SCIENTIFIC COMMENT

An extended equation to calculate NaCl contents from final clathrate melting temperatures in H₂O-CO₂-NaCl fluid inclusions: Implications for *P-T* isochore location

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Abstract—This report informs fluid inclusion researchers of an extended equation to calculate wt% NaCl from final CO_2-clathrate melting temperatures in H_2O-CO_2-NaCl fluid inclusions. This equation is valid only if melting occurs in the presence of CO_2-liquid, CO_2-vapor, and salt solution. Previous workers used the equation of BOZZO et al. (1973, 1975) for salinity calculations; however, their equation is limited to clathrate melting temperatures between 10 and about 0°C (0–16 wt% NaCl). Application of this equation to final clathrate melting temperatures from 0°C to the peritectic temperature of -10.0°C (16–24.2 wt% NaCl) yields significant errors in calculated NaCl content. Experimental data over the entire range of 10 to -10.0°C is provided by CHEN (1972b) and his best fit equation is

$$W = +0.00098241(10 - T)(T^2 + 45.385T + 1588.75),$$

where W is the wt% NaCl and T is the final clathrate melting temperature (°C). The values of W calculated by this equation are relative only to the salt solution (independent of CO_2 content) and have an average and maximum deviation of 1.33 and 5.61%, respectively (from the experimentally determined values of W). This equation should be used instead of the equation of BOZZO et al. (1973, 1975) in fluid inclusion data reduction programs such as HALWAT and CHNACL described by NICHOLLS and CRAWFORD (1985) and FLINCOR described by BROWN (1989). Without such correction, calculation of isochore position in *P-T* space using these programs may yield significant errors if fluid inclusions have final clathrate melting temperatures between 0 and -10.0°C.

INTRODUCTION

H_2O-CO_2-NaCl FLUID INCLUSIONS occur in rocks from a wide variety of geologic settings and their analysis and interpretation has been the subject of much scrutiny in recent years (BOWERS and HELGESON, 1983; PARRY, 1986; BROWN and LAMB, 1989). One of the fundamental microthermometric measurements in analysis of these inclusions is the final CO_2-clathrate melting temperature. COLLINS (1979) was the first to described how final clathrate melting temperatures could be used to estimate NaCl contents of inclusion fluids. He reproduced graphically the experimental results of CHEN (1972a) and BOZZO et al. (1973, 1975) who determined the decomposition temperature of CO_2-clathrate in the presence of CO_2-vapor and CO_2-liquid as a function of NaCl content. BOZZO et al. (1973, 1975) provide an equation to calculate NaCl contents but its validity is limited to clathrate melting temperatures in the range of 0 to 10°C and does not describe the experimental data at lower temperatures. This discrepancy results in significant errors in calculated NaCl contents for clathrate melting temperatures less than 0°C. Furthermore, the equation of BOZZO et al. (1973, 1975) is incorporated into at least three commonly employed fluid inclusion data reduction computer programs: HALWAT and CHNACL (NICHOLLS and CRAWFORD, 1985) and FLINCOR (BROWN, 1989). Application of these algorithms to H_2O-CO_2-NaCl fluid inclusions with final CO_2-clathrate melting temperatures

in the 0 to -10°C range result in significant errors in isochore location over some *P-T* ranges. This report is intended to clarify the limits of the equation of BOZZO et al. (1973, 1975) and to inform fluid inclusion researchers of another equation to calculate weight percent NaCl from final clathrate melting temperatures over the entire range from 10 to -10.0°C.

