Proceedings International Workshop on Mineral Scaling 2011
Manila, Philippines, 25-27 May 2011

Accurate Evaluation of Thermodynamic Properties of Geothermal Gases from an Equation of State with Field Applications

Joselito R. Ruaya and Caryl Joyce S. Mansing

Energy Development Corporation, Merritt Road, Ft. Bonifacio, 1201 Taguig City, Philippines

joselito.ruaya@gmail.com, mansing.cs@energy.com.ph

Keywords: Equation of state, geothermal gases, thermodynamic properties, gas solubility, CO_2

ABSTRACT

The equation of state (EOS) developed by Duan and co-workers has been adopted and proposed for calculating thermodynamic properties of geothermal gases. A spreadsheet-based simple calculation method is described, and sample calculations of compressibility, fugacity coefficients, gas partitioning coefficients and gas solubility in brines and its effects on the boiling curve of geothermal fluids are presented. Calculations of the solubility of the most important geothermal gas, CO_2, in brines of some Philippine geothermal fields are shown to demonstrate insights gained on well and reservoir processes.

1. INTRODUCTION

Naturally- occurring gases have been extensively used in geothermal exploration and development as a complement to the more popular water-based interpretation techniques. In the 1970s historical gas data have been used to interpret the behaviour of the Wairakei field (Glover, 1970) and some Italian fields (D'Amore and Nuti, 1977). By 1980, the most important aspects of geothermal gas equilibria have been elucidated clearly in a pioneering work (Giggenbach, 1980).

In early geothermal exploration stage, gas analysis has been used in deducing deep temperatures owing to the fact that gases are transported faster than the liquid phase of deep fluids and thus retain the fingerprints of deep conditions. D'Amore and Panichi (1980), Arnorsson and Gunnlaugsson (1985) and others have devised gas geothermometers based on gas analytical data. By the turn of the century, gas interpretative methods have been firmly established in the geothermal industry (e.g., Arnorsson, 2000).

Despite their widespread use, current gas techniques are invariably based on simplistic assumptions which may fail at the temperatures, pressures and fluid compositions encountered in many geothermal environments. For example, solubility and gas partitioning calculations are usually carried out using Henry's Law while salting out effects are estimated using Setchenow's correlation. In his otherwise excellent treatment of gas equilibria, Giggenbach (1980) had to assume fugacity coefficients close to unity in order to make progress. Other workers have invariably followed suit.

In the earth sciences including geothermal, application of EOS to solve geological problems is comparatively recent and it is only in the last two decades that it has gained acceptance. Examples include a proposed equation for methane (Kerrick and Jacobs, 1981), for the ternary H_2O-CO_2-NaCl (Bowers and Helgeson, 1983; Duan, Moller and Weare, 1995) and a highly accurate equation of state originally proposed for the CH_4-CO_2-H_2O system (Duan, Moller and Weare, 1992a) which has subsequently been extended to gas mixtures (Duan, Moller and Weare, 1992b), calculation of solubilities of gases in brines (Duan et al., 2007; Mao, and Duan, 2006; Duan, Moller and Weare, 1996; Mao, et al., 2005), applied to vapour-liquid phase equilibria (Mao, Duan and Hu, 2009), and coupled to chemical equilibrium calculations (Li and Duan, 2007; Duan and Li, 2008) which are essential to accurate evaluation of mineral scaling potential of geothermal fluids.

The last mentioned EOS of Duan and co-workers appears to have the required accuracy, predictive ability, self-consistency and comparative simplicity for geothermal applications. Most importantly, the temperatures, pressures and chemical compositions encountered in most geothermal systems are well within the range of conditions covered by the EOS.

Despite its success, this EOS has not been widely used or accepted by the geothermal community. The purposes of this paper are (1) to adopt a consistent set of EOS for gases of geothermal interest; (2) outline a simple spreadsheet-based calculation method; and (3) to give some examples of calculations and comparisons to actual field data.

2. THERMODYNAMIC CONSIDERATIONS

The equation of state proposed by Duan and co-workers is an adaptation of the Lee-Kesler equation (Lee and Kesler, 1975) which is expressed in terms of the compressibility factor Z as a function of P, T and V.

$$Z = \frac{\mathrm{P_r V_r}}{\mathrm{T_r}} = 1 + \frac{\mathrm{a_1} + (\mathrm{a_2}/\mathrm{T_r^2}) + (\mathrm{a_3}/\mathrm{T_r^2})}{\mathrm{V_r}} + \frac{\mathrm{a_4} + (\mathrm{a_5}/\mathrm{T_r^2}) + (\mathrm{a_6}/\mathrm{T_r^3})}{\mathrm{V_r^2}} + \frac{\mathrm{a_7} + (\mathrm{a_8}/\mathrm{T_r^2}) + (\mathrm{a_9}/\mathrm{T_r^3})}{\mathrm{V_r^4}} + \frac{\mathrm{a_{10}} + (\mathrm{a_{11}}/\mathrm{T_r^2}) + \left(\frac{\mathrm{a_{12}}}{\mathrm{T_r^3}}\right)}{\mathrm{V_r^5}} + \frac{\mathrm{a_{13}}}{\mathrm{T_r^3 V_r^2}}\left(\mathrm{a_{14}} + \frac{\mathrm{a_{15}}}{\mathrm{V_r^2}}\right)\exp\left(-\frac{\mathrm{a_{15}}}{\mathrm{V_r^2}}\right) \quad (1)$$

where

$$P_r = \frac{P}{P_c} \ (a);\ T_r = \frac{T}{T_c}\ (b);\ V_r = \frac{V}{V_c}\ (c);\ V_c = \frac{RT_c}{P_c}\ (d). \quad (2)$$

Table 1. Equation of state parameters for major geothermal gases and water.

