

## COMPUTER MODELLING OF GAS AND LIQUID TRACERS IN GEOTHERMAL RESERVOIRS

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### **ABSTRACT**

This paper describes models of the vapour/liquid phase partitioning behaviour of gas and liquid tracers. Each of these tracer types requires a distinct model. Henry's law is used to model the partitioning of gas tracers and Wilson's representation of the molar excess Gibbs free energy is used as the basis of a model for liquid partitioning. The implementation of these models in the TOUGH2 geothermal reservoir simulator is described and the modified version of TOUGH2 is used to simulate tracer movement in an idealised test problem. Test results show qualitatively expected behaviour.

### **INTRODUCTION**

Computer modelling of gas and liquid tracers is motivated by their widespread use in geothermal reservoir testing and management. Gas tracers are defined as those tracer chemicals that are highly volatile, sparingly soluble and are injected as vapour. Examples of gas tracers include the noble gases, refrigerants (e.g. R-12) and sulfur hexafluoride (SF<sub>6</sub>). In contrast, 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 phase partitioning behaviour similar or quite different to that of the geothermal water. Distinctive models of phase partitioning behaviour are required for each of these two tracer categories.

The models are currently being developed and implemented as part of the University of Auckland's version of the TOUGH2 geothermal reservoir simulation code. TOUGH2 was originally reported in Pruess (1991) and since then it has formed the basis of many publications regarding its methodology, use, capabilities and extensions (e.g. Oldenburg and Pruess (1993), Javeri (1995), Oldenburg and Pruess (1995), Boardman et al. (1996), Pruess (1997), Moridis and Pruess (1998), Pruess et al. (1998)).

There are two aspects to tracer modelling. Firstly, there is the transport of the tracer and the mathematical and discrete numerical representations of this. This includes issues of advection, molecular diffusion, adsorption, decay, physical dispersion and dispersion resulting from mathematical or numerical modelling. Secondly, there are the unique thermodynamic properties of the tracers. Here the focus is on the second aspect; issues in the modelling of tracer transport are discussed in Pruess et al. (2000).

One of the features of TOUGH2 is that it can be very easily extended to include extra chemical components. Thus, the basic mass, energy and tracer transport functions do not have to be modified to allow the modelling of different combinations of tracers. The modifications to TOUGH2 described here lie in the mass fraction calculations performed in the equation of state. General calculations for gas and liquid tracer components are combined in a single generic equation of state. Run-time parameters are specified to describe interactions between the specific tracers and the geothermal water. Any tracer for whom these interaction parameters are known can be modelled.

The majority of modelling work presented in the literature has considered the advective-diffusive transport of a single generic tracer with thermodynamic properties similar to that of the geothermal water. Modelling the partitioning behaviour of a tracer between liquid and vapour phases does not appear to be a recently significant area of study. Some references to modelling work are Akin and Okandan (1995), Fukuda et al. (1994), Birdsell and Robinson (1988), Bullivant (1988), Ramírez et al. (1988), Kocabas and Horne (1987), Menninger and Sageev (1987), Moench (1987) and Rívera et al. (1987). However, the modelling of gaseous tracers is conceptually similar to the modelling of CO<sub>2</sub> in geothermal reservoirs, considered by O'Sullivan et al. (1985). Those authors used Henry's Law to express the equilibrium of CO<sub>2</sub>

and the geothermal brine between the liquid and vapour phases.

In this paper, the interactions between gas tracers and the geothermal water are modelled by Henry's Law and the Harvey (1996) correlation for Henry's coefficients. The mixture models of liquid tracer and geothermal water interactions are based on Wilson's model of the molar excess Gibbs energy. This model is used to determine binary mixture activity coefficients. The activity coefficients are then applied to calculate liquid and vapour mass fractions of tracer.

## MIXTURE MODELS FOR GAS TRACERS IN WATER

### Assumptions

1. The concentration of the gas tracer is low. Thus the solubility of the gases in the geothermal brine can be modelled by Henry's law (Schotte 1985).
2. Fugacity can be replaced by the partial gas pressure (O'Sullivan et al. 1985). This is an assumption of ideal gas behaviour (Van Ness and Abbott 1997). Henry's law also is best applied at low gas partial pressures (Harvey 1996), perhaps less than 30 MPa (Fernandez-Prini and Crovetto 1985).

