LBL-29615
Preprint

Lawrence Berkeley Laboratory
UNIVERSITY OF CALIFORNIA

EARTH SCIENCES DIVISION

Submitted to Water Resources Research

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September 1990

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Prepared for the U.S. Department of Energy under Contract Number DE-AC03-76SF00098.

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Numerical Modeling of Steam Injection for the Removal of Nonaqueous Phase Liquids from the Subsurface
1. Numerical Formulation

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September 1990

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering and Geosciences Division, and in part by the U.S. Environmental Protection Agency, under Interagency Agreement DW89931336-01-07, through U.S. Department of Energy Contract DE-AC03-76SF00098.

ABSTRACT

A multidimensional integral finite difference numerical simulator is developed for modeling the steam displacement of nonaqueous phase liquid (NAPL) contaminants in shallow subsurface systems. This code, named STMVOC, considers three flowing phases: gas, aqueous, and NAPL; and three mass components: air, water, and an organic chemical. Interphase mass transfer of the components between any of the phases is calculated by assuming local chemical equilibrium between the phases, and adsorption of the chemical to the soil is included. Heat transfer occurs due to conduction and multiphase convection, and includes latent heat effects. A general equation of state is implemented in the code for calculating the thermophysical properties of the NAPL/chemical. This equation of state is primarily based on corresponding states methods of property estimation using a chemicals' critical constants. The necessary constants are readily available for several hundred hazardous organic liquid chemicals. In the second paper [Falta et al., this issue], the code is used to simulate two one-dimensional laboratory steam injection experiments, and to examine the effect of NAPL properties on the steam displacement process.

INTRODUCTION

Subsurface contamination by nonaqueous phase liquids (NAPLs) such as halogenated organic solvents and hydrocarbon fuels is a serious problem in the United States and other industrialized countries. Following the release of these liquids to the subsurface, significant amounts of the liquid become trapped in the soil by capillary forces. The complete removal of these trapped NAPLs by conventional technologies is difficult, time-consuming, and expensive. Recently, the sweeping of contaminated areas with steam has been examined as an alternative remediation method. Several laboratory-scale experiments [Hunt et al., 1988b; Basel and Udell, 1989; K. S. Udell, (personal communication, 1989)], and a field experiment [Udell and Stewart, 1989], have demonstrated that steam treatment may be an effective cleanup method. A schematic illustration of a possible steam injection remediation system is shown in Figure 1.

The process of steam injection for subsurface remediation involves several complex interacting phenomena. The system is characterized by strong heat transfer in a three-phase flow system (gas, water, NAPL) in which the mass transfer of components between the phases is significant. These complexities limit the general application of analytical solutions to steam injection problems.

In recent years, a number of numerical simulators have been developed for the purpose of modeling NAPL transport in multiphase systems [Little, 1983; Abriola and Pinder, 1985a,b; Faust, 1985; Osborne and Sykes, 1986; Pinder and Abriola, 1986; Baehr, 1987; Baehr and Corapcioglu, 1987; Corapcioglu and Baehr, 1987; Kuppusamy et al., 1987; Forsyth, 1988; Falta et al., 1989; Faust et al., 1989;

Kaluarachchi and Parker, 1989; Sleep and Sykes, 1989; Mendoza and Frind, 1990a,b]. While these codes have found fairly wide application in simulating NAPL transport in shallow systems, they were developed for use in isothermal problems, and do not consider heat transfer. This limitation precludes the use of these simulators for modeling steam injection processes.

In the field of petroleum engineering, steam injection is an established method for the enhanced recovery of crude oils. Beginning with an early field test reported by Stoval [1934], the use of steam injection for enhanced oil recovery has progressed to the point where by 1979, nearly 20% of the oil produced in California was attributable to steam injection processes [Prats, 1982]. For a review of petroleum engineering steam injection methods and case histories, the reader is referred to several recent texts [Prats, 1982; Burger et al., 1985; Boberg, 1988; Baibakov and Garushe, 1989].

As the use of steam injection became increasingly popular in the mid to late 1960s, researchers began developing numerical simulators capable of modeling non-isothermal three-phase flow. Starting with the one-dimensional three-phase model of Shulter [1969], simulation capabilities rapidly improved, and by the mid 1970's, three-dimensional three-phase steamflood simulators had been reported in the petroleum literature [Coats, 1974, 1976; Vinsome, 1974]. Present commercial steam injection simulators are quite sophisticated, and often include compositional effects (see, for example, Coats, [1980]; Hwang et al., [1982]; Pruess and Bodvarsson, [1983]; Rubin and Buchanan, [1985]). A description and comparison of contemporary steam injection simulators is given by Aziz et al., [1987]. Due to their

substantial commercial value in petroleum reservoir engineering, steam injection simulators are, as a rule, proprietary. The authors are not aware of any publicly available steam injection codes.

To a certain extent, the knowledge and techniques developed in petroleum engineering for modeling enhanced oil recovery by steam injection are applicable to the problem of steam treatment for subsurface remediation. There are, however, many significant differences in these applications. In enhanced oil recovery projects, the object is to remove as much oil from a formation as is economically feasible. If a small amount of oil is still present in the formation following a steamflood, it is probably of little consequence. In contrast, the object of remediation efforts is to remove all of the contaminant from the subsurface, down to parts per billion levels. The simulation of organic contaminant transport must include many subtle multi-phase processes that often operate on the pore level, and are usually ignored in petroleum reservoir engineering. Examples of such processes include dissolution and transport of organic compounds in the water phase, diffusion of organic vapors in the gas phase, the exchange of air, water, and chemical vapor between the vadose zone and the atmosphere, and phase partitioning of chemicals between the gas, water, and solid (soil) phases.

The conditions present in petroleum reservoirs tend to be different from those present in shallow contaminated sites. While petroleum reservoirs are usually very large in areal extent, and are confined at elevated pressures, sites which are subject to remedial action are smaller in extent, and are often unconfined and open to the atmosphere. Also, a wide variety of organic contaminants are encountered at

hazardous waste sites. Because the thermodynamic and transport properties of these different chemicals vary substantially, a flexible NAPL/organic chemical equation of state package is required to accurately describe the thermophysical characteristics of different chemicals of concern.

In order to gain a better quantitative understanding of the steam injection process, and to aid in the design and analysis of future experiments and remedial efforts, a numerical simulator has been developed that can model the complex mass and heat flow phenomena arising in a steam sweep cleanup operation. In this paper, the first of a two part series, details of the mathematical and numerical formulation of the simulator are given. The results of simulations of two laboratory column experiments will be presented in part 2 [Falta et al., this issue] along with an examination of the effect of different NAPL properties on the steam displacement process. Several two-dimensional laboratory scale experiments have been modeled using the simulator, and these results are presented in Falta [1990].

PHYSICAL PROCESSES AND ASSUMPTIONS

The numerical simulator, which will be referred to as STMVOC, has been developed for the purpose of modeling true three-phase flow in systems undergoing rapid changes in temperature. This code is based on a general integral finite difference method formulation known as MULKOM [Pruess, 1983; 1988]. Several versions of MULKOM have been developed for solving different multiphase flow problems. The features and capabilities of these different versions have been summarized by Pruess [1988]. The most well known and widely used version of

MULKOM is the TOUGH simulator [Pruess, 1987]. TOUGH (Transport of Unsaturated Groundwater and Heat) is a three-dimensional code (as are all of the MULKOM codes) for simulating the coupled transport of water, water vapor, air, and heat in porous and fractured porous media.

In the present formulation, the multiphase system is assumed to be composed of three mass components: air (or some other noncondensible gas), water, and a volatile, slightly water-soluble organic chemical. Although air consists of several components, here it is treated as a single "pseudo" component with averaged properties. These three components may be present in different proportions in any of the three phases, gas, water, and NAPL. The components and phases considered by the STMVOC simulator are listed in Table 1. Each phase flows in response to pressure and gravitational forces according to the multiphase extension of Darcy's law, including the effects of relative permeability and capillary pressure between the phases.

Transport of the three mass components occurs by advection in all three phases, and by multicomponent diffusion in the gas phase. It is assumed that the three phases are in local chemical and thermal equilibrium, and that there are no chemical reactions taking place other than interphase mass transfer and adsorption of the chemical component to the solid phase. Mechanisms of interphase mass transfer for the organic chemical component include evaporation and boiling of the NAPL, dissolution of the NAPL into the liquid water phase, condensation of the organic chemical from the gas phase into the NAPL, and equilibrium phase partitioning of the organic chemical between the gas, water, and solid phases. Interphase mass transfer of the

water component includes the effects of evaporation and boiling of the water phase, dissolution of water in the NAPL (not usually important), and condensation of water vapor from the gas phase. The interphase mass transfer of the air component consists of equilibrium phase partitioning of the air between the gas, liquid water, and NAPL phases.

Heat transfer occurs due to conduction, multiphase convection, and gaseous diffusion. The heat transfer effects of phase transitions between the NAPL, water and gas phases are fully accounted for by considering the transport of both latent and sensible heat. The overall porous media thermal conductivity is calculated as a function of water and NAPL saturation, and depends on the chemical characteristics of the NAPL.