	H_2O[1]	CO_2[1]	H_2S[2]	CH_4[1]	NH_3[3]	N_2[4]	C_2H_6[5]
a1	8.64449220E-02	8.99288497E-02	5.23860750E-02	8.72553928E-02	-2.17218056E-02	3.75504388E-02	1.17251079E-02
a2	-3.96918955E-01	-4.94783127E-01	-2.74639060E-01	-7.52599476E-01	-8.57922298E-02	-1.08730273E+04	-1.22755190E-01
a3	-5.73334886E-02	4.77922245E-02	-9.67601730E-02	3.75419887E-01	-2.60003585E-01	1.10964861E+06	-2.17900690E-01
a4	-2.93893000E-04	1.03808883E-02	1.36181040E-02	1.07291342E-02	2.39715057E-02	5.41589372E-04	3.88523929E-02
a5	-4.15775512E-03	-2.82516860E-02	-8.86817530E-02	5.49626360E-03	-7.08038210E-02	1.12094559E+02	-1.83005380E-01
a6	1.99496791E-02	9.49887563E-02	4.11769080E-02	-1.84772802E-02	9.11596169E-02	-5.92191393E+03	1.46315980E-01
a7	1.18901426E-04	5.20600880E-04	3.63540180E-04	3.18993183E-04	-9.01591089E-05	4.37200027E-06	-3.87281285E-04
a8	1.55212063E-04	-2.93540971E-04	2.27191940E-03	2.11079375E-04	5.59098353E-04	4.95790731E-01	4.60403075E-03
a9	-1.06855859E-04	-1.77265112E-03	-7.69625140E-04	2.01682801E-05	-9.13606670E-04	-1.64902948E+02	-3.73899089E-03
a10	-4.93197687E-06	-2.51101973E-05	-2.19485790E-05	-1.65606189E-05	1.22931050E-05	-7.07442825E-08	4.81844769E-05
a11	-2.73739155E-06	8.93353441E-05	-1.17076310E-04	1.19614546E-04	-1.40854901E-05	9.65727297E-03	-2.89809201E-04
a12	2.65571238E-06	7.88998563E-05	4.07569260E-05	-1.08087289E-04	3.88960952E-05	4.87945175E-01	2.55723237E-04
a13	8.96079018E-03	-1.66727022E-02	5.75822600E-02	4.48262295E-02	4.59318106E-03	1.62257402E+04	4.06315933E-02
a14	4.02000000E+00	1.39800000E+00	1.00000000E+00	7.53970000E-01	3.08000000E+00	1.00000000E+00	6.83486320E-01
a15	2.57000000E-02	2.96000000E-02	6.00000000E-02	7.71670000E-02	7.50000000E-02	8.99000000E-03	6.55999984E-02
T_c , K	647.25	304.2	373.6	190.6	405.55	(see text)	305.33
P_c , bar	221.19	73.825	90.08	46.41	112.8		48.718

[1] Duan et al. (1992). In anticipation for applications involving mixtures, the EOS parameters for water are included. [2] Duan et al. (2007). [3] Duan et al. (1996). [4] Mao and Duan (2006). [5] Mao et al. (2005). The EOS for nitrogen gas and for those using the generalized form set the value of a_{14} to 1, reducing the number of parameters by one. Thus, the original a_{15} becomes a_{14}. For consistency and ease of calculations we retain the original form, but set a_{14} to 1 as shown above.

P_c and T_c are the critical pressure and temperature, respectively, R is the universal gas constant at appropriate units and V_c is not the critical volume but is defined in terms of P_c and T_c as above. In the above equation, P and T (in terms of P_r and T_r) are assumed to be the independent variables while V (or V_r) is the dependent one.

The parameters a_1 to a_{15} are assumed to specific to a particular gas and have been evaluated from experimental data. Values for the major geothermal gases CO_2, H_2S, CH_4, and NH_3 taken from the original papers are collected and presented in Table 1. Parameters for ethane (Mao et al., 2005) are also included to represent the characteristics of heavier hydrocarbons which have gained increasing attention in geothermal studies (e.g., Tassi et al., 2005).

For the smaller-sized but important gases such as O_2, Ar, H_2 and CO, the applicability of the EOS has not been established. The reasons may include the lack of sufficiently accurate data at a wide range on pressure and temperature conditions for which the necessary parameters could be extracted, or simply the difficulty of obtaining such data. For example, CO and O_2 are highly reactive such that obtaining experimental data could be challenging. Nevertheless, an accurate solubility model covering an extended temperature and pressure range has been recently developed for O_2 (Geng and Duan, 2010).

Experimental difficulties in measuring H_2S solubilities, owing to the highly corrosive nature of the gas at high temperatures, have been noted by Suleimenov and Krupp (1994). Data obtained at these conditions were deemed highly uncertain by Duan et al. (2007) and they only modelled H_2S solubilities up to 500 K.

Hydrogen gas poses a fundamental problem in formulating a comprehensive EOS. Because each of the atoms in the gas molecule possesses a proton, the molecule could have two spin states. The molecules which have anti-parallel spins, called parahydrogen coexist which those which have parallel nuclear spins called orthohydrogen, and the two molecular states have completely different thermodynamic properties. Fortunately, at room conditions and higher temperature, H_2 exists as 25% parahydrogen and 25% orthohydrogen, and this mixture apparently extends to high temperatures (Jacobsen et al., 2007). Thus, H_2 gas under geothermal conditions should be considered as such, and any EOS would implicitly refer to this state. For example, the EOS for H_2 used in geologic applications (Spycher and Reed, 1988) and that of Zhou and Zhou (2001) fall in this category.

Table 2. Lennard-Jones parameters for gases of geothermal interest.