### The Gas Distribution Coefficient and Henry's Law

The gas distribution coefficient,  $\beta$ , is the ratio of the mass fraction of vapour that is the gas tracer,  $Y_g$ , to the mass fraction of liquid that is gas in solution,  $X_g$ . The parameter  $\beta$  is often expressed as a log-linear regression of experimental data (Giggenbach 1980):

$$\log \beta = aT + b \quad (1)$$

where  $a$  and  $b$  are regression coefficients and  $T$  is the temperature ( $^{\circ}\text{C}$ ).

With small gas densities and the fugacity approximated by the partial gas pressure,  $P_g$ , Henry's law describes the mass fraction of gas dissolved in the liquid phase. Given the temperature dependent Henry's coefficient,  $C_H$ , and the molecular weight of the gas,  $M_g$ , and water,  $M_{H_2O}$ , Henry's law is (Van Ness and Abbott 1997):

$$X_g = \frac{P_g}{C_H} \frac{M_g}{M_{H_2O}} \quad (2)$$

The mass fraction of gas in the vapour phase is the ratio of gas density,  $\rho_g$ , and steam density,  $\rho_s$ .

$$Y_g = \frac{\rho_g}{\rho_g + \rho_s} \approx \frac{\rho_g}{\rho_s} \quad (3)$$

since the gas concentration is small. Using the assumption of ideal gas behaviour:

$$\rho_g = \frac{P_g}{R T_a} M_g \quad (4)$$

where  $R$  is the universal gas constant (8.3143 kJ/kmol.K) and  $T_a$  is the absolute temperature. Combining the definition of  $\beta$  and (2), (3) and (4):

$$C_H(T) = \frac{\beta(T) R T_a \rho_s(T, P_s(T))}{M_{H_2O}} \quad (5)$$

Here,  $P_s$ , is the steam vapour pressure.

The gas distribution correlation data should not be used at excessively high temperatures. Here we assumed that the expression for  $\beta$  was valid in the range  $T \in [100, 300]^{\circ}\text{C}$ . To extend this range the semi-empirical correlation of Harvey (1996) was used. The correlation is:

$$\ln C_H = \ln P_s + A \frac{1}{T^*} + B \frac{(1-T^*)^{0.355}}{T^*} + C \exp(1-T^*)(T^*)^{-0.41} \quad (6)$$

where  $T^*$  is the temperature reduced by the critical temperature of water ( $T^c = 647.3 \text{ K}$ ). The coefficients  $A$ ,  $B$  and  $C$  are determined by the least squares fitting of (6) to data points generated from (5).

### Model Parameters

Solubility data for several gas tracers of interest has been obtained in the form of regression coefficients for the distribution coefficient,  $\beta$ . These values and the source are given in Table 1. The tracers R-12 and R-123 are refrigerants (halogenated alkanes).

<b>Tracer</b>	<b>a</b>	<b>b</b>	<b>Source</b>
SF <sub>6</sub>	-0.015910	7.263	Adams (1999)
R-12	-0.014307	6.267	Adams (1999)
R-123	-0.011080	5.066	Adams (1999)

Table 1. Regression coefficients for the gas distribution coefficient of some tracers.

The Harvey (1996) correlation coefficients, determined using linear least-squares fitting for each tracer given in Table 1, are presented in Table 2.

<b>Tracer</b>	<b>A</b>	<b>B</b>	<b>C</b>
SF <sub>6</sub>	-27.8787	0.8698	31.5
R-12	-23.5424	1.9532	25.8484
R-123	-17.5548	0.6613	20.2303

Table 2. Harvey (1996) correlation coefficients for Henry's coefficients of some tracers.

The data generated from the gas distribution regression and the Harvey (1996) correlation fits to the data are shown for the tracers in Figure 1. From these figures it can be seen that R-123 is the most

soluble gas, followed by R-12 and then SF<sub>6</sub>. Vapour flow velocities in geothermal reservoirs are usually larger than those for liquids, so tracers that partition more strongly into the vapour phase will tend to break through earlier and in larger concentrations. SF<sub>6</sub> is the least soluble of these three gas tracers and so will partition more strongly into the vapour phase.

