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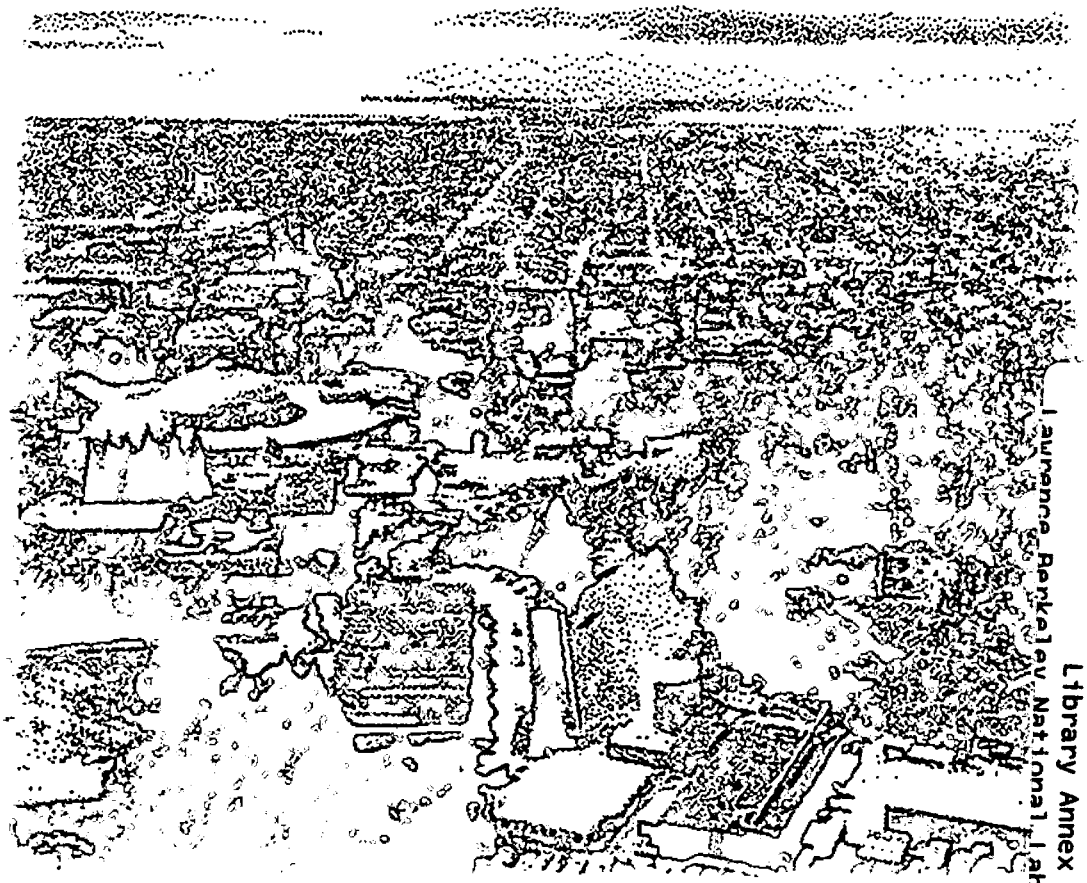
EOSN: A TOUGH2 Module for Noble Gases

Chao Shan and Karsten Pruess

Earth Sciences Division

March 2003



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Abstract

We developed a new fluid property module for TOUGH2, called EOSN, to simulate transport of noble gases in the subsurface. Currently, users may select any of five different noble gases as well as CO_2, two at a time. For the three gas components (air and two user-specified noble gases) in EOSN, the Henry's coefficients and the diffusivities in the gas phase are no longer assumed constants, but are temperature dependent. We used the Crovetto et al. (1982) model to estimate Henry's coefficients, and the Reid et al. (1987) correlations to calculate gas phase diffusivities. The new module requires users to provide names of the selected noble gases, which properties are provided internally. There are options for users to specify any (non-zero) molecular weights and half-lives for the gas components. We provide two examples to show applications of TOUGH2/EOSN. While temperature effects are relatively insignificant for one example problem where advection is dominant, they cause almost an order of magnitude difference for the other case where diffusion becomes a dominant process and temperature variations are relatively large. It appears that thermodynamic effects on gas diffusivities and Henry's coefficients can be important for low-permeability porous media and zones with large temperature variations.

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1. Introduction

Among many TOUGH2 fluid property modules, EOS7R is the one that can simulate two-phase, five-component flow and transport problems. The two phases are the water and gas phases, and the five components are water, brine, air and two radionuclides (Oldenburg and Pruess, 1995). Pruess et al. (2000) used TOUGH2 with the EOS7R module to simulate the transport of different tracers in a geothermal reservoir. These tracers included R-134a, tritium, neon, and xenon. The natural availability and chemical stability make some gases, especially noble gases, good tracers in studying transport processes in the subsurface. Phase partitioning and gas diffusion are two important mechanisms that affect transport processes. For trace gases, phase partitioning can be described using Henry's law, and gas diffusion using Fick's law. Each law is characterized by a coefficient: the Henry's coefficient and the gas diffusivity. Laboratory experiments have shown that both coefficients are temperature dependent. For noble gases and some other gases such as carbon dioxide (CO_2), this thermodynamic effect is so strong that it may significantly affect results in cases of large temperature variations. In fact, the dependence of noble gas solubility on temperature is sufficiently strong as to make monitoring of noble gas concentration in subsurface water of meteoric origin a useful tool for determining recharge temperature (Ballentine and Hall, 1999). Information on multi-phase processes (boiling, condensation) can also be obtained.

TOUGH2/EOS7R requires users to input Henry's coefficients and gas diffusivities as constant values, which is both inconvenient and inaccurate for strongly non-isothermal systems. In applying TOUGH2/EOSN, users only need to give the names of the two gases; all required thermodynamic properties are provided internally. There are, however, options for users to overwrite internal molecular weights for modeling user-specified isotopes. Currently there are six user-selectable gases: He (helium), Ne (neon), Ar (argon), Kr (krypton), Xe (xenon), and CO_2 (carbon dioxide). The capability to model radioactive decay by means of half-life is already included in EOSN. We provide the new capabilities by adding two subroutines into TOUGH2: NOHEN for calculating the temperature-dependent Henry's coefficients for the three gas components (air and two user-selected

gases), and GASDIF for calculating their temperature- and pressure- dependent diffusivities in the gas phase. We set diffusivities for the two other components (water and brine) to zero in both (aqueous and gas) phases. We also set a default value of 10^{-9} m^2/s for diffusivities of the three gas components (air and two user selected gases) in the aqueous phase. There is an option, however, for users to specify aqueous phase diffusivities for all five components through the data block, DIFFU (Pruess et al., 1999).

