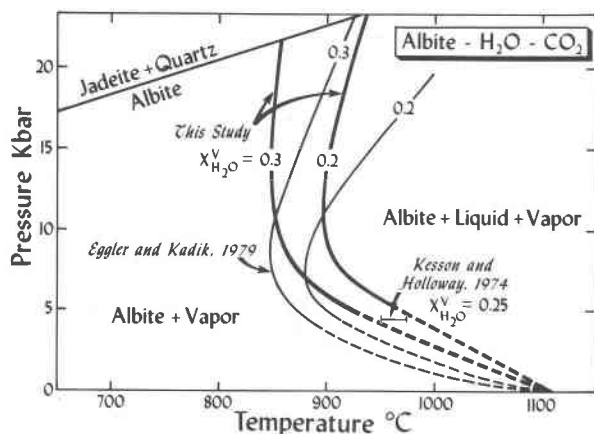


Fig. 3. Pressure-temperature projection of the various experimental determinations of the albite-vapor solidus for mole fractions of H₂O in the H₂O-CO₂ vapor of 0.2, 0.25, and 0.3.

albite + vapor = albite + liquid + vapor. Considering the full extent of experimental and analytical uncertainty in Eggler and Kadik's isothermal isobaric sections in the system Ab-H₂O-CO₂, most of their data can be brought into coincidence with our results. However, some differences still exist. For example, at 7 kbar and 850°C, Eggler and Kadik's data, considering maximum variation allowed by the experimental brackets, indicate the H₂O/H₂O-CO₂ ratio coexisting with the melt at the solidus to be $X_{H_2O}^V = 0.22-0.34$. However, our data, also including maximum experimental uncertainty, indicate the vapor composition to be $X_{H_2O}^V = 0.48 \pm 0.04$.

Regardless of the causes, the most striking differences between our data and those of Eggler and Kadik is that our results lack the pronounced minima in the albite solidi at 7-8 kbar for CO₂-rich compositions. Such minima would imply that CO₂-H₂O mixing is strongly non-ideal in the range 5-15 kbar, with non-ideality increasing with increasing temperatures. This is in conflict with other theoretical and experimental data (Holloway, 1977; Flowers, 1979; Kerrick and Jacobs, 1981; Smulovich *et al.*, 1982).

Ab-CO₂

The results of our experiments with Ab + CO₂ starting materials between 10 and 25 kbar are in Table 2 and Figure 1. Below 15 kbars, the beginning of melting of Ab-CO₂ is indistinguishable from that of Ab. Above that pressure, the solubility of CO₂ in the silicate liquid increases markedly, significantly lowering the melting temperature.

On the basis of IR spectra of quenched liquids, Mysen *et al.* (1976) suggested that CO₂ dissolves in feldspar liquids as molecular CO₂. Because the solubility is similar in K, Na, and Ca feldspars, they concluded that the formation of CO₃²⁻ is small, although an absorption band for CO₃²⁻ was detected in Ab-CO₂ glasses quenched from 1600°C and 20 kbar. Subsequent work (Mysen and Virgo, 1980a) indicates that CO₂ dissolves in albite liquids as both CO₂ and CO₃²⁻, predominantly, forming metal-carbonate complexes. A similar conclusion was reached in a study of CaMgSi₂O₆ and NaCaAlSi₂O₇ glasses (Mysen and Virgo, 1980b). The significant increase in freezing-point depression that we observed above 15 kbar may reflect a change from primarily CO₂ to primarily CO₃²⁻ in the Ab-CO₂ liquid. It may also simply reflect enhanced solubility of molecular CO₂ as a result of the rapid increase of f_{CO_2} with pressure.

