Geochimica et Cosmochimica Acta Vol. 56, pp. 1451–1460
Copyright © 1992 Pergamon Press Ltd. Printed in U.S.A.

0016-7037/92/$5.00 + .00

The prediction of methane solubility in natural waters to high ionic strength from 0 to 250°C and from 0 to 1600 bar

ZHENHAO DUAN, NANCY MØLLER, JERRY GREENBERG, and JOHN H. WEARE
Department of Chemistry (0340), University of California, San Diego, La Jolla, CA 92093, USA

(*Received May* 20, 1991; *accepted in revised form January* 15, 1992)

Abstract—A model for the solubility of methane in brines (0–6 m) for temperatures from 0 to 250°C and for pressures from 0 to 1600 bar (or slightly above) is presented. The model is based on Pitzer phenomenology for the liquid phase and a highly accurate equation of state recently developed for the vapor phase. Comparison of model predictions with experimental data indicates that they are within experimental uncertainty. Most experimental data sets are consistent within errors of about 7%. Although the parameters were evaluated from binary and ternary data, the model accurately predicts methane solubility in much more complicated systems like seawater and Salton geothermal brines. Application to fluid inclusion analysis is discussed. Minimum trapping pressures are calculated given the composition and homogenization temperature.

INTRODUCTION

METHANE-BEARING FLUIDS have been reported in many geological settings (e.g., geothermal systems, WHITE et al., 1963; geopressured-geothermal reservoirs, PRICE, 1981; KHARAKA et al., 1985; fluid inclusions of tectonic melanges, VROLIJK et al., 1988). Because of its importance, there have been many studies of the methane-salt-water system. The solubility varies with temperature, pressure, and brine composition. However, controversy over the reliability of data (BARTA and BRADLEY, 1985; DRUMMOND, 1981) and the lack of an equation of state for the gas phase has prevented the development of quantitatively reliable models. For many geological conditions, methane solubilities are still unknown. The empirical models published by PRICE (1981) and DRUMMOND (1981) are simple but accurate only in a T-P-m_{NaCl} range smaller than the data range. A specific interaction model introduced by BARTA and BRADLEY (1985) is no more accurate than the empirical model of PRICE (1981).

In this article we introduce a model for this system covering a large T-P-m range. The chemical potential of methane in the vapor phase is calculated using the equation of state recently reported by DUAN et al. (1992a), assuming ideal mixing of CH_4 and H_2O in the vapor phase. Little error arises from this assumption according to the equation of state for the CH_4-H_2O mixtures (DUAN et al., 1992b). The chemical potential of CH_4 in the liquid phase is described by specific interaction model established from solubility data. This is discussed in the next section. In order to disentangle the controversy over the experimental measurements, the available data are reviewed in the subsequent section. We found that most of the major data sets are consistent. Parameters are evaluated in Parameterization and comparison with experimental data section. Comparison with data indicates that the model can predict methane solubility to high ionic strength (6 m) from 0 to 250°C and from 0 to 1600 bar within experimental uncertainty. It also has reasonable accuracy when extrapolated up to 350°C. Application to seawater and Salton Sea geothermal brine illustrates its accuracy in complex systems. Finally we discussed the application of the model to fluid inclusion analysis.

NOTATION

T	absolute temperature in Kelvin
P	total pressure; $= P_{CH_4} + P_{H_2O}$ in bar
x	composition in vapor phase
R	univeral gas constant; =0.08314467 bar · l/mol · K
m	molality of CH_4 or salts in the liquid phase
ϕ	fugacity coefficient
γ	activity coefficient
μ	chemical potential
$\lambda_{CH_4\text{-ion}}$	interaction parameter
$\zeta_{CH_4\text{-cation-anion}}$	interaction parameter
Par	parameter

SUBSCRIPTS

a	anion
c	cation
h	homogenization

SUPERSCRIPTS

v	vapor
l	liquid
(0)	standard state

PHENOMENOLOGICAL DESCRIPTION OF GAS SOLUBILITY AS A FUNCTION OF COMPOSITION, PRESSURE, AND TEMPERATURE

Methane solubilities in aqueous solutions are determined by the balance of its chemical potentials in the liquid phase, $\mu^{aq}_{CH_4}$ and in the gas phase, $\mu^{v}_{CH_4}$. These can be written in terms of fugacity in the vapor phase and activity in the liquid phase as

$$\begin{aligned}\mu^{v}_{CH_4}(T, P, x) &= \mu^{v(0)}_{CH_4}(T) + RT \ln f_{CH_4}(T, P, x) \\ &= \mu^{v(0)}_{CH_4}(T) + RT \ln x_{CH_4}P + RT \ln \phi_{CH_4}(T, P, x)\end{aligned} \tag{1}$$

$$\begin{aligned}\mu^{l}_{CH_4}(T, P, m) &= \mu^{l(0)}_{CH_4}(T, P) + RT \ln a_{CH_4}(T, P, m) \\ &= \mu^{l(0)}_{CH_4}(T, P) + RT \ln m_{CH_4} + RT \ln \gamma_{CH_4}(T, P, m).\end{aligned} \tag{2}$$

At equilibrium, we obtain

$$\ln \frac{x_{CH_4}P}{m_{CH_4}} = \frac{\mu_{CH_4}^{l(0)}(T, P) - \mu_{CH_4}^{v(0)}(T)}{RT} - \ln \phi_{CH_4}(T, P, x) + \ln \gamma_{CH_4}(T, P, m). \quad (3)$$

The standard chemical potential of CH_4 in liquid phase, $\mu_{CH_4}^{l(0)}$, is the chemical potential in hypothetically ideal solution of unit molality (see DENBIGH, 1971). The vapor phase standard chemical potential, $\mu_{CH_4}^{v(0)}$, is the chemical potential when the fugacity is equal to 1 bar. In the following, $\mu_{CH_4}^{v(0)}$ is set to zero since solubility is only a function of the difference between $\mu_{CH_4}^{l(0)}$ and $\mu_{CH_4}^{v(0)}$. According to the equation of state by DUAN et al. (1992b), the fugacity coefficient of CH_4 in the vapor phase of CH_4-H_2O mixtures differs very little from that in pure CH_4 for temperature below 250°C (because the water concentration is relatively small). Therefore, $\ln \phi_{CH_4}$ can be calculated from the equation of state for pure CH_4 (see Appendix) or can be taken from tables (DUAN et al., 1992a). There are no vapor composition measurements in the ternary CH_4-H_2O-NaCl. We assume that water vapor pressure is not affected by the presence of NaCl and CH_4. Consequently, x_{CH_4} can be approximately calculated from

$$x_{CH_4} = (P - P_{H_2O})/P, \quad (4)$$

where P_{H_2O} is the pure water pressure, which can be calculated from the equation of state (DUAN, 1992a) or taken from the steam tables (HAAR et al., 1984). This assumption may lead to errors (up to about 5%) for $\mu_i^{l(0)}/RT$ and $\ln \gamma_{CH_4}^{l}$. However, their errors cancel approximately in our parameterization, and the effect on the calculation of methane solubility is vanishingly small. $\ln\gamma_{CH_4}$ is derived from a virial expansion of excess Gibbs Energy (PITZER, 1973):

$$\ln \gamma_{CH_4} = \sum_{c} 2\lambda_{CH_4\text{-}c} m_c + \sum_{a} 2\lambda_{CH_4\text{-}a} m_a + \sum_{c}\sum_{a} \zeta_{CH_4\text{-}a\text{-}c} m_c m_a. \quad (5)$$

Using Eqn. (5) in Eqn. (3) gives

$$\ln \frac{x_{CH_4}P}{m_{CH_4}} = \frac{\mu_{CH_4}^{l(0)}}{RT} - \ln \phi_{CH_4} + \sum_{c} 2\lambda_{CH_4\text{-}c} m_c + \sum_{a} 2\lambda_{CH_4\text{-}a} m_a + \sum_{c}\sum_{a} \zeta_{CH_4\text{-}c\text{-}a} m_c m_a. \quad (6)$$

In the above equation, λ's, ζ's, and the unitless standard chemical potential, $\mu_{CH_4}^{l(0)}/RT$, are dependent upon temperature and total pressure. Following PITZER et al. (1984), we select the following equation for the parameters,

$$\text{par}(T, P) = c_1 + c_2T + c_3/T + c_4T^2 + c_5/(680 - T) + c_6P + c_7P \ln T + c_8P/T + c_9P/(680 - T) + c_{10}P^2/T. \quad (7)$$

Eqns. (6) and (7) form the basis of our parameterization.

