

Modeling the Phase Partitioning Behavior of Gas Tracers Under Geothermal Reservoir Conditions

Mark Trew[†]
Michael O’Sullivan

Department of Engineering Science, University of Auckland, New Zealand

Yoshio Yasuda
JAPEx Research Center, Japan

Abstract

A model of the liquid-vapor phase partitioning behavior of gas tracers in water at geothermal temperatures and pressures is presented. This model uses Henry’s coefficient to describe the variation of the gas tracer solubility with temperature and pressure. A new method is described for the determination and representation of Henry’s coefficients. The method uses experimentally determined values of Henry’s coefficient and a theoretically predicted value of behavior at the critical point of water to provide data which can be fitted by a semi-empirical correlation. No assumptions regarding ideal behavior are necessary. The semi-empirical correlation is a modified version of that presented by Harvey (1996) and better accounts for high temperature and non-ideal behavior. Sets of model coefficients are given for a range of possible gas tracers. The resulting phase partitioning model is simple and may be easily implemented in a numerical geothermal simulator. The use and behavior of the model is illustrated by its application to a number of idealised test problems.

[†]Corresponding author. Email: m.trew@auckland.ac.nz

1 Introduction

Computer modelling of flows including geothermal tracers is motivated by the widespread use of tracers in geothermal reservoir testing and management. These tracer models are useful for both the design and interpretation of field tests. The tracers used in geothermal fields may be broadly categorised into gas tracers and liquid tracers. Gas tracers are defined as those tracer chemicals that are highly volatile, sparingly soluble and are injected as a vapor. Examples of gas tracers include the noble gases, refrigerants (e.g. R-23) and sulfur hexafluoride (SF_6). Liquid tracers have low or moderate volatility and may be injected as liquids. Examples include tritiated water, salt solutions (e.g. NaBr) and various alcohols (e.g. methanol). Liquid tracers may exhibit liquid-vapor phase partitioning behavior similar or quite different to that of the geothermal water. As discussed in Trew et al. (2000), distinctive models of phase partitioning behavior are required for each of these two tracer categories. This paper describes recent advances in models of the phase partitioning behavior of gas tracers.

The description of the liquid-vapor phase partitioning of gas tracers is based on their solubility in water. Gas solubility data in water at low temperatures are relatively abundant, however, they are scarce for the higher temperatures encountered in geothermal reservoirs (Schotte 1985, Japas and Levelt Sengers 1989). Suitable methods for extrapolating low temperature solubility data or relationships to high temperatures must be considered. In this research it is assumed that the gas tracer is only sparingly soluble and, hence, the gas tracer is close to infinite dilution in the liquid phase and its liquid-vapor partitioning behavior can be modelled by Henry's law (Schotte 1985). Henry's law has been used often in geothermal applications where gases are present; for example: O'Sullivan et al. (1985), Mroczek (1997) and Pruess et al. (2000). Henry's law requires the specification of Henry's coefficient which accounts for the solubility of the gas tracer in water varying with temperature and perhaps pressure. The representation of this coefficient is the key modeling consideration.

A geothermal flow simulator usually requires that a liquid-vapor phase partitioning model provide the liquid and vapor phase mass fractions of tracer for a given set of temperature and pressure conditions. Trew et al. (2000) describes the calculations required to implement a liquid-vapor partitioning model for gas tracers in the widely used TOUGH2 geothermal sim-

ulator program (Pruess 1991, Pruess et al. 1999). In developing the phase partitioning model described in Trew et al. (2000) it was assumed that gas behavior was ideal and that the concentration of gas tracers in both the liquid and vapor phases was very small. Consequently, given a temperature, T , and a partial gas pressure, P_g , the mass fractions of tracer in the liquid phase, X_g , and in the vapor phase, Y_g , were calculated as:

$$X_g = \frac{P_g}{C_H(T)} \frac{M_g}{M_{H_2O}} \quad (1)$$

$$Y_g = \frac{\rho_g(P_g, T)}{\rho_s(T)} \quad (2)$$

where $C_H(T)$ is Henry's coefficient as a function of temperature, M_g is the molecular weight of the gas, M_{H_2O} is the molecular weight of water, ρ_g is the density of the gas and ρ_s is the density of steam. The gas density was calculated using an ideal gas law. The value of Henry's coefficient is strongly temperature dependent. Henry's coefficient is also pressure dependent, however, in most cases a standard pressure state of water vapor pressure is adopted and the coefficient is given at the standard state pressure.

In Trew et al. (2000) the temperature dependence of C_H was represented by fitting discrete C_H values at a range of temperatures by the Harvey (1996) correlation. The Harvey correlation is attractive for its simplicity and only contains three unknown parameters that must be determined from experimental data. The discrete C_H values were determined for a given temperature, T , from regressions of the gas distribution coefficients, β (it was assumed that $\beta = Y_g/X_g$), by using:

$$C_H(T) = \frac{\beta(T)RT_a\rho_s}{M_{H_2O}} \quad (3)$$

where R is the universal gas constant and T_a is the absolute temperature. The gas distribution coefficients were obtained from low temperature (i.e. 20° C to 80° C) regressions provided by Adams (1999).

The gas tracer phase partitioning model described above and used by Trew et al. (2000) was easy to implement because of its simplicity. However, there were a number of limitations

to the model, including: the assumption of ideal gas behavior; the assumption of very small gas concentrations in all phases; the uncertain extrapolation of low temperature relationships to geothermal temperatures; no accounting for pressure effects in the specification of Henry's coefficient; and occasional problems with the Harvey correlation of the C_H values for some gas tracers. These limitations are addressed by the research presented in this paper.

A phase partitioning model is presented which contains some similarities to that of Trew et al. (2000). However, this model calculates mole fractions first and then converts them to mass fractions and most significantly uses a modified definition of Henry's coefficient that includes the effects of non-ideal behavior and pressure dependence.

The experimental calculation and semi-empirical fitting of this modified form of Henry's coefficient occupies a significant part of this paper. The determination and use of this coefficient does not assume ideal gas behavior and incorporates the theoretical behavior of Henry's coefficients at the critical point of water. A modified form of the semi-empirical Harvey (1996) correlation for Henry's coefficient is proposed that retains the simplicity of the original form but has improved fitting characteristics. The final expression given for Henry's coefficient correlates not only temperature effects, but also pressure effects. The necessary correlation coefficients are determined for a selection of gas tracers and finally some applications are presented.

No attempt has been made to include the effects of salinity of the geothermal brine on the phase partitioning behavior of gas tracers. In general it is expected that the solubility of the gas tracers in the liquid phase will decrease with increasing electrolyte concentration (Walas 1985, Hermann et al. 1995, Smits et al. 1998, Gao et al. 1999). This will be considered further in future work.

2 A Liquid-Vapor Phase Partitioning Model for Multiple Gas Tracers in Water

A liquid-vapor phase partitioning model that can be used in a geothermal flow simulator will generally provide expressions for the liquid and vapor phase mass fractions of gas tracer. How-

ever, the calculations are most easily performed to determine mole fractions and then the mole fractions of tracer in each phase are converted into mass fractions.

Consider a system with N gas tracers. Given a low solubility, Henry's law (Van Ness and Abbott 1997) can be used for tracer i to relate the liquid mole fraction, x_i , to the vapor phase mole fraction, y_i , the temperature, T , and the pressure, P , as:

$$x_i = \frac{y_i P}{C_H^*(T, P)_i}. \quad (4)$$

where $C_H^*(T, P)_i$ is a modified Henry's coefficient for tracer i that includes non-ideal behavior and accounts for the liquid phase solubility varying with temperature and pressure. The vapor mole fraction and the pressure can be conveniently combined into a single variable: $P_{gi} = y_i P$. This variable is identical to the partial pressure of an ideal gas component from Dalton's law of partial pressures. Thus, if the partial pressure is used as a dependent variable along with temperature and pressure, the liquid and vapor mole fractions of the gas tracer i are determined from:

$$x_i = \frac{P_{gi}}{C_H^*(T, P)_i} \quad (5)$$

$$y_i = \frac{P_{gi}}{P}. \quad (6)$$

Once the values of x and y have been determined for the N tracers, the liquid and vapor phase water mole fractions are:

$$x_w = 1 - \sum_{i=1}^N x_i \quad (7)$$

$$y_w = 1 - \sum_{i=1}^N y_i. \quad (8)$$

The mass fraction values that are necessary for modelling the phase partitioning of the gas

tracer are calculated as:

$$X_i = \frac{x_i M_i}{x_w M_w + \sum_{j=1}^N x_j M_j} \quad (9)$$

$$Y_i = \frac{y_i M_i}{y_w M_w + \sum_{j=1}^N y_j M_j}. \quad (10)$$

where M is the molecular weight, X is the liquid phase mass fraction and Y is the vapor phase mass fraction. The use of these mass fractions in the TOUGH2 geothermal simulator (Pruess 1991, Pruess et al. 1999) has been described in Trew et al. (2000). The key to this phase partitioning model is the modified Henry's coefficient which is discussed in the following sections.

3 Experimental Calculation and Fitting of a Modified Henry's Coefficient

3.1 Henry's law and a modified form of Henry's coefficient

This section shows how a modified form of Henry's coefficient can be obtained from experimental data and used with Henry's law to calculate liquid mole fractions of gas tracer in water for a general temperature and pressure state. No assumption of ideal behavior is made. The only assumption is that the solubility and, hence, liquid phase concentration of the gas tracer is sufficiently small so as to be approximately infinitely dilute.