The only other study of melting of Ab-CO₂ compositions is that of Eggler and Kadik (1979). They show a curve for the CO₂-saturated solidus

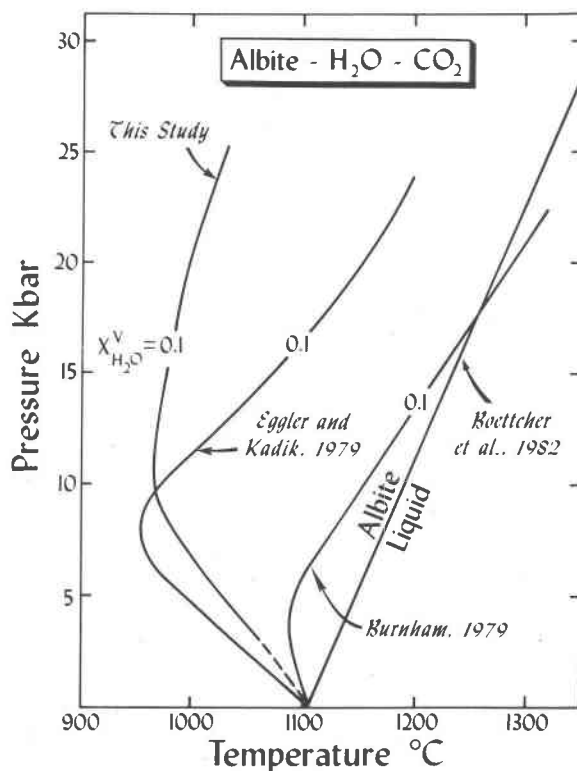


Fig. 4. Pressure-temperature projection of the various calculated and experimental determinations of the albite-vapor solidus in which the mole fraction of H₂O in the H₂O-CO₂ vapor is 0.1. The vapor-absent solidus of albite is from Boettcher *et al.*, 1982.

(their Fig. 5) that appears to be dissonant with their experimental results. Also, they report liquid at 1200°C and 20 kbar (not shown in their Fig 5), which is discordant with our results. The latter may result from H₂ entering the samples, lowering their melting temperatures. In addition, the experimental data of Eggler (1973), Holloway and Lewis (1974), and Mysen *et al.* (1976) indicate that addition of even small proportions of H₂O to Ab-CO₂ significantly increases the solubility of CO₂ in the liquid, which may also help to explain why Eggler and Kadik observed melting at least as low as 1200°C at 20 kbar.

Burnham (1979) contrasts the ability of H₂O to hydrolyze by reaction with bridging oxygen ions in the melt with that of CO₂, which cannot break Si-O-Si bridges. However, the data of Mysen (1976) show that the solubility of CO₂ increases from albite to jadeite to nepheline liquids in the range of 10 to 30 kbar, at least for high temperatures ($\geq 1450^\circ\text{C}$). The ratio CO₃²⁻/CO₂ in the liquid also appears to increase in the same direction through this series of compositions (Mysen, 1976). Burnham (1979) suggests that the solubility of CO₂ as CO₃²⁻ is also enhanced when Al in 4-fold coordination (Al^{IV}) transforms to Al^{VI}, breaking Al-O-Si bonds. Alternatively, the rupture of Al-O-Si bonds at high pressures may permit ingress of molecular CO₂ into the aluminosilicate liquid. We accept these as possible explanations for the marked increase in the solubility of CO₂ component at pressures in excess of ~ 15 kbar, but determination of the speciation of the liquid at high temperatures and pressures is necessary to solve the problem.

Activity of H₂O in CO₂-H₂O vapor

Thermodynamic calculations

One of the prime purposes of this experimental study was to determine activity coefficients for H₂O in CO₂-H₂O vapor. Because Burnham and Davis (1974) and Burnham (1979) have established the activity of water in an albite melt as a function of P , T , and water content of the liquid ($X_{\text{H}_2\text{O}}^1$) over much of the range of conditions in this study, the activity of H₂O in a coexisting vapor ($a_{\text{H}_2\text{O}}^V$) can be determined. The equation expressing equilibrium between pure crystalline albite and anhydrous albite liquid is (Burnham, 1979, eq. 16-12)

$$\mu_{\text{Ab}}^1 - \mu_{\text{Ab}}^s = \Delta G_{\text{mAb}}^\circ = 0 \sim \Delta G_{\text{mAb}}^\circ + P\Delta V_{\text{mAb}} + RT \ln a_{\text{Ab}}^1$$