REVIEW OF SOLUBILITY DATA OF METHANE

CH_4 solubility has been measured for a wide range of temperature, pressure, and NaCl concentration (Table 1). Our survey of the available measurements indicated that most data sets giving CH_4 solubility in pure water are consistent except for the MICHELS et al. (1936) data and some of the BLOUNT et al. (1979) data below 300 bar. The most comprehensive data set reported by BLOUNT et al. (1979) has a temperature, pressure, and NaCl concentration range of 100 to 240°C, 150–1540 bar, and 0 to 5.7 m. An experimental error in this data set was pointed out by PRICE (1981). We compared this data set with the empirical equation of PRICE (1981; which is based on the corrected data of BLOUNT et al., 1979), and other data sets. About 70% of the data points of BLOUNT et al. (1979) for pressure below 300 bar data have 10–35% higher solubility (these were not included in our evaluation of parameters). Those above 300 bar are consistent with the data sets reported by CULBERSON and MCKETTA (1951), O'SULLIVAN and SMITH (1970), and SULTANOV et al. (1972), with an error less than 8%, which is nearly within the experimental error. The BLOUNT et al. (1979) data are consistent with the data of O'SULLIVAN and SMITH (1970) in the overlapping *T-P-m* space with deviation of 2–10%. The data of CRAMER (1984) below 200°C and 3 m NaCl are compatible with BLOUNT et al. (1979) and O'SULLIVAN and SMITH (1970), with a deviation of 7–15%. The data of DUFFY et al. (1961) show large uncertainties, the deviation being as high as 30%. The MICHELS et al. (1936) data are not compatible with other data sets. Between 250 and 400°C, there is little data on methane solubility in salt solutions. This prevented us from extending the model to temperatures well above 250°C.

Methane solubility data in aqueous solutions with salt other than NaCl is very limited. The data of STOESSELL and BYRNE (1982) for 25°C and pressure below 50 bar includes almost all major salts in natural waters.

Table 1. Aqueous CH_4 Solubility Measurements

Authors	Solution	Temperature (C)	P(bar)	# of measurements
Winkler (1901)	pure water	0-40	1	6
Michels et al(1936)	NaCl(0-5.4m)	25-150	40-465	136
Culberson and Mcketta (1951)	pure water	25-171	20-680	71
Claussen Polglase(1952)	pure water	1-40	1.0	17
Mishnina et al(1961)	NaCl(0-5.3m)	4-90	1	44
Duffy et al(1961)	NaCl(0-5.4m)	25-	10-60	40
O'Sullivan and Smith(1970)	0-4 m NaCl	51-125	100-610	48
Sultanov et al(1972)	pure water	150-360	150-1080	64
Ben-Naim et al(1974)	pure water	10-30	1	5
Yamamoto et al(1976)	pure water	0-30	1.0	35
Blanco and Smith(1978)	1 m CaCl2	25-125	100-608	30
Wiesenburg et al(1979)	pure and seawater	0-30	1	180
Blount et al(1979)	0-5.7 m NaCl	100-240	100-1560	642
Price(1979)	pure water	154-354	16-1900	71
Cramer(1984)	0-4m NaCl	4-300	10-143	91
Krader and Frank(1987)	0-2 m NaCl	400-530	400-2500	137
Stoessell and Byme(1982)	all salts in Na- K-Mg-Ca-Cl-SO4 HCO3-CO3	25	20-50	96

Table 2 interaction parameters				
T-P coefficient	$\mu_{CH_4}^{l(o)}/RT$	$\lambda_{CH4,Na}$	$\lambda_{CH_4,Ca}$	$\zeta_{CH4,Na,Cl}$
c_1	4.30210345D+01	9.92230792D-02	-5.64278808D+00	-6.23943799D-03
c_2	-6.83277221D-02	2.57906811D-05	8.51392725D-03	
c_3	-5.68718730D+03		1.00057752D+03	
c_4	3.56636281D-05			
c_5	-5.79133791D+01			
c_6	6.11616662D-03		5.27816886D-05	
c_7	-7.85528103D-04			
c_8	-9.42540759D-02	1.83451402D-02		
c_9	1.92132040D-02			
c_{10}	-9.17186899D-06	-8.07196716D-06		

PARAMETERIZATION AND COMPARISON WITH EXPERIMENTAL DATA

In order to calculate the solubility of methane at a given temperature, pressure, and salt composition, we need to determine the parameters λ's and ζ's for each cation and anion in the liquid as well as the standard chemical potential $\mu_{CH_4}^{l(0)}$ (see Eqn. 6). Since measurements can only be made in neutral solutions, one of the parameters must be assigned arbitrarily (HARVIE and WEARE, 1984). We set λ_{CH_4Cl} to zero and fit the remaining parameters. $\mu_{CH_4}^{l(0)}/RT$ was first evaluated using the CH_4 solubility data in pure water. $\lambda_{CH_4,Na}$ and $\zeta_{CH_4,Na,Cl}$ were then evaluated simultaneously by least squares fitting of the solubility data in aqueous NaCl solutions in Table 1 (omitting the data of DUFFY et al., 1961, and MICHELS et al., 1936, and that of BLOUNT et al., 1979, below 300 bar) with a standard deviation $\sigma = 0.067$. $\lambda_{CH_4,Ca}$ was determined from methane solubility data (BLANCO and SMITH, 1978) in $CaCl_2$ aqueous solutions and are valid from 25 to 125°C and from 100 to 600 bar. All these parameters vary with temperature and pressure. However, the variations in the λ and ζ with *T* and *P* are small (see Fig. 1a,b). The temperature- and pressure-dependent coefficients are listed in Table 2. The third virial parameter, $\zeta_{CH_4,Ca,Cl}$ is only necessary at relatively high concentrations (usually above 2 m) and cannot be evaluated from the BLANCO and SMITH (1978) data.

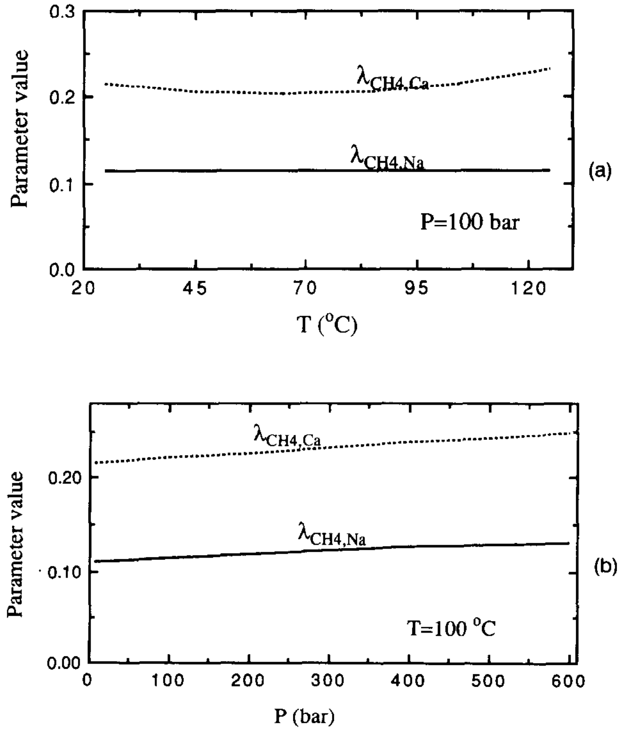

FIG. 1. The values of $\lambda_{CH_4,Na}$ and $\lambda_{CH_4,Ca}$ as functions of (a) temperature and (b) pressure.