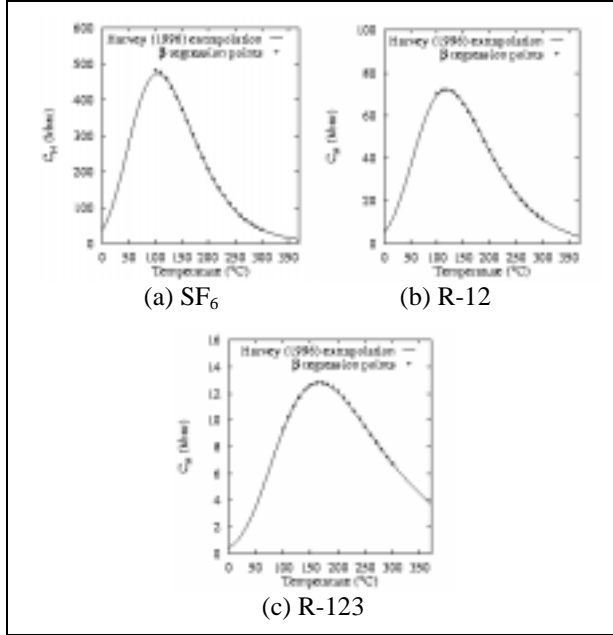


Figure 1. The temperature dependence of Henry's coefficients for various gas tracers in water.

## MIXTURE MODELS FOR LIQUID TRACERS IN WATER

### Assumptions

1. There are very low concentrations of liquid tracers and thus the formation of non-aqueous phases due to any partial-miscibility or non-miscibility of the tracers will be ignored as a first approximation. This is important from both the perspective of modelling complexity and the capabilities of the Wilson model (Reid et al. 1977).
2. Because of the low concentrations, the interactions between the liquid tracers are negligible and thus, only those between the liquid tracers and water are important.
3. As a first approximation, fugacity is near unity.
4. The mixture of liquid tracer and water is only moderately non-ideal, enabling the molar excess Gibbs energy to be modelled by a two-parameter Wilson model (Reid et al. 1977).
5. The primary temperature influence is in the pure component vapour pressures. Thus, the uncertain and difficult to model temperature dependence of the molar excess Gibbs energy, is assumed to be

dominated by the temperature dependence of the pure component vapour pressures (Reid et al. 1977).

### Molar Excess Gibbs Free Energy, the Wilson Model and Activity Coefficients

The interactions between components in a mixture can be described by activity coefficients,  $\gamma$ , and related to liquid mole fractions,  $x$ , by the Gibbs-Duhem differential equation (Hala et al. 1967). An additional useful concept that unites the activity coefficients, liquid mole fractions and temperature is the molar excess Gibbs energy,  $g^E$ . This quantity is the observed Gibbs energy, per mole of a mixture, beyond what it would be for an ideal solution at the same temperature, pressure and composition (Reid et al. 1977). The relationship between the molar excess Gibbs energy, the liquid mole fractions of liquid tracer and water,  $x_l$  and  $x_w$  respectively, and the activity coefficients,  $g_l$  and  $g_w$ , is (Reid et al. 1977):

$$\frac{g^E}{RT} = x_l \ln \gamma_l + x_w \ln \gamma_w \quad (7)$$

The molar excess Gibbs energy can also be represented by a model, one such being Wilson's model (Reid et al. 1977):

$$\frac{g^E}{RT} = -x_l \ln(x_l + \Lambda_{lw}x_w) - x_w \ln(x_w + \Lambda_{wl}x_l) \quad (8)$$

where  $\Lambda_{lw}$  and  $\Lambda_{wl}$  are binary interaction parameters. The binary interaction parameters are determined from the non-linear fitting of (8) to experimentally determined values of the molar excess Gibbs energy for various liquid mole fractions of the tracer.

Using (7) and (8) together with the Gibbs-Duhem relation, the Wilson expressions for the activity coefficients of a binary mixture are:

$$\ln \gamma_l = -\ln(x_l + \Lambda_{lw}x_w) + x_w \left( \frac{\Lambda_{lw}}{x_l + \Lambda_{lw}x_w} - \frac{\Lambda_{wl}}{\Lambda_{wl}x_l + x_w} \right) \quad (9)$$

$$\ln \gamma_w = -\ln(x_w + \Lambda_{wl}x_l) - x_l \left( \frac{\Lambda_{lw}}{x_l + \Lambda_{lw}x_w} - \frac{\Lambda_{wl}}{\Lambda_{wl}x_l + x_w} \right) \quad (10)$$

A mixture vapour pressure can then be determined from pure component vapour pressures,  $P_{vp_l}(T)$  and  $P_{vp_w}(T)$ , as:

$$P_{vp_{mixture}}(T) = \gamma_l x_l P_{vp_l}(T) + \gamma_w x_w P_{vp_w}(T). \quad (11)$$

The vapour mole fraction of liquid tracer is then:

$$y_l = \frac{\gamma_l x_l P_{vp_l}(T)}{P_{vp_{mixture}}(T)}. \quad (12)$$

This is the mixture-partitioning model that is used in the work presented in this paper.