Thermophysical properties of the aqueous and NAPL phases such as saturated vapor pressure and viscosity are calculated as functions of temperature, while parameters such as specific enthalpy and density are computed as functions of both temperature and pressure. Vapor pressure lowering effects due to capillary forces are not presently included in the simulator. Gas phase thermophysical properties such as specific enthalpy, viscosity, density, and component molecular diffusivities are considered to be functions of temperature, pressure, and gas phase composition. The solubility of the organic chemical in water may be specified as a function of temperature, and the gas-water Henry's constant for the organic chemical is calculated as a function of temperature. The gas-water and gas-NAPL Henry's constant for air is assumed to be constant, as is the water solubility in the NAPL phase.

The necessary NAPL/organic chemical thermophysical and transport properties are computed by means of a very general equation of state. This equation of state is largely based on semi-empirical corresponding states methods in which chemical parameters are calculated as functions of the critical properties of the chemical such as the critical temperature and pressure. Because these data are available for hundreds of organic compounds, the NAPL/organic chemical equation of state is quite flexible in its application.

By virtue of the fact that the integral finite difference method [Narasimhan and Witherspoon, 1976] is used for spatial discretization, the present formulation makes no reference to a global coordinate system other than the direction of the gravitational acceleration vector, and no particular dimensionality is required. The STMVOC simulator may therefore be used for one, two, or three-dimensional anisotropic, heterogenous porous or fractured systems having complex geometries. The porous media porosity may be specified to be a function of pore pressure and temperature, but no stress calculations are made.

GOVERNING EQUATIONS

In a nonisothermal system containing three mass components, three mass balance equations and an energy balance equation are needed to fully describe the system. The following summary of the governing transport equations follows Pruess [1987; 1988] with extensions to account for a NAPL phase and a chemical component. The balance equations are written in integral form for some flow region, V_l, having a surface area Γ_l, as follows

$$\frac{d}{dt}\int_{V_l} M^K \, dV_l = \int_{\Gamma_l} \mathbf{F}^K \cdot \mathbf{n} \, d\Gamma_l + \int_{V_l} q^K \, dV_l \tag{1}$$

$$K = a: air; \;\; K = w: water; \;\; K = c: chemical; \;\; K = h: heat$$

where M^K is the amount of component K per unit porous medium volume, $\mathbf{F}^K$ is the total flux of component K into V_l, $\mathbf{n}$ is the outward unit normal vector, and q^K is the rate of generation of component K per unit volume. For $K=a,w,c$, M^K is the mass of component K per unit porous media volume, $\mathbf{F}^K$ is the mass flux of component K, and q^K is the rate of mass generation of component K per unit volume. For $K=h$, M^K is the amount of energy (heat) per unit porous media volume, $\mathbf{F}^K$ is the heat flux, and q^K is the rate of heat generation per unit volume.

Accumulation Terms

The mass accumulation terms for air and water ($K=a,w$) contain a sum over the gas, water, and NAPL phases

$$M^K = \phi \sum_{\beta} S_\beta \rho_\beta \omega_\beta^K \tag{2}$$

$$\beta = g: gas; \;\; \beta = w: aqueous; \;\; \beta = n: NAPL$$

where ϕ is the porosity, S_β is the β phase saturation, ρ_β is the β phase density, and ω_β^K is the mass fraction of component K in phase β. The organic chemical accumulation term ($K=c$) includes the effect of linear equilibrium adsorption

$$M^c = \rho_b \rho_w \omega_w^c K_D + \phi \sum_{\beta} S_\beta \rho_\beta \omega_\beta^c \tag{3}$$

where ρ_b is the dry bulk density of the soil, ω_w^c is the mass fraction of the chemical

in the aqueous phase, and K_D is the soil water distribution coefficient for the organic chemical [Freeze and Cherry, 1979]. The last term in (3) implies that

$$C_s^c = \rho_b K_D C_w^c \tag{4}$$

where C_s^c is the adsorbed mass of chemical per unit volume of soil, and C_w^c is the chemical mass concentration in the aqueous phase. The use of (4) assumes that some liquid water is present in the system, and that the soil is preferentially wetted by the water phase. In very dry systems, the use of (4) to describe vapor adsorption may lead to some error. Because it has been found that the degree of adsorption of organic chemicals depends largely on the amount of organic carbon present in the soil, K_D is often written as

$$K_D = K_{oc} f_{oc} \tag{5}$$

where K_{oc} is the organic carbon partition coefficient, and f_{oc} is the organic carbon fraction in the soil [Karickhoff et al., 1979; Schwarzenbach and Westall, 1981].

The heat accumulation term ($K=h$) includes contributions from both the solid and the fluid phases

$$M^h = (1 - \phi)\rho_R C_R T + \phi \sum_\beta S_\beta \rho_\beta u_\beta \tag{6}$$

where ρ_R is the soil grain density, C_R is the heat capacity of the soil grains, T is the temperature, and u_β is the specific internal energy of phase β. Because the mass fractions of air and organic chemical in the aqueous phase are small, the specific internal energy of the aqueous phase is assumed to be independent of composition. Likewise, because the mass fractions of air and water in the NAPL phase are small,

the specific internal energy of the NAPL phase is also assumed to be independent of composition. The gas phase internal energy is a very strong function of composition, and is calculated by

$$u_g = \sum_{K=a,w,c} \omega_g^K u_g^K \tag{7}$$

where u_g^K is the specific internal energy of component K in the gas phase.

Flux Terms

The three mass flux terms (air, water, chemical) sum over the three phases (gas, aqueous, NAPL)

$$\mathbf{F}^K = \sum_\beta \mathbf{F}_\beta^K \tag{8}$$

The mass flux of each component in the gas phase includes both advection and diffusion

$$\mathbf{F}_g^K = \frac{-kk_{rg}\rho_g}{\mu_g} \omega_g^K (\nabla P_g - \rho_g \mathbf{g}) + \mathbf{J}_g^K \tag{9}$$

where k is the absolute permeability, k_{rg} is the gas phase relative permeability, μ_g is the gas phase dynamic viscosity, P_g is the gas phase pressure, $\mathbf{g}$ is the gravitational acceleration vector, and $\mathbf{J}_g^K$ is the diffusive mass flux of component K in the gas phase. The diffusive mass fluxes of water and organic chemical vapor, $\mathbf{J}_g^w$, and $\mathbf{J}_g^c$ are calculated by

$$\mathbf{J}_g^K = -\phi S_g \tau_g D_g^K \rho_g \nabla \omega_g^K \tag{10}$$

where D_g^K is the multicomponent molecular diffusion coefficient of component K in

the gas phase, and τ_g is the gas phase tortuosity computed from the Millington and Quirk [1961] model

$$\tau_g = \phi^{1/3} S_g^{7/3} \tag{11}$$

The use of (11) to predict the gas phase tortuosity does not account for possible enhancements to the diffusive flow of condensible vapors which may occur when the liquid condensate is also present [Walker et al., 1981]. With the water and chemical diffusive mass fluxes given by (10), the air diffusive mass flux, $\mathbf{J}_g^a$ is determined from the requirement that

$$\mathbf{J}_g^a + \mathbf{J}_g^w + \mathbf{J}_g^c = 0 \tag{12}$$

The use of (12) ensures that the total gas phase diffusive mass flux summed over the three components is zero with respect to the mass average velocity [Bird et al., 1960]. Then, the total gas phase mass flux is the product of the gas phase Darcy velocity and the gas phase density.

The component mass fluxes in the water and NAPL phases are calculated by considering only advection,

$$\mathbf{F}_w^K = \frac{-kk_{rw}\rho_w}{\mu_w}\,\omega_w^K\,(\nabla P_w - \rho_w \mathbf{g}) \tag{13}$$

$$\mathbf{F}_n^K = \frac{-kk_{rn}\rho_n}{\mu_n}\,\omega_n^K\,(\nabla P_n - \rho_n \mathbf{g}) \tag{14}$$

The water phase pressure in (13) is related to the gas phase pressure in (9) by

$$P_w = P_g - P_{cgw} \tag{15}$$

where P_{cgw} is the gas-water capillary pressure. The NAPL phase pressure in (14) is

related to the gas phase pressure by

$$P_n = P_g - P_{cgn} \tag{16}$$

where P_{cgn} is the gas-NAPL capillary pressure. It follows that the NAPL-water capillary pressure, P_{cnw}, is

$$P_{cnw} = P_{cgw} - P_{cgn} = P_n - P_w \tag{17}$$

The heat flux includes both conduction and convection

$$\mathbf{F}^h = -\lambda \nabla T + \sum_{\beta} h_\beta \mathbf{F}_\beta \tag{18}$$

where λ is the overall porous media thermal conductivity, h_β is the β phase specific enthalpy, and $\mathbf{F}_\beta$ is the total β phase mass flux (not to be confused with the component mass flux). As in the case of the aqueous and NAPL phase internal energies, the aqueous and NAPL phase specific enthalpies are assumed to be independent of composition. The gas phase specific enthalpy is calculated as

$$h_g = \sum_{K=a,w,c} \omega_g^K h_g^K \tag{19}$$

and is a very strong function of composition. From thermodynamics, the relationship between the enthalpy and the internal energy of a fluid is $h = u + P/\rho$ [Sonntag and van Wylen, 1982].

PRIMARY VARIABLES AND VARIABLE SUBSTITUTION

In order to describe the thermodynamic state of a four-component system in which local thermal and chemical phase equilibrium is assumed, it is necessary to

choose four primary variables. In addition to the four primary variables, a complete set of "secondary variables" is needed for the solution of the four coupled balance equations. These secondary variables include thermodynamic and transport properties such as enthalpies, densities, relative permeabilities, viscosities, and mass fractions. The four primary variables must be chosen so that the entire set of secondary variables may be calculated as functions of the primary variables.