2. Treatment of Diffusion in TOUGH2

TOUGH2 uses an "advective-diffusive model" (ADM) in which total mass flux of a component is computed as the sum of advective and diffusive fluxes. It is well established that for gases the advective and diffusive fluxes are coupled, as given by the dusty gas model (Mason and Malinauskas, 1983; Webb, 1998). However, Webb and Pruess (2001) have shown that for trace gases the dusty gas model reduces to the ADM, and this is the approximation used here. The diffusive flux of component κ in phase β (= aqueous, gas) is written as (Pruess et al., 1999)

$$\mathbf{f}_\beta^\kappa = -\phi\tau_0\tau_\beta\rho_\beta d_\beta^\kappa \nabla X_\beta^\kappa \tag{1}$$

where ϕ is porosity, $\tau_0\tau_\beta$ is the tortuosity which includes a porous medium-dependent factor τ_0 and a coefficient τ_β that depends on phase saturation S_β [i.e., $\tau_\beta = \tau_\beta(S_\beta)$], ρ_β is density, d_β^κ is the diffusion coefficient of component κ in the bulk fluid phase β, and X_β^κ is the mass fraction of component κ in phase β. According to Eq. (1), each fluid component diffuses separately under its own mass fraction gradient and with its own diffusion coefficient. Diffusion coefficients for gases are calculated internally as functions of pressure and temperature (see Section 3), while aqueous phase diffusion coefficients are taken as constants, with no provisions for temperature dependence of these parameters.

It is convenient to define a single diffusion strength factor that combines all material constants and tortuosity factors into a single effective multiphase diffusion coefficient, as follows.

$$\Sigma_\beta^\kappa = \phi\tau_0\tau_\beta\rho_\beta d_\beta^\kappa \tag{2}$$

For general two-phase conditions, the total diffusive flux can then be written as the sum of diffusive fluxes in aqueous and gas phases.

$$\mathbf{f}^\kappa = -\Sigma_l^\kappa \nabla X_l^\kappa - \Sigma_g^\kappa \nabla X_g^\kappa \tag{3}$$

Space discretization of Eq. (3) in multiphase conditions raises some subtle issues (Pruess et al., 1999). Generally speaking, it is not permissible to evaluate space-discretized

expressions separately in gas and aqueous phases and then add them, because this ignores the coupling between diffusion and phase partitioning. The default option in TOUGH2, selected with MOP(24) = 0, fully accounts for such coupling and can cope with the most general case of diffusion across a phase boundary. As an alternative, by setting MOP(24) = 1, diffusive fluxes can be evaluated separately in gas and aqueous phases and then added.

Tortuosity effects have a porous medium-dependent part τ_0 and a saturation-dependent part τ_β, as indicated in Eq. (1). The following three alternative formulations are available.

1. Relative permeability model

   For domains whose tortuosity parameter $\tau_0 =$ TORTX $\neq 0$ is specified in data block ROCKS, tortuosity will be taken as $\tau_0 \tau_\beta (S_\beta) = \tau_0 k_{r\beta} (S_\beta)$. Here, $k_{r\beta}$ is the relative permeability to phase β.

2. Millington model

   For domains where TORTX = 0, the Millington (1959) model will be used

$$\tau_0 \tau_\beta = \phi^{1/3} S_\beta^{10/3} \tag{4}$$

3. Constant diffusivity model

   Diffusivities d_β^κ may optionally be user-specified as negative numbers. Then $\tau_0 \tau_\beta = S_\beta$ will be used for tortuosity, and the absolute values of the users' input will be taken as the diffusivities.

Alternative 3 corresponds to the formulation for gas diffusion in earlier versions of TOUGH2. In the absence of phase partitioning and adsorptive effects, it amounts to effective diffusivity being approximately equal to d_β^κ, independent of saturation. This can be seen by noting that in the mass balance equation for component κ (Pruess et al., 1999) the contribution to the accumulation term from phase β is given by $\phi S_\beta \rho_\beta X_\beta^\kappa$, approximately canceling out the $\phi S_\beta \rho_\beta$ coefficient in the diffusive flux.

A crude (saturation-independent) enhancement of vapor diffusion can be chosen by specifying a suitable value, typically of order 1, for the parameter group $B = \phi\tau_0\tau_\beta$. This is to be entered as parameter BE in the first record in data block PARAM.

3. Gas Diffusivity Model

The thermodynamic noble gas diffusivity is calculated using the following equation modified from Reid et al. (1987):

$$D_{AB} = 0.01881 \times T^{3/2} \cdot M_{AB} / (P \cdot \sigma_{AB}{}^{2} \cdot \Omega_D) \tag{5}$$

Equation (5) requires fixed units for all parameters. D_{AB} is the diffusivity of Gas A (air or the noble gas of interest) in Gas B (water vapor in TOUGH2), in m^2/s. T is temperature, in K. P is pressure, in Pa. M_{AB} is defined by:

$$M_{AB} = \sqrt{(M_A + M_B)/(M_A \cdot M_B)} \tag{6}$$

where M_A and M_B are the molecular weights of Gases A and B, respectively.

The other two parameters in (5) are: σ_{AB}, a characteristic length, in angstrom; and Ω_D, a dimensionless coefficient defined by

$$\Omega_D = A \cdot (T^*)^{-B} + C \cdot e^{-DT^*} + E \cdot e^{-FT^*} + G \cdot e^{-HT^*} \tag{7}$$

where A through H are eight gas-independent constants, and T^* is a modified temperature that is defined by:

$$T^* = T / (\varepsilon_{AB} / k) \tag{8}$$

where ε_{AB} is the geometric mean characteristic Lennard-Jones energy of gas A and B (Reid et al., 1987); k is the Boltzmann constant.