where ΔG_{mAb} is the Gibbs free energy of fusion, a_{Ab}^1 is the activity of NaAlSi₃O₈ in the liquid relative to pure NaAlSi₃O₈ liquid at P and T (K), $\Delta G_{\text{mAb}}^\circ$ is the free energy of fusion for albite at T and 1 bar, and ΔV_{mAb} is the average volume change of melting over the P - T range of interest. Given $\Delta G_{\text{mAb}}^\circ$ and ΔV_{mAb} , the activity of NaAlSi₃O₈ in the liquid can then be calculated for the equilibrium between crystalline albite and liquid at any P - T . From the relations (Burnham, 1979; eq. 16-13 and 16-14)

$$\text{for } X_{\text{H}_2\text{O}}^1 \leq 0.5$$

$$a_{\text{Ab}}^1 = (1 - X_{\text{H}_2\text{O}}^1)^2$$

$$\text{and for } X_{\text{H}_2\text{O}}^1 > 0.5$$

$$\ln a_{\text{Ab}}^1 = (6.52 - 2667/T)[\ln(1 - X_{\text{H}_2\text{O}}^1) + X_{\text{H}_2\text{O}}^1] - \frac{515}{T} - 0.127$$

the H₂O content of the silicate liquid may be determined and hence $a_{\text{H}_2\text{O}}^1 (= a_{\text{H}_2\text{O}}^V)$ derived from Burnham's (1979) expressions 16-17, 16-18, and the data in his Figure 16-3.

In these calculations we have assumed the following:

(1) $\Delta V_{\text{mAb}} = 0.2$ cal/bar. Although this value is somewhat higher than that of Burnham (1979) ($= 0.187$ cal/bar), it agrees within 10% with the experimental data of Burnham and Davis (1971) and $\Delta V_{\text{mAb}}^{1\text{bar}}$ calculated from the partial molal volumes of Bottinga and Weill (1970) and Nelson and Carmichael (1979).

(2) $\Delta G_{\text{mAb}}^\circ$ can best be calculated from experimental data for the melting of albite for $a_{\text{H}_2\text{O}}^V \sim 1$ as well as with the data and thermodynamic formalism outlined above. This approach has the advantage that it is unnecessary to assume (as did Burnham, 1979 and Eggler and Kadik, 1979) that the free energy function for the vitrification of crystalline albite corresponds to that of $\Delta G_{\text{mAb}}^\circ$.

(3) The small solubility of CO₂ in the albite liquid has a small effect on a_{mAb} and can be ignored.

(4) The silicate component of the vapor phase has negligible effects on $a_{\text{H}_2\text{O}}^V$ (Burnham, 1979; Eggler and Kadik, 1979; Kesson and Holloway, 1974).

Results

Values of the activity coefficients of H₂O in the vapor ($a_{\text{H}_2\text{O}}^V$) calculated from our experimental data and those of Millhollen *et al.* (1971) are listed in

Table 3. There are five major sources of uncertainty in these values:

(1) The assumed uncertainty in ΔV_{mAb} would introduce a maximum error of 150 cal/mole (at 15 kbar) in the free energy of fusion of Ab ($\Delta G_{\text{mAb}}^{\circ}$).

(2) Assigning $\pm 10^{\circ}\text{C}$ uncertainties to the experimental temperatures for the albite solidus with $X_{\text{H}_2\text{O}}^{\text{V}} = 1$ introduces potential errors of about ± 100 cal/mole in both $\Delta G_{\text{mAb}}^{\circ}$ and ΔG_{mAb} , these values being considerably larger than contributions from errors in the experimental pressures.

(3) Additional uncertainties in $\Delta G_{\text{mAb}}^{\circ}$ and ΔG_{mAb} derive from the activity-composition relations for hydrous albite melts (Burnham, 1979; Burnham and Davis, 1974). These authors state that their P - V - T data are unlikely to introduce errors of more than ± 100 cal/mole in the free energies of such liquids over the P - T - X_{Ab}^{I} range considered in this study. They cite the agreement of measured and calculated solubilities of H₂O in albite liquids (see also Eggler and Kadik) and also small discrepancies between calculated and experimental Ab-H₂O melting curves. A generous estimate of the overall uncertainty of the free energy data for albite melting used

to derive the activity-composition relations of the coexisting hydrous melt is ± 200 cal/mole.