To account for a non-ideal component i in a non-ideal mixture, the quantities of fugacity, f , and the partial fugacity of component i , \hat{f}_i , are necessary. The fugacity may be either that of the mixture or that of the pure component i , i.e. f_i . The fugacity and partial fugacity are defined as those quantities that replace pressure and partial pressure in the ideal pressure, temperature and molar volume relationships in order to maintain the validity of these relationships for non-ideal components and mixtures (Walas 1985). When multiple phases are present, the partial fugacities of component i in the liquid and vapor phases become equal when the vapor and

liquid phases are in equilibrium (Van Ness and Abbott 1997), i.e.:

$$\hat{f}_i^v = \hat{f}_i^l = \hat{f}_i. \quad (11)$$

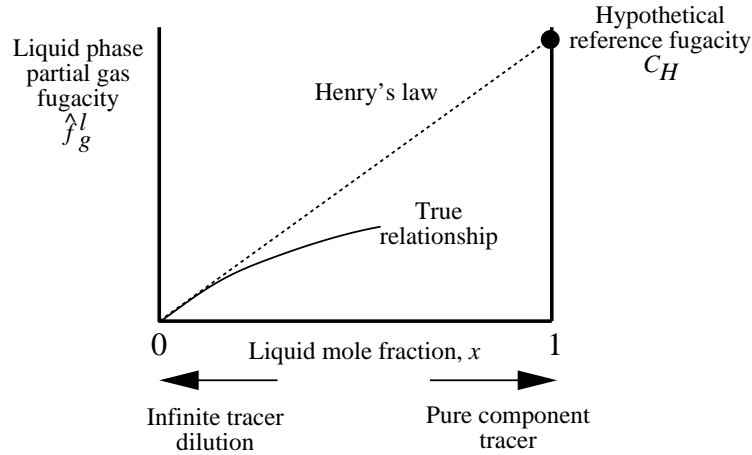


Figure 1: Henry's law.

Henry's law is based on the relationship between the gas tracer partial liquid fugacity and its liquid mole fraction, x . This is shown in Figure 1. Henry's law defines a hypothetical linear liquid phase partial fugacity and liquid mole fraction relationship for the gas tracer which corresponds to the true state at infinite liquid dilution of the gas tracer (Benson and Krause, Jr. 1989). The slope of this relationship is the value of Henry's coefficient, C_H . The formal definition of Henry's coefficient is (Benson and Krause, Jr. 1989, Van Ness and Abbott 1997):

$$C_H = \lim_{x \rightarrow 0} \frac{\hat{f}_g^l}{x} \quad (12)$$

where \hat{f}_g^l is the partial fugacity of the gas tracer in the liquid phase.

Although Henry's coefficient is temperature and pressure dependent it is usually given at a standard pressure state of water vapor pressure. Pressure dependence is recovered by using a Poynting correction factor (PCF) to reference the standard state Henry's coefficient at the water vapor pressure, $C_H(T, P_w^s)$, to the general pressure state, $C_H(T, P)$ (Benson and Krause,

Jr. 1989):

$$C_H(T, P) = C_H(T, P_w^s) \exp \left[\frac{\hat{V}_g^l (P - P_w^s)}{RT_a} \right] \quad (13)$$

where \hat{V}_g^l is the partial liquid molar volume at infinite dilution and the standard pressure state, R is the universal gas constant and T_a is the absolute temperature. The PCF is determined by integrating an expression for the rate of change of fugacity with pressure, using the assumption that the partial liquid molar volume varies negligibly with pressure (Walas 1985, Benson and Krause, Jr. 1989).

The vapor phase partial fugacity coefficient of the gas tracer, $\hat{\phi}_g^v$, is defined as (Van Ness and Abbott 1997):

$$\hat{\phi}_g^v = \frac{\hat{f}_g^v}{yP} \quad (14)$$

where \hat{f}_g^v is the partial fugacity of the gas tracer in the vapor phase and y is the mole fraction of the gas tracer in the vapor phase. Rearrangement and division by the liquid phase mole fraction of tracer, x , gives:

$$\frac{\hat{f}_g^v}{x} = \frac{\hat{\phi}_g^v y P}{x} \quad (15)$$

Assuming that the solubility and mass of the gas tracer is sufficiently small so that it is approximately infinitely dilute in the liquid phase, (12) may be used to give the general pressure state Henry's coefficient as:

$$C_H(T, P) = \frac{\hat{\phi}_g^v y P}{x} \quad (16)$$

A Poynting correction factor can then be used to express the standard state Henry's coefficient as:

$$C_H(T, P_w^s) = \frac{\hat{\phi}_g^v y P}{x} \exp \left[\frac{-\hat{V}_g^l (P - P_w^s)}{RT_a} \right] \quad (17)$$

Experimental gas solubility data is usually available for gas-solvent binary mixtures as the mole fraction of gas in the liquid solvent, x , at a given pressure, P and temperature, T . Equation (17) can be used to determine experimental values of C_H using T , P , and x , if y , $\hat{\phi}_g^v$ and \hat{V}_g^l can be determined by auxiliary calculations. Section 3.2 describes the calculation of y , sections 3.4 and 3.5 describe the calculation of $\hat{\phi}_g^v$ and \hat{V}_g^l and other quantities necessary to evaluate y . The experimentally derived values of $C_H(T, P_w^s)$ are fitted by a semi-empirical relationship which describes their variation with temperature.

When the semi-empirical relationship between $C_H(T, P_w^s)$ and temperature is defined, Henry's law is used to calculate the liquid mole fractions at a given temperature and pressure. Equation (17) can be rearranged to:

$$x = \frac{P_g}{\frac{C_H(T)}{\hat{\phi}_g^v(T)}} \exp \left[\frac{-\hat{V}_g^l(P - P_w^s)}{RT_a} \right] \quad (18)$$

where $P_g = yP$ is the partial gas pressure. This expression for x accounts for non-ideal behavior as well as temperature and pressure effects. It can be observed that if this equation is further rearranged to:

$$x = \frac{P_g}{C_H^*(T) \exp \left[\frac{\hat{V}_g^l(P - P_w^s)}{RT_a} \right]} \quad (19)$$

then the modified standard state Henry's coefficient, $C_H^*(T)$, implicitly contains the partial fugacity coefficient necessary to account for non-ideal behavior. Equation (19) is identical to (5). It is proposed then that the modified Henry's coefficient $C_H^* = C_H(T, P_w^s)/\hat{\phi}_g^v(T, P_w^s)$ rather than C_H be fitted using a semi-empirical fit. This approach has the attractive feature that once C_H^* is fitted, the partial fugacity coefficient does not need to be calculated every time the liquid mole fraction of the gas tracer, x , at a given temperature and pressure is required.

3.2 The vapor phase mole fraction of gas tracer

This section describes the derivation of the calculations required to determine the vapor phase mole fraction of gas tracer, y , given TPx experimental data. The derivation assumes that the

experimental data is for a binary mixture of gas tracer and water and that the solubility and mass of the gas tracer is sufficiently small so as to be approximately infinitely dilute in the liquid phase. This means that the activity coefficient of the water component is very close to unity for all temperatures and does not need to be modelled (Fernandez-Prini and Crovetto 1985, Mroczek 1997). In order to take advantage of this, the expression for the vapor phase mole fraction of gas tracer is based on relationships involving the water component.

The liquid phase activity coefficient for water, γ_w , is defined as (Van Ness and Abbott 1997):

$$\gamma_w = \frac{\hat{f}_w^l}{x_w f_w} \quad (20)$$

The vapor phase partial fugacity coefficient, $\hat{\phi}_w^v$, is (Van Ness and Abbott 1997):

$$\hat{\phi}_w^v = \frac{\hat{f}_w^v}{y_w P} \quad (21)$$

where y_w is the vapor phase mole fraction of water. At equilibrium:

$$\hat{f}_w^l = \hat{f}_w^v \quad (22)$$

With rearrangement, and using the fact that the activity coefficient of water is one, the vapor phase mole fraction of water is:

$$y_w = \frac{x_w f_w}{\hat{\phi}_w^v P} \quad (23)$$

By definition the pure component fugacity at the standard pressure state, P_w^s , is: $f_w^s = \phi_w^s P_w^s$. The pure component fugacity of water may be referred to a general pressure state through the use of a PCF:

$$f_w = \phi_w^s P_w^s \exp \left[\frac{\hat{V}_w^l (P - P_w^s)}{RT_a} \right] \quad (24)$$

Assuming that x and y refer to the liquid and vapor mole fractions of gas tracer respectively, the expression relating the liquid mole fraction of gas tracer to the vapor mole fraction of gas

tracer in a binary mixture with water at a given experimental temperature is:

$$1 - y = \frac{\gamma_w(1 - x)\phi_w^s P_w^s}{\hat{\phi}_w^v P} \exp \left[\frac{\hat{V}_w^l (P - P_w^s)}{RT_a} \right] \quad (25)$$

An important feature of (25) is its non-linearity. The value of $\hat{\phi}_w^v$ also depends on the unknown vapor mole fraction of tracer y , therefore y must be determined iteratively. The calculations required for the auxiliary values: ϕ_w^s , $\hat{\phi}_w^v$ and \hat{V}_w^l ; are described in sections 3.4 and 3.5.

3.3 Calculating the Henry coefficient, $C_H(T, P_w^s)$ when only β is known

For the gas tracers R-134a, R-124 and R-125 considered in this research, experimental TPx data was not available. However, regressions of the gas distribution coefficient, β , with temperature were provided by Adams (1999). The gas distribution coefficient represents the distribution of the gas tracer between the liquid and vapor phases and is the ratio of the vapor phase concentration to the liquid phase concentration. If this ratio is expressed in units of molality, it can be rearranged to give a distribution ratio in terms of the vapor and liquid phase mole fractions of the gas tracer:

$$\beta = \frac{y(1 - x)}{x(1 - y)} \quad (26)$$

This ratio can be rearranged to give an expression for the liquid phase mole fraction of gas tracer:

$$x = \frac{y}{\beta + y(1 - \beta)} \quad (27)$$

The expression for x can be used together with:

$$1 - y = \frac{\gamma_w(1 - x)\phi_w^s P_w^s}{\hat{\phi}_w^v P} \exp \left[\frac{V_w^{sl}(P - P_w^s)}{RT_a} \right] \quad (28)$$

to iteratively determine x and y values from β values derived at low temperatures from a β regression. The x and y values can then be used to determine the standard state Henry's coeffi-

cients using (17).