The values of the eight constants are given in Table 1.

Table 1. Constants for calculating the dimensionless parameter Ω_D

A	*B*	*C*	*D*	*E*	*F*	*G*	*H*
1.06036	0.1561	0.193	0.47635	1.03587	1.52996	1.764744	3.89411

The other three parameters, M_{AB}, σ_{AB}, and ε_{AB}/k are gas-specific. Their values for five noble gases, CO_2, and air are given in Table 2. Although air is a mixture of different gases (mainly nitrogen and oxygen), here we treat it as a single pseudo-component.

Table 2. Gas parameters

	He	Ne	Ar	Kr	Xe	CO_2	Air
M_{AB}	0.552594	0.317797	0.288662	0.259692	0.251205	0.279742	0.300064
σ_{AB}	2.596	2.7305	3.0915	3.148	3.344	3.291	3.176
ε_{AB}/k	90.93405	162.9064	274.7527	380.4576	432.3218	397.412	252.181

We define water vapor as Gas B and calculate these gas-specific constants. The rationale is that the thermodynamic effect on gas diffusivity is significant only in an environment with large temperature variation such as in geothermal reservoirs, where water vapor is the dominant component in the gas phase. For most other groundwater problems, temperature is in the range of 10 °C to 20 °C, and air is likely the dominant component in the gas phase. As a result, using the above constants may cause some error. However, the thermodynamic effect is usually insignificant for those problems and users may not want to consider it at all.

Equation (5) is programmed in the subroutine GASDIF of TOUGH2/EOSN, and the constants listed in the two tables are used in the subroutine GASDIF. For two-phase conditions in a pure water system, P is a function of T so that D_{AB} in (5) is actually a function of temperature only. Figure 1 shows the calculated temperature-dependent diffusivity in saturated water vapor for all seven gases.

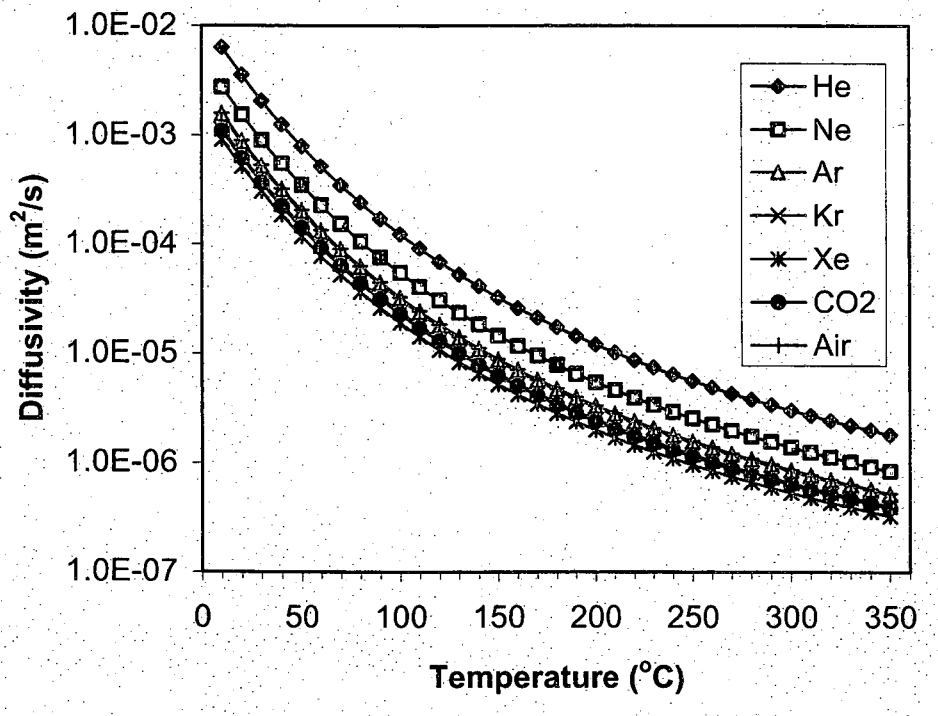

Figure 1. Diffusivity in saturated water vapor as a function of temperature for air and six gases

4. Model for Henry's Coefficients

According to Henry's law, the partial pressure of a non-condensable gas (NCG) in the gas phase is proportional to the mole fraction of the dissolved NCG in the aqueous phase (Prausnitz et al., 1986)

$$P_{NCG} = K_h \cdot x_{aq}^{NCG} \tag{9}$$

The coefficient K_h in (9) is the Henry's coefficient and has units of pressure (Pa in TOUGH2). We use the model introduced by Crovetto et al. (1982) to calculate the Henry's coefficient as a function of temperature for gases.

$$K_h = 10^9 \cdot e^{a_0 + a_1/t + a_2/t^2 + a_3/t^3} \tag{10}$$

where the variable t is one thousandth of temperature in K, i.e.

$$t = 0.001 \times T \tag{11}$$

Equation (10) is an empirical one that is fitted against the calculated K_h using experimental data of Crovetto et al. (1982). The four coefficients in (10) are gas-specific, and their values for seven gases used in TOUGH2 are given in Table 3.

Table 3. Coefficients used to calculate Henry's coefficients for seven gases

	He	Ne	Ar	Kr	Xe	CO_2	Air
a_0	-8.792806	-7.2590	-9.5200	-6.2920	-3.9020	-18.0239	-20.0899
a_1	7.847946	6.9500	8.8300	5.6120	2.4390	18.6643	21.6153
a_2	-1.573777	-1.3826	-1.8959	-0.8881	0.3863	-6.1679	-6.8549
a_3	0.075541	0.0538	0.0698	-0.0458	-0.2211	0.6078	0.7116

The coefficients for Ne, Ar, Kr, and Xe are taken directly from Crovetto et al. (1982). The coefficients for He are obtained by fitting the Smith (1985) data for He to the Crovetto et al. (1982) model. For CO_2 and air we chose four data points for each gas from Naumov et al. (1974), and substituted them into (10). This provided four linear equations for a_0 through a_3, which were solved simultaneously to obtain the coefficients for CO_2 and

air as shown in Table 3. Naumov et al. (1974) only provided the Henry's coefficient data for oxygen and nitrogen (D'Amore and Truesdell, 1988). We assumed that air is simply a mixture of 21% oxygen and 79% nitrogen, and used the following formula to estimate the Henry's coefficient for air (Pruess and Battistelli, 2002):

$$K_{h(Air)} = 1/\left(0.21/K_{h(O_2)} + 0.79/K_{h(N_2)}\right) \tag{12}$$

The data points used for calculating the coefficients for CO_2 and air are listed in Tables 4a, and 4b, respectively.