Although our calculated $\Delta G_{\text{mAb}}^{\circ}$ function agrees with that derived by Burnham (1979) from thermochemical data for temperatures above 800°C , our values for $\Delta G_{\text{mAb}}^{\circ}$ at 700°C are 500–700 cal/mole lower. This results from our reliance on the high-pressure melting data for Ab-H₂O rather than on tabulated values for the vitrification of albite. Utilizing a finite-difference method, we derive $\Delta G_{\text{mAb}}^{\circ}/\Delta T \sim \Delta S_{\text{mAb}}^{\circ}$ of 12 – 13 cal $\cdot$ mole⁻¹ $\cdot$ K⁻¹ for temperatures near the melting of albite at atmospheric pressure. This value of $\Delta S_{\text{mAb}}^{\circ}$ is about 10% higher than that of Weill *et al.* (1980), and it indicates an initial $dP/dT = 50$ – 65 bars $\cdot$ K⁻¹ for the anhydrous melting curve of albite. Boettcher *et al.* (1982) experimentally determined the slope for this reaction to be ~ 120 bar $\cdot$ K⁻¹ at pressures above several kbar. The discrepancy between the calculated and experimental slopes requires that the atmospheric values of entropy or volume of fusion, or both, are incorrect or change significantly at high pressures. Boettcher *et al.* (1982) concluded that the published values of $\Delta H_{\text{mAb}}^{\circ}$ are correct because of the agreement among various calorimetric determinations (see Weill *et al.*, 1980). The specific volumes of crystalline albite were determined with great accuracy ($2\sigma = 0.002$ cm³gr⁻¹) by Burnham and Davis (1971) to 8.5 kbar and about 700°C . However, their determination of the specific volumes of albite liquid is less reliable. Data were obtained only on albite liquids with 8.25 and 10.9 wt% H₂O; the data for anhydrous liquid was obtained from the density of albite glass, applying the thermal-expansion data of such glass (Orlowski and Koenig, 1941) and assuming a compressibility 10% greater than that of crystalline albite. Phase transformations in albite liquid at high temperatures and high pressures would also change the specific volumes.

The apparent discrepancy between the calculated and experimental fusion of albite at high pressures may also be the result of differences in the behaviors of hydrous liquids (upon which our calculations are based) and the anhydrous liquids. H₂O tends to depolymerize the liquid by breaking Al-O-Si bonds, enhancing the transformation of Al from 4-fold to 6-fold sites (see Burnham, 1979). Thus, the structures of hydrous aluminosilicate liquids will differ from those of the anhydrous counterparts at equivalent pressures. However, our calculated P - T - $a_{\text{H}_2\text{O}}$ curves for albite melting should have largely

Table 3. Activity coefficients of H₂O in H₂O-CO₂ vapor

P kbar	T°C	$X_{\text{H}_2\text{O}}^{\text{V}}$	$a_{\text{H}_2\text{O}}^{\text{m}}$ *	$\gamma_{\text{H}_2\text{O}}^{\text{V}}$
5	725 $\pm$ 10	1.0	1.0	1.0
5	785	0.8 $\pm$ 0.02	0.93	1.2 $\pm$ 0.1
5	865	0.5	0.73	1.45 $\pm$ 0.15
5	915	0.3	0.59	2.0 $\pm$ 0.3
5	965	0.2	0.44	2.2 $\pm$ 0.5
5	1035	0.1	0.23	2.3 $\pm$ 0.8
7	695	1.0	1.0	1.0
7	755	0.8	0.90	1.1 $\pm$ 0.1
7	845	0.5	0.76	1.5 $\pm$ 0.15
7	875	0.3	0.68	2.3 $\pm$ 0.3
7	915	0.2	0.59	3.0 $\pm$ 0.5
7	995	0.1	0.38	3.7 $\pm$ 0.8
10	675	1.0	1.0	1.0
10	725	0.8	0.86	1.1 $\pm$ 0.1
10	795	0.5	0.79	1.6 $\pm$ 0.15
10	855	0.3	0.69	2.3 $\pm$ 0.3
10	895	0.2	0.64	3.1 $\pm$ 0.6
10	965	0.1	0.49	4.9 $\pm$ 1.0
15	635	1.0	1.0	1.0
15	715	0.8	0.88	1.1 $\pm$ 0.2
15	795	0.5	0.80	1.6 $\pm$ 0.3
15	845	0.3	0.74	2.5 $\pm$ 0.4
15	905	0.2	0.66	3.3 $\pm$ 0.67
15	975	0.1	0.52	5.2 $\pm$ 1.0
2*	935	0.5		1.2
3**	905	0.5		1.25
4**	805	0.5		1.4
4.4***	955	0.25		1.66