The data for KCl, $MgCl_2$, sulphate, and carbonate solutions are available for 25°C below 50 bar (STOESSELL and BYRNE, 1982). These data were used in the evaluation of the parameters in Table 3.

Substituting the parameters into Eqn. (6), the methane solubility in pure water, NaCl aqueous solutions (0–250°C, 0–1600 bar, and 0–5.7 m), and in NaCl-$CaCl_2$ aqueous solutions (25–125°C, 100–600 bar, and 0–1 m) can be calculated. The methane solubilities for a wide *T*-*P*-m_{NaCl} range have been compiled in Table 4. Figures 2 to 4 show the agreement between the experimental data and the model of this study. It can be seen from these figures that experimental data are adequately represented by this model. Figure 5 indicates that the isobaric minimum solubility varies from about 120°C for low pressures to about 65°C at high pressures. Although no data above 250°C were included in the parameterization, predictions for temperatures up to 350°C are still reasonable (Fig. 6).

The partial volume of CH_4 in aqueous solution can be derived from Eqn. (2):

$$\begin{aligned}\frac{\bar{V}_{CH_4(l)}}{RT} &= \left(\frac{\partial \mu^{0(l)}/RT}{\partial P}\right)_{T,m} + \left(\frac{\partial \ln \gamma_{CH_4}}{\partial P}\right)_{T,m} \\ &= \left(\frac{\partial \mu^{0(l)}/RT}{\partial P}\right)_{T,m} + \sum_{c} 2m_c\left(\frac{\partial \lambda_{CH_4\text{-}c}}{\partial P}\right)_{T,m} \\ &\quad + \sum_{a} 2m_a\left(\frac{\partial \lambda_{CH_4\text{-}a}}{\partial P}\right)_{T,x} + \sum_{c}\sum_{a} m_c m_a\left(\frac{\partial \lambda_{CH_4\text{-}c\text{-}a}}{\partial P}\right)_{T,m}. \quad (8)\end{aligned}$$

The derivatives in the above equation are obtained by taking the derivative of Eqn. (7) with respect to *P* fixing *T*:

Table 3. CH_4- ion interaction parameters at 25 °C			
parameter	P=24.1bar	P=38.bar	P=51.7 bar
λ_{Na-CH4}	0.14296	0.15161	0.14821
λ_{K-CH4}	0.13509	0.14362	0.13856
λ_{Ca-CH4}	0.26526	0.24426	0.24727
λ_{Mg-CH4}	0.24798	0.25019	0.24216
λ_{Cl-CH4}	0.	0.	0.
$\lambda_{SO4-CH4}$	0.03023	0.02983	0.03116
$\lambda_{CO3-CH4}$	0.15208	0.17633	0.16947
$\lambda_{HCO3-CH4}$	0.00650	0.00708	0.00650
$\zeta_{Na-Cl-CH4}$	-0.00501	-0.00599	-0.00529
$\zeta_{K-Cl-CH4}$	-0.00906	-0.00126	-0.00113
$\zeta_{Ca-Cl-CH4}$	-0.00958	-0.00132	-0.00314
$\zeta_{Mg-Cl-CH4}$	-0.01683	-0.01350	-0.00935

Table 4 Methane solubilities (m/kg water) in NaCl aqueous solutions

P (bar)					NaCl=0	T (°C)				
	0	30	60	90	120	150	180	210	240	270
1	0.0023	0.0012	0.0008	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
50	0.0974	0.0547	0.0412	0.0380	0.0401	0.0455	0.0523	0.0556	0.0431	0.0000
100	0.1623	0.0949	0.0736	0.0697	0.0755	0.0892	0.1103	0.1368	0.1614	0.1625
150	0.2060	0.1249	0.0993	0.0957	0.1055	0.1271	0.1614	0.2092	0.2678	0.3245
200	0.2382	0.1481	0.1202	0.1177	0.1314	0.1603	0.2068	0.2742	0.3640	0.4715
300	0.2876	0.1840	0.1531	0.1530	0.1740	0.2160	0.2840	0.3859	0.5309	0.7280
400	0.3285	0.2129	0.1793	0.1813	0.2084	0.2615	0.3477	0.4788	0.6705	0.9435
500	0.3657	0.2381	0.2017	0.2053	0.2375	0.2999	0.4017	0.5576	0.7892	1.1267
600	0.4010	0.2613	0.2218	0.2264	0.2628	0.3332	0.4482	0.6255	0.8913	1.2837
700	0.4351	0.2830	0.2402	0.2454	0.2854	0.3626	0.4891	0.6848	0.9799	1.4193
800	0.4684	0.3037	0.2574	0.2629	0.3057	0.3888	0.5252	0.7369	1.0573	1.5368
900	0.5012	0.3236	0.2735	0.2789	0.3242	0.4124	0.5574	0.7829	1.1252	1.6390
1000	0.5337	0.3429	0.2888	0.2939	0.3412	0.4338	0.5862	0.8237	1.1848	1.7278
1100	0.5659	0.3616	0.3034	0.3079	0.3568	0.4531	0.6120	0.8600	1.2372	1.8050
1200	0.5982	0.3799	0.3174	0.3211	0.3712	0.4708	0.6353	0.8922	1.2833	1.8718
1300	0.6303	0.3978	0.3308	0.3335	0.3846	0.4869	0.6562	0.9208	1.3236	1.9294
1400	0.6626	0.4154	0.3437	0.3452	0.3970	0.5016	0.6751	0.9462	1.3588	1.9788
1500	0.6949	0.4326	0.3561	0.3563	0.4086	0.5150	0.6920	0.9686	1.3894	2.0207
1600	0.7274	0.4497	0.3681	0.3668	0.4193	0.5273	0.7072	0.9884	1.4158	2.0560
1700	0.7601	0.4665	0.3798	0.3767	0.4293	0.5385	0.7207	1.0057	1.4384	2.0852
1800	0.7930	0.4831	0.3910	0.3862	0.4386	0.5487	0.7329	1.0208	1.4575	2.1090
P (bar)					NaCl=1 m	T (°C)				
	0	30	60	90	120	150	180	210	240	270
1	0.0019	0.0010	0.0006	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
50	0.0788	0.0442	0.0332	0.0306	0.0323	0.0366	0.0420	0.0446	0.0345	0.0000
100	0.1304	0.0762	0.0591	0.0559	0.0605	0.0714	0.0882	0.1093	0.1288	0.1296
150	0.1645	0.0997	0.0793	0.0764	0.0842	0.1014	0.1286	0.1666	0.2131	0.2579
200	0.1891	0.1177	0.0955	0.0935	0.1044	0.1274	0.1643	0.2176	0.2887	0.3737
300	0.2260	0.1449	0.1206	0.1207	0.1373	0.1705	0.2242	0.3045	0.4187	0.5739
400	0.2557	0.1662	0.1402	0.1420	0.1634	0.2052	0.2729	0.3758	0.5263	0.7404
500	0.2824	0.1845	0.1567	0.1598	0.1851	0.2341	0.3137	0.4357	0.6168	0.8805
600	0.3075	0.2012	0.1714	0.1754	0.2039	0.2589	0.3486	0.4868	0.6940	0.9997
700	0.3317	0.2168	0.1847	0.1893	0.2205	0.2807	0.3791	0.5312	0.7606	1.1021
800	0.3554	0.2317	0.1972	0.2020	0.2355	0.3001	0.4059	0.5702	0.8187	1.1906
900	0.3790	0.2461	0.2090	0.2138	0.2492	0.3176	0.4299	0.6046	0.8697	1.2676
1000	0.4027	0.2603	0.2203	0.2249	0.2618	0.3336	0.4516	0.6353	0.9147	1.3348
1100	0.4267	0.2742	0.2312	0.2355	0.2736	0.3483	0.4712	0.6629	0.9547	1.3937
1200	0.4510	0.2882	0.2419	0.2456	0.2847	0.3619	0.4891	0.6878	0.9903	1.4454
1300	0.4759	0.3021	0.2523	0.2553	0.2953	0.3746	0.5057	0.7104	1.0221	1.4909
1400	0.5015	0.3162	0.2627	0.2648	0.3053	0.3865	0.5210	0.7311	1.0508	1.5310
1500	0.5279	0.3304	0.2731	0.2740	0.3150	0.3978	0.5352	0.7499	1.0765	1.5664
1600	0.5553	0.3449	0.2834	0.2831	0.3244	0.4086	0.5486	0.7674	1.0999	1.5977
1700	0.5838	0.3598	0.2938	0.2922	0.3335	0.4189	0.5612	0.7835	1.1210	1.6254
1800	0.6136	0.3751	0.3043	0.3012	0.3425	0.4289	0.5731	0.7985	1.1403	1.6499