In multiphase flow problems involving phase transitions (ie. appearance or disappearance of a phase), the number of possible phase combinations may become large. In a system in which a maximum of three fluid phases may be present, there are seven possible phase combinations. These combinations include three single phase systems (eg. gas, water, NAPL), three two-phase systems (eg. gas-water, gas-NAPL, water-NAPL), and one three-phase system (eg. gas-water-NAPL). The appropriate choice of primary variables depends on which combination of phases is present.

For example, in a non-isothermal three-phase system (gas-water-NAPL), the primary variables could be chosen to be a reference phase pressure, P, gas saturation, S_g, water saturation, S_w, and temperature, T. Under conditions of local thermal and chemical equilibrium between the phases, this choice of variables would completely define the state of the system, and the entire set of secondary variables could be determined from the primary variables. Because all three phases are present, the mass fraction (or concentration) of every mass component in every phase would be determined by local equilibrium considerations. The mass fraction of the organic chemical in the gas phase would be determined by the saturated vapor pressure of

the NAPL at the prevailing temperature, and the mass fraction of the organic chemical in the water phase would be calculated using Henry's constant for gas-water equilibrium at the given temperature.

Suppose, however, that the NAPL phase disappeared due to evaporation into the gas phase or dissolution into the water phase. Because S_n=0, it would no longer be appropriate to calculate the mass fraction of the organic chemical in the gas phase from the saturated vapor pressure. Also, S_g and S_w would no longer be independent. For these reasons, the system would not be fully defined by the primary variables P, S_g, S_w, and T.

One method of dealing with this problem is employed by Abriola and Pinder [1985b]. This method involves the specification of a minimum value for the NAPL saturation, on the order of 10^{-4}. Next, a "pseudo" saturated chemical vapor concentration, $\hat{C}_g^c$, is defined as

$$\hat{C}_g^c = \left[\frac{S_n}{S_n + 10^{-4}}\right]\overline{C}_g^c \tag{20}$$

where $\overline{C}_g^c$ is the true saturated vapor concentration of the chemical. In the numerical simulator, $\overline{C}_g^c$ is replaced by $\hat{C}_g^c$. As the NAPL saturation becomes very small, the value of $\hat{C}_g^c$ is reduced, limiting the amount of evaporation which may take place. The use of (20) along with Henry's constant for the water concentration prevents complete evaporation or dissolution of the NAPL phase [Forsyth, 1988], and the concentration of the chemical in each phase is known at all times. Abriola and Pinder [1985b] found this method to be satisfactory, and this technique was used by Falta and Javandel [1987] for three-phase multicomponent simulations. Forsyth [1988]

reports that this method has also been used in petroleum reservoir simulation.

A drawback of this method is that it is not possible to rigorously simulate the complete removal of the NAPL from the porous medium. Even though the minimum S_n value of 10^{-4} is quite small, this is still a relatively high level of contamination. Consider a system which has a porosity of 0.4. A NAPL saturation of 10^{-4} corresponds to 40 ml of NAPL per m^3 of porous medium. For toxic organic chemicals, this is a significant level of contamination.

A more robust approach to this problem involves the use of primary variable substitution during phase transitions. From the earlier example in which the NAPL phase disappeared from a three phase system, if the primary variables are switched from P, S_g, S_w, and T to P, χ_g^c, S_w, and T, where χ_g^c is the mole fraction of the organic chemical in the gas phase, a complete description of the system is once again possible in terms of the primary variables. This technique of variable switching during phase transitions has been employed in various versions of MULKOM [Pruess, 1988], TOUGH [Pruess, 1987], and is used in the TOUGH VOC simulator described by Falta et al. [1989]. This technique was also used by Forsyth [1988] for a two-phase isothermal simulator.

While the technique of variable substitution during phase transitions is quite attractive, implementing this procedure for a three-phase system with seven possible phase combinations would require seven sets of primary variables and would be cumbersome to code.

In the present work, a compromise is made between the robustness and elegance of the variable substitution method, and the simplicity of the minimum

saturation method. To reduce the number of phase combinations, it is assumed that the gas and aqueous phases never totally disappear, although the phase saturations may be quite small ($\approx 10^{-4}$). In regions where the NAPL phase is present, the system is considered to be under three-phase conditions (gas-water-NAPL), and the primary variables are P, S_g, S_w, and T. The disappearance of the NAPL phase is recognized when $S_g + S_w \geq 1$. In this case, the system is under two-phase conditions (gas-water), and the variables are switched to P, χ_g^c, S_w, and T where χ_g^c is the mole fraction of the organic chemical in the gas phase. If at any point, the partial pressure of the chemical ($\chi_g^c P_g$) becomes greater than the saturated vapor pressure of the chemical (P_{sat}^c), the NAPL phase evolves and the variables are switched to the three-phase set of variables. In either case, the minimum saturation method is used for the gas and water phases in order to prevent complete disappearance of these phases. This is done by using equations similar to (20) for the water saturated vapor pressure, the water solubility in the NAPL phase, the air solubility in water, and the air solubility in the NAPL phase.

SECONDARY VARIABLES

In non-isothermal multiphase flow simulations, major nonlinearities in the governing equations occur due to large variations of secondary thermodynamic and transport parameters from changes in the values of the primary variables. For this reason, the accurate calculation of secondary variables from the primary variables is of considerable importance. In the formulation of STMVOC an effort has been made to include all of the secondary variables which significantly contribute to the

nonlinearity of the problem. A complete list of all of the variable secondary parameters along with their dependence on the primary variables is given in Table 2. The dependence of the secondary variables on specific primary variables may change under different phase conditions due to the primary variable switching. In Table 2, it is assumed that the pressure used as a primary variable is the gas phase pressure. For this reason, it is not necessary to compute a gas phase capillary pressure.

Gas Phase Density and Mass Fractions

By assuming that all components of the gas phase obey the ideal gas law, and that the total pressure is equal to the sum of the partial pressures, the gas density is calculated as the sum of the component gas concentrations. The partial pressure of water in the gas phase, P_g^w, is equal to the saturated vapor pressure of water at the local temperature, P_{sat}^w. This value is calculated using steam table equations given by the International Formulation Committee [1967]. From the ideal gas law, the concentration of water in the gas phase (i.e., the vapor density), C_g^w is

$$C_g^w = \frac{P_g^w M_{wt}^w}{RT} \tag{21}$$

where M_{wt}^w is the molecular weight of water, and R is the universal gas constant.

Next, the partial pressure of the organic chemical is calculated. If the NAPL phase is not present, then

$$P_g^c = \chi_g^c P_g \tag{22}$$

where χ_g^c is the chemical mole fraction in the gas phase, and P_g is the gas phase

pressure. If the NAPL phase is present, then P_g^c is set equal to the saturated vapor pressure of the chemical which is calculated as a function of temperature by the Wagner equation [Reid et al., 1987]

$$P_{sat}^c = P_{crit} \exp\left[\frac{ax + bx^{1.5} + cx^3 + dx^6}{1 - x}\right] \tag{23}$$

$$x = 1 - \frac{T}{T_{crit}}$$

In (23), P_{crit} and T_{crit} are the critical pressure and critical temperature of the organic compound, and a, b, c, and d are empirically determined constants. Values of these constants for about 500 compounds are given by Reid et al. [1987]. Figure 2 shows the variation of saturated vapor pressure with temperature for several compounds. Using the ideal gas law for the chemical concentration results in

$$C_g^c = \frac{P_g^c M_{wt}^c}{RT} \tag{24}$$

where M_{wt}^c is the molecular weight of the chemical.

Given the total gas phase pressure, and the water and chemical partial pressures, the air partial pressure is calculated by

$$P_g^a = P_g - P_g^w - P_g^c \tag{25}$$

The air concentration, C_g^a is then calculated from the ideal gas law as

$$C_g^a = \frac{P_g^a M_{wt}^a}{RT} \tag{26}$$

where M_{wt}^a is the mixture molecular weight of air. The gas density is then calculated as the sum of the component concentrations

$$\rho_g = C_g^a + C_g^w + C_g^c \tag{27}$$

and the gas phase mass fractions are simply

$$\omega_g^a = \frac{C_g^a}{\rho_g} \tag{28}$$

$$\omega_g^w = \frac{C_g^w}{\rho_g} \tag{29}$$

$$\omega_g^c = \frac{C_g^c}{\rho_g} \tag{30}$$

The use of the ideal gas law for calculating the gas density and mass fractions is a reasonable approximation as long as the total pressure is less than about two or three atmospheres. For instance, the error in the calculated water vapor density at a pressure of five atmospheres using the ideal gas law is less than five percent. In cases where the pressure is very high, as in petroleum reservoirs, the real gas law should be used instead of the ideal gas law.

Gas Phase Viscosity

The gas viscosity is computed as a function of temperature, pressure, and composition. In areas where only air and water vapor are present, the gas viscosity is calculated using a modified version of the kinetic gas theory formulation given by Hirschfelder et al. [1954] in which the water vapor viscosity is calculated from steam table equations [Pruess, 1987].