Species	ϵ (K)	σ A)	Refs.
H_2O	510	2.88	Duan, Moller and Weare, 1996
CO_2	235.0	3.69	Duan, Moller and Weare, 1996
H_2S	289.5	3.693	Duan, Moller and Weare, 1996
CH_4	154.0	3.691	Duan, Moller and Weare, 1996
NH_3	182.9	3.376	Eckl, Vrabec and Hasse, 2009
N_2	101.0	3.63	Duan, Moller and Weare, 1996
H_2	34.6	2.91	Duan, Moller and Weare, 1996
CO	98.0	3.66	Duan, Moller and Weare, 1996
O_2	115.7	3.365	Duan, Moller and Weare, 1996
Ar	113.5	3.465	Mourits and Rummens, 1977
He	3.78	2.63	Hirschfelder, Curtiss and Bird, 1964
SO_2	139.23	3.312	Eckl, Vrabec and Hasse, 2008
SF_6	212	5.199	Mourits and Rummens, 1977
C_2H_6	227.9	4.407	Mourits and Rummens, 1977
C_6H_6	401.2	5.455	Mourits and Rummens, 1977

For gases whose individual parameters for the EOS have not been fully evaluated, we adopt the generalized equation of state proposed by Duan, Moller and Weare, 1995a, 1992c). It is the same equation used here except that only one set of parameters characteristic of a reference gas—chosen by the authors to be methane—is used for all the gases. If the molecular interactions in each gas are described by a Lennard-Jones potential V_{LJ} ,

$$V_{LJ}(pair) = 4\epsilon\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^{6}\right] \qquad (3)$$

the reduced temperature T* = kT/ϵ and reduced volume V* = V/σ^3 would be the same for all systems, and where the L-J parameters ϵ and σ would be characteristics of a particular gas. In eq. 3, *r* is the intermolecular distance between a pair of gas molecules.

Such scaling property of the L-J potential allows a generalization of the reduced pressure P_r, reduced temperature T_r and reduced volume V_r to

$$P_r = \frac{3.062\sigma^3 P}{\epsilon} \qquad (4)$$

$$T_r = \frac{154T}{\epsilon} \qquad (5)$$

$$V_r = \left(\frac{3.691}{\sigma}\right)^3 V \qquad (6)$$

For the case of polyatomic molecules, e.g., ammonia, an "effective" L-J potential is used; that is, a unified-atom approach is used where the interaction involving H are not explicitly included. In such treatment, the center of mass and charge would lie on the central atom like N in ammonia or S in SF_6. For molecules with no well-defined central atom such as ethane or benzene, the center-of-mass would be considered the center of charge also. In any case, the treatment used by Duan et al. (1995) considers the L-J parameters as adjustable to fit existing vapour-liquid equilibrium data.

The L-J parameters for gases of geothermal interest, or which could be applied in the industry (such as SF_6 for fluid flow measurements), are listed on Table 2. For many of these gases, the applicability of the approach here has not been validated.

A major impetus for this study is to calculate accurate vapour-liquid and mineral equilibria involving gases. Such calculation requires evaluating the fugacity coefficient φ of a gas which is related to compressibility Z by the relation:

$$ln\varphi(T,P) = \int_0^P (Z-1)\frac{dP}{P} \, . \qquad (7)$$

The explicit form of φ follows directly from the EOS and is given by Duan, Moller and Weare, (1992a).

For thermodynamic self-consistency, it is important to adopt a single form of EOS for all gases especially in calculating mixture properties. Using appropriate mixing rules, the proposed equation of state has been extended to mixtures (Duan, Moller and Weare, 1992b).

3. CALCULATION PROCEDURE

One of our objectives in this work is to provide a simple method of implementing the required calculations on a stand-alone or notebook computer since many geothermal workers simply want to generate results without recourse to computer programming. We have therefore implemented the required calculations on a spreadsheet such as MS Excel or the OpenOffice suite.

The basic procedure requires the calculation of V_r in Eq. 1 which is a nonlinear function in the independent variable. From the available numerical solutions of such an equation, a simple method using the Newton-Rhapson procedure is found to be robust and convergences to a unique solution within a few iterations. This is implemented by solving the objective function $f(V_r) = Z - P_r V_r / T_r = 0$ for V_r. The solution at the ith iteration in given by $V_{r,i} = V_{r,i-1} - f(V_{r,i-1}) / f'(V_{r,i-1})$ where $f'(V_{r,i-1})$ is the derivative of the objective function with respect to V_r.

Initially, we set a convergence criterion to a very small number (e.g., 10^{-8}), but the solutions converge rapidly to 0 within the computational limits of the computer. The simplest procedure to implement the iteration is to manually copy the V_i result (on a given column) to the V_{i-1} column and keeping track of the value of $f(V_r)$ until the latter becomes 0.

Implementation using a spreadsheet also has the advantage of tracking the steps of the calculations and flagging unacceptable or spurious results (e.g., at pressures below the saturated water vapour line), especially during debugging and plotting the results immediately.

4. COMPRESSIBILITY AND FUGACITY COEFFICIENTS

Using the above procedure, we calculated the compressibility factors for two of the most important geothermal gases, CO_2 and H_2S, at three selected temperatures and the results are shown in Figs. 1 and 2.

The temperatures were chosen to check the correctness of the calculations against the results of Duan, Moller and Weare (1992a) for CO_2, who also showed that their EOS reproduces experimentally-determined values. It can be seen from the plots that the gases are far from ideal even at comparatively low pressures encountered in geothermal environment or at very high temperatures where gas behaviour should be approaching ideal. It is therefore inappropriate to consider gas compressibility values to be near unity (near ideal) for chemical equilibrium calculations, for example.

Representative plots of calculated fugacity coefficients of some geothermal gases at selected temperatures up to moderate pressure of 2000 bars are shown below. It is clear that even at these comparatively mild conditions, fugacity coefficients deviate significantly from unity even for non-polar gases CH_4 and N_2. For the polar and highly reactive NH_3, fugacity coefficients are below unity for much of the geothermal range of temperatures and pressure. There is therefore no basis for assuming that fugacity coefficients are near unity under these conditions

5. GAS SOLUBILITY IN BRINES

In every stage of geothermal development from exploration to power generation, there is a need to calculate the solubility of gases in brines or gas partitioning between the liquid and the steam phases. The chemical potential of a gas in the gaseous phase is expressed in terms of its fugacity while in the aqueous phase it is expressed in terms of its activity. By equating these two expressions, the solubility of, say CO_2, is given as (Duan and Sun, 2003)

$$ln\frac{y_{CO2}P}{m_{CO2}} = \frac{\mu^{l(0)}_{CO2} - \mu^{v(0)}_{CO2}(T)}{RT} - ln\varphi_{CO2}(T,P,y) + ln\gamma_{CO2}(T,P,m) \qquad (8)$$

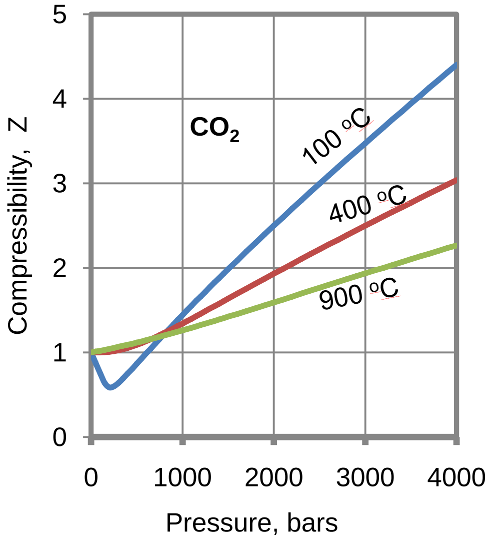

Figure 1: Compressibility factors for CO2 as functions of T and P.