3.4 The Peng-Robinson equation of state

A relationship between the pressure, temperature and molar volume of a gas tracer and water mixture is necessary to successfully determine the auxiliary values ($\hat{\phi}_g^v$, \hat{V}_g^l , ϕ_w^s , $\hat{\phi}_w^v$ and \hat{V}_w^l) necessary for calculating y , C_H and C_H^* . One such relationship is the theoretical Peng-Robinson equation of state (Peng and Robinson 1976). This equation of state has been widely used in chemical engineering applications, and was used by Mroczek (1997) in his experimental work with SF₆ at geothermal temperatures and pressures.

For a mixture, the Peng-Robinson equation of state (PREOS) (Peng and Robinson 1976) is:

$$P = \frac{RT_a}{V - b} - \frac{a(T_a)}{V(V + b) + b(V - b)} \quad (29)$$

where P is the mixture pressure, T_a is the absolute temperature, V is the mixture molar volume and a and b are mixture parameters depending on the pure component critical parameters (T_i^c , P_i^c), the acentric factor (ω_i) and the temperature. For component i in a multi-component mixture, a_i and b_i are defined as:

$$a_i(T) = 0.45724 \frac{R^2 T_i^{c2}}{P_i^c} \alpha(T_i^r, \omega_i) \quad (30)$$

$$b_i(T) = 0.07780 \frac{RT_{ci}}{P_{ci}} \quad (31)$$

where T_i^r is the temperature reduced by the critical temperature of component i , i.e. $T_i^r = T_a/T_i^c$.

A number of choices of the $\alpha(T_i^r, \omega_i)$ function have been presented in the literature (Peng and Robinson 1976, Tsai and Chen 1998), derived by fitting pure component vapor pressure values and finding the values of α such that the liquid and vapor phase fugacities match along the saturation curve. In this research a generalised α function given by Twu et al. (1995) has been used. The α function for each component is expanded as a power series in the acentric factor and the unknown functions fitted from vapor pressure values. The results are (Twu

et al. 1995):

$$\alpha = \alpha^{(0)} + \omega (\alpha^{(1)} - \alpha^{(0)}) \quad (32)$$

$$T^r \leq 1 \begin{cases} \alpha^{(0)} = T^{r-0.171813} e^{0.125283(1-T^{r1.77634})} \\ \alpha^{(1)} = T^{r-0.607352} e^{0.511614(1-T^{r2.20517})} \end{cases} \quad (33)$$

$$T^r > 1 \begin{cases} \alpha^{(0)} = T^{r-0.792615} e^{0.401219(1-T^{r-0.992615})} \\ \alpha^{(1)} = T^{r-1.98471} e^{0.024955(1-T^{r-9.98471})} \end{cases} \quad (34)$$

The mixture values of a and b are (Peng and Robinson 1976):

$$a = \sum_i \sum_j z_i^k z_j^k a_{ij} \quad (35)$$

$$a_{ij} = (1 - \gamma_{ij}) \sqrt{a_i a_j} \quad (36)$$

$$b = \sum_i z_i^k b_i \quad (37)$$

where z_i^k is the mole fraction of component i in phase k of the mixture. The binary interaction component, γ_{ij} , characterises the binary formed by components i and j . Its value was set to 0.5 in this work, following Mroczek (1997). In addition to these original mixture rules for a and b given by Peng and Robinson (1976) other rules have been proposed, including those derived from combining Gibbs free energy models with an equation of state such as the PREOS (Fischer and Gmehling 1996, Dahl and Michelsen 1990, Gupte et al. 1986, Dahl et al. 1991, Larsen et al. 1987).

The PREOS may be expressed as a cubic equation in the mixture compressibility factor, Z :

$$Z^3 - (1 - B)Z^2 + (A - 3B^2 - 2B)Z - (AB - B^2 - B^3) = 0 \quad (38)$$

where:

$$A = \frac{a_m P}{R^2 T_a^2} \quad (39)$$

$$B = \frac{b_m P}{RT_a} \quad (40)$$

$$Z = \frac{PV}{RT_a}. \quad (41)$$

The largest root of this equation is the vapor phase compressibility and the smallest positive root is the liquid phase compressibility. The partial fugacity coefficient for component i in phase k , necessary for further calculations, may be calculated as:

$$\ln \phi_i^k = \frac{b_i}{b} (Z^k - 1) - \ln (Z^k - B) - \frac{A}{2\sqrt{2}B} \left(\frac{2 \sum_j z_j^k a_{ji}}{a} - \frac{b_i}{b} \right) \ln \left(\frac{Z^k + (1 + \sqrt{2})B}{Z^k + (1 - \sqrt{2})B} \right) \quad (42)$$

3.5 Partial molar volumes

The partial molar volumes are necessary for the determination of the Poynting correction factors, i.e. pressure dependence, in the calculation of the vapor phase mole fraction and the standard state Henry coefficient. The molar volume of phase k of a mixture is related to the mixture compressibility for that phase (see Equation (41)) as:

$$V^k = \frac{Z^k RT}{P} \quad (43)$$

$$\Rightarrow \frac{\partial V^k}{\partial z^k} = \frac{RT}{P} \frac{\partial Z^k}{\partial z^k} \quad (44)$$

where z^k is the mole fraction of gas tracer in phase k . For an N component mixture, the partial molar volume for component i is found from the mixture volume as (Walas 1985):

$$\hat{V}_i^k = V^k - \sum_{j \neq i}^N z_j^k \frac{\partial V^k}{\partial z_j^k} \quad (45)$$

For a binary mixture, if the liquid mole fraction of the gas tracer is x , then the water and

gas components partial molar volumes in the liquid phase are:

$$\hat{V}_w^l = V^l - x \frac{\partial V^l}{\partial x} \quad (46)$$

$$\hat{V}_g^l = V^l + (1 - x) \frac{\partial V^l}{\partial x} \quad (47)$$

The mixture molar volume derivative with respect to the gas tracer mole fraction is found from Equation (44) and the PREOS cubic equation for the compressibility:

$$\frac{\partial}{\partial x} \left(Z^{l^3} - (1 - B)Z^{l^2} + (A - 3B^2 - 2B)Z^l - (AB - B^2 - B^3) \right) = 0 \quad (48)$$

$$\Rightarrow \frac{\partial Z^l}{\partial x} = \frac{-Z^{l^2} \frac{\partial B}{\partial x} - Z^l \left(\frac{\partial A}{\partial x} - 2(1 + 3B) \frac{\partial B}{\partial x} \right) + B \frac{\partial A}{\partial x} + (A - 2B - 3B^2) \frac{\partial B}{\partial x}}{\left(3Z^{l^2} - 2Z^l(1 - B) + A - 2B - 3B^2 \right)} \quad (49)$$

To evaluate $\frac{\partial Z^l}{\partial x}$, the PREOS must be solved to find Z^l (the liquid phase root of the cubic PREOS), and mixture values for A , B , $\frac{\partial A}{\partial x}$ and $\frac{\partial B}{\partial x}$ are required. Using a single coefficient mixing rule (equations (35) to (37)) these mixture values are:

$$A = \frac{P}{R^2 T^2} \left((1 - x)^2 a_1 + 2x(1 - x)(1 - \gamma_{12})\sqrt{a_1 a_2} + x^2 a_2 \right) \quad (50)$$

$$\Rightarrow \frac{\partial A}{\partial x} = \frac{P}{R^2 T^2} \left(-2(1 - x)a_1 + 2(1 - 2x)(1 - \gamma_{12})\sqrt{a_1 a_2} + 2xa_2 \right) \quad (51)$$

and

$$B = \frac{P}{RT} ((1 - x)b_1 + xb_2) \quad (52)$$

$$\Rightarrow \frac{\partial B}{\partial x} = \frac{P}{RT} (b_2 - b_1) \quad (53)$$

3.6 The modified Harvey correlation for Henry's coefficients

The Harvey semi-empirical correlation for Henry's coefficients (Harvey 1996, Harvey 1998) used by Trew et al. (2000) has the form:

$$\ln C_H = \ln P_w^s + \frac{A}{T_w^r} + B \frac{(1 - T_w^r)^{0.355}}{T_w^r} + C(T_w^r)^{-0.41} e^{(1 - T_w^r)} \quad (54)$$

where A , B and C are correlation coefficients determined by fitting experimental data. This correlation was based on a number of previous works (Japas and Levelt Sengers 1989, Harvey and Levelt Sengers 1990) and was found to be effective for both interpolation and extrapolation of Henry's coefficients for a number of gases over a wide temperature range (Harvey 1996, Mroczek 1997, Harvey 1998).

The term $B(1 - T_w^r)^{0.355}/T_w^r$ is important as it correctly reproduces the divergent behavior of $\ln C_H$ at the solvent (water) critical point, i.e. (Schotte 1985):

$$\left. \frac{d \ln C_H}{dT} \right|_{T=T_w^c} = -\infty. \quad (55)$$

However, it is also known that at the solvent (water) critical point (Beutier and Renon 1978, Schotte 1985, Japas and Levelt Sengers 1989):

$$C_H(T_w^c, P_w^c) = \hat{\phi}_g^v(T_w^c, P_w^c) P_w^c \quad (56)$$

In this research it has been found through experimentation that the limiting value of C_H is not represented by the Harvey correlation in the form of (54), although the divergent behavior of $\ln C_H$ is correctly represented. To represent the limiting value, given in (56), it is necessary that: $A + C = \ln \hat{\phi}_g^v(T_w^c, P_w^c)$. In practice, this constraint has been found to give a poor fit to the predominantly low temperature experimentally derived C_H values.