* Calculated from Burnham (1979)

** Experimental data of Millhollen *et al.* (1971)

*** Experimental data of Kesson and Holloway (1974)

compensated for these effects because we utilized Burnham's activity-composition data for the H₂O and albite components of the silicate melt. At present, the most reliable fusion temperatures for anhydrous liquids at high pressures are those directly determined experimentally.

(4) Another term that contributes to uncertainties in $\gamma_{\text{H}_2\text{O}}^V$ is the measured $X_{\text{H}_2\text{O}}^V$. For possible errors of $X_{\text{H}_2\text{O}}^V = \pm 0.02$ this term has negligible effect at high $X_{\text{H}_2\text{O}}^V$ but is a major source of uncertainty for low $X_{\text{H}_2\text{O}}^V$.

(5) The fifth uncertainty in the calculation of $\gamma_{\text{H}_2\text{O}}^V$ is dependent on the extent to which assumption (3) is correct. There are several studies on the solubility of CO₂ in hydrous (Eggler, 1973; Holloway and Lewis, 1974; Mysen *et al.*, 1976) and anhydrous (Mysen and Virgo, 1980a) melts of albite composition. With the exception of these studies, the primary source of solubility data for CO₂ in hydrous albite melts within the range of pressures and temperatures of interest is the synthesis experiments of Eggler and Kadik (1979). If it is assumed that their synthesis experiments yield equilibrium CO₂ contents in the melt and that CO₂ mixes ideally in the albite melt, the magnitude of the effect of dissolved CO₂ on calculated $\gamma_{\text{H}_2\text{O}}^V$ can be estimated from the formalism of Burnham outlined above with substitution of $a_{\text{mAb}} = 1 - X(\text{CO}_2)^m$. Such calculations are similar to those given by Eggler and Kadik (1979) and differ only in values of $\Delta G_{\text{mAb}}^\circ$. The calculations indicate that small but significant amounts of CO₂ in hydrous albite melt may reduce the $\gamma_{\text{H}_2\text{O}}^V$ by 0.4–0.7 for H₂O-poor vapor compositions. The lack of CO₂ solubility data for H₂O-rich vapor compositions prevents similar calculations at high $X_{\text{H}_2\text{O}}^V$. However, for $X_{\text{H}_2\text{O}}^V \leq 0.3$, values of $\gamma_{\text{H}_2\text{O}}^V$ in Table 3 should be regarded as upper limits, although the amount by which the values should be reduced is uncertain as a result of the lack of reversed experiments on the solubility of CO₂.

With the knowledge that values of ΔV_{mAb} and ΔS_{mAb} are unknown at high pressures, we combined the above sources of uncertainty (1–4) in the calculation of $\gamma_{\text{H}_2\text{O}}^V$, leading to the error limits given in Table 3. The largest uncertainties in $X_{\text{H}_2\text{O}}^V$ are for CO₂-rich vapor compositions. However, for the P - T - $X_{\text{H}_2\text{O}}^V$ range considered in this study, $a_{\text{H}_2\text{O}}^V$ should be reliable to within ± 0.1 .

Our $\gamma_{\text{H}_2\text{O}}^V$ values derived from the NaAlSi₃O₈-H₂O-CO₂ system exhibit trends broadly similar to those of Eggler and Kadik (1979). The $\gamma_{\text{H}_2\text{O}}^V$ values generally increase with increasing pressure and

exhibit marked positive deviations from ideality for $X_{\text{H}_2\text{O}}^V \leq 0.2$, the largest values of $\gamma_{\text{H}_2\text{O}}^V$ being for low values of $X_{\text{H}_2\text{O}}^V$. The data overlap with that calculated from Kesson and Holloway (1974) for $X_{\text{H}_2\text{O}}^V = 0.25$ in a C-O-H-N vapor. The main discrepancies between Eggler and Kadik's data and our own derive from systematic differences in our experimentally determined phase relations and to a lesser extent in our values for $\Delta G_{\text{mAb}}^\circ$. In view of the better agreement of our experimental data with those of Millhollen *et al.* (1971) and Kesson and Holloway (1974), and the more extensive character and good internal consistency of our data, we believe our values of $\gamma_{\text{H}_2\text{O}}^V$ should be preferred.