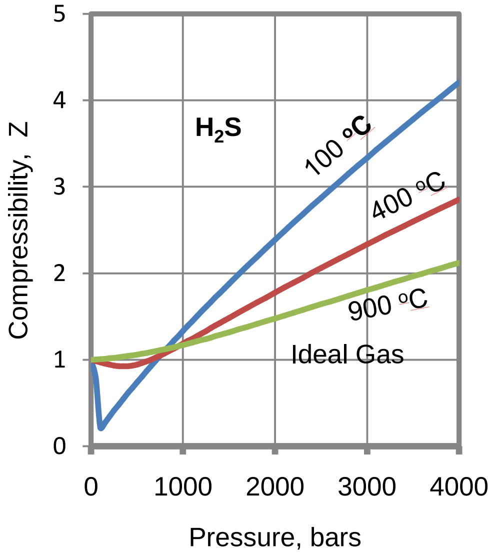

Figure 2: Compressibility factors for H2S as functions of T and P.

where y_{CO2} is the fraction of the gas in the steam phase, P is the total pressure, m_{CO2} is the liquid solubility, $\varphi_{CO2}(T,P,y)$is the fugacity coefficient, $\gamma_{CO2}(T,P,m)$ is the activity coefficient in the liquid phase, R is the universal gas constant, and $\mu^{l(0)}_{CO2}$ and $\mu^{v(0)}_{CO2}(T)$ are the standard chemical potentials of CO$_2$ in the liquid and vapour phases, respectively.

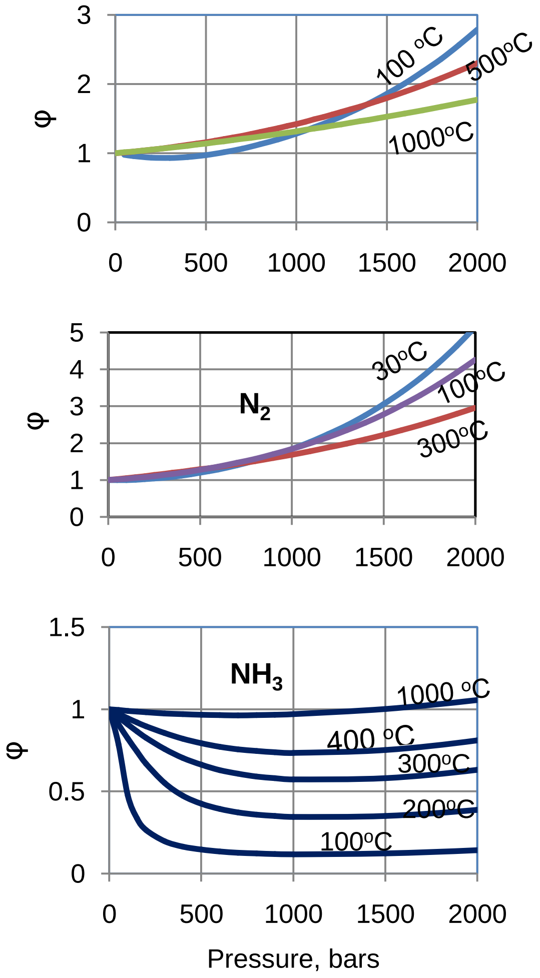

Figure 3: Fugacity coefficients for N$_2$, CH$_4$, NH$_3$.

Given P, the gas fraction y for a dominant gas such as CO$_2$ can be approximated as y =(P – P$_{H2O}$)/P where P$_{H2O}$ is the saturated water vapour pressure which is only a function of T, and can be taken from standard steam tables. For more accurate work, and if experimental data are available for H$_2$O-gas mixtures, the mole fraction of H$_2$O (and consequently of the gas since y = 1 – y$_{H2O}$ for binary mixtures) can be calculated from empirical correlations. Thus, for the N$_2$-H$_2$O system, the mole fraction for H$_2$O is calculated using the equation (Mao and Duan, 2006)

$$y_{H_2O} = \frac{\gamma_{H_2O}\, x_{H_2O}\, P^S_{H2O}}{\varphi_{H_2O}} \exp\left(\frac{v^l_{H2O}(P-P^S_{H2O})}{RT}\right) \qquad (9)$$

where γ_{H_2O} is the activity coefficient of water in the liquid phase which can be taken to be 1 since the amount of dissolved gas in invariably much smaller than that of water; x_{H_2O} the mole fraction of water, is also taken as one for a gas-water system and 1 – 2x$_{NaCl}$ for a solution containing NaCl; v^l_{H2O} , the molar volume of liquid water, can be approximated as being equal to the molar volume of steam at saturated water vapour pressure; and P^S_{H2O} is the saturation pressure of water. The fugacity coefficient of water, φ_{H_2O} , can be obtained from semi-empirical correlations from experimental data which has the form, e.g., for N$_2$:

$$\varphi_{H_2O} = \exp(c_1 + c_2P + c_3\,P^2 + c_4PT + \frac{c_5P}{T} + \frac{c_6P^2}{T}). \qquad (10)$$

Because only the difference between the chemical potentials given above is meaningful, $\mu_{CO2}^{v(0)}$ can be conveniently set to zero and only $\mu_{CO2}^{l(0)}$ needs to be evaluated. At the conditions prevalent in most geothermal systems, Duan et al. (1992) has shown that the fugacity coefficient of CO_2 in CO_2-H_2O mixtures differs very little from that of the pure gas. Therefore, this quantity can be calculated directly from the EOS.