In some instances, the liquid tracer will be injected as part of a cocktail of tracers with varying properties. The returns from such a test give additional information concerning the structure and qualities of the geothermal reservoir. Experimental data for ternary, and higher, mixtures is difficult (and perhaps impossible) to locate in the literature. An alternative is to build a mixture-partitioning model based solely on binary interactions between the mixture components.

Reid et al. (1977) give a Wilson model for the activity coefficient for component  $i$  of a multi-component liquid mixture (with  $N_i$  components), in terms of the binary Wilson interaction parameters,  $\Lambda_{ij}$ . This model is:

$$\ln \gamma_i = 1 - \ln \left( \sum_j^{N_i} x_j \Lambda_{ij} \right) - \sum_k^{N_i} \left( \frac{x_k \Lambda_{ki}}{\sum_j^{N_i} x_j \Lambda_{kj}} \right). \quad (13)$$

Currently the interaction parameters are calculated using binary mixture experimental vapour-liquid equilibrium data. Future work will consider theoretical methods for determining vapour-liquid equilibrium behaviour, based on molecular structure and the interactions between molecular groups (Pierotti et al. 1959, Reid et al. 1977) or various equations of state (Wu and Prausnitz 1998). These methods will allow the flexibility to model tracers for whom experimental data is currently not available.

With the activity coefficients calculated from the multi-component version of Wilson's model, the mixture vapour pressure can be determined in terms of the pure component vapour pressure at a given temperature as:

$$P_{vp_{mixture}}(T) = \sum_i^{N_i} \gamma_i x_i P_{vp_i}(T). \quad (14)$$

The vapour mole fraction of component  $i$  is then:

$$y_i = \frac{\gamma_i x_i P_{vp_i}(T)}{P_{vp_{mixture}}(T)}. \quad (15)$$

Once the vapour mole fraction  $y_i$  has been determined, it is then converted to the vapour mass fraction,  $Y_i$ , to be used in further calculations.

### Model Parameters

Here we consider two alcohol tracers, methanol and n-propanol. Experimental data for isothermal methanol vapour-liquid equilibria were obtained from Griswold and Wong (1952) and McGlashan and Williams (1976). For n-propanol, experimental data were obtained from Reid et al. (1977) and Morrison et al. (1990). The fitting of the Wilson model binary interaction parameters to this experimental data was performed using a non-linear least-squares fit. This

non-linear minimisation was based on the algorithm of Hooke and Jeeves (1961) (see also Kaupe Jr. (1963)). The experimental data and the non-linear fits for methanol and n-propanol are shown in Figure 2.

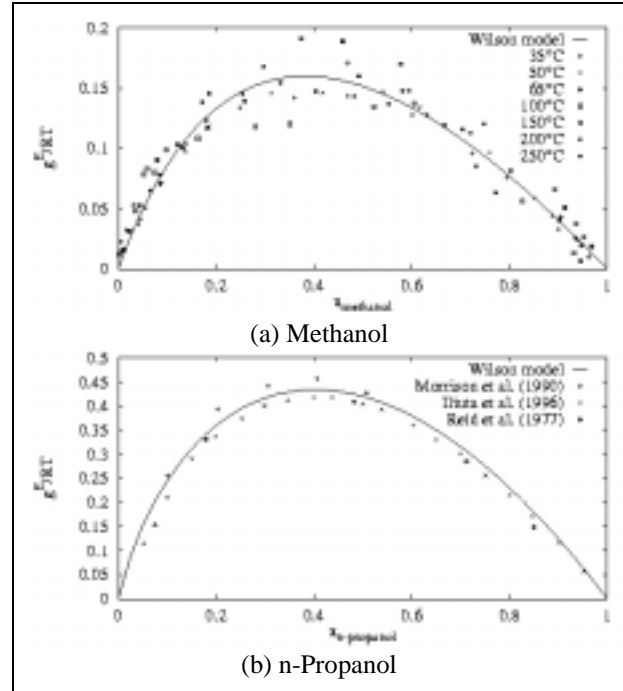


Figure 2. Experimentally determined molar excess Gibbs free energy and the Wilson model.