$$\left(\frac{\partial \operatorname{Par}(T, P)}{\partial P}\right)_{T,m} = a_6 + a_7 \ln T + a_8/T + a_9/(680 - T) + 2a_{10}P/T. \quad (9)$$

Table 5 compares the experimental partial volume (O'SULLIVAN and SMITH, 1970; KOBAYASHI and KATZ, 1955) with the results calculated from Eq. (8).

METHANE SOLUBILITY IN SEAWATER-TYPE BRINES TO HIGH TEMPERATURES AND PRESSURES

The advantage of the specific interaction approach is that the model, though evaluated from binary and ternary data, can be applied to more complex systems (WEARE, 1987). Natural waters often contain NaCl, KCl, $MgCl_2$, $CaCl_2$, and sulphate and carbonate salts, though NaCl is often the major component. Because of data limitations, a model directly fit to experimental measurements is possible only for the CH_4-NaCl-H_2O system. In order to treat more complex systems, we include Ca, K, Mg, SO_4, CO_3, and HCO_3 to 250°C and 1600 bar with an approximation approach.

CH_4-ions interaction parameters are summarized in Table 3. Note that the interaction parameters of the same charge have roughly the same value. The CH_4-bivalent cation interaction parameters are about twice as large as CH_4-monovalent interaction parameters within the accuracy of exper-

Table 4 (continued)

P (bar)	NaCl=2 m T (°C)									
	0	30	60	90	120	150	180	210	240	270
1	0.0016	0.0008	0.0005	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
50	0.0645	0.0361	0.0271	0.0250	0.0263	0.0298	0.0341	0.0362	0.0280	0.0000
100	0.1061	0.0620	0.0480	0.0454	0.0491	0.0579	0.0714	0.0884	0.1041	0.1046
150	0.1330	0.0807	0.0641	0.0618	0.0680	0.0819	0.1038	0.1343	0.1717	0.2075
200	0.1520	0.0947	0.0769	0.0753	0.0840	0.1025	0.1321	0.1749	0.2319	0.2999
300	0.1797	0.1155	0.0963	0.0964	0.1097	0.1363	0.1792	0.2433	0.3344	0.4581
400	0.2015	0.1313	0.1110	0.1126	0.1297	0.1630	0.2169	0.2987	0.4182	0.5882
500	0.2207	0.1448	0.1233	0.1260	0.1462	0.1850	0.2481	0.3447	0.4880	0.6967
600	0.2387	0.1569	0.1341	0.1375	0.1602	0.2037	0.2745	0.3837	0.5471	0.7883
700	0.2560	0.1682	0.1438	0.1478	0.1726	0.2200	0.2975	0.4173	0.5979	0.8665
800	0.2731	0.1790	0.1530	0.1572	0.1837	0.2345	0.3177	0.4467	0.6419	0.9340
900	0.2903	0.1896	0.1616	0.1660	0.1939	0.2477	0.3358	0.4728	0.6807	0.9927
1000	0.3077	0.2000	0.1701	0.1743	0.2034	0.2598	0.3522	0.4962	0.7151	1.0442
1100	0.3257	0.2106	0.1784	0.1823	0.2125	0.2710	0.3673	0.5174	0.7459	1.0897
1200	0.3443	0.2213	0.1866	0.1901	0.2211	0.2816	0.3813	0.5369	0.7738	1.1302
1300	0.3638	0.2323	0.1949	0.1979	0.2295	0.2918	0.3945	0.5550	0.7993	1.1666
1400	0.3844	0.2437	0.2034	0.2056	0.2378	0.3016	0.4071	0.5719	0.8227	1.1995
1500	0.4061	0.2555	0.2120	0.2134	0.2459	0.3111	0.4192	0.5879	0.8446	1.2295
1600	0.4293	0.2679	0.2209	0.2213	0.2541	0.3206	0.4309	0.6033	0.8651	1.2571
1700	0.4541	0.2810	0.2302	0.2294	0.2624	0.3299	0.4424	0.6181	0.8846	1.2828
1800	0.4807	0.2948	0.2399	0.2378	0.2708	0.3394	0.4538	0.6325	0.9033	1.3069
P (bar)	NaCl=4 m T (°C)									
	0	30	60	90	120	150	180	210	240	270
1	0.0011	0.0006	0.0004	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000	0.0000
50	0.0448	0.0251	0.0188	0.0173	0.0181	0.0205	0.0234	0.0248	0.0191	0.0000
100	0.0728	0.0425	0.0329	0.0311	0.0335	0.0395	0.0486	0.0601	0.0706	0.0707
150	0.0902	0.0548	0.0436	0.0419	0.0461	0.0554	0.0702	0.0907	0.1156	0.1395
200	0.1020	0.0636	0.0517	0.0507	0.0565	0.0689	0.0887	0.1173	0.1553	0.2005
300	0.1181	0.0761	0.0637	0.0638	0.0727	0.0904	0.1188	0.1612	0.2215	0.3031
400	0.1299	0.0852	0.0723	0.0735	0.0849	0.1068	0.1422	0.1959	0.2742	0.3855
500	0.1401	0.0925	0.0792	0.0813	0.0946	0.1199	0.1611	0.2240	0.3172	0.4529
600	0.1494	0.0990	0.0852	0.0878	0.1027	0.1309	0.1768	0.2474	0.3530	0.5089
700	0.1584	0.1050	0.0905	0.0935	0.1097	0.1403	0.1902	0.2673	0.3834	0.5561
800	0.1674	0.1109	0.0955	0.0988	0.1160	0.1487	0.2020	0.2847	0.4097	0.5967
900	0.1767	0.1167	0.1004	0.1038	0.1219	0.1564	0.2127	0.3001	0.4329	0.6320
1000	0.1865	0.1227	0.1053	0.1086	0.1275	0.1635	0.2225	0.3142	0.4537	0.6633
1100	0.1970	0.1289	0.1102	0.1135	0.1330	0.1704	0.2317	0.3273	0.4727	0.6915
1200	0.2083	0.1355	0.1153	0.1184	0.1384	0.1771	0.2406	0.3397	0.4905	0.7174
1300	0.2207	0.1426	0.1207	0.1235	0.1439	0.1838	0.2493	0.3516	0.5073	0.7414
1400	0.2344	0.1503	0.1265	0.1288	0.1496	0.1906	0.2581	0.3634	0.5236	0.7643
1500	0.2495	0.1586	0.1327	0.1344	0.1556	0.1976	0.2669	0.3751	0.5397	0.7864
1600	0.2663	0.1678	0.1394	0.1404	0.1619	0.2049	0.2760	0.3871	0.5557	0.8080
1700	0.2851	0.1779	0.1467	0.1469	0.1686	0.2125	0.2855	0.3993	0.5719	0.8295
1800	0.3063	0.1891	0.1546	0.1539	0.1757	0.2206	0.2954	0.4120	0.5885	0.8513