THE SALT SOLUTION + CO₂-VAPOR + CO₂-LIQUID + CO₂-CLATHRATE UNIVARIANT

The salt solution + CO_2-vapor + CO_2-liquid + CO_2-clathrate univariant was experimentally determined by CHEN (1972a) in the temperature range of 10 to 0°C (0–16 wt% NaCl). Confusion arises because BOZZO et al. (1973, 1975) show graphically the experimental results between 10 and -10.0°C (0.0 and 24.2 wt% NaCl), but provide an equation that is valid only from 0–16 wt% NaCl, and no experimental data. Their least squares regression is

$$W = +0.05286(10 - T)(T + 29.361), \tag{1}$$

where W is the wt% NaCl and T is the final clathrate melting temperature (°C). While Eqn. (1) is valid for fluid inclusions with final clathrate melting temperatures between 10 and about 0°C, it fails to describe the experimental data for the 0 to -10.0°C range (Fig. 1). The experimental data along the univariant illustrated by BOZZO et al. (1973, 1975) was
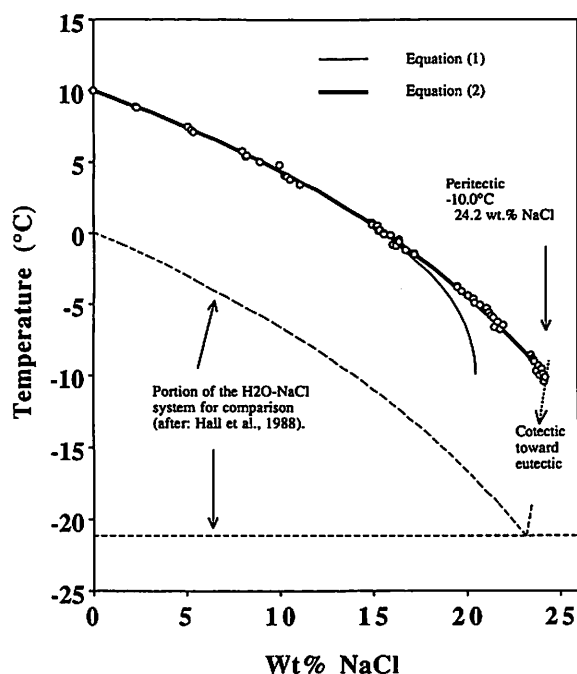
FIG. 1. NaCl effect on dissolution temperature of CO_2-clathrate in the presence of CO_2-vapor and CO_2-liquid. Modified after BOZZO et al. (1973, 1975). Circles represent experimental data along the salt solution + CO_2-vapor + CO_2-liquid + CO_2-clathrate univariant (Table 1). Heavy solid line is Eqn. (2) in text (from CHEN, 1972b, p. 19). Light solid line is Eqn. (1) in text (from BOZZO et al., 1973, 1975). Light dotted line is position of salt solution + CO_2-vapor + CO_2-clathrate + hydrohalite univariant (see CHEN, 1972b, Table 11 for experimental data). Dashed line is a portion of the H_2O-NaCl system (CO_2-free) for comparison (see HALL et al., 1988, for experimental data). See text for further details.

completed by CHEN (1972b). These data are not readily available and are reproduced here (Table 1) for immediate use to fluid inclusion researchers. CHEN (1972b) provides a least squares regression that describes the experimental data over the entire temperature range of 10 to −10.0°C (0 to 24.2 wt% NaCl):

$$W = +0.00098241(10 - T)$$

$$\times (T^2 + 45.385T + 1588.75), \quad (2)$$

where W is the wt% NaCl and T is the final clathrate melting temperature (°C). The values of W calculated by Eqn. (2) are only relative to the salt solution (i.e., a CO_2-free basis). Equation (2) deviates from the experimentally determined values of W by an average of 1.33% and a maximum of 5.61% (CHEN, 1972b). Equation (2) should be used to calculate NaCl contents for all final CO_2-clathrate melting temperatures between 10 and −10.0°C provided melting occurs in the presence of CO_2-vapor, CO_2-liquid, and salt solution.