In areas where the chemical vapor is present, the viscosity is calculated from a modified version of the Wilke semi-empirical method for multicomponent gas

viscosity [Bird et al., 1960].

$$\mu_g = \frac{\mu_g^c}{1+\Phi_{c,aw}\left[\frac{\chi_g^{aw}}{\chi_g^c}\right]} + \frac{\mu_g^{aw}}{1+\Phi_{aw,c}\left[\frac{\chi_g^c}{\chi_g^{aw}}\right]} \tag{31}$$

In (31), μ_g^{aw} is the air-water vapor viscosity calculated from the modified kinetic gas theory formulation [Hirschfelder et al., 1954], μ_g^c is the viscosity of pure chemical vapor, χ_g^{aw} is the sum of the air and water vapor mole fractions, and χ_g^c is the chemical vapor mole fraction. The interaction parameters, $\Phi_{c,aw}$ and $\Phi_{aw,c}$ are

$$\Phi_{c,aw} = \frac{[1 + (\mu_g^c/\mu_g^{aw})^{1/2}(M_{wt}^{aw}/M_{wt}^c)^{1/4}]^2}{[8(1 + M_{wt}^c/M_{wt}^{aw})]^{1/2}} \tag{32}$$

and

$$\Phi_{aw,c} = \frac{[1 + (\mu_g^{aw}/\mu_g^c)^{1/2}(M_{wt}^{aw}/M_{wt}^c)^{1/4}]^2}{[8(1 + M_{wt}^{aw}/M_{wt}^c)]^{1/2}} \tag{33}$$

in which M_{wt}^c is the chemical molecular weight, and M_{wt}^{aw} is the air-water vapor mixture molecular weight. The chemical vapor viscosity (μ_g^c) in (31) is computed from the corresponding states method [Reid et al., 1987]. Details of this method are given in Appendix A.

The method of calculating the gas phase viscosity described above is expected to give good accuracy over the entire range of composition. As the mole fraction of chemical vapor tends towards zero, (31) reduces to the air-water viscosity calculated by the kinetic gas theory model. Comparisons with experimental data over the range

of air-water composition and at temperatures up to 150 ^{o}C have shown this model to be accurate to within four percent. As the mole fraction of chemical vapor tends towards one, the formulation reduces to the corresponding states method for the chemical vapor viscosity which has an average error of about three percent [Reid et al., 1987]. For intermediate compositions, Bird et al. [1960] report that the use of (31) results in an average error of about two percent given accurate values for the individual viscosities.

Aqueous and NAPL Phase Densities and Viscosities

Due to the low solubility of most organic liquids in water, and to the low solubility of water and air in organic liquids, variations of aqueous and NAPL densities and viscosities with composition are neglected. The aqueous phase density is taken to be equal to that of pure water at the same temperature and pressure, and aqueous and NAPL viscosities are calculated as a function of temperature. The density and viscosity of liquid water are calculated from steam table equations given by the International Formulation Committee [1967].

The variation of NAPL density with temperature is computed using the Modified Rackett technique [Reid et al., 1987]

$$\rho_{ns} = \rho_{nsR} Z_{RA}^{[(1 - T_{rR})^{2/7} - (1 - T_r)^{2/7}]} \tag{34}$$

where

$$Z_{RA} = 0.29056 - 0.08775\omega$$

with

$$T_{rR} = \frac{T_R}{T_{crit}}$$

and

$$T_r = \frac{T}{T_{crit}}$$

In (34), ρ_{nsR} is a known NAPL density at a temperature of T_R and a pressure equal to the NAPL saturation pressure, and ω is the Pitzer acentric factor for the chemical. The NAPL density calculated by (34), ρ_{ns} is the density at a pressure equal to the NAPL saturation pressure at the prevailing temperature. Because the total pressure often differs from the NAPL saturation pressure, the NAPL density, ρ_n, at a pressure of P is calculated by

$$\rho_n = \rho_{ns}(1 + \varepsilon_n(P - P_{sat}^c)) \tag{35}$$

where ε_n is the NAPL compressibility, and P_{sat}^c is calculated from (23).

The NAPL viscosity is calculated using one of two semi-empirical methods suggested by Reid et al. [1987]. When sufficient experimental data is available, the viscosity may be accurately calculated by

$$\mu_n = \exp(a + b/T + cT + dT^2) \tag{36}$$

where a, b, c, and d are empirically determined constants. Values of these constants for about 350 organic liquids are given by Reid et al. [1987]. If only one viscosity data point is available, the viscosity in units of centipoise is calculated from

$$\mu_n = \left[\mu_{nR}^{-.2661} + \frac{T - T_R}{233}\right]^{-3.758} \tag{37}$$

where μ_{nR} is the viscosity (in cP) at a temperature of T_R. This expression is only approximate, and errors in the calculated viscosity may be as high as 15 percent in some cases [Reid et al., 1987]. A plot of liquid viscosity versus temperature for several liquids is shown in Figure 3. In this figure, the viscosity curves for n-pentane, toluene, o-xylene, n-decane, and water were calculated using (36) while the curves for trichloroethylene and 1-methylnapthalene were computed from (37).

Specific Enthalpies

The specific enthalpy of the water and NAPL phases is assumed to be independent of compositional effects, and is calculated as a function of temperature and pressure only. The liquid water specific enthalpy is computed from steam table equations given by the International Formulation Committee [1967]. The specific enthalpy of the NAPL is calculated from

$$h_n = \int_{T_{ref}}^{T} C_{pn} d\zeta \tag{38}$$

where T_{ref} is the temperature at which the enthalpy is zero (enthalpy and internal energy are relative quantities). The reference temperature is normally chosen to be 0 ^oC, but the choice of T_{ref} is not important as long as a consistent value is used in all of the other heat calculations. The heat capacity of the NAPL, C_{pn} is calculated in two stages. First, the ideal gas molar heat capacity is computed using the method of Joback [Reid et al., 1987]

$$C_{pn}^o = a + bT + cT^2 + dT^3 \tag{39}$$

where a, b, c, and d are empirically determined constants provided by Reid [1987] for about 500 organic compounds. The liquid heat capacity is calculated from the ideal gas heat capacity by the Rowlinson-Bondi method [Reid et al., 1987]

$$C_{pn} = \frac{1}{M_{wt}^{c}}(C_{pn}^{o} + R(1.45 + 0.45(1 - T_r)^{-1} \tag{40}$$

$$+ 0.25\omega[17.11 + 25.2(1 - T_r)^{1/3}T_r^{-1}$$

$$+ 1.742(1 - T_r)^{-1}]))$$

where T_r is the reduced temperature (T/T_{crit}), R is the universal gas constant, and ω is Pitzer's acentric factor. In (40), C_{pn} has units of $kJ/kg\ K$. Because the heat capacity of a liquid is only a weak function of temperature, the integral in (38) is numerically evaluated using the two-point Gaussian quadrature method [Burden et al., 1981].

The specific enthalpy of the gas phase is a very strong function of composition. The gas enthalpy is calculated as the mass fraction weighted sum of the component enthalpies given by (19). As with the previously discussed water thermophysical properties, the water vapor specific enthalpy is calculated from steam table equations provided by the International Formulation Committee [1967]. The specific enthalpy of the chemical vapor is calculated as the sum of the liquid enthalpy and the latent heat of vaporization

$$h_g^c = h_n + h_{vap}^c \tag{41}$$

where h_n is given by (38). The latent heat of vaporization of the chemical is calculated in two parts. First, the heat of vaporization at the normal boiling point is

computed by the Chen method [Reid et al., 1987]

$$h^c_{vap,b} = \frac{RT_{crit}T_{br}}{M^c_{wt}}\left[\frac{3.978T_{br} - 3.958 + 1.555\ln(P_{crit})}{1.07 - T_{br}}\right] \tag{42}$$

where T_{br} is equal to the normal boiling temperature of the chemical, T_b divided by the critical temperature, and $h^c_{vap,b}$ has units of kJ/kg. The heat of vaporization is then calculated as a function of temperature by the Watson relation [Reid et al., 1987]

$$h^c_{vap}=h^c_{vap,b}\left[\frac{1 - T_r}{1 - T_{br}}\right]^{.375} \tag{43}$$

The specific enthalpy of the air (a noncondensible gas) is

$$h^a_g = C_{va}T + \frac{P^a_g}{C^a_g} \tag{44}$$

In (44), the temperature dependence of the air heat capacity, C_{va}, is neglected. It should be noted that this formulation corresponds to the air internal energy, $u^a_g=C_{va}T$, being normalized to zero at $T=0^oC$. The overall gas specific enthalpy is calculated from (19) to be

$$h_g = \omega^a_g h^a_g + \omega^w_g h^w_g + \omega^c_g h^c_g \tag{45}$$

It is interesting to note that the specific gas enthalpy of most organic compounds is smaller than that of water by a factor of roughly five. This is mainly due to the smaller latent heat of vaporization of the organic liquids. In Figure 4, the specific gas and liquid enthalpy of toluene is shown as a function of temperature. For comparison, the specific enthalpy of saturated water vapor at 100 ^oC is 2676 kJ/kg,

and the liquid enthalpy is 419 kJ/kg [Sonntag and van Wylen, 1982].

Henry's Constants and Water and NAPL Phase Mass Fractions

Under conditions of local chemical equilibrium, the concentration of a compound in a phase is related to the concentration in another phase by a constant. Strictly speaking, this constant is a function of both temperature and concentration. In situations where the compound is only slightly soluble in one or more of the phases, the equilibrium constant is often independent of concentration.