iment. This is also true for different temperatures and pressures (see Fig. 1a,b). The CH_4-anion interaction parameters are, with the exception of λ_{CH_4,CO_3}, relatively small and therefore contribute little to the calculations. The amount of CO_3 and the contribution from $2m_{CO_3}\lambda_{CH_4,CO_3}$ term is usually small in natural waters. The ternary interaction parameters, ζ's, are important only when their corresponding concentrations are over $2m$, which except for NaCl is seldom the case in natural waters. So approximating all CH_4-monovalent cation and CH_4-bivalent cation interaction parameters as $\lambda_{CH_4,Na}$ and $2\lambda_{CH_4,Na}$, respectively, and neglecting all ternary parameters but $\zeta_{CH_4,Na,Cl}$, the following equation is obtained:

$$\ln m_{CH_4} = \ln x_{CH_4}\phi_{CH_4}P - \mu^{0(l)}_{CH_4}/RT - 2\lambda_{CH_4,Na}(m_{Na} + m_K + 2m_{Ca} + 2m_{Mg}) - 0.06m_{SO_4} + 0.00624m_{Na}m_{Cl}. \quad (10)$$

In order to test this approximation, we compared Eqn. (10) with experimental data of methane solubility in $CaCl_2$ solutions—seawater and Salton Sea geothermal brines, respectively. Figure 7 indicates that this approximate approach is within an error of 7%, which is about the experimental error. The chemical composition of seawater is from HOLLAND (1978) and that of Salton Sea geothermal brines is from

Table 4 (continued)

P (bar)	NaCl=6 m T (°C)									
	0	30	60	90	120	150	180	210	240	270
1	0.0008	0.0004	0.0003	0.0001	0.0015	0.0018	0.0022	0.0030	0.0041	0.0058
50	0.0328	0.0183	0.0137	0.0126	0.0132	0.0148	0.0169	0.0178	0.0137	0.0058
100	0.0526	0.0307	0.0237	0.0223	0.0241	0.0283	0.0348	0.0429	0.0503	0.0503
150	0.0644	0.0391	0.0311	0.0299	0.0329	0.0395	0.0499	0.0643	0.0819	0.0986
200	0.0719	0.0450	0.0366	0.0358	0.0400	0.0487	0.0626	0.0827	0.1093	0.1409
300	0.0815	0.0528	0.0442	0.0444	0.0507	0.0630	0.0828	0.1123	0.1541	0.2107
400	0.0881	0.0581	0.0495	0.0505	0.0584	0.0735	0.0980	0.1350	0.1890	0.2656
500	0.0934	0.0622	0.0535	0.0551	0.0643	0.0818	0.1099	0.1530	0.2168	0.3095
600	0.0982	0.0657	0.0569	0.0589	0.0692	0.0884	0.1196	0.1676	0.2395	0.3453
700	0.1030	0.0690	0.0599	0.0622	0.0733	0.0941	0.1278	0.1800	0.2585	0.3752
800	0.1079	0.0722	0.0627	0.0653	0.0771	0.0991	0.1350	0.1907	0.2749	0.4007
900	0.1131	0.0756	0.0656	0.0682	0.0806	0.1038	0.1416	0.2003	0.2894	0.4230
1000	0.1189	0.0791	0.0685	0.0712	0.0840	0.1082	0.1477	0.2092	0.3025	0.4430
1100	0.1253	0.0830	0.0716	0.0742	0.0875	0.1126	0.1537	0.2176	0.3149	0.4613
1200	0.1325	0.0872	0.0749	0.0775	0.0911	0.1171	0.1596	0.2259	0.3268	0.4786
1300	0.1408	0.0920	0.0786	0.0809	0.0949	0.1217	0.1657	0.2342	0.3385	0.4954
1400	0.1502	0.0974	0.0827	0.0847	0.0990	0.1266	0.1720	0.2427	0.3503	0.5119
1500	0.1611	0.1035	0.0873	0.0890	0.1035	0.1319	0.1787	0.2516	0.3625	0.5287
1600	0.1737	0.1105	0.0924	0.0936	0.1084	0.1376	0.1858	0.2610	0.3752	0.5459
1700	0.1882	0.1184	0.0982	0.0988	0.1138	0.1439	0.1936	0.2711	0.3886	0.5639
1800	0.2051	0.1276	0.1048	0.1047	0.1199	0.1508	0.2021	0.2821	0.4030	0.5829

CRAMER (1984). Calculated CH_4 solubilities are compared to experimental data in Tables 6 and 7, respectively. It can be seen that the agreement between this model and the experiment is excellent.

We note that the above three examples may not be sufficient to prove that Eqn. (10) is within experimental uncertainty at all the temperatures and pressures of interest. More tests are needed if data become available.

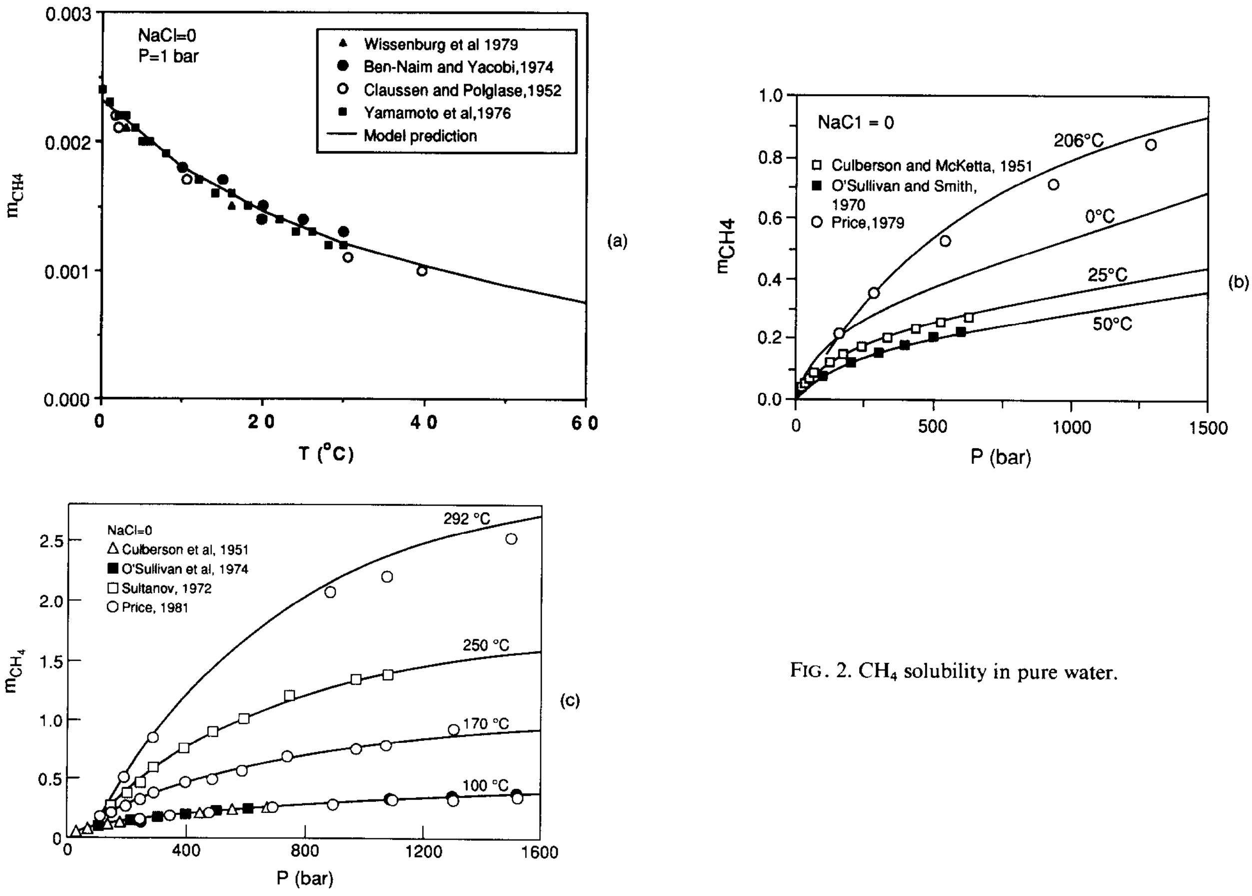

FIG. 2. CH_4 solubility in pure water.