The Wilson model binary interaction parameters calculated for a methanol-water mixture and an n-propanol-water mixture are given in Table 3.

Mixture	$\Lambda_{lw}$	$\Lambda_{wl}$
methanol-water	0.205294	1.451029
n-propanol-water	0.015448	0.700203

Table 3. The Wilson model binary interaction parameters for selected alcohol-water mixtures.

## IMPLEMENTATION OF THE MIXTURE MODELS IN TOUGH2

### The TOUGH2 Equation of State

A general equation of state (EOS) module for TOUGH2 has been constructed which allows for multiple liquid components (including the geothermal water) and multiple gas components. A routine is included for calculating the mass fractions in the liquid and vapour phases of each component. The sequence of calculations in the EOS is:

1. Determine the phase state.
2. Calculate thermodynamic properties for each component.
3. Determine mass fractions.

Within the mass fraction routine, the gas tracer calculations are performed first, followed by the liquid mass fraction of water, the vapour mass fraction of water and then any liquid components other than the geothermal water. The calculations are summarised in a following section.

### Assumptions

1. The concentrations of tracers are low, and the mixture thermodynamic properties of viscosity and enthalpy remain identical to those of water and steam. The density of the liquid mixture remains identical to that of water and the vapour density is the sum of the steam and gas tracer densities.
2. Additivity may be used for gas and steam partial pressures in the vapour phase.

### The Primary Solution Variables for Each Phase

1. Compressed liquid: pressure,  $P$ , temperature,  $T$ , partial pressure of gas  $i$ ,  $P_{g_i}$ , and the mass fraction of additional liquid  $j$  in the liquid phase,  $X_{l_j}$ .
2. Superheated vapour: pressure,  $P$ , temperature,  $T$ , partial pressure of gas  $i$ ,  $P_{g_i}$ , and the mass fraction of additional liquid  $j$  in the liquid phase,  $X_{l_j}$ .
3. Two-phase mixture: vapour pressure,  $P_v$ , vapour saturation,  $S_v$ , partial pressure of gas  $i$ ,  $P_{g_i}$  and the mass fraction of additional liquid  $j$  in the liquid phase,  $X_{l_j}$ .

### Calculations Performed in the Mass Fraction Routine

The mass fraction routine requires on input: partial gas pressures, liquid tracer mass fractions, steam pressure and density and the pure component vapour pressures. The quantities returned on output are: water liquid and vapour mass fractions, gas tracer liquid and vapour mass fractions and liquid tracer vapour fractions.

When there are  $N_l$  liquids (including water) and  $N_g$  gases in the total mixture, the calculations that the mass fraction routine performs, in order, are shown in Table 4. When gas tracers are present, the mass fraction of liquids in the vapour phase is less than that calculated using the Wilson model, since the gas tracers are not included in these calculations. To account for the reduced mass fraction, the liquid component vapour mass fraction is multiplied by the overall fraction of the vapour occupied by the liquid components, i.e.

$$\left(1 - \sum_{i=1}^{N_g} Y_{g_i}\right).$$

1. Mass fraction of gas tracer  $i$  in liquid phase,

$X_{g_i}$ : $X_{g_i} = \frac{P_{g_i} M_g}{C_H M_{H_2O}} \quad (16)$
2. Mass fraction of gas tracer $i$ in the vapour phase, $Y_{g_i}$ : $Y_{g_i} = \frac{\rho_{g_i}}{\sum_{j=1}^{N_g} \rho_{g_j} + \rho_s} \quad (17)$ where $\rho_{g_i} = \frac{P_{g_i} M_g}{RT_a} \quad (18)$
3. Mass fraction of water in the liquid phase, $X_w$ : $X_w = 1 - \sum_{i=1}^{N_g} X_{g_i} - \sum_{j=1}^{N_l} X_{l_j} \quad (19)$
4. Mass fraction of water/liquid tracer $j$ in the vapour phase, $Y_{l_j}$ : $Y_{l_j} = \left(1 - \sum_{i=1}^{N_g} Y_{g_i}\right) \left(\frac{M_{l_j}}{\sum_{k=0}^{N_l} y_{l_k} M_{l_k}}\right) y_{l_j} \quad (20)$ where $l_0 \Leftrightarrow w \quad (21)$ $y_{l_j} = \frac{\gamma_{l_j} x_{l_j} P_{vp_{l_j}}}{P_{vp_{mixture}}} \quad (22)$ $x_{l_j} = \frac{X_{l_j}}{\left(M_{l_j} \sum_{k=0}^{N_l} \frac{X_{l_k}}{M_{l_k}}\right)} \quad (23)$ $P_{vp_{mixture}} = \sum_{k=0}^{N_l} \gamma_{l_k} x_{l_k} P_{vp_{l_k}} \quad (24)$