Although our melting curves for Ab-H₂O-CO₂ cover a range of temperatures, the temperature dependence of $\gamma_{\text{H}_2\text{O}}^V$ cannot be retrieved from these data because isobars cross the melting curves only once (Fig. 1). However, our $\gamma_{\text{H}_2\text{O}}^V$ values join smoothly with those of Chou and Williams (1979). Also, our values and those of Chou and Williams (at 2 kbar) do not show the strong temperature dependence implied by Eggler and Kadik. Smulovich *et al.* (1982) tabulated activity-composition relations for CO₂-H₂O mixtures to 5 kbar, based primarily on *PVT* data. Their $\gamma_{\text{H}_2\text{O}}^V$ (like ours) are largest for high $X_{\text{CO}_2}^V$ and also increase with increasing pressure. However, at any given pressure and $X_{\text{CO}_2}^V$, the Smulovich *et al.* values of $\gamma_{\text{H}_2\text{O}}^V$ decline monotonically with increasing temperature and hence are unlikely to be consonant with our higher-temperature values. Whereas complete, accurate *PVT* data for fluid mixtures should generally yield better mixing properties than phase-equilibrium-based data, it should be noted that their values of $\gamma_{\text{H}_2\text{O}}^V$ for pressures above 1 kbar are derived from *PVT* measurements for 3 mixtures at 400°C and only two compositions at 500°C. The *PVT* data were fit, interpolated, and extrapolated using empirical functions. However, Smulovich *et al.* give no indication of overall uncertainties for their $\gamma_{\text{H}_2\text{O}}^V$, which are most poorly constrained at high $X_{\text{CO}_2}^V$, where the disagreement with our data is probably greatest. These discrepancies are disturbing and may indicate problems with the model-based aspects of our activity-composition relations or those of Smulovich *et al.* CO₂-H₂O may exhibit distinctly unusual behavior, with $\gamma_{\text{H}_2\text{O}}^V$ declining from near solvus-temperature values and then increasing at higher temperatures. In any case it seems that at this stage we cannot make unequivocal statements as to the temperature dependence of $\gamma_{\text{H}_2\text{O}}^V$.

Comparisons of our derived values of $\gamma_{\text{H}_2\text{O}}^V$ can be made with those calculated from semi-empirical equations of state such as modified Redlich-Kwong (MRK) expression (Holloway, 1977; Flowers, 1979; Kerrick and Jacobs, 1981). If our model-dependent, water-activity coefficients are correct, then such comparisons cast considerable doubt on the power of these formulations to predict mixing relations in these H₂O-CO₂ systems. The MRK $\gamma_{\text{H}_2\text{O}}^V$ values are significantly lower than those in Table 3 and do not exhibit the large deviations from ideality for the H₂O component at low $X_{\text{H}_2\text{O}}^V$. Existing MRK formulations fit the P - V - T data for pure H₂O and CO₂ (Wall and Holloway, in preparation) moderately well, so the problem appears to lie in the nature of the empirical terms involved in predicting the behavior of mixtures.

Given some additional determinations of $\gamma_{\text{H}_2\text{O}}^V$ over the pressure range of our data, application of the Gibbs-Duhem relation would lead to evaluation of $\gamma_{\text{CO}_2}^V$. The mixing relations for H₂O-CO₂ indicated by our data suggest that the CO₂ component of the fluid should exhibit the largest positive deviations from ideality for high values of $X_{\text{H}_2\text{O}}^V$. A similar conclusion was reached by Chou and Williams (1979) and Smulovich *et al.* (1982).