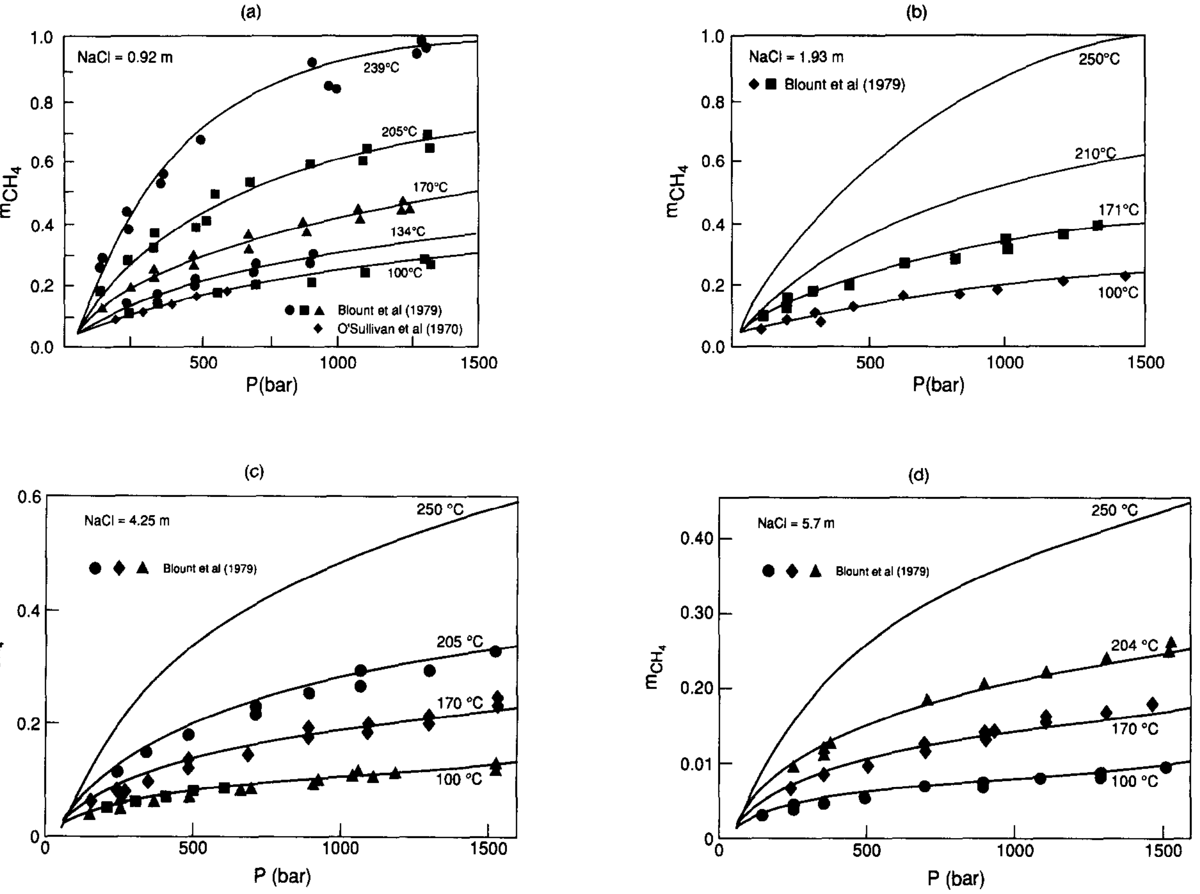

FIG. 3. CH_4 solubility in NaCl aqueous solution.

FLUID INCLUSION ANALYSIS

A central problem in geochemistry is the determination of the formation conditions of geological terrain. A record of the fluids present at formation may be preserved in small cavities or fluid inclusions in the minerals. In most systems the size of these fluid inclusions is so small that it is difficult to measure their properties directly. However, the temperature at which a fluid inclusion transforms to a single phase (homogenization temperature) often can be observed. This temperature is usually taken as the lower limit to the formation temperature of the terrane. If the composition of the fluid can be determined, more information is available from a model calculation. Recently this information has been obtained by *in situ* measurement of composition by spectroscopic techniques such as the Raman microprobe (e.g., RAMBOZ et al., 1985). The bulk composition and homogenization temperature of the inclusion completely defines the thermodynamic state of the system and thus the homogenization pressure. For fluid inclusions which homogenize to the liquid, this is the total pressure required to prevent the formation of a bubble in the liquid. Given the model, it may

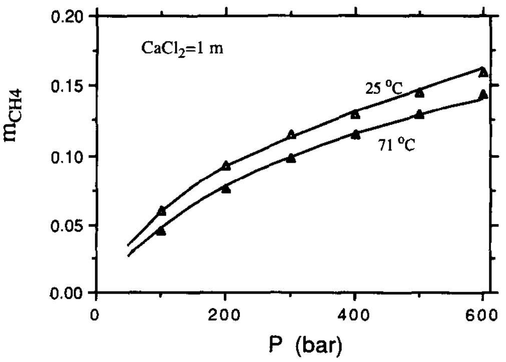

FIG. 4. CH_4 solubility in $CaCl_2$ aqueous solution.

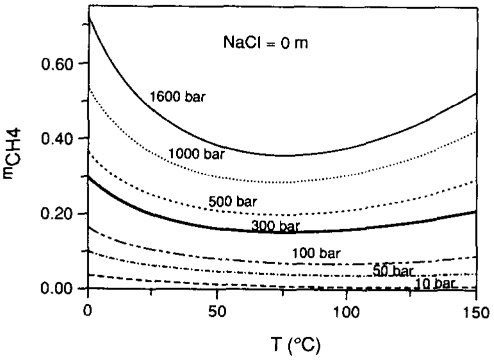

FIG. 5. The isobaric minimum solubilities of CH_4.

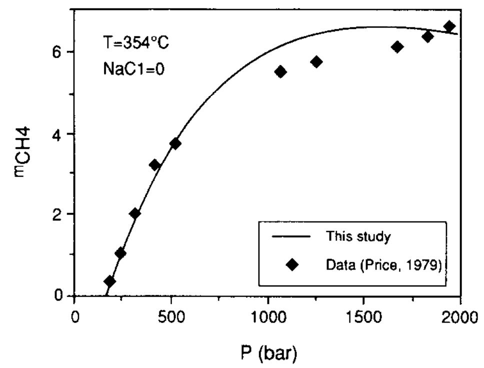

FIG. 6. Comparison of experimental methane solubility with model predictions at 354°C.