The remaining quantity that needs to be evaluated is the activity coefficient in the liquid phase. In recent years, the specific ion interaction model of Pitzer (see e.g., Weare, 1987) to calculate activity coefficients in the aqueous phase has been a huge success in terms of its accuracy and predictive capability. For charged species, the Pitzer formulation for the activity coefficient contains a Debye-Hückel term and ion-ion or ion-neutral species interaction parameters. For a (neutral) gas species *i* in solution the expression for its activity coefficient takes on a simple form:

$$ln\gamma_i = \sum_c 2\lambda_{ic}\, m_c + \sum_a 2\lambda_{ia}\, m_a + \sum_c \sum_a \xi_{ica}\, m_c m_a \quad (11)$$

where λ and ξ are the second-order and third order interaction parameters, respectively; and *c* and *a* refer to cation and anion, respectively.

In theory, all the interaction parameters need to be known to adequately describe thermodynamically the aqueous portion of the geothermal fluid. For many of the major components like the chloride salts, the interaction parameters have been determined at geothermal conditions. Comparatively less is known regarding the gas-ion interaction parameter except those involving the major gases and NaCl. But since NaCl is the predominant ionic species in solution, a thermodynamic model which approximates geothermal solution as NaCl brine may prove to be adequate to describe gas solubility in brines. Many workers have shown that the Pitzer formulation can be extended to complex electrolyte solutions such as oil brines, geothermal fluids and seawater (Weare, 1987) even if some of the parameters are poorly known.

For more rigorous calculations, other dissolved species may be included by adding the appropriate interaction parameters. The specific-ion interaction parameters involving gases and NaCl as functions of temperature and pressure are given as empirical equations in the original papers cited in Table 1.

Examples of calculation of solubility of CO_2 in brines are shown in Fig. 4. It can be seen that at moderate salinities, the salting-out effect cannot be neglected, especially at increasing temperatures and pressures. Also shown are the possible inaccuracies that may result when using simple Henry's Law approach in calculating gas solubilities in brines as in the case of H_2S (Fig. 5). The effects of pressures and salinity on solubility even for sparingly soluble gas such as N_2 cannot be neglected (Fig. 6).

6. GAS PARTITION COEFFICIENTS

During geothermal fluid production, lowering of fluid pressures causes preferential partitioning of the gases into the gaseous phase. Such distribution is a complicated function of temperature, pressure and composition. The distribution coefficient *B* is defined as B = x^v/x^l where x^v and x^l are the mole fractions of the gas in the vapour and liquid phases respectively.

The usual practice in determining the extent of distribution of gases is the use of distribution or Henry's Law coefficients valid near water saturation. But as Duan et al. (1996) have shown, the B values for CO_2 at 200°C calculated from Giggenbach's (1980) regression equation may be in error in the order of 100% even for pressures slightly higher than saturation when compared to experimental data.

We have extended such calculation using the present approach for some geothermal gases and the results for CO_2 and N_2 are shown as examples in Figs. 7 and 8. It can be noted that in general, values of B drop rapidly as pressures increase from saturation. The implication is that gas distribution calculations cannot be reliable using simple regression equations. A common assumption that all the gases essentially partition into the steam phase can cause large errors in calculations if proper distribution is neglected.

7. BOILING CURVES FOR CO_2-H_2O-NACL MIXTURES

Duan et al. (1996) calculated the boiling curves of the CO_2-H_2O system using the EOS of the mixture who noted that these are dramatically different from that of pure water. Rather than using the mixture EOS, we have chosen the obtain similar curves by using the same calculation procedure outlined above and the solubility model of Mao et al. (2009) to cover the temperatures above 250°C. This was achieved by adjusting both the total pressure ($P = P_{H2O} + P_{CO2}$) using the saturated vapour pressure of water from steam tables, and the reduced volume V_r until the desired solubility of CO_2 is obtained. The procedure has the advantage of calculating the effect of dissolved NaCl (salting-out effect) on the boiling curve. Results of such calculation are shown in Fig. 8. Without the NaCl, the plot essentially reproduces Fig. 3 of Duan et al. (1996).

It can be seen that the effect of NaCl on the boiling curve, while smaller than that of CO_2, can still be significant.

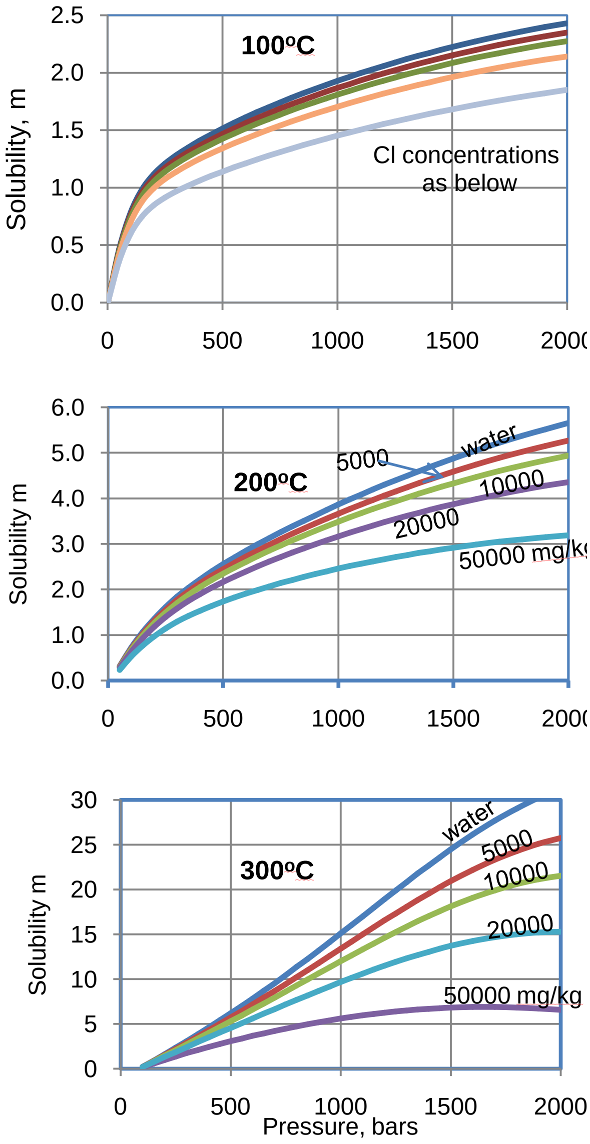

Figure 4: Solubility of CO_2 in brines (as ppm Cl) at different temperatures: (a)100°C, (b) 200°C, (c) 300°C.