The equilibrium expression for the gas-liquid distribution of a dilute compound is known as Henry's law, and may be written for the air and chemical components in a gas-water system as

$$P_g^K = H_{gw}^K \chi_w^K \qquad (K = a, c) \tag{46}$$

where P_g^K is the partial pressure of component K in the gas phase, χ_w^K is the mole fraction of K in the aqueous phase, and H_{gw}^K is Henry's constant for K, a function of temperature. In this context, Henry's constant has units of pressure. If Henry's constant is assumed to be independent of concentration, and K is a slightly soluble organic compound, Henry's constant may be determined by

$$H_{gw}^c = \frac{P_{vap}^c}{\overline{\chi}_w^c} \tag{47}$$

where P_{vap}^c is the saturated vapor pressure of the organic chemical given as a function of temperature by (23), and $\overline{\chi}_w^c$ is the solubility of the chemical in water (mole fraction). The solubility of a chemical in water is a complex function of temperature

which may increase or decrease with increasing temperature (see for example, [API, 1977]). As a general rule, the solubility of organic liquids tends to increase with increasing temperature, while the solubility of noncondensible gases tends to decrease with increasing temperature. In some cases, the solubility of organic liquids decreases with temperature to some minimum value and then increases with temperature [API, 1977]. If data for the chemical solubility are available, the solubility may be approximated by

$$\bar{\chi}_w^c = a + bT + cT^2 + dT^3 \tag{48}$$

where a, b, c, and d are determined by fitting the data. Unfortunately, data for the solubility of most organic chemicals are only available for a narrow temperature range. Estimation methods are available for computing aqueous solubilities (see for example, Fredenslund et al., [1977]; Prausnitz et al., [1986]; Reid et al., [1987]), but these methods are complex and do not always give accurate results. In the present work, if experimental solubility data are only available at one temperature, then the solubility is assumed to be constant, and b, c, d in (48) are set equal to zero.

The gas-water distribution of the air component is calculated using (46) with a constant value for Henry's constant of 10^{10} Pa. Although the variation of H_{gw}^a with temperature is neglected, this value is accurate to within 10 percent at temperatures ranging from 40 to 100 ^oC [Loomis, 1928].

The solubilities of air and water in the NAPL are assumed to be very small, and independent of temperature. The air mole fraction in the NAPL, χ_n^a, is calculated using an equation similar to (46) with H_{gn}^a equal to an experimentally determined constant. The water mole fraction in the NAPL is calculated using (46) with

Henry's constant calculated as in (47) by the ratio of the saturated vapor pressure to the solubility. In most instances, the mole fractions of air and water in the NAPL are very small, and $\chi_n^c \approx 1$.

Given the dissolved mole fractions in the water and NAPL phases, the remaining mole fractions are determined from the requirement that the sum of the mole fractions in all phases is equal to one.

$$\sum_{K=a,w,c} \chi_\beta^K = 1 \tag{49}$$

From the mole fractions, the mass fractions in the water and NAPL phases are calculated by

$$\omega_\beta^K = \frac{\chi_\beta^K M_{wt}^K}{\sum_{K=a,w,c} \chi_\beta^K M_{wt}^K} \tag{50}$$

Capillary Pressures and Relative Permeabilities

Of the various secondary variables, the multiphase capillary pressures and relative permeabilities are among the most important parameters affecting the multiphase flow. Unfortunately, these parameters are also very difficult to predict in a general fashion due to the variability of the pore space geometry in natural media, and the complexity of the different fluid interactions. Further compounding the situation is the fact that it is very difficult to experimentally measure capillary pressures and relative permeabilities under three phase conditions. For these reasons, it is a common practice to develop three-phase capillary pressure and relative permeability functions from two-phase relationships [Leverett, 1941; Leverett and Lewis, 1941;

Stone, 1970; Stone, 1973; Aziz and Settari, 1979; Parker et al., 1987].

By assuming that order of fluid wettability in a three-phase system is unique and follows the pattern of water > NAPL > gas, Parker et al. [1987] propose a three-phase capillary pressure formulation based on the two-phase method developed by van Genuchten [1980]. In this formulation, the NAPL-water capillary pressure, P_{cnw} is assumed to be a function of water saturation, while the gas-NAPL capillary pressure, P_{cgn}, is assumed to be a function of the gas saturation. These assumptions were originally proposed by Leverett and Lewis [1941], and have been widely used in petroleum reservoir engineering [Aziz and Settari, 1979]. The NAPL-water capillary pressure function may be written as

$$P_{cnw} = \frac{\rho_w g}{\alpha_{nw}} \left[\left[\frac{S_w - S_m}{1 - S_m} \right]^{-1/m} - 1 \right]^{1/n} \tag{51}$$

where $m = 1 - 1/n$, and n, α_{nw}, and S_m are empirically determined constants given by Parker et al. [1987]. The gas-NAPL capillary pressure function is

$$P_{cgn} = \frac{\rho_w g}{\alpha_{gn}} \left[\left[\frac{S_w + S_n - S_m}{1 - S_m} \right]^{-1/m} - 1 \right]^{1/n} \tag{52}$$

where α_{gn} is an experimentally determined constant.

With P_{cnw} from (51) and P_{cgn} from (52), the gas-water capillary pressure, P_{cgw} is calculated from

$$P_{cgw} = P_{cnw} + P_{cgn} \tag{53}$$

or

$$P_{cgw} = \frac{\rho_w g}{\alpha_{nw}} \left[\left[\frac{S_w - S_m}{1 - S_m} \right]^{-1/m} - 1 \right]^{1/n} + \frac{\rho_w g}{\alpha_{gn}} \left[\left[\frac{S_w + S_n - S_m}{1 - S_m} \right]^{-1/m} - 1 \right]^{1/n} \tag{54}$$

In regions where the NAPL is not present (S_n=0), the van Genuchten [1980] equation is used for the gas-water capillary pressure

$$P_{cgw} = \frac{\rho_w g}{\alpha_{gw}} \left[\left[\frac{S_w - S_m}{1 - S_m} \right]^{-1/m} - 1 \right]^{1/n} \quad . \tag{55}$$

where α_{gw} is found experimentally. If α_{nw} and α_{gn} are related to α_{gw} by

$$\frac{1}{\alpha_{gw}} = \frac{1}{\alpha_{nw}} + \frac{1}{\alpha_{gn}} \tag{56}$$

then the expression for the three-phase P_{cgw} given by (54) becomes the two-phase relationship given by (55) as $S_n \rightarrow 0$.

Methods developed for calculating three-phase relative permeabilities follow a logic similar to that used in the capillary pressure formulation. Early three-phase experimental work conducted by Leverett and Lewis [1941], Corey et al. [1956], and Snell [1962] showed that the dependence of relative permeability on phase saturation may be approximated by [Aziz and Settari, 1979]

$$k_{rw} = f(S_w) \tag{57}$$

$$k_{rg} = f(S_g) \tag{58}$$

and

$$k_{rn} = f(S_w, S_g) \tag{59}$$

The functions for the water and gas phase relative permeabilities required by (57) and (58) are normally determined by fitting two-phase laboratory data. Usually, the data for the water phase relative permeability may be fitted by a function of the form

$$k_{rw} = \left[\frac{S_w - S_{wr}}{1 - S_{wr}} \right]^n \tag{60}$$

where S_{wr} is the irreducible water saturation, and n has a value of between about 2 and 4 [Fatt and Klikoff, 1959; Frick, 1962; Grant, 1977; Verma, 1986; Faust et al., 1989]. Similar equations are often used for the gas phase relative permeability, although some studies suggest that the gas relative permeability is larger than would be predicted by equations of the form of (60) [Grant, 1977; Verma, 1986].

Because the NAPL phase relative permeability depends on both the water and gas phase saturations, a direct experimental determination of the three-phase permeability relationship is not usually possible. In practice, the three-phase NAPL relative permeability is computed from two-phase data for NAPL-water and NAPL-gas systems where

$$k_{rnw} = f(S_w) \tag{61}$$

and

$$k_{rng} = f(S_g) \tag{62}$$

The functional forms of (61) and (62) are often found to be similar to (60). The three-phase NAPL relative permeability may be calculated from these two-phase relative permeabilities by using methods developed by Stone [1970, 1973] and modified by Aziz and Settari [1979].

In the first method [Stone, 1970], k_{rn} is written as

$$k_{rn} = k_{rncw} S_n^* \beta_w \beta_g \tag{63}$$

where

$$\beta_w = \frac{k_{rnw}(S_w)}{k_{rncw}(1 - S_w^*)} \tag{64}$$

and

$$\beta_g = \frac{k_{rng}(S_g)}{k_{rncw}(1 - S_g^*)} \tag{65}$$

In (63), (64), and (65), k_{rncw} is the NAPL phase relative permeability in the presence of an irreducible water saturation. The two-phase NAPL-gas relative permeability required by (64) is assumed to have been measured in the presence of this irreducible water. With this assumption, and through the use of k_{rncw}, the three-phase NAPL relative permeability will reduce to the appropriate two-phase relationships if two-phase conditions are present [Aziz and Settari, 1979]. The scaled phase saturations needed in (63), (64), and (65) are

$$S_n^* = \frac{S_n - S_{nr}}{(1 - S_{wr} - S_{nr})} \tag{66}$$

$$S_w^* = \frac{S_w - S_{wr}}{(1 - S_{wr} - S_{nr})} \tag{67}$$

and

$$S_g^* = \frac{S_g}{(1 - S_{wr} - S_{nr})} \tag{68}$$

where S_{nr} is the irreducible (residual) NAPL saturation, and S_{wr} is the irreducible water saturation.