A NOTE ON THE H_2O-CO_2-NaCl PERITECTIC

The five-phase invariant in the H_2O-CO_2-NaCl system where salt solution, CO_2-liquid, CO_2-vapor, CO_2-clathrate, and hydrohalite are in equilibrium was determined by CHEN (1972b) and presented in BOZZO et al. (1973, 1975). These

authors describe the invariant as the eutectic for the H_2O-CO_2-NaCl system, but this point is probably not a ternary minimum but rather a peritectic (I-MING CHOU and PAUL B. BARTON JR., pers. commun.) and is referred to as such in this report. Both CHEN (1972b) and BOZZO et al. (1973, 1975) describe the same two methods of approaching the peritectic: (1) by intersection of the two univariants, (a) salt solution, CO_2-liquid, CO_2-vapor, CO_2-clathrate, and (b) salt solution, CO_2-vapor, CO_2-clathrate, hydrohalite in pressure-temperature space and (2) intersection of the same two univariants in temperature-composition space. The two methods give peritectic conditions of −9.6°C and 24.2 wt% NaCl and −10.0°C and 24.2 wt% NaCl, respectively. Peritectic conditions of the latter method are used in this report because of the direct applicability (of T-X space) to final CO_2-clathrate melting temperatures in the study of fluid inclusions. However, CHEN (1972b) and BOZZO et al. (1973, 1975) preferred peritectic conditions of −9.6°C and 24.2 wt% NaCl because their measurements of pressure and temperature were more accurate than measurements of NaCl content.

ERRORS IN CALCULATED NaCl CONTENT

The difference in calculated salinities between Eqns. (1) and (2) is shown in Fig. 1. Both equations adequately describe the experimental data between about 0 and 10.0°C, yet significant errors in predicted NaCl content occur with Eqn. (1) for temperatures in the 0 to −10.0°C range. The greatest amount of error occurs at the peritectic temperature of −10°C where Eqn. (1) predicts an NaCl content of 20.47 wt% and Eqn. (2) predicts 24.26 wt% NaCl, a difference of 3.79 wt% or 15.6% of the total.

TABLE 1. Experimental data along the salt solution + CO_2-vapor + CO_2-liquid + CO_2-clathrate univariant (From: Tables 5 and 10 of CHEN, 1972b). Temperatures and NaCl content have associated errors of ±0.025°C and ±1.0%, respectively (CHEN, 1972b, pp. 8, 10).

| Temp. (°C)	Wt % NaCl	Temp. (°C)	Wt % NaCl	Temp. (°C)	Wt % NaCl
10.00	0.00	0.20	15.28	−5.63	21.18
8.94	2.28	0.03	15.56	−5.80	21.28
8.79	2.35	−0.07	15.57	−6.00	21.42
7.52	5.05	−0.23	15.94	−6.27	21.64
7.31	5.23	−0.56	16.39	−6.55	21.92
7.08	5.38	−0.56	16.38	−6.60	21.47
5.78	8.00	−0.82	16.02	−6.80	21.72
5.53	8.20	−0.92	16.20	−8.60	23.45
5.36	8.14	−1.16	16.75	−8.80	23.50
5.00	8.90	−1.34	16.94	−8.90	23.58
4.75	9.98	−1.44	17.19	−9.00	23.63
4.13	10.25	−1.49	17.21	−9.28	23.83
4.00	10.37	−3.68	19.47	−9.50	23.99
3.84	10.53	−3.75	19.48	−9.73	23.74
3.44	11.09	−4.05	19.73	−9.92	24.08
0.66	14.94	−4.44	20.07	−9.97	23.89
0.64	14.94	−4.62	20.33	−10.08	24.21
0.52	15.20	−4.87	20.42	−10.40	24.11
0.48	15.16	−5.10	20.69		
0.20	15.34	−5.32	21.02		
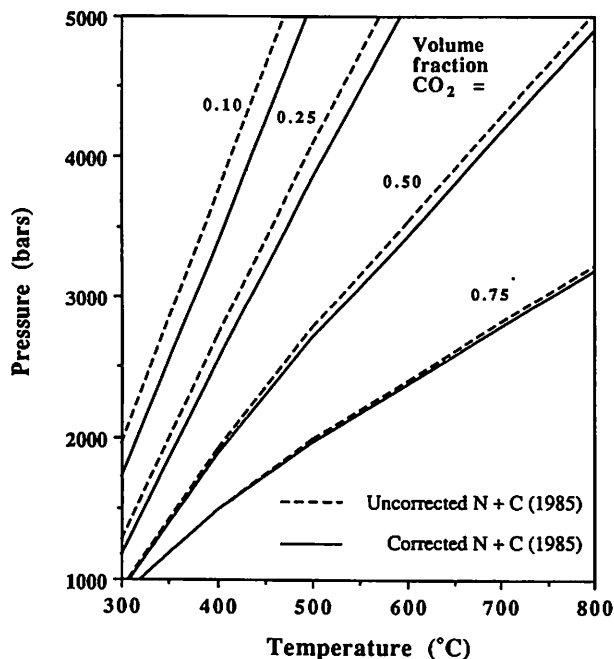
FIG. 2. Isochores calculated by the program CHNACL of NICHOLLS and CRAWFORD (1985) and a modified version of the same program. Dashed isochores (uncorrected) were calculated with Eqn. (1) in text. Solid isochores (corrected) calculated with Eqn. (2) in text. Isochores calculated for CO_2 volume fractions of 0.10, 0.25, 0.50, 0.75. See text for further details.