Table 4. Steps in the mixture partitioning calculations.

The terms

$$\left(\frac{M_{l_j}}{\sum_{k=0}^{N_l} y_{l_k} M_{l_k}}\right) \text{ and } \left(M_{l_j} \sum_{k=0}^{N_l} \frac{X_{l_k}}{M_{l_k}}\right)^{-1}$$

represent the conversions from mole to mass fractions and mass to mole fractions, respectively.

### QUALITATIVE RESULTS FOR TWO-PHASE FLOWS

#### A Three-dimensional Idealised Test Problem

An idealised test problem with isotropic matrix properties has been considered. The reservoir volume

is  $1 \text{ km}^3$  and it is discretely represented by 3375 regular computational blocks. The porous media is homogeneous with a permeability of  $10^{-14} \text{ m}^2$  and a porosity of 0.1. Energy is introduced in the bottom layers of the reservoir so as to produce steady convective two-phase flow. No-flux boundary conditions are imposed at the bottom and side boundaries. The top surface is an atmosphere boundary. The steady state  $200 \text{ }^\circ\text{C}$  temperature and 10% vapour saturation solutions for this problem are shown in Figure 3.

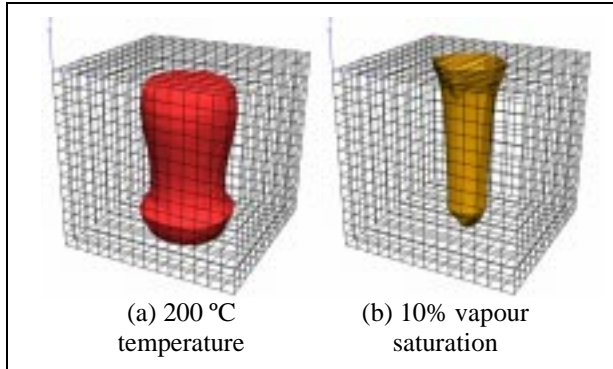


Figure 3. Steady state iso-surfaces.

### **Tracer Cocktail of Three Gas Tracers**

A cocktail of three gas tracers is injected into a  $0.008 \text{ km}^3$  region in the centre of the reservoir. The gas tracers are  $\text{SF}_6$ , R-123 and R-12. 100 kg of each tracer is injected at a constant rate for 20 minutes. For the purpose of this test problem, no geothermal water is injected with the tracers and the steady state convective flow is undisturbed. Results for the gas tracers are shown in Figure 4. The iso-surfaces drawn are for  $10^{-12}$  mass fraction of the tracer. A cutting plane parallel to the y-axis has been used to clearly show the surfaces relative to each other.

The tracers have moved up and out with the convective flow. The relative vapour phase partitioning characteristics of these three gas tracers, coupled with the relative phase flow velocities are clearly seen. The sparingly soluble  $\text{SF}_6$  tracer has been transported further by the vapour than the more soluble R-12 and R-123 tracers. Consequently it is detected over a wider volume in both the vapour and the liquid phases after 100 days of simulation. These features are expected of the gas tracers used here.