The second method [Stone, 1973; Aziz and Settari, 1979] is written as

$$k_{rn} = k_{rncw}[(k_{rnw}/k_{rncw} + k_{rw})(k_{rng}/k_{rncw} + k_{rg}) - (k_{rw} + k_{rg})] \tag{69}$$

As with the first method, if the NAPL-gas relative permeability is measured in the presence of a residual water saturation, the formulation will reduce to the appropriate

two-phase relationship under two-phase conditions.

In the numerical simulator, either (63) or (69) may be used to compute the three-phase NAPL relative permeability. The two-phase relative permeabilities may be calculated by a number of methods, although in most cases equations of the form of (60) are used.

Other Secondary Variables

Additional secondary variables include the porous medium thermal conductivity, gas phase multicomponent molecular diffusivities, and the porosity.

The thermal conductivity of the porous medium, λ, is a function of the rock grain thermal conductivity, λ_r, the water thermal conductivity, λ_w, the NAPL thermal conductivity, λ_n, the porosity and pore geometry, and the water and NAPL saturations. In general, λ is a complex function of these parameters, and researchers have developed theoretical [Walsh and Decker, 1966; Beck, 1976; Zimmerman, 1989] and empirical [Somerton, 1958; Sugawara and Yoshizawa, 1962; Somerton et al., 1973; 1974] methods for predicting λ. One method for estimating the overall thermal conductivity is known as the parallel model [Bejan, 1984]. With this model, the overall thermal conductivity is a combination of the individual conductivities

$$\lambda = \lambda_r (1 - \phi) + \lambda_w \phi S_w + \lambda_n \phi S_n \tag{70}$$

where λ_r is usually measured experimentally, λ_w is about 0.61 $W/m\ K$, and λ_n is calculated by the method of Sato and Riedel [Reid et al., 1987]

$$\lambda_n = \frac{(1.11/(M_{wt}^c)^{1/2})[3 + 20(1-T_r)^{2/3}]}{3 + 20(1 - T_{br})^{2/3}} \tag{71}$$

where T_r is the reduced temperature (T/T_{crit}), and T_{br} is the reduced NAPL boiling temperature (T_b/T_{crit}). The first term in (70) is usually several times larger than the second and third terms. Additionally, because the thermal conductivity of water is about four times larger than the thermal conductivity of most organic liquids, the last term in (70) is usually small compared to the second term.

The multicomponent diffusivities for water and chemical vapor in the gas phase are calculated from the three sets of binary diffusivities by the Wilke method [API, 1977]

$$D_g^w = \frac{1 - \chi_g^w}{\dfrac{\chi_g^a}{D_g^{aw}} + \dfrac{\chi_g^c}{D_g^{cw}}} \tag{72}$$

and

$$D_g^c = \frac{1 - \chi_g^c}{\dfrac{\chi_g^w}{D_g^{cw}} + \dfrac{\chi_g^a}{D_g^{ac}}} \tag{73}$$

where D_g^{aw} is the binary air-water vapor diffusivity, D_g^{cw} is the binary chemical-water vapor diffusivity, and D_g^{ac} is the binary air-chemical vapor diffusivity. Due to the condition specified by (12), it is not necessary to calculate the multicomponent air diffusivity, D_g^a. The binary air-water and air-chemical diffusivities are calculated as functions of temperature and pressure by [Vargaftik, 1975; Walker et al., 1981]

$$D_g^{ij} = D_g^{ijR}\left[\frac{P_R}{P_g}\right]\left[\frac{T}{T_R}\right]^{\theta_{ij}} \tag{74}$$

where D_g^{ijR} is the experimentally determined i-j binary diffusivity at a temperature of

T_R and a pressure of P_R, and θ_{ij} is an experimentally determined constant. For air-water diffusion, θ_{aw} has a value of 1.80 [Vargaftik, 1975]. For the diffusion of organic compounds in air, the value of θ_{ca} is typically about 1.6 [Vargaftik, 1975]. Because direct experimental data for the water-chemical vapor diffusivity are not usually available, the diffusivity is calculated using the Wilke and Lee empirical correlation [Reid et al., 1987]. Details of this method are given in Appendix B.

Changes in the porous medium porosity are calculated in response to pressure and temperature variations by assuming a constant pore compressibility, ε_P, and expansivity, ε_T. The porosity is then

$$\phi = \phi_R [1 + \varepsilon_P (P - P_R) + \varepsilon_T (T - T_R)] \tag{75}$$

where ϕ_R is the porosity at a reference pressure, P_R, and temperature, T_R.

NUMERICAL SOLUTION METHOD

The numerical solution method described in this section follows Pruess [1987; 1988] with extensions to account for a NAPL phase and a chemical component.

Discretized Equations

The mass and energy balance equations given by (1) are discretized in space using the integral finite difference method [Edwards, 1972; Narasimhan and Witherspoon, 1976]. For element l with a volume of V_l, the mass and energy accumulation terms in (1) are

$$\frac{d}{dt}\int_{V_l} M^K dV_l = \frac{d}{dt} V_l M_l^K \tag{76}$$

where M_l^K is the average value of M^K over the volume V_l. Similarly, the source term in (1) becomes

$$\int_{V_l} q^K dV_l = q_l^K V_l \tag{77}$$

The surface integrals in (1) are approximated as the sum of averages over discrete surface areas connecting element l with other elements m

$$\int_{\Gamma_l} \mathbf{F}^K \cdot \mathbf{n} d\Gamma_l = \sum_m A_{lm} F_{lm}^K \tag{78}$$

in which A_{lm} is the area of the interface between elements l and m, and F_{lm}^K is the flux of component K from element l to element m. Using a first order finite difference approximation in space for the gradients, the gas phase mass flux equations given by (9) are

$$F_{g,lm}^K = -k_{lm} \left[\frac{k_{rg} \rho_g}{\mu_g} \right]_{lm} (\omega_g^K)_{lm} \left[\frac{P_{g,l} - P_{g,m}}{d_{lm}} - \rho_{g,lm} g_{lm} \right] + J_{g,lm}^K \tag{79}$$

where d_{lm} is the distance between the centers of elements l and m. The quantity g_{lm} is the component of gravitational acceleration along nodal lines. The diffusive mass fluxes for water and chemical vapor are

$$J_{g,lm}^K = -(\phi S_g \tau_g D_g^K \rho_g)_{lm} \frac{\omega_{g,l}^K - \omega_{g,m}^K}{d_{lm}} \tag{80}$$

In (79) and (80), the subscript lm indicates that the quantity is evaluated at the interface between elements l and m. Different parameters require different interface weighting procedures. In order to avoid numerical stability problems, upstream weighting is used to evaluate phase mobilities, mass fractions, and enthalpies at

element interfaces. Other interface quantities are calculated using harmonic weighting or spatial interpolation.

The component mass fluxes in the water and NAPL phases given by (13) and (14) in discretized form are

$$F^K_{w,lm} = -k_{lm}\left[\frac{k_{rw}\rho_w}{\mu_w}\right]_{lm}(\omega^K_w)_{lm}\left[\frac{P_{w,l} - P_{w,m}}{d_{lm}} - \rho_{w,lm}g_{lm}\right] \tag{81}$$

$$F^K_{n,lm} = -k_{lm}\left[\frac{k_{rn}\rho_n}{\mu_n}\right]_{lm}(\omega^K_n)_{lm}\left[\frac{P_{n,l} - P_{n,m}}{d_{lm}} - \rho_{n,lm}g_{lm}\right] \tag{82}$$

The discretized form of the heat flux equation, (18), is

$$F^h_{lm} = -\lambda_{lm}\frac{T_l - T_m}{d_{lm}} + \sum_\beta h_{\beta,lm}F_{\beta,lm} \tag{83}$$

where $F_{\beta,lm}$ is the total β phase mass flux across the lm interface.

Time is discretized as a fully implicit first order finite difference. This ensures the numerical stability necessary for an efficient simulation of multiphase flow. The mass and energy balance equations given by (1) may be written in a discretized form in terms of the residual of each component in each element

$$R^{K(t+\Delta t)}_l \equiv M^{K(t+\Delta t)}_l - M^{K(t)}_l - \frac{\Delta t}{V_l}\left[\sum_m A_{lm}F^{K(t+\Delta t)}_{lm} + V_l q^{K(t+\Delta t)}_l\right] = 0 \tag{84}$$

$$K = air,\ water,\ chemical,\ heat$$

For a flow region discretized into N volume elements, (84) represents a system of $4N$ coupled non-linear algebraic equations. The unknowns in these equations are the $4N$ primary variables at the time level $t+\Delta t$.