Table 4a. Set of data points used for calculating the coefficients for CO_2

T (°C)	10	90	170	350
K_h (MPa) – CO_2	103.76	492.95	718.60	235.88

Table 4b. Set of data points used for calculating the coefficients for air

T (°C)	50	80	210	350
K_h (MPa) – air	9439.48	10083.7	4918.15	1017.06

The coefficients of Table 3 are stored in data blocks in subroutine NOHEN of TOUGH2/EOSN for calculating K_h using (10). The resulting Henry's coefficients as functions of temperature are shown in Figure 2.

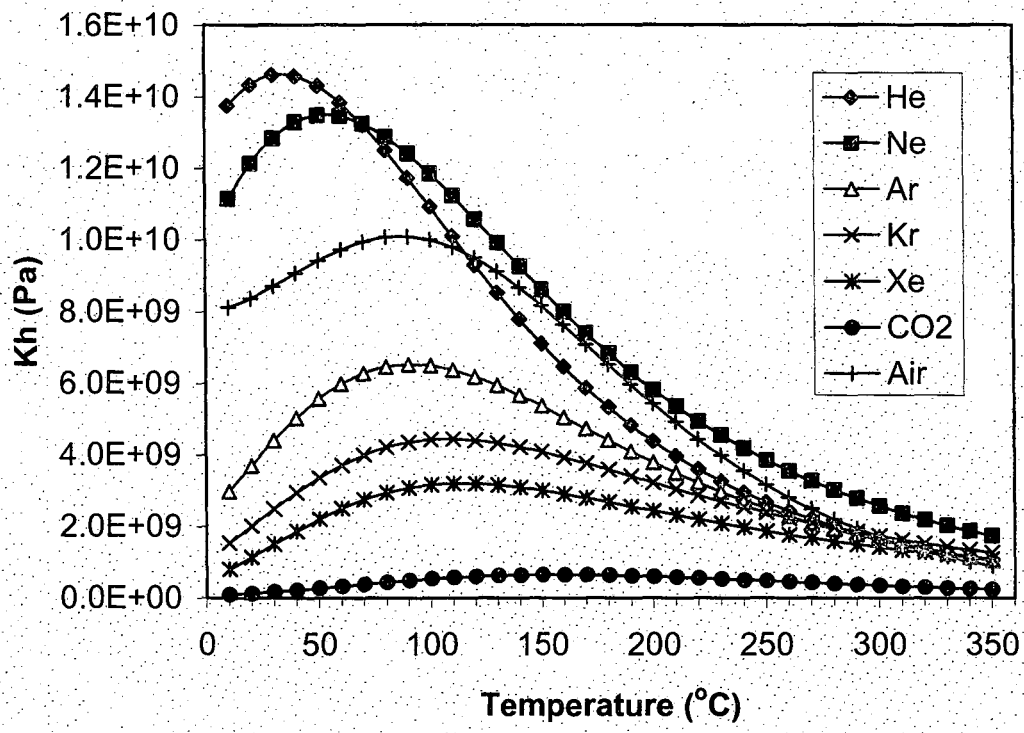

Figure 2. Henry's coefficient as a function of temperature for air and six gases

5. New Data Block

A major change in preparing TOUGH2/EOSN input files is the new data block NOBLE that requires two records, one for the two user-selected gases. Users need to choose two gases from the six gases: He, Ne, Ar, Kr, Xe, and CO_2, and input one name on each line. Users may also specify the molecular weight and half-life of the selected gases, partly or wholly.

In most cases, the new data block NOBLE is sufficient for providing modeling data. In some rare cases, users may want to use two optional data blocks SELEC and DIFFU. SELEC is needed only when brine properties are different from internally provided data. If there is a need for such a specification, users are recommended to specify IE(1) = 1 or 2 in Record SELEC.1 such that only the required number of additional records (SELEC.2 and SELEC.3) will be read. The use of DIFFU is for specifying the diffusivities in **water** for the five components: water, brine, noble gas #1, noble gas #2, and air, respectively. If DIFFU is not used, default diffusivities for five components (1 - water, 2 - brine, 3 - noble gas #1, 4 – noble gas #2, and 5 – air) in water will be used as follows: $D_{w1} = D_{w2} = 0$, $D_{w3} = D_{w4} = D_{w5} = 10^{-9}$ m^2/s. The formats of SELEC, DIFFU, and all other data blocks are the same as those in standard TOUGH2 (Pruess et al., 1999). The data formats and instructions for NOBLE are as follows.

NOBLE: keyword to introduce a data block with names of two user-selected gases, as well as (optionally) their molecular weights and half-lives.

<u>Record NOBLE.1</u>

Format (A3, 7X, 2E10.4, I2)

GASNAME(1), GMW1, THALF1, INOBLE

GASNAME(1): the name of the first selected gas. Currently users may choose from only six gases. They are He, Ne, Ar, Kr, Xe, and CO2. Names are case-sensitive and must be entered exactly as indicated. All names must be typed starting from the first column.

GMW1: the molecular weight (g/mole) of the first selected gas. This input is **optional** and can be left blank (or set 0) so that TOUGH2/EOSN will use the internally stored standard value for the first selected gas.

THALF1: the half-life of the first selected gas, in seconds. This input is **optional** and can be left blank (or set 0) so that TOUGH2/EOSN will use the internally stored default value of 10^{50}, which implies no decay.

INOBLE: an **optional** index to turn off temperature dependence of Henry's coefficients and gas phase diffusivities. If users input a non-zero integer such as 1, the program will keep using the Henry's coefficients and gas phase diffusivities that are calculated at the user-specified initial temperature. This option is provided for comparison only, and should not be used for field applications.