It can, however, be observed that if $C_H(T, P_w^s)/\hat{\phi}_g^v(T, P_w^s)$ is to be fitted by a correlation similar to that of Harvey (1996), then the final three terms must disappear as the solvent critical point is reached, i.e. $T_w^r \rightarrow 1$. A modified Harvey correlation (MHC) with these characteristics is proposed here:

$$\ln \frac{C_H}{\hat{\phi}_g^v(T, P_w^s)} = \ln P_w^s + a \frac{(1 - T_w^r)^{0.8}}{T_w^r} + b \frac{(1 - T_w^r)^{0.355}}{T_w^r} + c(1 - T_w^r)^{0.8} (T_w^r)^{-0.41} e^{(1 - T_w^r)} \quad (57)$$

The MHC retains the simplicity of only three unknown coefficients, a , b and c , that must be fitted. The exponent of 0.8 has been arrived at by experimentation and gives good behaviour.

At the solvent critical point:

$$\ln C_H = \ln \hat{\phi}_g^v(T_w^c, P_w^c) + \ln P_w^c \quad (58)$$

as required.

3.7 An empirical correlation for the liquid phase partial molar volumes of gas tracers

As shown in (19), if pressure effects are to be included in the liquid-vapor partitioning model, then the partial molar gas volume at any given temperature is required to determine the Poynting correction factor. The calculations required for partial molar volumes given in Section 3.5 are overly cumbersome to use in an implementation of the partitioning model in a geothermal flow simulator. In addition, the effect of the Poynting correction factor is usually small. Therefore, it was decided to investigate a correlation for the liquid phase partial molar volumes in terms of temperature and molecular weight. A collection of gas tracers identical to those considered later in Section 4 (SF₆, R-13, R-14, R-22, R-23, R-116, R-C318, R-134a, R-124 and R-125) were used to develop the correlation.

Equation (47) was used to calculate the partial molar volumes of the gas tracers under consideration. The results over a temperature range from 0° C to approximately 370° C are shown in Figure 2(a). The expected behavior is seen. For example, the molar volume of SF₆ at its normal boiling point (-64° C) is estimated to be $0.73 \times 10^{-4} \text{m}^3 \text{mol}^{-1}$ (Mroczek 1997), so a simple extrapolation suggests that the partial molar volumes for SF₆ derived from Equation (47) and the PREOS are quantitatively correct, at least at low temperatures. Furthermore, it has been shown that the partial molar volume of a gas solute diverges at the critical temperature of the solvent (Schotte 1985). So the partial molar volume behavior of the gas tracers is at least qualitatively correct at the critical point of water. A study of various infinite dilution partial molar volume models, including the PREOS, has shown that the models are only suitable for qualitative predictions around the solvent critical point (Liu and Macedo 1995).

The mean partial molar volumes for the 10 gas tracers under consideration have been sam-

pled at a large number of temperature sample points and have been fitted by the non-linear empirical function:

$$\hat{V}_g^l(T_w^r) \approx \frac{-6.7 \times 10^{-4} T_w^r + 8.1 \times 10^{-4}}{15(1 - T_w^r)^{1.28}} \quad (59)$$

This is shown in Figure 2(b).

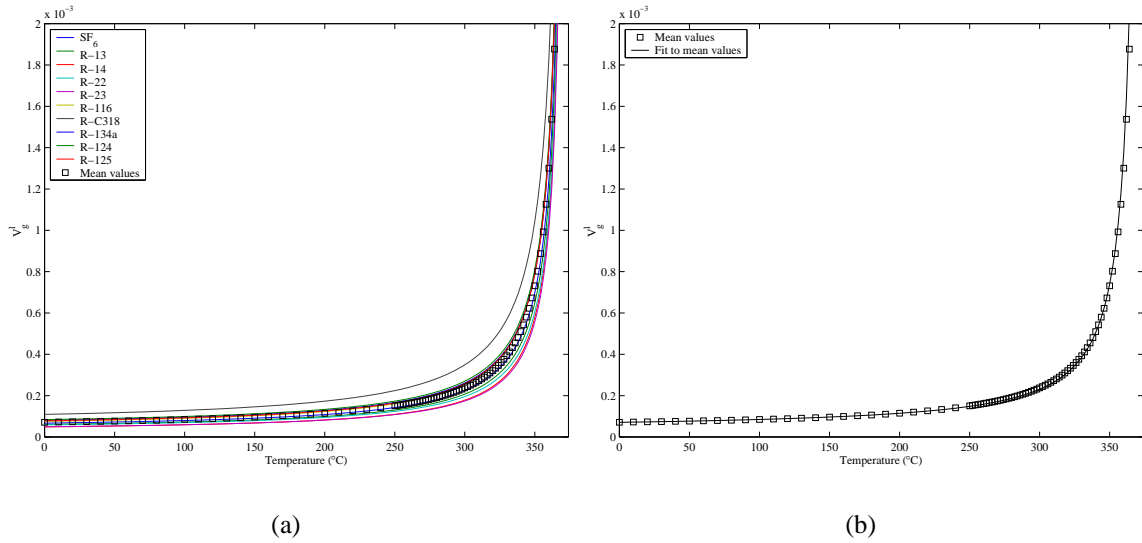


Figure 2: Infinite dilution partial molar volumes for gas tracers. Also shown in are the mean values for each temperature.

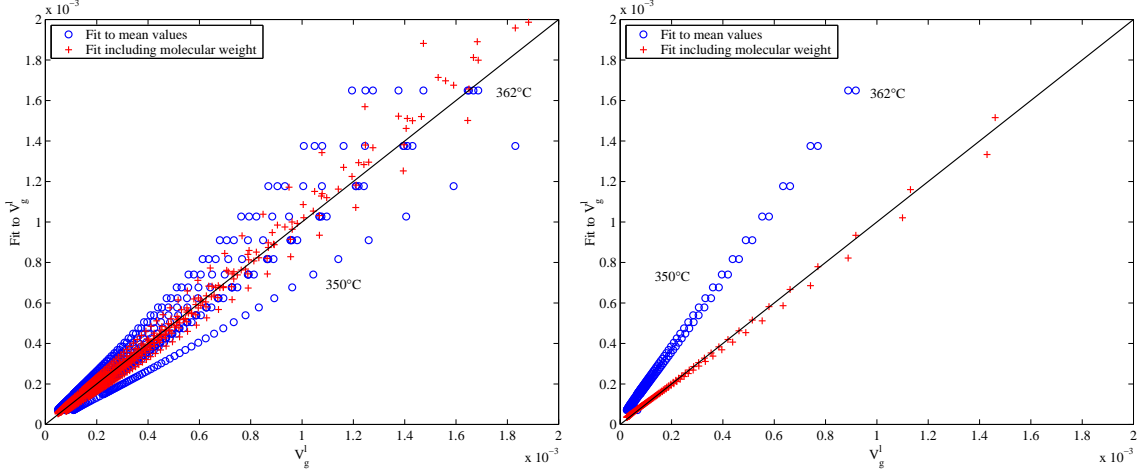
The fit of the mean partial molar volumes by a function of T_w^r has been further moderated by a linear function of the molecular weight of the gas, M_g , to account for deviations from the mean values. The coefficients of the moderating function have been fitted to all the data in a least squares sense. The final form of the empirical partial molar volume function is:

$$\hat{V}_g^l(T_w^r, M_g) \approx (6.20M_g + 0.34) \frac{-6.7 \times 10^{-4} T_w^r + 8.1 \times 10^{-4}}{15(1 - T_w^r)^{1.28}} \quad (60)$$

This moderation provides improved representation at no extra cost of parameter specification.

The quality of the fit to the mean values and the molecular weight moderated fit is shown in Figure 3. In both plots, the fitted partial molar volumes are plotted against the values calculated using the Peng-Robinson equation of state. A perfect fit would lie along the diagonal line shown in Figure 3. Figure 3(a) clearly indicates that a significant improvement in the empirical

correlation for these gas tracers has been achieved through the use of the molecular weight, at almost negligible extra computational expense. In particular, the fit is quite good up to 350° C. Figure 3(b) shows some interesting results for CO₂ and O₂. Although (59) was not determined using CO₂ or O₂, the final correlation (60) is good at predicting their partial molar volumes.



(a) SF₆, R-13, R-14, R-22, R-23, R-116, R-C318, R-134a, R-124 and R-125.

(b) O₂ and CO₂.

Figure 3: Characteristics of the mean partial molar volume fit and the successful moderation by the molecular weight.

3.8 Summary of the steps require to fit the modified Henry's coefficients

This section presents an outline and summary of the steps required to determine the modified Harvey correlation coefficients.

1. As described in sections 3.2 to 3.5, experimental TPx or $TP\beta$ data are used to calculate \hat{V}_w^l , ϕ_w^v , y (and x if unknown), \hat{V}_g^l , $\hat{\phi}_w^v$ and $\hat{\phi}_g^v$. The calculation of y is non-linear as y and $\hat{\phi}_w^v$ are inter-dependent. These values are determined iteratively. The experimental values of Henry's coefficient at the standard state, $C_H(T, P_w^s)$, are determined from:

$$C_H^{\text{expt}}(T, P_w^s) = \frac{\hat{\phi}_g^v y P}{x} \exp \left[\frac{-\hat{V}_g^l (P - P_w^s)}{RT_a} \right]. \quad (61)$$

2. Due to the sparsity of experimental data, it has been found best to scale $C_H^{\text{expt}}(T, P_w^s)$ by the partial fugacity coefficient of the gas tracer at the critical point and fit these values in

a least squares sense by the modified Harvey correlation (MHC) described in Section 3.6.

The result of this fit is the intermediate quantity: $C_H^1(T, P_w^s)$.