Newton-Raphson Iteration

The non-linear balance equations given by (84) are linearized using a residual-based Newton-Raphson iterative technique. The Newton-Raphson technique is a very powerful technique which has been widely used for the solution of sets of non-linear equations. Given sufficiently accurate starting values for the unknowns, the method generally gives quadratic convergence to the solution [Burden et al., 1981]. Denoting the vector of primary variables in each element as **X**, (84) may be written as

$$\mathbf{R}(\mathbf{X}) = 0 \tag{85}$$

where **R** is the $4N$ vector of component residuals. Performing a Taylor series expansion of (85) about an assumed solution, $\mathbf{X}^{p+1}$, and neglecting the higher order terms results in

$$\mathbf{R}(\mathbf{X}^{p+1}) \simeq \mathbf{R}(\mathbf{X}^{p}) + \left[\frac{\partial \mathbf{R}(\mathbf{X})}{\partial \mathbf{X}}\right]^{p} (\mathbf{X}^{p+1} - \mathbf{X}^{p}) \tag{86}$$

where p is the iteration level. From the requirement that the residuals at the iteration index $p+1$ must vanish, (86) leads to the linearized matrix equation

$$\left[\left[\frac{\partial \mathbf{R}(\mathbf{X})}{\partial \mathbf{X}}\right]^{p}\right][\mathbf{X}^{p+1} - \mathbf{X}^{p}] = [-\mathbf{R}(\mathbf{X}^{p})] \tag{87}$$

Equation (87) represents a linear system of $4N$ simultaneous equations. These equations may be written in a more expanded matrix form as

$$\begin{bmatrix} \mathbf{Y}_{1,1} & \mathbf{Y}_{1,2} & \mathbf{Y}_{1,3} & \cdots & \mathbf{Y}_{1,N} \\ \mathbf{Y}_{2,1} & \mathbf{Y}_{2,2} & \mathbf{Y}_{2,3} & \cdots & \mathbf{Y}_{2,N} \\ \mathbf{Y}_{3,1} & \mathbf{Y}_{3,2} & \mathbf{Y}_{3,3} & \cdots & \mathbf{Y}_{3,N} \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \cdot & \cdot & \cdot & \cdots & \cdot \\ \mathbf{Y}_{N,1} & \mathbf{Y}_{N,2} & \mathbf{Y}_{N,3} & \cdots & \mathbf{Y}_{N,N} \end{bmatrix} \times \begin{bmatrix} \Delta\mathbf{X}_1 \\ \Delta\mathbf{X}_2 \\ \Delta\mathbf{X}_3 \\ \cdot \\ \cdot \\ \cdot \\ \Delta\mathbf{X}_N \end{bmatrix} = \begin{bmatrix} -\mathbf{R}_1 \\ -\mathbf{R}_2 \\ -\mathbf{R}_3 \\ \cdot \\ \cdot \\ \cdot \\ -\mathbf{R}_N \end{bmatrix} \tag{88}$$

where [**Y**] is the Jacobian matrix, [Δ**X**] is the vector of unknown changes in the primary variables in each element from the previous iteration, and [**R**] is the vector of residuals of each component in each element.

Each of the Jacobian matrix elements, **Y**, is actually a four-by-four submatrix. The diagonal terms ($\mathbf{Y}_{l,l}$) represent the partial derivatives of the residuals in an element with respect to the primary variables in that element. For an element, l, in which the primary variables are P, S_g, T, and S_w (three-phase gas-water-NAPL), the submatrix, $\mathbf{Y}_{l,l}$, is

$$\mathbf{Y}_{l,l} = \begin{bmatrix} \frac{\partial R_l^{w(t+\Delta t)}}{\partial P_l} & \frac{\partial R_l^{w(t+\Delta t)}}{\partial S_{g,l}} & \frac{\partial R_l^{w(t+\Delta t)}}{\partial T_l} & \frac{\partial R_l^{w(t+\Delta t)}}{\partial S_{w,l}} \\ \frac{\partial R_l^{a(t+\Delta t)}}{\partial P_l} & \frac{\partial R_l^{a(t+\Delta t)}}{\partial S_{g,l}} & \frac{\partial R_l^{a(t+\Delta t)}}{\partial T_l} & \frac{\partial R_l^{a(t+\Delta t)}}{\partial S_{w,l}} \\ \frac{\partial R_l^{c(t+\Delta t)}}{\partial P_l} & \frac{\partial R_l^{c(t+\Delta t)}}{\partial S_{g,l}} & \frac{\partial R_l^{c(t+\Delta t)}}{\partial T_l} & \frac{\partial R_l^{c(t+\Delta t)}}{\partial S_{w,l}} \\ \frac{\partial R_l^{h(t+\Delta t)}}{\partial P_l} & \frac{\partial R_l^{h(t+\Delta t)}}{\partial S_{g,l}} & \frac{\partial R_l^{h(t+\Delta t)}}{\partial T_l} & \frac{\partial R_l^{h(t+\Delta t)}}{\partial S_{w,l}} \end{bmatrix} \tag{89}$$

The partial derivatives in (89) are calculated numerically by successively incrementing each of the primary variables. As each primary variable is incremented, all of the secondary variables (see Table 2) are recalculated. These are used in

conjunction with the incremented primary variable to calculate a new value of $R_l^{K(t+\Delta t)}$. The partial derivative is then calculated by subtracting the original value of $R_l^{K(t+\Delta t)}$ from the incremented value, and dividing by the amount of the primary variable increment.

The off-diagonal submatrices in the Jacobian matrix, $\mathbf{Y}_{l,m}$ contain the partial derivatives of the residuals in element l with respect to the primary variables in element m. If the primary variables in element m are P, T, χ_g^c, and S_w (two-phase gas-water), then submatrix $\mathbf{Y}_{l,m}$ is

$$\mathbf{Y}_{l,m} = \begin{bmatrix} \frac{\partial R_l^{w(t+\Delta t)}}{\partial P_m} & \frac{\partial R_l^{w(t+\Delta t)}}{\partial T_m} & \frac{\partial R_l^{w(t+\Delta t)}}{\partial \chi_{g,m}^c} & \frac{\partial R_l^{w(t+\Delta t)}}{\partial S_{w,m}} \\ \frac{\partial R_l^{a(t+\Delta t)}}{\partial P_m} & \frac{\partial R_l^{a(t+\Delta t)}}{\partial T_m} & \frac{\partial R_l^{a(t+\Delta t)}}{\partial \chi_{g,m}^c} & \frac{\partial R_l^{a(t+\Delta t)}}{\partial S_{w,m}} \\ \frac{\partial R_l^{c(t+\Delta t)}}{\partial P_m} & \frac{\partial R_l^{c(t+\Delta t)}}{\partial T_m} & \frac{\partial R_l^{c(t+\Delta t)}}{\partial \chi_{g,m}^c} & \frac{\partial R_l^{c(t+\Delta t)}}{\partial S_{w,m}} \\ \frac{\partial R_l^{h(t+\Delta t)}}{\partial P_m} & \frac{\partial R_l^{h(t+\Delta t)}}{\partial T_m} & \frac{\partial R_l^{h(t+\Delta t)}}{\partial \chi_{g,m}^c} & \frac{\partial R_l^{h(t+\Delta t)}}{\partial S_{w,m}} \end{bmatrix} \tag{90}$$

Naturally, if element l is not connected to element m, all of the partial derivatives in (90) will be equal to zero. For this reason, the Jacobian matrix tends to have a sparse structure with large areas of zeros.

The partial derivatives in (90) are calculated in a manner similar to those in (89). In succession, each of the primary variables in element m is incremented by a small amount. The secondary variables in element m are recomputed and used with the incremented primary variable in m, along with the original primary and secondary variables in l to calculate a new $R_l^{K(t+\Delta t)}$. The value of $R_l^{K(t+\Delta t)}$ calculated

using the non-incremented primary variables in l and m is subtracted from the new value, and the difference is divided by the amount of the increment in the primary variable in m to obtain the partial derivative. All of the partial derivatives in (89) and (90) are evaluated at iteration level p.

The vector of unknown changes in the primary variables in (88) consists of N groups of four-component vectors. For an element, l, in which the primary variables are P, S_g, T, and S_w, $\Delta\mathbf{X}_l$ in (88) is

$$\Delta\mathbf{X}_l = \begin{bmatrix} P_l^{p+1} - P_l^p \\ S_{g,l}^{p+1} - S_{g,l}^p \\ T_l^{p+1} - T_l^p \\ S_{w,l}^{p+1} - S_{w,l}^p \end{bmatrix} \tag{91}$$

The vector of residuals in (88) also consists of N groups of four component vectors. For element l, $-\mathbf{R}_l$ in (88) is

$$-\mathbf{R}_l = \begin{bmatrix} -R_l^{w(t+\Delta t)}(\mathbf{X}^p) \\ -R_l^{a(t+\Delta t)}(\mathbf{X}^p) \\ -R_l^{c(t+\Delta t)}(\mathbf{X}^p) \\ -R_l^{h(t+\Delta t)}(\mathbf{X}^p) \end{bmatrix} \tag{92}$$

In (92), each of the residuals is evaluated at iteration level p.

At the beginning of each time step, the converged values of $\mathbf{X}$ from the previous time step are used as the initial solution for the first iteration. The system of simultaneous equations is solved with a direct solver which uses sparse storage techniques, and only stores the non-zero members of the Jacobian matrix. This solver, known as MA28, performs a sparse version of LU-decomposition with partial

pivoting and back substitution [Duff, 1977]. Iteration is continued until all residuals are reduced to a small fraction of the accumulation terms.

$$\left[\frac{\mathbf{R}_l^{K(t+\Delta t)}(\mathbf{X}^{p+1})}{M_l^{K(t+\Delta t)}(\mathbf{X}^{p+1})}\right] \leq \varepsilon_1 \tag{93}$$

In most cases, the relative convergence criterion, ε_1 is chosen to be on the order of 10^{-5}.

The initial time step size, Δt is chosen by the user. If during a time step convergence does not occur within a specified number of iterations (the default is 8), the time step size is reduced by a factor of four, and a new iteration process is started. Any failure in solving the linear equations or in computing the secondary variables will also result in an automatic reduction of the time step size, and the start of a new iterative process. If convergence occurs in less than a specified number of iterations (usually 4 or 5), the next time step size is automatically doubled. At the end of a simulation, a disk file called SAVE is written. This file contains the values of all primary variables in all elements, and may be used as initial conditions for a continuation run.