Record NOBLE.2

Format (A3, 7X, 2E10.4)

GASNAME(2), GMW2, THALF2

GASNAME(2): the name of the second selected gas. Currently users may choose from only six gases. They are He, Ne, Ar, Kr, Xe, CO2. Names are case-sensitive and must be entered exactly as indicated. All names must be typed starting from the first column.

GMW2: the molecular weight (g/mole) of the second selected gas. This input is **optional** and can be left blank (or set 0) so that TOUGH2/EOSN will use the internally stored standard value for the second selected gas.

THALF2: the half-life of the second selected gas, in seconds. This input is **optional** and can be left blank (or set 0) so that TOUGH2/EOSN will use the internally stored default value of 10^{50}, which implies no decay.

6. Sample Problems

Here we use TOUGH2/EOSN to demonstrate temperature effects in two different problems under different conditions. The first problem was previously presented by Pruess et al. (2000). The second is a simple one-dimensional advection-diffusion problem with relatively large temperature variations. For both problems, we ran the simulation twice: with full temperature dependence of gas diffusivities and Henry's coefficients (INOBLE = 0) and without such temperature dependence (INOBLE = 1).

6.1. Sample Problem 1 - *Transport of Noble Gases to an Extraction Well*

A central well in a geothermal reservoir with a uniform thickness of 500 meters produces at a constant rate of 20 kg/s. The reservoir is homogeneous and the flow is radial. An impermeable boundary is set at a radial distance of 1000 meters. The reservoir has the following initial conditions: pressure of 33.479 bar, gas saturation of 20%, temperature of 240 °C, and aqueous phase mass fractions of 10^{-12}, 2.44×10^{-11}, and 2.142×10^{-11} for brine, neon (Ne), and xenon (Xe), respectively. The mass fractions of the noble gases correspond to equilibrium solubility at T = 10 °C for atmospheric abundances of isotopes, ^{22}Ne and ^{132}Xe. Our interests are the variations of mass fractions (in the gas phase) of Ne and Xe at the production well.

Using MESHMAKER we divided the domain into 31 elements along the radial direction. We then simulated the production process for 30 years. The input file for the case with full temperature dependence (INOBLE = 0) is given in Figure 3A.

Part of the printout after 50 time steps is given in Figure 3B, where we see clear decreasing trends for pressure, temperature, water saturation, and mass fractions of noble gases towards the production well.

```
*SAM1B* ... 1-D radial flow with Ne & Xe. Case B: INOBLE=0
MESHMAKER1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
RZ2D
RADII
    1
      5.46
EQUID
    1            0.3
LOGAR
   20           1.e2
LOGAR
   10           1.e3
LAYER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
      500.

ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
POMED    2     2600.        .04  43.2e-15  43.2e-15  43.2e-15      2.51     1000.

    7          .4438      0.80        1.        .05
    7          .4438   0.00E-2 8.734e-05      5.e8       1.0

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    5    6    2    8
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
PARAM----1 MOP: 123456789*123456789*1234 ---*----5----*----6----*----7----*----8
   2 300      501000 000000000 30   2
           946.728e6       -1. 31.5576e6
      1.e3      9.e3
     1.e-5     1.e-5
            33.479e5              1.e-12           2.440e-11           2.142e-11
               10.20                240.
SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
     -1.e5
NOBLE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
Ne               22.        0. 0
Xe              132.        0.
INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

FOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A1  1

GOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
A1  1wel 1                          MASS       -20.

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 3A. TOUGH2 input file for sample problem 1

```
*****************************************************************************************************************************