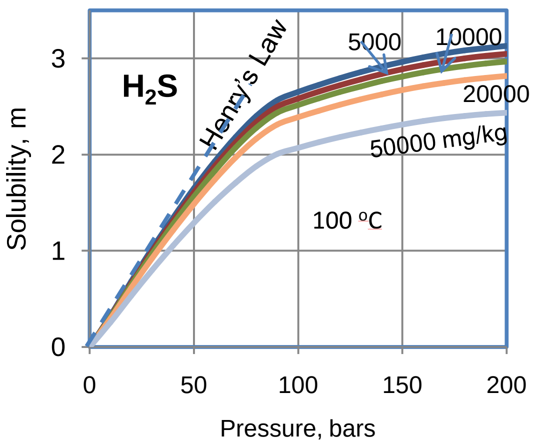

Figure 5: Solubility of H_2S in NaCl brines at 100°C. Shown as dashed line is the solubility using Henry's law.

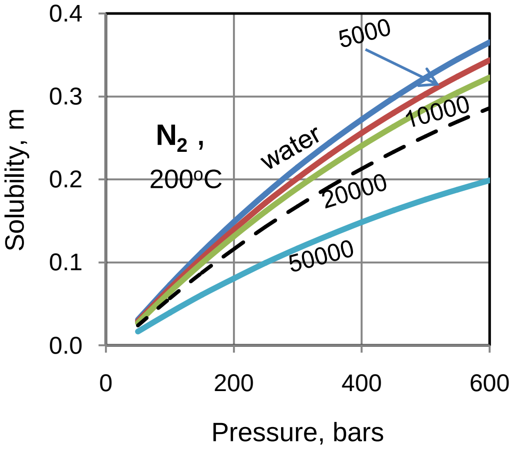

Figure 6: Solubility of N_2 in NaCl brines at 200°C.

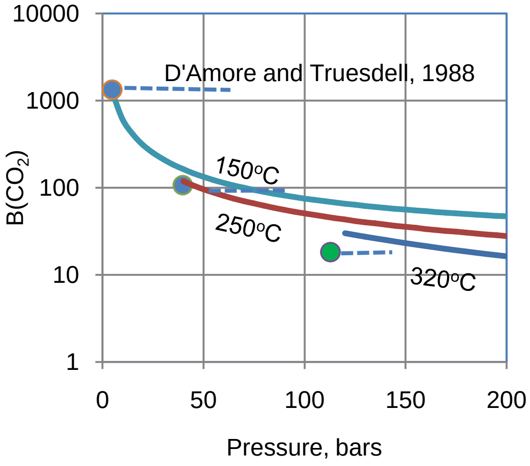

Figure 7: Distribution coefficients of CO_2 at various temperatures.

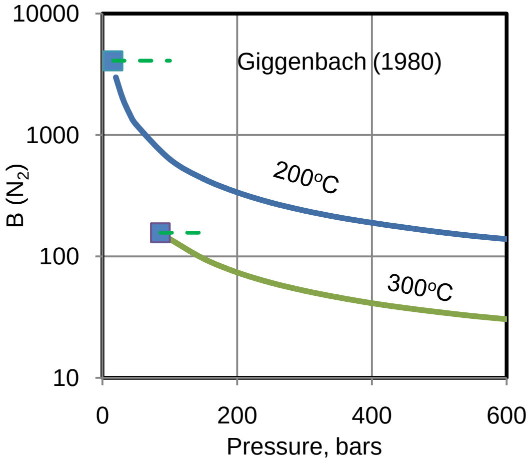

Figure 8: Distribution coefficients of N_2 at various temperatures.

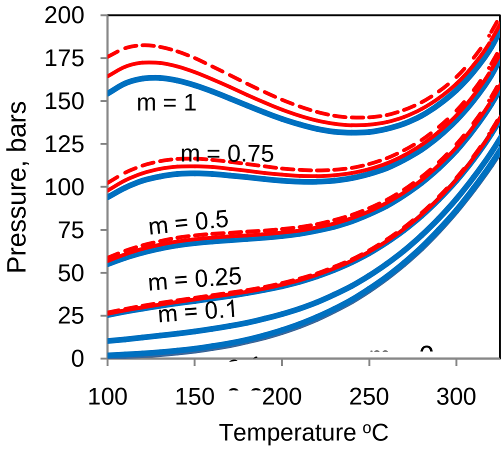

Figure 9: Boiling pressures of the system CO_2-H_2O-NaCl calculated from the solubility model of Mao et al. (2009).The effect of dissolved NaCl is shown by the dashed lines (m_{Cl} = 5000 mg/kg) or dot-dash lines (m_{Cl} = 10000 mg/kg) which are typical Cl values in geothermal fluids.

8. SOME FIELD APPLICATIONS

We applied the calculation procedure to problems involving carbon dioxide, which is by far the most significant gas in most geothermal systems.

8.1. Effect of high gas content on boiling depth at well OP-4D, Bacman Geothermal Field

Well OP-4D is one of the hottest and most productive wells at the Bacman geothermal field, Philippines. Measured enthalpy is at 1478 kJ/kg, which is equivalent to the temperature of 320°C measured at the main production zone; the CO_2 concentration is significant at 833 mmol/100 mol steam (2.07 wt %) at total discharge; and the brine has about 10,000 mg/kg Cl. The measurements were taken when the well was "producing from the major feed zone at stabilized conditions" (D'Amore et al., 1993). The corresponding pressure was read as 150 bars from the pressure-temperature plot of Austria (2008).