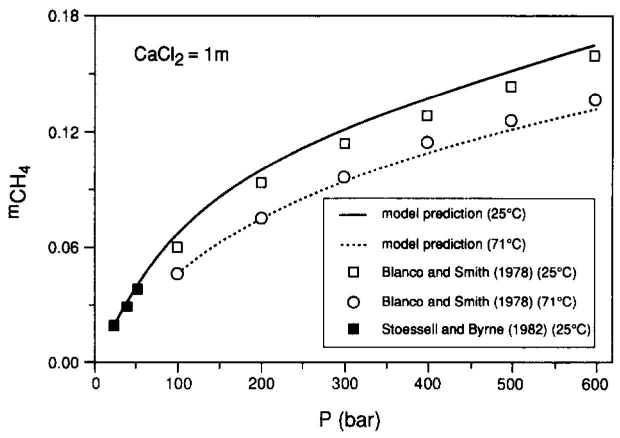

FIG. 7. Prediction of methane solubility in $CaCl_2$ aqueous solutions using Eqn. (10).

be calculated as the sum of the pressure of the dissolved gas plus the vapor pressure of water at the temperature of homogenization.

In order to illustrate the application of the model to a problem of this sort, we use the fluid inclusion data and the model to calculate the trapping pressure of the quartz crystal from central alpine mineral clefts. Fluid inclusion compositions and homogenization temperatures for this system have been reported by MULLIS (1979) and are presented in Table 8. Also included are the homogenization pressures that we have calculated using the model.

MULLIS (1979) also calculated the trapping pressure using a somewhat different approach. In addition to the water-rich inclusions, the compositions of which are given in Table 8, he identified pure methane inclusions which he asserted were formed simultaneously with the water-rich inclusions. Knowing the homogenization temperatures from water-rich inclusions and the density from methane inclusion, he estimated the trapping pressures. The results of these calculations are included in Table 8. They generally fall within the range of pressures we calculate from the uncertainty in total composition. There are sources of error resulting from inaccuracy in the compositions in both our approach and that of MULLIS (1979). For example, there may be dissolved salts in the fluids in the water-rich inclusions which would increase the trapping pressures we predict. Or as MULLIS (1979) has suggested, there may be other gases in the methane inclusions.

There is another empirical approach that has been used to calculate trapping pressures. That is to use available Henry's law data with water-rich inclusions to calculate pressures at the trapping temperature. As we show in Figure 8, this will lead to substantial underestimations of the trapping pressure. For example using the first data point in Table 8 and Henry's law constant calculated from the SULTANOV et al. data (1972), a trapping pressure range would be 444 to 611 bar if Henry's law is used compared against 900 to 1800 bar calculated from our model calculation.

CONCLUSIONS

This methane solubility model has been developed based on the equation of state by DUAN et al. (1992a) and the

Table 5 The partial volume of CH_4 dissolved in liquid solution

(T(°C)	P(atm)	NaCl(m)	$\bar{V}_{CH4(l)}$(a)	$\bar{V}_{CH4(l)}$ (b)	$\bar{V}_{CH4(l)}$ (c)
51.5	200	0	37.1	37.2	35.8
51.5	200	4	36.61	-	45.85
51.5	600	0	37.1	37.2	35.18
51.5	600	4	36.61	-	40.95
102	200	0	45.9	40.2	39.37
102	200	4	49.3	-	49.42
102	600	0	36.2	40.2	38.76
102	600	4	49.3	-	44.51
125	200	0	54.4	41.4	40.9
125	200	4	66.1	-	50.96
125	600	0	38.7	41.4	40.29
125	600	4	36.5	-	46.05

a. O'Sullivan and Smith (1970); b. Kobayashi et al (1955); c. This study

Table 6. Solubility of CH_4 in seawater (25 °C)

	P=24.1	P=37.9	P=51.7 bar
Eq.(10)	0.02681	0.0404	0.05282
Data (Stoessell,1982)	0.0263	0.040	0.0514

Table 7. Solubility of CH_4 in Salton Sea Geothermal Brine

T(°C)	P(bar)	ln(f/m) Eq.(10)	ln(f/m) data(Cramer, 1974)
60.2	11.4	7.88	7.908
88.1	11.6	7.957	7.929
121.7	13.2	7.88	7.860
166.8	34.2	7.60	7.829

Table 8 The formation pressure of the 'Fadenquartz' in Central Alps.

locality	T(°C)	x_{CH_4}	Formation pressure (bar) this study	Formation pressure (bar) Mullis(1979)
Val d'lliez	249	0.022-0.03	900-1800	1570
Chöex	242	0.017-0.023	650-1180	1370
Les Monte	241	0.016-0.022	600-1090	1120
Metholz	230	0.014-0.020	595-1190	1090
Jour De Duin	244	0.013-0.017	425-630	810

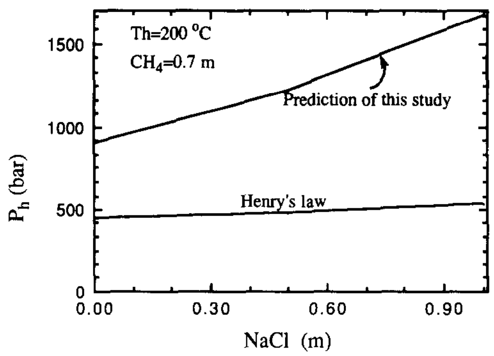

FIG. 8. Homogenization pressure calculated from homogenization temperature and composition analysis.

theory of Pitzer (1973). Comparison with data demonstrates that this model is within experimental uncertainty (about 7%) for temperatures from 0 to 250°C, for pressures from 0 to 1600 bar, and for ionic strength from 0 to 6 m. It can be extrapolated to 300°C and 1800 bar with some loss of accuracy. Because the parameters represent interactions of particles, and some close relationship was found between the values of different parameters, an approximate approach (Eqn. 10) was suggested to extend the model to complex brines. It is shown that this approach agrees with the available data very well. Our comprehensive reviewing of data indicates that most data sets are consistent within an error of about 7% except for a few data sets (see Review of Solubility Data of Methane section). The model can be used in fluid inclusion studies. If bulk homogenization temperature and bulk composition are determined, the minimum trapping pressure can be obtained.

Acknowledgments—We thank Prof. Kenneth Pitzer for his valuable comments. This work has been supported by funds from the Department of Energy (DOE-DE-AC03-88SF), American Chemical Society (ACS PRF 18991 AC2) and Central Canada Potash. Dr. J. Dubessy and Dr. M. Sterner are acknowledged for their constructive reviews.

Editorial handling: T. S. Bowers

REFERENCES

Barta L. and Bradley D. J. (1985) Extention of the specific interaction model to include gas solubilities in high temperature brines. *Geochim. Cosmochim. Acta* **49**, 195–203.

Ben-Naim A. and Yaacobi M. (1974) Effects of solutes on the strength of hydrophobic interaction and its temperature dependence. *J. Phys. Chem.* **78**, 170–175.

Blanco L. H. and Smith N. O. (1978) The high pressure solubility of methane in aqueous calcium chloride and aqueous tetraethylammonium bromide. Partial molar properties of dissolved methane and nitrogen in relation to water structure. *J. Phys. Chem.* **82**, 186–191.

Blount C. W., Price L. C., Wenger L. M., and Tarullo M. (1979) Methane solubility in aqueous NaCl solutions at elevated temperatures and pressures. *Proc. 4th US Gulf Coast Geopressured-geothermal Energy Conference* **3**, 1225–1262.

Claussen W. F. and Polglase M. F. (1952) Solubilities and structures in aqueous aliphatic hydrocarbon solutions. *J. Amer. Chem. Soc.* **74**, 4817–4819.

Cramer S. D. (1984) Solubility of methane in brines from 0 to 300 C. *Ind. Eng. Chem. Process Des. Dev.* **23**, 533–538.

Culberson O. L. and McKetta J. J., Jr. (1951) Phase equilibria in hydrocarbon-water systems. III—The solubility of methane in water pressures to 10,000 psi. *Petrol. Trans. AIME* **192**, 223–226.

Denbigh K. (1971) *The Principles of Chemical Equilibrium*, 3d ed. Cambridge University Press.