...ITERATING...  AT [   1,  1] --- DELTEX = 0.100000E+04   MAX. RES. = 0.103827E+02  AT ELEMENT A1  1  EQUATION   5
...ITERATING...  AT [   1,  2] --- DELTEX = 0.100000E+04   MAX. RES. = 0.758958E+00  AT ELEMENT A1  5  EQUATION   5
...ITERATING...  AT [   1,  3] --- DELTEX = 0.100000E+04   MAX. RES. = 0.808232E-01  AT ELEMENT A1  2  EQUATION   5
A1  2(   1,  4) ST = 0.100000E+04 DT = 0.100000E+04 DX1= -.216495E+05 DX2= 0.213770E-13 T = 239.632 P =  3326250. S = 0.217241E+00
...ITERATING...  AT [   2,  1] --- DELTEX = 0.900000E+04   MAX. RES. = 0.257404E+01  AT ELEMENT A1  1  EQUATION   5
...ITERATING...  AT [   2,  2] --- DELTEX = 0.900000E+04   MAX. RES. = 0.751154E+00  AT ELEMENT A1 10  EQUATION   5
...ITERATING...  AT [   2,  3] --- DELTEX = 0.900000E+04   MAX. RES. = 0.958358E-01  AT ELEMENT A1  1  EQUATION   5
A1  2(   2,  4) ST = 0.100000E+05 DT = 0.900000E+04 DX1= -.548908E+05 DX2= 0.589594E-13 T = 238.689 P =  3271360. S = 0.261158E+00
...ITERATING...  AT [   3,  1] --- DELTEX = 0.900000E+04   MAX. RES. = 0.223814E+00  AT ELEMENT A1  8  EQUATION   5
...ITERATING...  AT [   3,  2] --- DELTEX = 0.900000E+04   MAX. RES. = 0.777234E+00  AT ELEMENT A1  9  EQUATION   5
...ITERATING...  AT [   3,  3] --- DELTEX = 0.900000E+04   MAX. RES. = 0.679020E-02  AT ELEMENT A1  1  EQUATION   5
A1  4(   3,  4) ST = 0.190000E+05 DT = 0.900000E+04 DX1= -.277743E+05 DX2= 0.313204E-13 T = 238.538 P =  3262618. S = 0.268169E+00
...ITERATING...  AT [   4,  1] --- DELTEX = 0.900000E+04   MAX. RES. = 0.937637E-01  AT ELEMENT A1 12  EQUATION   5
...ITERATING...  AT [   4,  2] --- DELTEX = 0.900000E+04   MAX. RES. = 0.661534E+00  AT ELEMENT A1  9  EQUATION   5
...ITERATING...  AT [   4,  3] --- DELTEX = 0.900000E+04   MAX. RES. = 0.206486E-02  AT ELEMENT A1  1  EQUATION   5
A1  2(   4,  4) ST = 0.280000E+05 DT = 0.900000E+04 DX1= -.200681E+05 DX2= 0.250557E-13 T = 237.832 P =  3222075. S = 0.300755E+00
...ITERATING...  AT [   5,  1] --- DELTEX = 0.900000E+04   MAX. RES. = 0.658156E-01  AT ELEMENT A1 13  EQUATION   5
...ITERATING...  AT [   5,  2] --- DELTEX = 0.900000E+04   MAX. RES. = 0.619808E+00  AT ELEMENT A1  9  EQUATION   5
...ITERATING...  AT [   5,  3] --- DELTEX = 0.900000E+04   MAX. RES. = 0.105861E-02  AT ELEMENT A1  1  EQUATION   5
A1  1(   5,  4) ST = 0.370000E+05 DT = 0.900000E+04 DX1= -.154866E+05 DX2= 0.218244E-13 T = 237.405 P =  3197732. S = 0.322943E+00
...ITERATING...  AT [   6,  1] --- DELTEX = 0.900000E+04   MAX. RES. = 0.514660E-01  AT ELEMENT A1 14  EQUATION   5
...ITERATING...  AT [   6,  2] --- DELTEX = 0.900000E+04   MAX. RES. = 0.438910E+00  AT ELEMENT A1  8  EQUATION   5
...ITERATING...  AT [   6,  3] --- DELTEX = 0.900000E+04   MAX. RES. = 0.687613E-03  AT ELEMENT A1  1  EQUATION   5
A1  3(   6,  4) ST = 0.460000E+05 DT = 0.900000E+04 DX1= -.125018E+05 DX2= 0.164330E-13 T = 237.520 P =  3204262. S = 0.315107E+00
...ITERATING...  AT [   7,  1] --- DELTEX = 0.900000E+04   MAX. RES. = 0.405896E-01  AT ELEMENT A1 15  EQUATION   5
...ITERATING...  AT [   7,  2] --- DELTEX = 0.900000E+04   MAX. RES. = 0.471397E+00  AT ELEMENT A1  7  EQUATION   5
...ITERATING...  AT [   7,  3] --- DELTEX = 0.900000E+04   MAX. RES. = 0.508508E-03  AT ELEMENT A1  1  EQUATION   5
A1  2(   7,  4) ST = 0.550000E+05 DT = 0.900000E+04 DX1= -.106709E+05 DX2= 0.147948E-13 T = 237.153 P =  3183400. S = 0.331941E+00
...ITERATING...  AT [   8,  1] --- DELTEX = 0.900000E+04   MAX. RES. = 0.367082E-01  AT ELEMENT A1 15  EQUATION   5
...ITERATING...  AT [   8,  2] --- DELTEX = 0.900000E+04   MAX. RES. = 0.404409E+00  AT ELEMENT A1  4  EQUATION   5
...ITERATING...  AT [   8,  3] --- DELTEX = 0.900000E+04   MAX. RES. = 0.416910E-03  AT ELEMENT A1  1  EQUATION   5
A1  4(   8,  4) ST = 0.640000E+05 DT = 0.900000E+04 DX1= -.915444E+04 DX2= 0.123266E-13 T = 237.375 P =  3196015. S = 0.321759E+00
...
...


*SAM1B* ... 1-D radial flow with Ne & Xe. Case B: INOBLE=0

        OUTPUT DATA AFTER (  50,  4)-2-TIME STEPS                                                  THE TIME IS 0.188657E+02 DAYS

@@@
```

A time series of simulation variables at the production well were recorded in file FOFT, and gas phase mass fractions of noble gases are plotted in Figure 3C. Results with and without temperature dependence are virtually identical in this problem.

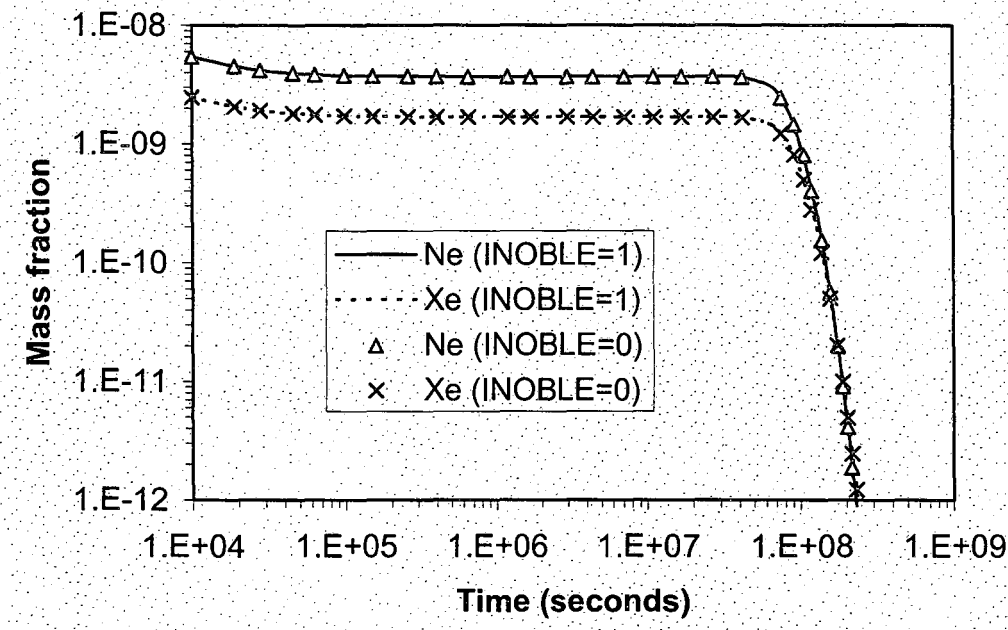

Figure 3C. Produced noble gas mass fractions in the gas phase for sample problem 1

6.2. Sample Problem 2 - *One-Dimensional Noble Gas Transport*

In this hypothetical problem we have a 10-meter long horizontal homogeneous porous rock column with a uniform cross-sectional area of 1 m^2. The column has a low permeability of 10^{-18} m^2 (1 microdarcy) and is initially at equilibrium conditions with a pressure of 24 bar, a gas saturation of 10%, and a temperature of 200 °C. The initial mass fractions for brine and two noble gases (Ne and Xe) are exactly the same as those in sample problem 1. Mass and heat are removed at the surface of one end of the column by setting constant pressure of 1 bar and temperature of 50 °C at the surface, where noble gas concentrations are assumed to be zero (Figure 4A). A no-flow boundary condition is assigned to the other end of soil column. We are interested in the variations of mass fractions of Ne and Xe in the column.

Starting from the no-flow end we divided the domain into 10 elements along its length. Each element is one meter long, numbered sequentially from the no-flow end. The input file is given in Figure 4A.

Part of the printout after 100 time steps is given in Figure 4B, where we see a clear decreasing trend for pressure, temperature, and water saturation towards the discharge boundary at BND 1. The mass fractions of air and noble gases in the gas phase, however, show a non-monotonic behavior. This occurs because the lowered temperature causes water vapor condensation and thus the mass fractions for non-condensable components to increase. The process is simulated for 5 years.