Using the above conditions and the calculation method outlined, the CO_2 solubility in the brine was found to be 2.01 wt. % which is quite consistent with the measured values assuming that all the gases were initially dissolved in the liquid phase. If the aqueous phase were assumed to be pure water, the calculated solubility becomes 2.27 wt. %, which is 13% higher compared to that in brine. Thus, accurate solubility calculation should take into account the salting-out effect of the brine.

The effect of the presence of CO_2 on the boiling point depth can be estimated by noting that essentially, $P = P_{sat} + P_{CO2}$ and using the regression equation of Arnorsson and D'Amore (2000) for the boiling point with depth for pure water. By taking into account the pre-exploitation water level in the well, the boiling point is calculated to be depressed to -2380 m (vertical) depth. This point plots beyond the last measurement of Austria (2008), but is consistent with the temperature profile during discharge.

The change in boiling point with depth is about 700 m deeper compared to that of a column of pure water. This calculation is quite significant in designing calcite inhibition systems where typically, the inhibitor injection point should be below the boiling point of the hot brine.

8.2. Thermodynamic structure of a high gas field

The development of the Northern Negros geothermal field (NNGF) poses major challenges, both political and technical. Production well drilling has been constrained to a limited area within the geothermal reservation but outside a protected national park where most of the resource is thought to the located (Yglopaz at al., 2005). The wells are spaced closely such that well interference has been observed.

In addition, potential calcite scaling and pressure drawdown have been noted early on. For example, well PT-5D, the hottest well at 290°C, experiences a pressure drop of 40 bars when going from static to discharging conditions which is attributed partly to poor recharge (Yglopaz et al., 2005). This explanation seems to be incompatible with the observation during drilling and completion tests that good productivity is exhibited by most wells in Pataan sector (the most productive sector of the field) (Dulce and Zaide-Delfin, 2005).

It has been noted that even during the pre-exploitation stage, the subsurface pressures of the NNGF wells at similar depths are higher by about 20 bars compared to those of wells in other projects (unpublished data). To assess the role played by gas concentrations on the above observations, we examined the chemical data from a recently- drilled well located two kilometres southeast of the main production area.

During testing, the following information was obtained: (1) the main permeable zone was at 2200-2225 m (measured depth) at a measured pressure of 105 bars; (2) the average chloride concentration of the geothermal water taken at atmospheric pressure was 5600-5700 mg/kg; and (3) silica geothermometry gave an average fluid temperature of of 267°C. Assuming a single phase inflow into the well, the deep chloride concentration was taken to be 3800 mg/kg.

At the given conditions, the calculated solubility of CO_2 is 2.67 % by weight. This gives rise to a P_{CO2} of approximately 53 bars which is also equal to the saturated water vapour pressure at this temperature. If this CO_2-saturated fluid is flashed at a design pressure of 6 bars, this would result in 11.2% by weight of gas in steam which compares very well with measured values of 10-13 % by weight (unpublished results) of CO_2 taken during discharge testing.

It can be concluded therefore that the apparent overpressure of the Northern Negros reservoir can be accounted solely by the presence of dissolved CO_2 in the geothermal brine. Such seemingly anomalous thermodynamic structure finds support in a geological study which shows that the fresh Canlaon Volcanics is relatively thick here (~ 1800 m) in comparison with similar Pleistocene deposits in other Philippine geothermal fields that have an average thickness of only 250-350 m, which effectively seals off the hot reservoir that is hosted by sedimentary Talave Formation (Dulce and Zaide-Delfin, 2005).

The presence of elevated CO_2 can also explain the rapid pressure drop observed in some wells (Yglopaz et al., 2005) since, according to simulation studies (Bodvarsson and Gaulke, 1986), CO_2 greatly affects the fluid recovery from matrix blocks: the higher the initial partial pressure of CO_2, the less the recoverable reserves.

ACKNOWLEDGEMENT

We thank the management of Energy Development Corporation for allowing us to use company data in this paper.

REFERENCES

Arnorsson, S., D'Amore, F., 2000. Estimation of aquifer steam fraction, in: Arnorsson, S. (ed.) Isotopic and chemical techniques in geothermal exploration, development and use. International Atomic Energy Agency, Vienna, pp. 267-308.

Arnorsson, S., Gunnlaugsson, E., 1985. New gas geothermometers for geothermal exploration—calibration and application. Geochim. Cosmochim. Acta 49, 1307-1325.

Austria, J. J. ,2008. Production capacity assessment of the Bacon-Manito geothermal reservoir, Philippines. Report 2, United Nations University, Geothermal Training Programme, Reykjavik, Iceland. 81 p.

Bodvarsson, G. S., Gaulke, S., 1986. Effects of noncondensible gases on fluid recovery in fractured geothermal reservoirs. SPE 15121, 273-280.

Bowers, T. S., Helgeson, H. C., 1983. Calculation of the thermodynamic and geochemical consequences in the system H_2O-CO_2-NaCl on phase relations: Equation of state for H_2O-CO_2-NaCl fluids at high pressures and temperatures. Geochim. Cosmochim. Acta 47, 1247-1275.

D'Amore, F., Maniquis-Buenviaje, M., Solis, R.P., 1993. An evaluation of the deep reservoir conditions of the Bacon-Manito geothermal field, Philippines using well gas chemistry. Proceedings Eighteenth Workshop on Geothermal Engineering, Stanford University, Stanford, California, January 26-28, 1993, pp. 235-240.

D'Amore, F. Nuti, S., 1977. Notes on the chemistry of geothermal gases. Geothermics 6, 39-45.

D'Amore, F., Panichi , C., 1980. Evaluation of deep temperatures in hydrothermal systems by a new gas geothermometer. Geochim. Cosmochim. Acta 44, 549-556.

Duan, Z., Li, D., 2008. Coupled phase and aqueous species equilibrium of the H_2O-CO_2-NaCl-$CaCO_3$ system from 0 to 250°C, 1 to 1000 bar with NaCl concentrations up to saturation of halite. Geochim. Cosmochim. Acta 72, 5128-5145.

Duan, Z. , Moller, N., Weare, J. H., 1996. Equation of state for the NH_3-H_2O system. J. Solution Chem. 25, 43-50.