Drummond S. E. (1981) Boiling and mixing of hydrothermal fluids: Chemical effects on mineral precipitation. Ph.D. dissertation, The Pennsylvania State Univ.

Duan Z., Møller N., and Weare J. H. (1992a) An equation of state (EOS) for CH_4, CO_2 and H_2O: I. Pure systems from 0 to 1000°C and from 0 to 8000 bar. *Geochim. Cosmochim. Acta* (submitted)

Duan Z., Møller N., and Weare J. H. (1992b) An equation of state (EOS) for CH_4, CO_2 and H_2O II: Mixtures from 0 to 1000°C and from 0 to 1000 bar. *Geochim. Cosmochim. Acta.* (submitted)

Duffy J. R., Smith N. O., and Nagy B. (1961) Solubility of natural gases in aqueous salt solutions: I. Liquidus surfaces in the system CH_4-H_2O-NaCl-$CaCl_2$ at room temperatures and at pressures below 1000 psi. *Geochim. Cosmochim. Acta* **24**, 23–31.

Haar L., Gallagher J. S., and Kell G. S. (1984) *Steam Tables: Thermodynamic and Transport Properties and Computer Programs for Vapor and Liquid States of Water in SI Units.* Hemisphere Publishing Co.

Harvie C. E. and Weare J. H. (1984) The prediction of mineral solubility in natural waters: The Na-K-Mg-Ca-H-Cl-SO_4-OH-HCO_3-CO_3-CO_2-H_2O system from zero to high concentration at 25°C. *Geochim. Cosmochim. Acta* **48**, 723–751.

Holland H. D. (1978) *The Chemistry of the Atmosphere and Oceans.* Wiley-Interscience.

Kharaka Y. K., Carothers W. W., and Law L. M. (1985) Origin of gaseous hydrocarbons in geopressured geothermal waters. *Proc. 6th US Gulf Coast Geopressured-geothermal Energy Conference* **6**, 125.

Kobayashi R. and Katz D. L. (1955) Metastable equilibrium in the dew point determination of natural gases in the hydrate region. *Trans. AIME*, 51–52.

Krader T. and Frank E. U. (1987) The ternary systems H_2O-CH_4-NaCl and H_2O-CH_4-$CaCl_2$ to 800 K and 250 bar. *Ber. Bunsenges. Phys. Chem.* **91**, 627–634.

Mashnina T. A., Avdeeva O. I., and Bozhovskaya T. K. (1961) The solubility of methane in NaCl agueous solutions. *Mater. Vses. Nauchno. Issled. Geol. Inst.* **46**, 93–110.

Michels A., Gerver J., and Bijl A. (1936) The influence of pressure on the solubility of gases. *Physica* **3**, 797–807.

Mullis J. (1979) The system methane-water as a geologic thermometer and barometer from external part of central part of Central Alps. *Bull. Soc. Fr. Mineral. Crystallogr.* **102**, 526–536.

O'Sullivan T. D. and Smith N. O. (1970) The solubility and partial molar volume of nitrogen and methane in water and in aqueous sodium chloride from 50 to 125°C and 100 to 600 atm. *J. Phys. Chem.* **74**, 1460–1466.

Pitzer K. S. (1973) Thermodynamics of electrolytes: I. Theoretical basis and general equations. *J. Phys. Chem.* **77**, 268–277.

Pitzer K. S., Peiper J. C., and Busey R. H. (1984) Thermodynamic properties of aqueous sodium chloride solutions. *J. Phys. Chem. Ref. Data* **13**, 1–102.

Price L. C. (1979) Aqueous solubility of methane at elevated pressures and temperatures. *AAPG Bull.* **632**, 1527–1533.

Price L. C. (1981) Methane solubility in brines with application to the geopressured resource. *Proc. 5th Geopressured-geothermal Energy Conference* **5**, 205–214.

Ramboz C., Schnapper D., and Dubessy J. (1985) The P-$\bar{V}$T-X-fO_2 evolution of H_2O-CO_2-CH_4-bearing fluid in a wolframite vein: Reconstruction from fluid inclusion studies. *Geochim. Cosmochim. Acta* **49**, 205–219.

Stoessell R. K. and Byrne P. A. (1982) Salting out of methane in single-salt solutions at 25°C and below 800 psi. *Geochim. Cosmochim. Acta* **46**, 1327–1332.

Sultanov R. C., Skripka V. E., and Namiot A. Yu. (1972) Solubility of methane in water at high temperatures and pressures. *Gazova Promyshlennost* **17**, 6–7 (in Russian).

Vrolijk P., Myers G., and Moore J. C. (1988) Warm fluid migration along tectonic melanges in the Kodiak accretionary complex, Alaska. *J. Geophys. Res.* **93**, 10,313–10,324.

WEARE J. H. (1987) Models of mineral solubility in concentrated brines with application to field observations. *Rev. Mineral.* **17**, 143.

WHITE D. E., ANDERSON E. T., and GRUBBS D. K. (1963) Geothermal brine well: Mile-deep drill hole may tap ore-bearing magmatic water and rocks undergoing metamorphism. *Science* **139**, 919–922.

WIESENBURG D. A. and GUINASSO N. L. (1979) Equilibrium solubilities of methane, carbon monoxide and hydrogen in water and seawater. *J. Chem. Eng. Data* **24**, 356–360.

WINKLER L. W. (1901) Bunsen coefficient of methane. *Chem. Ber.* **34**, 1408–1422.

YAMAMOTO S., ALCAUSKAS J. B., and CROZIER T. E. (1976) Solubility of methane in distilled water and seawater. *J. Chem. Eng. Data* **21**, 78–80.

APPENDIX: THE EQUATION OF STATE FOR CH_4

$$Z = \frac{P_r V_r}{T_r} = 1 + \frac{B}{V_r} + \frac{C}{V_r^2} + \frac{D}{V_r^4} + \frac{E}{V_r^5} + \frac{F}{V_r^2}\left(\beta + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right), \quad (A1)$$

$$\ln \phi_{CH_4} = Z - 1 - \ln Z + \frac{B}{V_r} + \frac{C}{2V_r^2} + \frac{D}{4V_r^4} + \frac{E}{5V_r^5} + G, \quad (A2)$$

where:

$$P_r = P/46.41$$

$$T_r = T/190.6$$

$$V_r = V/0.34146$$

$$B = a_1 + \frac{a_2}{T_r^2} + \frac{a_3}{T_r^3}$$

Table A1. EOS parameters for CH_4

parameters	CH_4
a_1	8.72553928D-02
a_2	-7.52599476D-01
a_3	3.75419887D-01
a_4	1.07291342D-02
a_5	5.49626360D-03
a_6	-1.84772802D-02
a_7	3.18993183D-04
a_8	2.11079375D-04
a_9	2.01682801D-05
a_{10}	-1.65606189D-05
a_{11}	1.19614546D-04
a_{12}	-1.08087289D-04
α	4.48262295D-02
β	7.53970000D-01
γ	7.71670000D-02

$$C = a_4 + \frac{a_5}{T_r^2} + \frac{a_6}{T_r^3}$$

$$D = a_7 + \frac{a_8}{T_r^2} + \frac{a_9}{T_r^3}$$

$$E = a_{10} + \frac{a_{11}}{T_r^2} + \frac{a_{12}}{T_r^3}$$

$$F = \frac{\alpha}{T_r^3}$$

$$G = \frac{F}{2\gamma}\left[\beta + 1 - \left(\beta + 1 + \frac{\gamma}{V_r^2}\right)\exp\left(-\frac{\gamma}{V_r^2}\right)\right],$$

given T (°K) and P (bar), Z and V_r or V (dm^3) can be obtained through Eqn. (A1). $\ln \phi_{CH_4}$ can be calculated by substituting V_r, Z, and the parameters, A, B, . . . , into Eqn. (A2). The parameters are listed in Table A1.