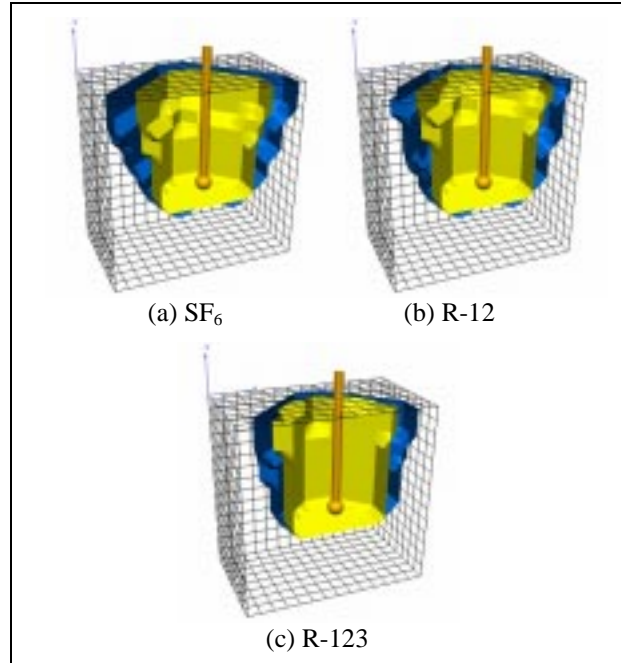


Figure 4.  $10^{-12}$  iso-surfaces, 100 days after the injection of the gas tracers. The light coloured surfaces are the tracer in the liquid phase. The dark coloured surfaces are the tracer in the vapour phase.

### **Tracer Cocktail of One Water-Like Liquid, Two Alcohols and One Gas**

This test involved the injection of a cocktail of one water-like tracer (e.g. tritium), methanol, n-propanol and  $\text{SF}_6$ . An identical injection regime to the previous test was used with 100 kg of each tracer injected at a constant rate for 20 minutes. Results are shown in Figure 5. The iso-surfaces drawn are for  $10^{-12}$  mass fraction of the tracer.

The water-like tracer is transported an equal distance in the liquid and vapour phases and the extent of its movement is shown by a single iso-surface in Figure 5(a). The remaining tracers which are more volatile than the water-like tracer and so partition more strongly into the vapour phase are transported further by the vapour flow and then partition back to the liquid phase as the temperature cools at the top of the reservoir. This is observed in figures 5(b), 5(c) and 5(d). At these low liquid tracer mass fractions, the n-propanol tracer fractionates more readily into the vapour phase than methanol as observed in 5(b) and 5(c). Thus, the methanol tracer is detected at equal times in the liquid and the vapour phases, whereas n-propanol is detected sooner in the vapour phase than in the liquid phase. Figure 5(d) shows that as expected,  $\text{SF}_6$  displays comparatively more volatility than either of the alcohols. These are the expected behavioural features of this collection of tracers.

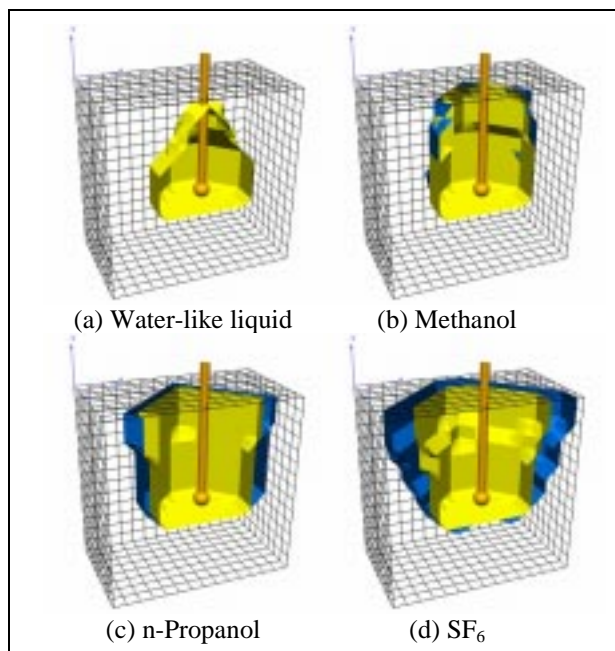


Figure 5.  $10^{-12}$  iso-surfaces, 100 days after the injection of the liquid and gas tracers. The light coloured surfaces are the tracer in the liquid phase. The dark coloured surfaces are the tracer in the vapour phase.

## SUMMARY AND CONCLUSIONS

Mixture liquid and vapour partitioning models have been developed for gas and general liquid tracers. These models have been implemented in TOUGH2 as a general EOS.

Preliminary testing with  $\text{SF}_6$ , refrigerant and alcohol tracers has shown that the phase partitioning models for gas and liquid tracers qualitatively give the expected results. Further work is required to obtain vapour-liquid equilibrium and phase distribution data so that a wider range of tracers can be represented.

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