Geochemical applications

H₂O-CO₂ mixtures have been widely used in high-pressure, phase-equilibrium studies of subsolidus and melting reactions as a means of controlling $a_{\text{H}_2\text{O}}$ and a_{CO_2} in the experimental environment (*e.g.* Holloway *et al.*, 1968; Boettcher *et al.*, 1973). The marked deviations from ideality exhibited by H₂O (and presumably CO₂) make it imperative that activity coefficients for the volatile components be applied to extract accurate thermodynamic data from the experimental phase relations and to extrapolate them to other P - T - $X_{\text{H}_2\text{O}}$ conditions. For example, for $X_{\text{H}_2\text{O}}^V = 0.2$ at about 800–900°C and 19 kbar, $a_{\text{H}_2\text{O}} = 0.5$ – 0.6 . If $\gamma_{\text{H}_2\text{O}}$ were not applied, an error of approximately 2.0 kcal · mole⁻¹ H₂O would be contributed to the free energy of a reaction involving H₂O. Similarly, calculation of high-pressure P - T - $X_{\text{H}_2\text{O}}$ relations for equilibria involving H₂O-CO₂ mixtures using fugacity data for pure H₂O and CO₂ requires adjustment for $\gamma_{\text{H}_2\text{O}}$ and/or γ_{CO_2} . Such considerations are important in the quantitative evaluation of the chemistry of lower-crustal and upper-mantle fluids.

Estimates of the H₂O contents of magmas based on experimentally determined phase relations in the

presence of H₂O-CO₂ vapors and the assumption of ideal mixing of these volatile components (*e.g.* Eggler and Burnham, 1973; Clemens and Wall, 1981) would need to be revised upwards in the light of our $\gamma_{\text{H}_2\text{O}}^V$ data. Consider, for example, a granitic melt coexisting with a H₂O-CO₂ vapor of $X_{\text{H}_2\text{O}}^V = 0.2$ at 900°C and 10 kbar. Using Burnham's (1979) model, this melt would have a H₂O content of approximately 2.5 wt% if ideal mixing of H₂O-CO₂ were assumed. Application of our values of $\gamma_{\text{H}_2\text{O}}^V$ would require 6 wt% H₂O in the liquid. The systematics of equilibria between crystalline hydrates and liquid (*e.g.* Holloway, 1973) may also require re-examination in view of the large $\gamma_{\text{H}_2\text{O}}^V$ for the more CO₂-rich fluid compositions used in such experimental studies.

High-grade regional metamorphic reactions and partial melting in the lower crust and upper mantle commonly involve C-O-H components. Over a wide range of redox conditions, high-pressure C-O-H fluids are dominated by H₂O and CO₂ (Eugster and Skippen, 1967; Ohmoto and Kerrick, 1977). On the basis of fluid inclusion studies Touret (1971), Hollister and Burruss (1976) and others suggested that the apparently relatively "dry" metamorphic conditions indicated by many granulite facies assemblages resulted from CO₂-rich metamorphic fluids. If these compositions can be taken as representative of fluids present during metamorphism, values of $a_{\text{H}_2\text{O}}$ could be much higher than might be anticipated from supposing ideal mixing of H₂O and CO₂. For example, our values of $\gamma_{\text{H}_2\text{O}}$ imply that for temperatures of 800–900°C, pressures of 7 to 15 kbar, and $X_{\text{H}_2\text{O}}$ in the range of 0.1–0.3, $a_{\text{H}_2\text{O}}$ in H₂O-CO₂ fluid ranges between about 0.4 and 0.7. Fluids approaching pure CO₂ would be compatible with water fugacities of a few hundred bars inferred for some granulites (*e.g.* Wones and Eugster, 1965; Bohlen *et al.*, 1980b) or vapor-absent situations could have prevailed in these terranes. The moderate values of $a_{\text{H}_2\text{O}}$ required for the development of granitic melts (under typical granulite facies conditions 7 to 10 kbar, 800°C) could be achieved even in the presence of relatively CO₂-rich fluids. Indeed, preferential dissolution of H₂O relative to CO₂ in these silicate melts could lead to the evolution of such CO₂-rich fluids (Holloway, 1976).

There are many other applications and implications of H₂O-CO₂ mixing relations in the evaluation of physicochemical conditions and processes in igneous and metamorphic systems. In view of the importance of these volatile components for quanti-

tative petrogenetic modeling, there is an urgent need for the determination of additional H₂O-CO₂ activity-composition data to complement ours. Such investigations should concentrate on lower temperatures and higher pressures than in our study.

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