3. The $C_H^1(T, P_w^s)$ function is evaluated for a number of temperatures from 0° C to 374° C and a modified Henry coefficient is calculated as:

$$C_H^{1*}(T, P_w^s) = \frac{C_H^1(T, P_w^s)}{\hat{\phi}_g^v(T, P_w^s)} \hat{\phi}_g^v(T_w^c, P_w^c). \quad (62)$$

4. In order to obtain a function for modeling purposes, the $C_H^{1*}(T, P_w^s)$ values are fitted in a least-squares sense using the MHC described in Section 3.6. The resulting correlation gives $C_H^*(T, P_w^s)$ which is a standard state Henry's coefficient modified to account for non-ideality through the inclusion of the standard state fugacity coefficient.
5. The Poynting correction factor using the empirical correlation for the liquid phase partial molar volumes (Section 3.7) is added to give a representation of a modified Henry coefficient applicable to a general temperature and pressure state:

$$\begin{aligned} \ln C_H^*(T, P) = \ln P_w^s + a \frac{(1 - T_w^r)^{0.8}}{T_w^r} + b \frac{(1 - T_w^r)^{0.355}}{T_w^r} + \\ c(1 - T_w^r)^{0.8} (T_w^r)^{-0.41} \exp(1 - T_w^r) + \\ (6.20M_g + 0.34) \frac{(-6.7 \times 10^{-4} T_w^r + 8.1 \times 10^{-4})}{15(1 - T_w^r)^{1.28} T_w^c T_w^r} (P - P_w^s). \end{aligned} \quad (63)$$

This is the modified Henry's coefficient which is used in (5) for calculating the gas tracer phase partitioning.

4 Modified Henry's Coefficients for a Selection of Gas Tracers

The selection of possible gas tracers that have been specifically considered in this work are: SF₆, R-13, R-14, R-22, R-23, R-116, R-C318, R-134a, R-124 and R-125. The HCFC gases considered have low ozone-depletion potentials and are not to be phased out under the Montreal

Protocol (Adams et al. 1991). The key properties of these possible gas tracers and the modified Harvey correlation coefficients resulting from the fitting process described in Section 3.8 are given in Table 1. A comparison of Henry's coefficients determined using the methods presented in this paper and the methods described in (Trew et al. 2000) is given for SF₆, R-134a and R-23 in Figure 4. These examples illustrate that the improved theoretical foundations and empirical fitting process for Henry's coefficients presented in this research are clearly superior to those of (Trew et al. 2000) at the temperatures found in geothermal reservoirs.

<i>Compound</i>	<i>M(kg/mol)</i>	<i>T^c(° C)</i>	<i>P^c(MPa)</i>	<i>ω</i>	<i>a</i>	<i>b</i>	<i>c</i>
H ₂ O	0.018016	374	22.06	0.742	-	-	-
SF ₆	0.146056	45.54	3.76	0.215	-42.0138	16.1840	30.0582
R-13	0.104459	28.81	3.946	0.180	-60.0736	11.1937	51.7480
R-14	0.088005	-45.65	3.739	0.186	-66.1391	4.7463	66.3009
R-22	0.086468	96.15	4.97	0.221	-56.3330	4.5208	53.9459
R-23	0.070014	25.74	4.836	0.267	-82.3196	8.7996	73.3207
R-116	0.138012	19.85	3.06	0.28	-79.9564	5.1976	79.3443
R-C318	0.200031	115.35	2.78	0.356	-86.7454	6.0113	84.0756
R-134a	0.102031	106.85	3.690	0.239	-59.0986	6.8705	54.0940
R-124	0.13648	126.75	3.72	0.281	-84.7575	8.5418	76.0311
R-125	0.120022	68.85	3.44	0.259	-127.7211	11.4972	112.2099

Table 1: Key properties and MHC coefficient values.

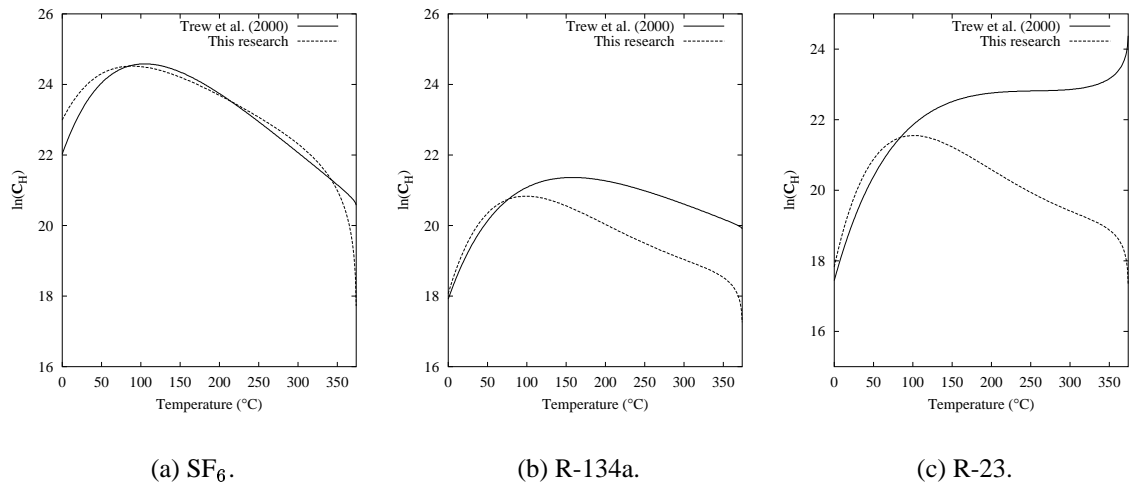


Figure 4: Comparison of Henry's coefficient correlations using the method given in Trew et al. (2000) with those derived using the methodology presented in this research.

Figures 5 to 14 show the temperature and pressure variations of the Henry coefficient correlations. Also shown is the available experimental data and the fit at each step in the process.

The results indicate that non-ideal behavior becomes significant at approximately 200° C. In addition, it can be observed that in general the variation in the modified Henry's coefficient with pressure from the standard state pressure is small. The exception to this is near the critical temperature of water. It may be expected that for most practical simulations the pressure correction term in (63) is not necessary, however, given that it adds negligible computational overhead it can be retained for completeness.

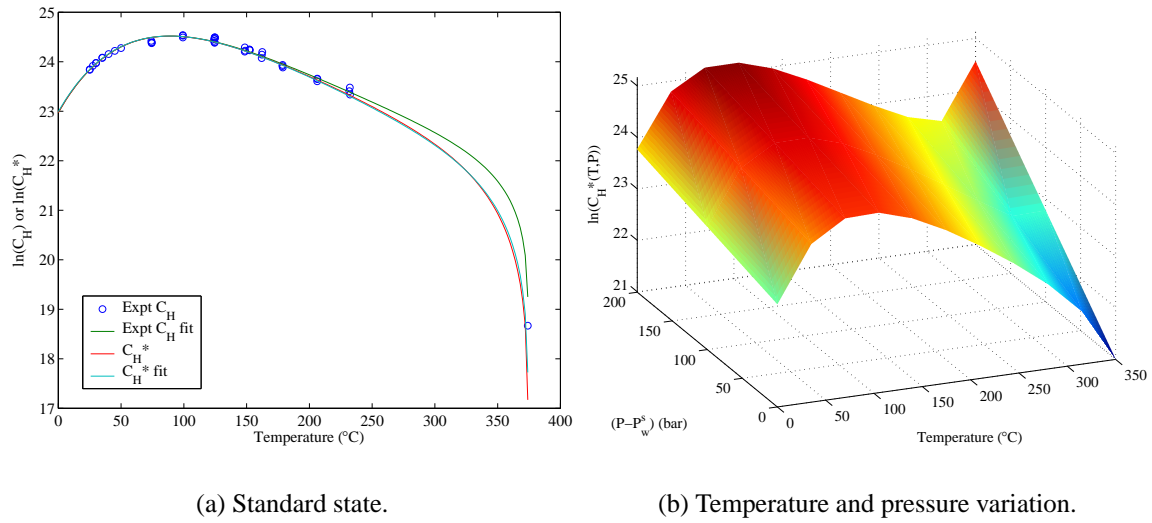


Figure 5: SF₆.

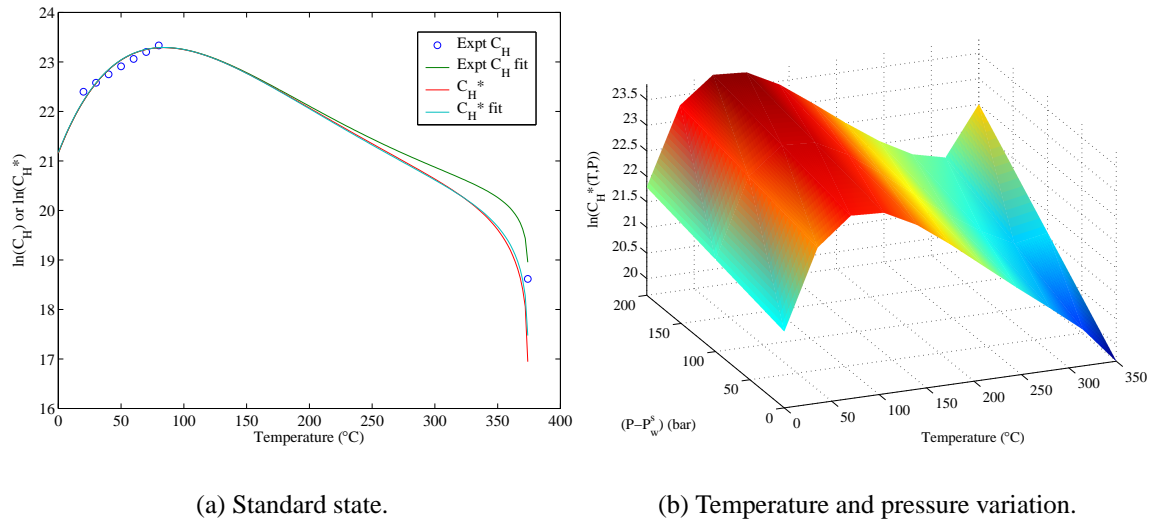
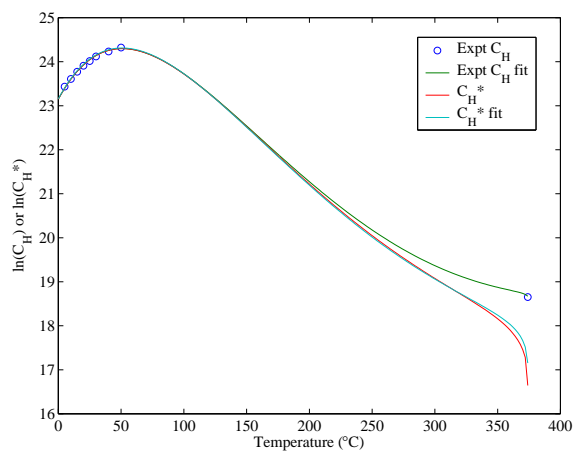
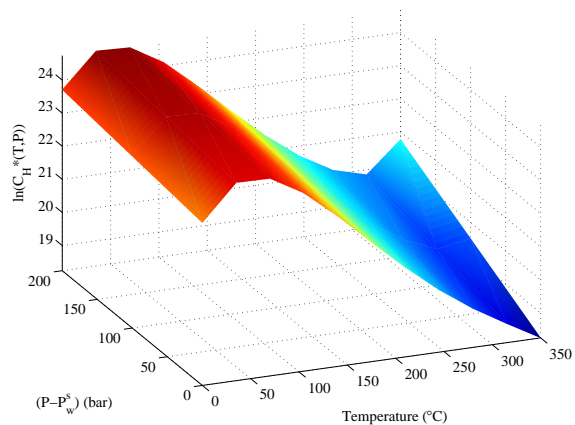