Duan, Z. , Moller, N., DeRocher, T., Weare, J. H., 1996. Prediction of boiling, scaling and formation conditions in geothermal reservoirs using computer programs TEQUIL and GEOFLUIDS. Geothermics 25, 663-678.

Duan, Z., Moller, N., Weare, J. H.,1995a. A general equation of state for supercritical fluid mixtures and molecular dynamics simulation of mixture PVTX properties. Geochim. Cosmochim. Acta 60, 1209-1216.

Duan, Z., Moller, N., Weare, J. H.,1995b. Equation of state for the NaCl-H_2O-CO_2 system: Prediction of phase equilibria and volumetric properties. Geochim. Cosmochim. Acta 59, 2869-2882.

Duan, Z., Moller, N.; Weare, J. H.,1992a. An equation of state for the CH_4-CO_2-H_2O system: I. Pure systems from 0 to 1000 °C and 0 to 8000 bar. Geochim. Cosmochim. Acta 56, 2605-2617.

Duan, Z.; Moller, N., Weare, J. H.,1992b. An equation of state for the CH_4-CO_2-H_2O system: II. Mixtures from 50 to 1000°C and 0 to 1000 bar. Geochim. Cosmochim. Acta 56, 2619-2631.

Duan, Z.; Moller, N.; Weare, J. H.,1992c. Molecular dynamics simulation of PVT properties of geological fluids and a general equation of state of nonpolar and weakly polar gases up to 2000 K and 20,000 bar. Geochim. Cosmochim. Acta 56, 3839-3845.

Duan, Z., Sun, R., 2003. An improved model calculating CO_2 solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar. Chem. Geol. 193, 257-271.

Duan, Z., Sun, R., Liu, R., Zhu, C., 2007. Accurate thermodynamic model for the calculation of H_2S solubility in pure water and brines. Energy and Fuels 21, 2056-2065.

Dulce, R. G.; Zaide-Delfin, M. C.; 2005. Exploration and delineation drilling in a high-temperature geothermal reservoir: Northern Negros geothermal field, Central Philippines. Proceedings World Geothermal Congress 2005, Antalya, Turkey, 24-29 April 2005.

Eckl, B.; Vrabec, J.; Hasse, H., 2009. An optimized molecular model for ammonia. Mol. Phys. 106, 1039-1046.

Eckl, B.; Vrabec, J.; Hasse, H., 2008. Set of molecular models based on quantum mechanical *ab initio* calculations and thermodynamic data. J Phys. Chem. B 112, 12710-12721.

Giggenbach, W.F., 1980. Geothermal gas equilibria. Geochim. Cosmochim. Acta 45, 2021-2032.

Geng, M.; Duan, Z. , 2010. Prediction of oxygen solubility in pure water and brines up to high temperatures and pressures. Geochim. Cosmochim. Acta 74, 5631-5640.

Glover, R. B., 1970. Interpretation of gas compositions from the Wairakei field over 10 years. Geothermics 2, 1355-1366.

Jacobsen, R. T.; Leachman, J. W.; Penoncello, S. G.; Lemmon, E. W., 2007. Current status of thermodynamic properties of hydrogen. Int. J. Thermophysics 28, 758-772.

Kerrick, D. M.; Jacobs, G. K., 1981. A modified Redlich-Kwong equation for H_2O, CO_2, and H_2O-CO_2 mixtures at elevated pressures and temperatures. Am. J. Sci. 281, 735-767.

Lee, B. I.; Kesler, M. G., 1975. A generalized thermodynamic correlation based on three-parameter corresponding states. AIChE J. 21, 510-527.

Li, D.; Duan, Z.; 2007. The speciation equilibrium coupling with phase equilibrium in the H_2O-CO_2-NaCl system from 0 to 250^oC, from 0 to 1000 bar, and from 0 to 5 molality of NaCl. Chem. Geol. 244, 730-751.

Mao, S.; Duan, Z., 2006. A thermodynamic model for calculating nitrogen solubility, gas phase composition and density of the N_2-H_2O-NaCl system. Fluid Phase Equilibria 248, 103-114.

Mao, S., Duan, Z., Hu, W., 2009. A vapor-liquid phase equilibrium model for binary CO_2-H_2O and CH_4-H_2O systems above 523 K for application to fluid inclusions. J. Supercritical Fluids 50, 13-21.

Mao, S.; Zhang, Z.; Hu, J.; Sun, R.; Duan, Z., 2005. An accurate model for calculating C_2H_6 solubility in pure water and aqueous NaCl solutions. Fluid Phase Equilibria 238, 77-86.

Mourits, F. M.; Rummens, F. H. A., 1977. A critical evaluation of Lennard-Jones and Stockmayer potential parameters and of some correlation methods. Can. J. Chem. 55, 3007-3020.

Spycher, N. F.; Reed, M. H., 1988. Fugacity coefficients of H_2, CO_2, CH_4, H_2O and of H_2O- CO_2-CH_4 mixtures: A virial equation treatment for moderate pressures and temperatures applicable to calculations of hydrothermal boiling. Geochim. Cosmochim. Acta 52, 739-749.

Suleimenov, O. M.; Krupp, R. E., 1994. Solubility of hydrogen sulphide in pure water and in NaCl solutions from 20 to 320^oC and at saturation pressures. Geochim. Cosmochim. Acta 58, 2433-2444.

Tassi, F.; Martinez, C.; Vaselli, O.; Capaccioni, B.; Viramonte, J., 2005. Light hydrocarbons as redox and temperature indicators in the geothermal field of El Tatio (Northern Chile). Applied Geochemistry 20, 2049-2062.

Weare, J. H., 1987. Models of mineral solubility in concentrated brines with application to field observations. Rev. Miner. 17, 143.

Yglopaz, D. M.; Malate, R. C. M.; Amistoso, A. E.; Aqui, A. R.; Orizonte; R. G.; Sanchez, D. R.; 2005. Field management strategies for the development of the Northern Negros geothermal field, Philippines. Proceedings World Geothermal Congress 2005, Antalya, Turkey, 24-29 April 2005.

Zhou, L.; Zhou, Y., 2001. determination of compressibility factor and fugacity coefficient of hydrogen in studies of adsoptive storage. International Journal of Hydrogen Energy 26, 597-601.