```
*SAM2B* ... 1-D diffusion with Ne & Xe. Case B: INOBLE=0
ROCKS----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
MATRX    2     2600.      0.25    1.e-18    1.e-18    1.e-18      2.51     1000.

    7            0.5       0.1        1.      0.05
    7            0.5      0.09    1.e-04      5.e8       1.0

MULTI----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    5    6    2    8
START----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
PARAM----1-MOP:-123456789*123456789*1234 ---*----5----*----6----*----7----*----8
   29000     1001000 000000000 30   2
            1.5768e8      600.   360000.
     1.e-5
               24.e5              1.e-12          2.440e-11           2.142e-11
               10.10                200.
ELEME----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AAA 1    9    1    1        1.
BND 1              1

CONNE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AAA 1AAA 2    8    1    1    1       0.5       0.5       1.0
AAA10BND 1                 1       0.5    1.e-10       1.0

INCON----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
BND 1
                1.e5              1.e-12                 0.                  0.
               10.10                50.

SOLVR----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
5  Z1   O0    8.0e-1    1.0e-7
SELEC----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
    1
     -1.e5
NOBLE----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
Ne               22.        0. 0
Xe              132.        0.
FOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
AAA10

GOFT ----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

GENER----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8

ENDCY----1----*----2----*----3----*----4----*----5----*----6----*----7----*----8
```

Figure 4A. TOUGH2 input file for sample problem 2

```
*****************************************************************************************************************************

...ITERATING...  AT [   1,  1] --- DELTEX = 0.600000E+03   MAX. RES. = 0.820133E-03  AT ELEMENT AAA10  EQUATION   6
AAA10(   1,  2) ST = 0.600000E+03 DT = 0.600000E+03 DX1= -.678788E+04 DX2= -.644325E-18 T = 199.840 P =  2393212. S = 0.100213E+00
...ITERATING...  AT [   2,  1] --- DELTEX = 0.120000E+04   MAX. RES. = 0.163889E-02  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [   2,  2] --- DELTEX = 0.120000E+04   MAX. RES. = 0.840432E-04  AT ELEMENT AAA10  EQUATION   5
AAA10(   2,  3) ST = 0.180000E+04 DT = 0.120000E+04 DX1= -.131450E+05 DX2= -.102950E-17 T = 199.521 P =  2380067. S = 0.100637E+00
...ITERATING...  AT [   3,  1] --- DELTEX = 0.240000E+04   MAX. RES. = 0.327231E-02  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [   3,  2] --- DELTEX = 0.240000E+04   MAX. RES. = 0.183286E-03  AT ELEMENT AAA10  EQUATION   5
AAA10(   3,  3) ST = 0.420000E+04 DT = 0.240000E+04 DX1= -.258947E+05 DX2= -.218106E-17 T = 198.888 P =  2354172. S = 0.101476E+00
...ITERATING...  AT [   4,  1] --- DELTEX = 0.480000E+04   MAX. RES. = 0.652281E-02  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [   4,  2] --- DELTEX = 0.480000E+04   MAX. RES. = 0.424592E-03  AT ELEMENT AAA10  EQUATION   5
AAA10(   4,  3) ST = 0.900000E+04 DT = 0.480000E+04 DX1= -.502583E+05 DX2= -.481425E-17 T = 197.636 P =  2303914. S = 0.103114E+00
...ITERATING...  AT [   5,  1] --- DELTEX = 0.960000E+04   MAX. RES. = 0.129590E-01  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [   5,  2] --- DELTEX = 0.960000E+04   MAX. RES. = 0.106128E-02  AT ELEMENT AAA10  EQUATION   5
AAA10(   5,  3) ST = 0.186000E+05 DT = 0.960000E+04 DX1= -.947639E+05 DX2= -.111766E-16 T = 195.194 P =  2209150. S = 0.106247E+00
...ITERATING...  AT [   6,  1] --- DELTEX = 0.192000E+05   MAX. RES. = 0.255768E-01  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [   6,  2] --- DELTEX = 0.192000E+05   MAX. RES. = 0.282569E-02  AT ELEMENT AAA10  EQUATION   5
AAA10(   6,  3) ST = 0.378000E+05 DT = 0.192000E+05 DX1= -.169126E+06 DX2= -.268198E-16 T = 190.541 P =  2040025. S = 0.111992E+00
...ITERATING...  AT [   7,  1] --- DELTEX = 0.384000E+05   MAX. RES. = 0.498277E-01  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [   7,  2] --- DELTEX = 0.384000E+05   MAX. RES. = 0.753809E-02  AT ELEMENT AAA10  EQUATION   5
...ITERATING...  AT [   7,  3] --- DELTEX = 0.384000E+05   MAX. RES. = 0.103458E-04  AT ELEMENT AAA10  EQUATION   5
AAA10(   7,  4) ST = 0.762000E+05 DT = 0.384000E+05 DX1= -.273028E+06 DX2= -.622423E-16 T = 182.073 P =  1766997. S = 0.121767E+00
...ITERATING...  AT [   8,  1] --- DELTEX = 0.384000E+05   MAX. RES. = 0.473175E-01  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [   8,  2] --- DELTEX = 0.384000E+05   MAX. RES. = 0.706127E-02  AT ELEMENT AAA10  EQUATION   5
AAA10(   8,  3) ST = 0.114600E+06 DT = 0.384000E+05 DX1= -.210699E+06 DX2= -.601664E-16 T = 174.359 P =  1556298. S = 0.130056E+00
...ITERATING...  AT [   9,  1] --- DELTEX = 0.768000E+05   MAX. RES. = 0.897857E-01  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [   9,  2] --- DELTEX = 0.768000E+05   MAX. RES. = 0.138344E-01  AT ELEMENT AAA10  EQUATION   5
...ITERATING...  AT [   9,  3] --- DELTEX = 0.768000E+05   MAX. RES. = 0.326306E-04  AT ELEMENT AAA10  EQUATION   5
AAA10(   9,  4) ST = 0.191400E+06 DT = 0.768000E+05 DX1= -.298292E+06 DX2= -.117253E-15 T = 161.421 P =  1258005. S = 0.142666E+00
...ITERATING...  AT [  10,  1] --- DELTEX = 0.768000E+05   MAX. RES. = 0.810462E-01  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [  10,  2] --- DELTEX = 0.768000E+05   MAX. RES. = 0.988582E-02  AT ELEMENT AAA10  EQUATION   5
...ITERATING...  AT [  10,  3] --- DELTEX = 0.768000E+05   MAX. RES. = 0.150359E-04  AT ELEMENT AAA10  EQUATION   5
AAA10(  10,  4) ST = 0.268200E+06 DT = 0.768000E+05 DX1= -.196902E+06 DX2= -.904798E-16 T = 150.532 P =  1061104. S = 0.152281E+00
...ITERATING...  AT [  11,  1] --- DELTEX = 0.768000E+05   MAX. RES. = 0.729294E-01  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [  11,  2] --- DELTEX = 0.768000E+05   MAX. RES. = 0.631091E-02  AT ELEMENT AAA10  EQUATION   5
AAA10(  11,  3) ST = 0.345000E+06 DT = 0.768000E+05 DX1= -.137479E+06 DX2= -.719525E-16 T = 141.336 P =   923625. S = 0.159755E+00
...ITERATING...  AT [  12,  1] --- DELTEX = 0.153600E+06   MAX. RES. = 0.130917E+00  AT ELEMENT AAA10  EQUATION   6
...ITERATING...  AT [  12,  2] --- DELTEX = 0.153600E+06   MAX. RES. = 0.103361E-01  AT ELEMENT AAA10  EQUATION   5
...ITERATING...  AT [  12,  3] --- DELTEX = 0.153600E+06   MAX. RES. = 0.224911E-04  AT ELEMENT AAA10  EQUATION   5
AAA10(  12,  4) ST = 0.498600E+06 DT = 0.153600E+06 DX1= -.164505E+06 DX2= -.977301E-16 T = 127.725 P =   759119. S = 0.169785E+00
...
...