Figure 6: R-13.

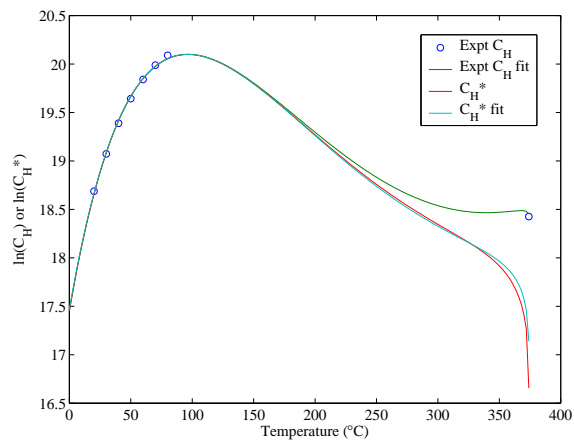


(a) Standard state.

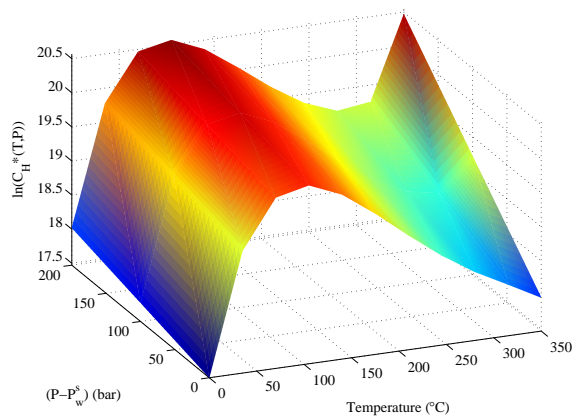


(b) Temperature and pressure variation.

Figure 7: R-14.

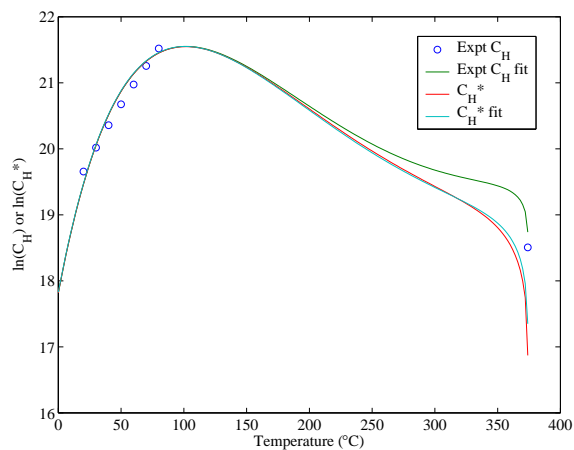


(a) Standard state.

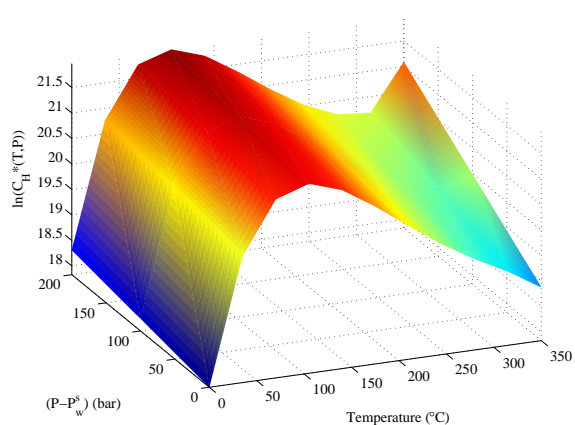


(b) Temperature and pressure variation.

Figure 8: R-22.

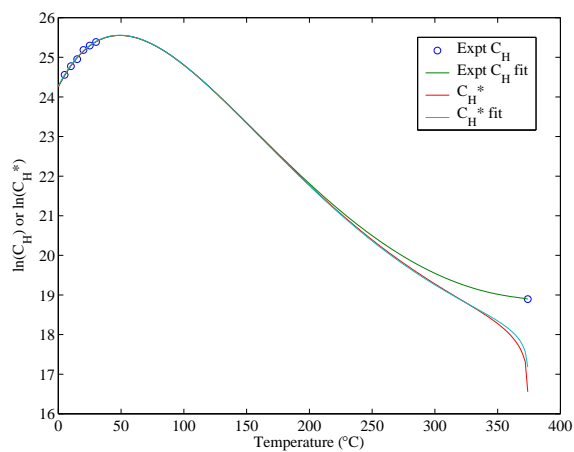


(a) Standard state.

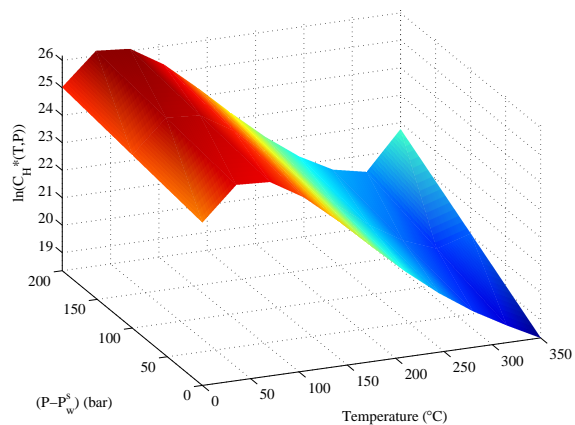


(b) Temperature and pressure variation.

Figure 9: R-23.

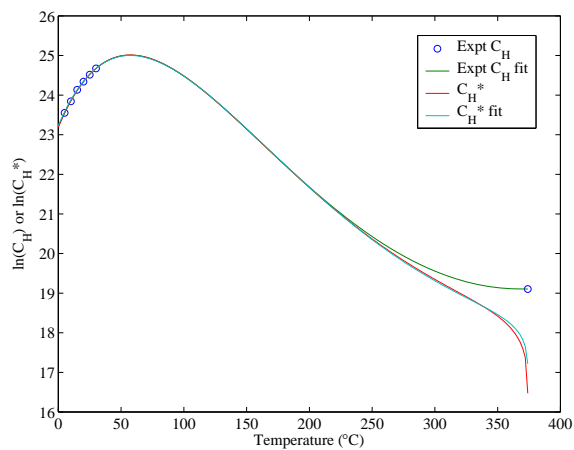


(a) Standard state.

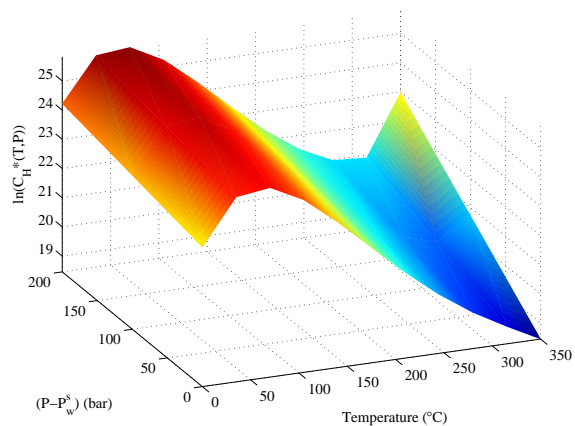


(b) Temperature and pressure variation.

Figure 10: R-116.

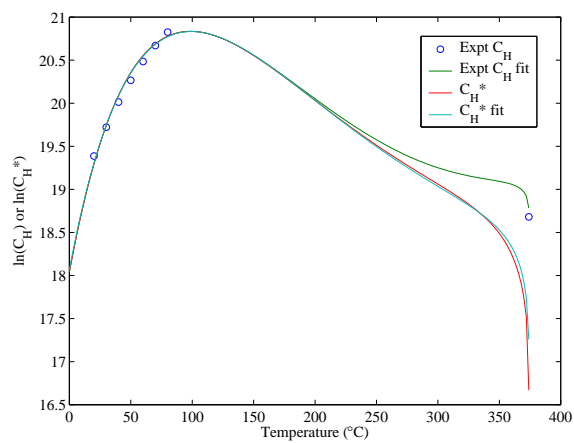


(a) Standard state.