IMPLICATIONS FOR ISOCHORE POSITION IN P-T SPACE

Figure 2 illustrates the difference in isochore position in P-T space calculated by two versions of the program CHNACL of NICHOLLS and CRAWFORD (1985). Dashed isochores (uncorrected) were calculated with the original version of CHNACL that uses Eqn. (1) while solid isochores (corrected) were calculated with a modified version of CHNACL that uses Eqn. (2). All isochores in Fig. 2 were constructed for a fluid inclusion with (1) a final CO_2-clathrate melting temperature of $-10.0°C$ (peritectic temperature); (2) an arbitrarily chosen CO_2 density of 0.6 gm/cm³ ($ThCO_{2(liquid)}$ = 29.8968°C), and (3) CO_2 volume fraction ($V_{CO_2}/V_{total fluid}$) estimates of 0.10, 0.25, 0.50, and 0.75 (estimated at 40°C). Figure 2 illustrates that all isochores are shifted to lower pressures for any given temperature when using the equation of CHEN (1972b; i.e., when higher NaCl contents are predicted). The shift of isochores to lower pressures is greatest in those inclusions with low volume fraction of CO_2. For example, a fluid inclusion with 10 vol% CO_2 will have its corrected isochore positioned 360 bars lower at 400°C than the uncorrected isochore. The shift is greater at higher temperatures, pressures, and lower volume fractions of CO_2. Fluid inclusions with higher volume fractions of CO_2 (e.g., V_{CO_2} = 0.75) show little deviation in isochore position between corrected and uncorrected programs. Similar errors in isochore position are generated by the program FLINCOR (BROWN, 1989) which also uses the equation of BOZZO et al. (1973, 1975) for determination of NaCl content.

CONCLUSIONS

Determination of wt% NaCl by final CO_2-clathrate melting temperatures in H_2O-CO_2-NaCl fluid inclusions should not use Eqn. (1) but rather Eqn. (2). This method of determining NaCl contents is valid only if the CO_2-clathrate melted in the presence of CO_2-vapor, CO_2-liquid, and salt solution. Any computer program that calculates position of isochores in P-T space for H_2O-CO_2-NaCl fluid inclusions should be corrected to account for the experimental data over the entire 10 to $-10°C$ temperature range. Equation (2) should replace Eqn. (1) in programs such as HALWAT (Line 135) and CHNACL (Line 177) of NICHOLLS and CRAWFORD (1985) and FLINCOR.C (equations in FUNCTION: TernaryDlg and FUNCTION: TernBLDlg) of BROWN (1989).

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