*SAM2B* ... 1-D diffusion with Ne & Xe. Case B: INOBLE=0

        OUTPUT DATA AFTER ( 100,  3)-2-TIME STEPS                                                THE TIME IS 0.368826E+03 DAYS

@@@
```

The transient conditions close to the surface grid block AAA10 were recorded in the file FOFT, from which we obtained the data for Figure 4C that shows the mass fractions of Ne and Xe in the gas phase as functions of time. Results with temperature dependence (INOBLE = 0) and those without temperature dependence (INOBLE = 1) agree at early times (note that both axes are logarithmic) when both diffusion and temperature drop are insignificant, and start departing later when both diffusion and temperature drop become significant. The temperature in the column falls to about 50 °C at the end of the simulation, when diffusivities for both neon and xenon are more than 50 times larger than the corresponding diffusivities at 200 °C (Figure 1). That is why the mass fractions accounting for temperature effects (the markers) decrease faster in Figure 4C.

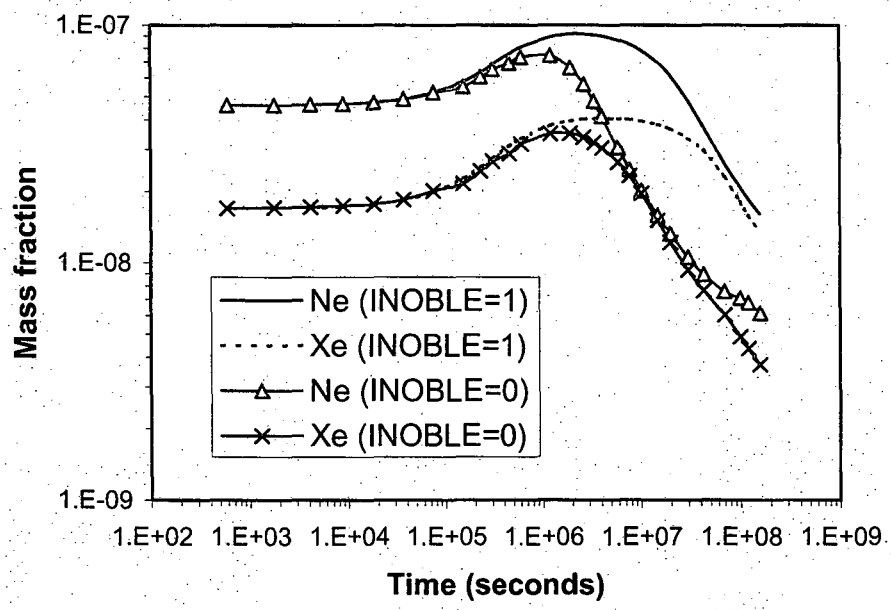

Figure 4C. Noble gas mass fractions in the gas phase at production end for sample problem 2

7. Conclusions

TOUGH2/EOSN can simulate noble gas transport in the subsurface, which may provide useful information on reservoir processes and conditions. The temperature effect may play an important role in gas diffusion-dominated processes and in fluid exchange between matrix blocks and surrounding fractures. The solubility/diffusivity difference between two different noble gases leads to a difference in resulting noble gas mass fractions (or concentrations), which may provide additional information for subsurface studies. Vaporization and condensation of water may greatly affect mass fractions of gases, which is a factor to be considered in data analyses. The study of noble gases may be extended to any other non-condensable gases or even volatile organic chemicals (VOCs).

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