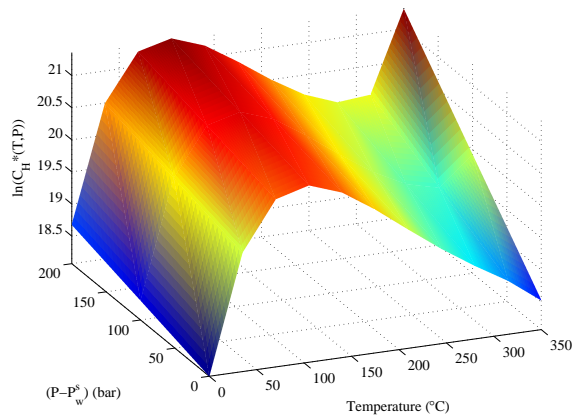


(b) Temperature and pressure variation.

Figure 11: R-C318.

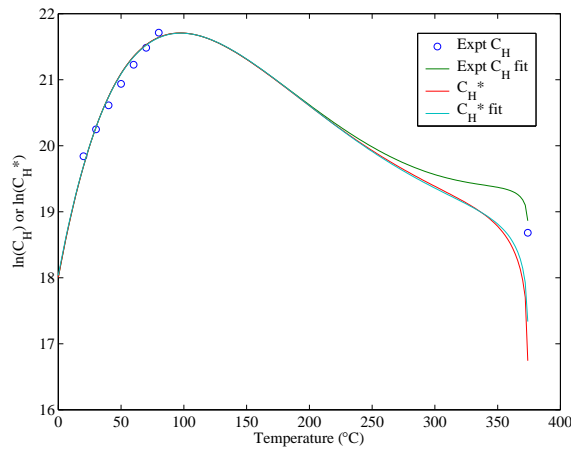


(a) Standard state.

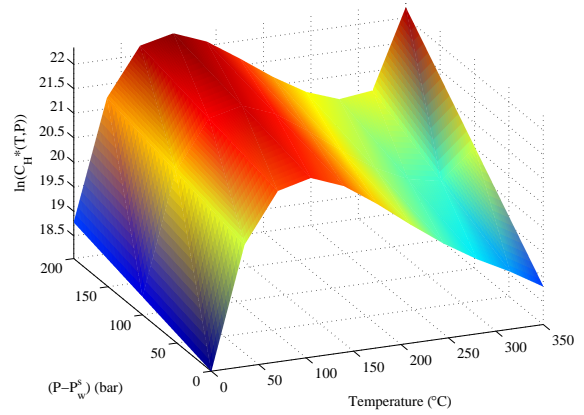


(b) Temperature and pressure variation.

Figure 12: R-134a.

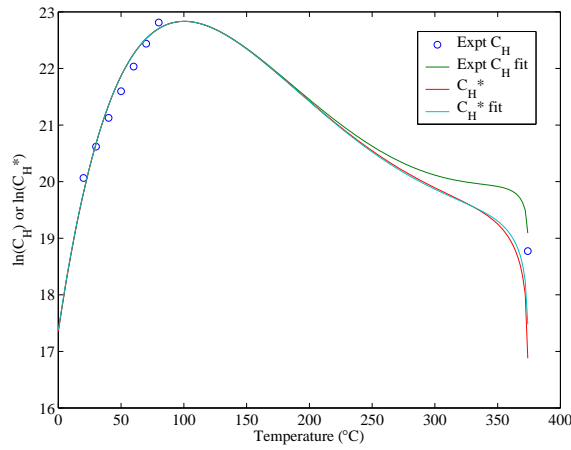


(a) Standard state.

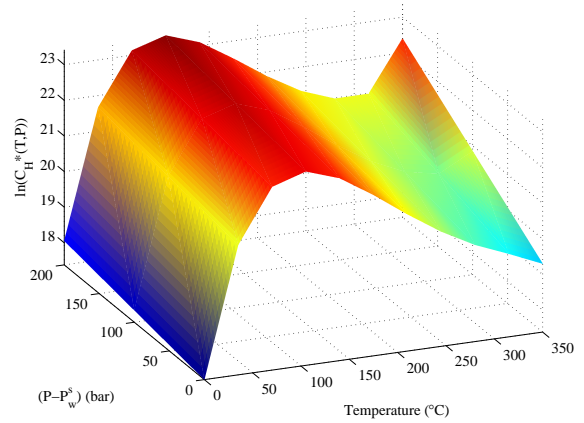


(b) Temperature and pressure variation.

Figure 13: R-124.



(a) Standard state.



(b) Temperature and pressure variation.

Figure 14: R-125.

5 Applications

5.1 Two-phase stream-tube flow

The comparative liquid and vapor behavior of gas tracers is best observed in a simple stream-tube test problem. The problem and its specifications are shown in Figure 15.

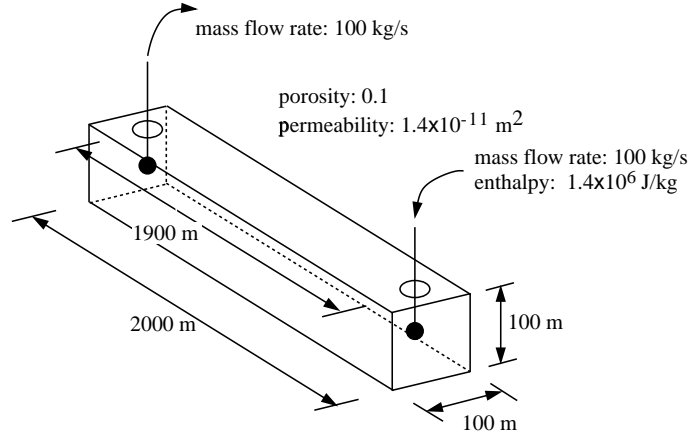


Figure 15: The stream-tube test problem specifications.

Fluid is injected with an enthalpy of $1.4 \times 10^6 \text{ Jkg}^{-1}$, generating a two-phase flow regime. The steady state pressure, vapor pressure, temperature and vapor saturation distributions are shown in Figure 16.

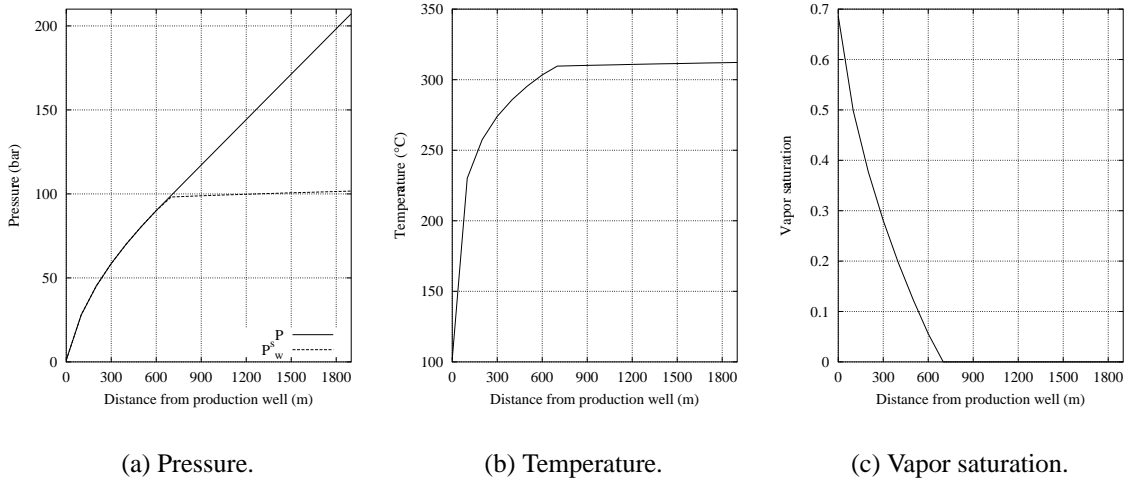


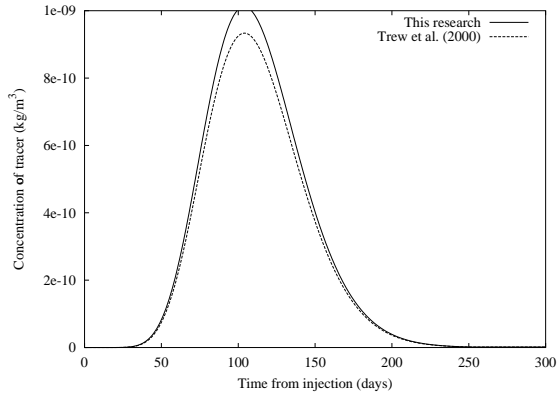
Figure 16: Two-phase flow conditions at steady state.

Three gas tracers are considered: SF_6 , R-134a and R-23. The standard pressure state variations of Henry's coefficients with temperature for these tracers are shown in Figure 4. This figure also shows that at the temperatures considered in this problem (100°C to 300°C) the C_H value for SF_6 derived in this research and those of Trew et al. (2000) are similar. It is expected then that the the phase partitioning model presented here and that of Trew et al. (2000) will give similar results since the key differences lie in the determination of Henry's coefficients.

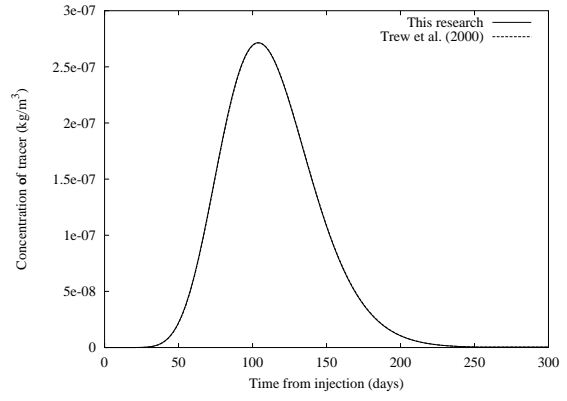
The gas tracers are each injected at a rate of 0.1 kg s^{-1} for 20 minutes. The liquid and vapor phase tracer concentration time histories at the production well are shown for the two-phase flow in figures 17 to 19. Partitioning behavior calculated using the Harvey correlation coefficients derived with the methods given in Trew et al. (2000) is compared to the models presented in this research. The implementation of the partitioning models in TOUGH2 has been validated by comparison with known analytic solutions for single phase transport and convergence analysis for multiple phases.

As expected from the low gas tracer solubility, at the production well the concentrations of the gas tracers in the liquid phase are at least an order of magnitude less than those in the vapor phase. Also, the expected minimal difference between the SF_6 mass fractions determined from the model presented in this research and that of (Trew et al. 2000) can be observed in figures 17(a) and 17(b). The differences lie in the peak predicted tracer concentration and not in a time shift of the tracer pulse, thus suggesting that these arise due to the emergence of non-ideal behavior of the SF_6 tracer as the concentration increases. In the case of R-134a and R-23 gas tracers, the Henry coefficient models of Trew et al. (2000) predict lower solubilities at higher temperatures than those of this research and, particularly in the case of R-23, this is clearly erroneous behavior. Figures 17 to 19 shows that the impact of the new models is to retard the breakthrough times of the gas tracers.

In the single phase region, Figure 16(a) shows that the difference $P - P_w^s$ varies from close to zero at the production to over 100 bar at the injection well. Although the value of $P - P_w^s$ is not negligible, its impact on the final results through the Poynting correction factor remains negligible and for most practical simulations the influence of pressure variations on the phase partitioning models may be neglected. However, given that its inclusion in the phase partitioning model presents negligible computational overhead, the term can be quite easily retained for completeness.

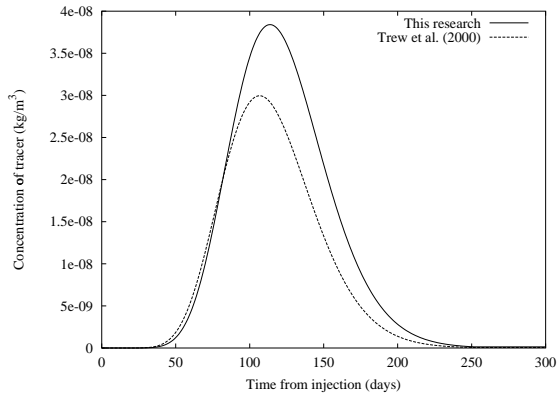


(a) Liquid phase.

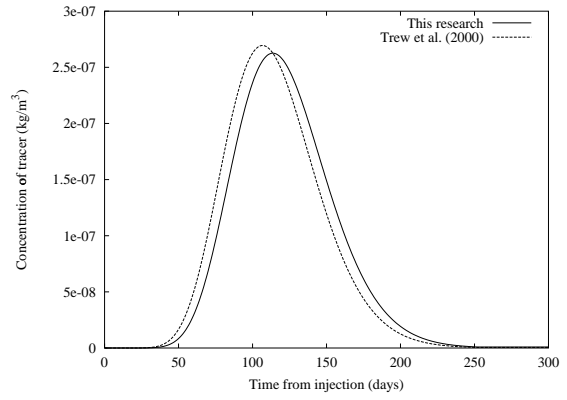


(b) Vapor phase.

Figure 17: Tracer breakthrough time history for SF₆.

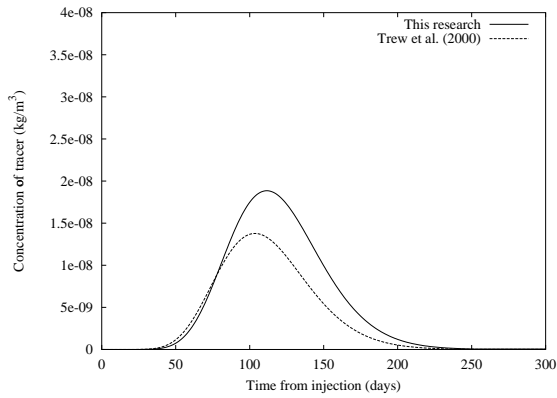


(a) Liquid phase.

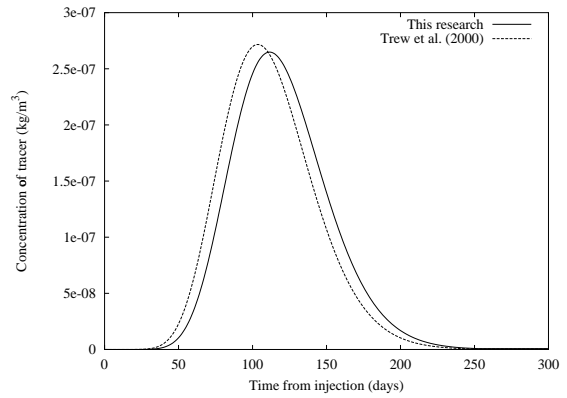


(b) Vapor phase.

Figure 18: Tracer breakthrough time history for R-134a.



(a) Liquid phase.

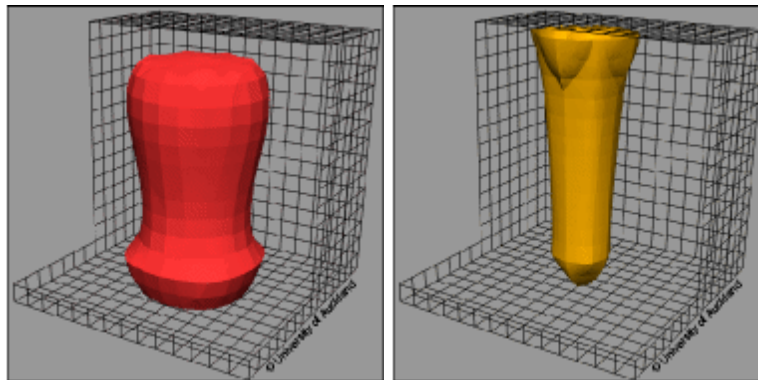


(b) Vapor phase.

Figure 19: Tracer breakthrough time history for R-23.

5.2 An idealised three-dimensional reservoir

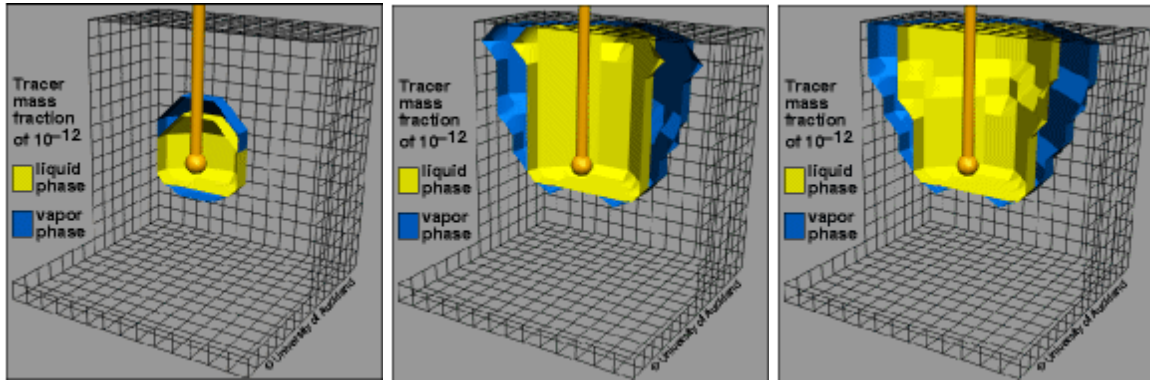
The utility and value of gas tracer phase partitioning models coupled with a geothermal reservoir simulator is illustrated by the following problem. Steady state two-phase convective flow is formed in an idealised reservoir of volume 1 km^3 . The steady state temperature and vapor saturation iso-surfaces are shown in Figure 20. 100 kg of SF_6 is introduced into the center of the reservoir. The predicted transport over time of the gas tracer in the liquid and vapor phases is shown in Figure 21. The sparingly soluble SF_6 tracer is preferentially transported in the vapor phase, however, the flow is two-phase and local equilibrium exists between the phases at every point. Consequently, SF_6 is also detected in the liquid phase further from the injection point than would be the case for a fully soluble tracer. For this example the cut-off detection point has been nominally set to a mass fraction of 10^{-12} . This problem shows how models of tracer transport in geothermal reservoirs can be used as predictive and correlative tools to enhance both the design and the interpretation of field tracer tests.



(a) 200° C iso-surface.

(b) 10% vapor saturation iso-surface.

Figure 20: Temperature and vapor saturation iso-surfaces.



(a) Soon after injection.

(b) Approximately 50 days.

(c) Approximately 100 days.

Figure 21: Predicted spread of SF_6 in the vapor and liquid phases over 100 days.

6 Summary and Conclusions

A model of liquid-vapor phase partitioning of gas tracers in water at geothermal temperatures and pressures has been presented. The key feature of this model is the definition and determination of the Henry's coefficients that are used in Henry's law to model the liquid phase mole fraction of gas tracers. This coefficient has been derived from first principles and no assumption of ideal gas behavior has been necessary. The definition of Henry's coefficient has been modified so that non-ideal behavior can be easily included in Henry's law. Experimental values of Henry's coefficient derived from solubility data have been fitted in two steps by a modified semi-empirical Harvey correlation that accounts for the theoretical behavior at the critical point of water. The semi-empirical correlation also accounts for pressures other than the vapor pressure of water, which is the standard state pressure. The new methods have been used to determine correlation coefficients for a range of gas tracers and the liquid-vapor phase partitioning models have been applied to some test problems.

The models and experimental reduction methods described in this research retain the simplicity and attractions of those presented in previous research by Trew et al. (2000). However, this new research has reduced levels of uncertainty in the process of determining the experimental values of Henry's coefficients and has proposed a new correlation of Henry's coefficients which is satisfactory for geothermal temperatures and pressures.

Acknowledgements

This study has been funded in part by the New Energy & Industrial Technology Development Organisation of Japan (NEDO). We also acknowledge the input of Mike Adams (EGI Utah), who provided gas solubility data and helpful comments.

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