Incorporation of Source Terms and Initial and Boundary Conditions

Several options are available in the STMVOC simulator for specifying the injection or production of fluids and heat. For the injection of fluids, any of the three mass components (air, water, chemical) may be injected in an element at a constant or time-dependent rate. Alternately, a total gas or aqueous phase mass

injection rate may be specified in which the injected phase composition (water and air components only) is given by the user. The specific enthalpy of the injected fluid is input by the user as either a constant or time-dependent value. Heat sources/sinks (with no mass injection) may be either constant or time-dependent.

Fluid production from an element is handled using one of two options. With the first option, the total mass rate of production is given as a constant or time-dependent value. In this case, the phase composition of the produced fluids may be determined by the relative phase mobilities in the source element. Alternately, the produced phase composition may be specified to be the same as the phase composition in the producing element. In either case, the mass fraction of each component in each of the produced phases is determined by the component mass fractions in each phase in the producing element.

The second production option is a well deliverability model in which production occurs against a prescribed flowing wellbore pressure, P_{wb}, with a productivity index PI [Coats, 1977; Aziz et al., 1987]. With this option, the mass production rate of phase β is

$$q_\beta = \frac{k_{r\beta}}{\mu_\beta}\rho_\beta \cdot PI \cdot (P_\beta - P_{wb}) \tag{94}$$

and the rate at which each mass component ($K \neq h$) is removed is

$$q^K = \sum_\beta \omega_\beta^K q_\beta \tag{95}$$

For wells which are screened in more than one layer (element), the flowing wellbore pressure is approximately corrected for gravity effects according to the depth-

dependent flowing density in the wellbore. Further details of this method are given by Pruess [1987].

During fluid production or injection, the rate of heat removal or injection is determined by

$$q^h = \sum_\beta q_\beta h_\beta \tag{96}$$

where h_β is the specific enthalpy of phase β.

The initial conditions for a simulation are introduced by specifying the values of the four primary variables in all volume elements. As discussed earlier, the choice of these primary variables depends on the phase conditions in a given element. In many instances, it is convenient to use the results of an earlier simulation as the initial conditions for a later simulation. This feature is particularly useful for simulations in which the initial conditions consist of a steady-state flow field, or static equilibrium.

Boundary conditions are normally applied through the use of appropriately chosen volume elements, node to interface distances, and source/sink terms. Boundary conditions of the "no flow" type are applied by simply not including any elements beyond the "no flow" boundary. Specified flux boundary conditions (Neumann) are maintained by means of source/sink terms in elements adjacent to the boundary on the outside of the flow region. Boundary conditions in which the primary variables are constant (Dirichlet) are specified by introducing boundary elements having a very large volume. In this case, the nodal distance from the boundary element to the boundary is given a very small value. Specifying a very large

volume for the boundary element ensures that the primary variables at the boundary will not change during the course of the simulation. Several other types of boundary conditions are made possible by assigning special values of certain parameters such as capillary pressures, relative permeabilities, or heat capacity to the boundary elements. In the assembly and solution of the linear equations, (87), boundary elements are not distinguished from other elements, and no special numerical treatment is required.

CONCLUSIONS

A numerical simulator, STMVOC, has been developed for modeling nonisothermal three phase contaminant transport. This code is based on an existing integral finite difference formulation for multiphase heat and mass transport known as MULKOM [Pruess, 1983; 1988]. The STMVOC code has been specifically designed for simulating steam injection for the removal of NAPLs from shallow subsurface formations. Using a general equation of state to calculate the properties of a NAPL/chemical under various thermodynamic conditions, the simulator models three phase flow and chemical transport with equilibrium interphase mass transfer between phases.

APPENDIX A. VISCOSITY OF A PURE GAS

The chemical vapor viscosity (μ_g^c) in (31) is computed from the corresponding states method [Reid et al., 1987]

$$\mu_g^c = \frac{0.606 T_r F_p^o}{0.176\left[\dfrac{T_{crit}}{(M_{wt}^c)^3 (P_{crit})^4}\right]^{1/6}} \tag{A1}$$

where T_r is the reduced temperature equal to T/T_{crit}, and μ_g^c has units of centipoise. The value of the polarity correction factor, F_p^o, depends on the value of the reduced dipole moment of the chemical

$$\eta_{dr} = 52.46 \frac{(\eta_d)^2 P_{crit}}{(T_{crit})^2} \tag{A2}$$

in which η_d is the dipole moment of the chemical. The polarity correction factor is then

$$F_p^o = 1 \qquad 0 \le \eta_{dr} < 0.022 \tag{A3}$$

$$F_p^o = 1 + 30.55(0.292 - Z_{crit})^{1.72} \qquad 0.022 \le \eta_{dr} < 0.075$$

$$F_p^o = 1 + 30.55(0.292 - Z_{crit})^{1.72} |0.96 + 0.1(T_r - 0.7)| \qquad \eta_{dr} \ge 0.075$$

where Z_{crit} is the critical compressibility factor.

APPENDIX B. CALCULATION OF BINARY GAS DIFFUSIVITIES

If direct experimental data for the binary gas diffusivity of two chemicals are not available, the diffusivity may be estimated by using the Wilke and Lee empirical correlation [Reid et al., 1987]. Considering a binary system containing water and chemical vapor

$$D_g^{cw} = \frac{100[3.03 - (0.98/(M_{wt}^{cw})^{1/2})] T^{3/2}}{P (M_{wt}^{cw})^{1/2} \sigma_{cw}^2 \Omega_d} \tag{B1}$$

where

$$M_{wt}^{cw} = \frac{2}{1/M_{wt}^{c} + 1/M_{wt}^{w}} \tag{B2}$$

The scale parameter, σ_{cw}, may be computed as

$$\sigma_{cw} = \frac{1.18(.285(V_{crit}^{c})^{1.048})^{1/3} + 1.18(.285(V_{crit}^{w})^{1.048})^{1/3}}{2} \tag{B3}$$

while the diffusion collision integral, Ω_d may be accurately calculated from

$$\Omega_d = \frac{A}{(T^*)^B} + \frac{C}{exp\,(DT^*)} + \frac{E}{exp\,(FT^*)} + \frac{G}{exp\,(HT^*)} \tag{B4}$$

where

$$T^* = \frac{T}{\left[(1.15T_b)(1.15T_b^w)\right]^{1/2}} \tag{B5}$$

In (B3), V_{crit}^{c} is the critical molar volume of the chemical and V_{crit}^{w} is the critical molar volume of water. In (B5), T_b is the boiling temperature of the chemical, T_b^w is the boiling point of water, A=1.06036, B=0.15610, C=0.19300, D=0.47635, E=1.03587, F=1.52996, G=1.76474, and H=3.89411. The diffusivity calculated by this method is usually within ten percent of the experimental value [Reid et al., 1987].

NOTATION

A_{lm} area of the interface between elements l and m, m^2.

C_{pn} NAPL heat capacity, $J/kg\ K$.

C_{pn}^{o} ideal gas molar heat capacity for chemical, $J/mole\ K$.

C_R soil grain heat capacity, $J/kg\ K$.

C_{va} air heat capacity at constant volume, $J/kg\ K$.

C_s^c concentration of chemical in the solid phase, kg/m^3.

C_β^K concentration of mass component K in phase β, kg/m^3.

$\bar{C}_g^c$ saturated chemical vapor concentration, kg/m^3.

$\hat{C}_g^c$ pseudo saturated vapor concentration, kg/m^3.

d_{lm} distance between the centers of elements l and m, m.

D_g^K molecular diffusivity of mass component K in a multicomponent gas, m^2/s.

D_g^{ij} binary i-j mixture molecular gas diffusivity, m^2/s.

D_g^{ijR} reference binary i-j mixture molecular gas diffusivity, m^2/s.

$\mathbf{F}^K$ total flux of component K; for $K \neq h$: kg/m^2s; for $K=h$: J/m^2s.

$\mathbf{F}_\beta$ total mass flux in the β phase, kg/m^2s.

$\mathbf{F}_\beta^K$ flux of component K in the β phase; for $K \neq h$: kg/m^2s; for $K=h$: J/m^2s.

F_p^o polarity correction factor for pure vapor viscosity calculation.

f_{oc} fraction of organic carbon in the soil.

g_{lm} component of gravitational acceleration along the nodal line connecting elements l and m, m/s^2.

$\mathbf{g}$ gravitational acceleration vector, m/s^2.

h specific enthalpy, J/kg.

h_β specific enthalpy of phase β, J/kg.

h_g^K specific enthalpy of mass component K in the gas phase, J/kg.

h_{vap}^c chemical latent heat of vaporization, J/kg.

$h_{vap,b}^c$ chemical latent heat of vaporization at the normal boiling point, J/kg.

H_{gw}^K Henry's constant for gas-water partitioning of mass component K, Pa.

H_{gn}^K Henry's constant for gas-NAPL partitioning of mass component K, Pa.

$\mathbf{J}_g^K$ diffusive mass flux of component K in the gas phase, kg/m^2s.

K component index, K = a: air; w: water; c: chemical; h: heat.

K_D chemical-solid distribution coefficient, m^3/kg.

K_{oc} chemical-organic carbon partition coefficient, m^3/kg.

k porous media permeability, m^2.

$k_{r\beta}$ relative permeability of the β phase.

k_{rncw} NAPL relative permeability in the presence of an irreducible water saturation.

k_{rnw} NAPL relative permeability in a two phase NAPL-water system.

k_{rng} NAPL relative permeability in a two phase NAPL-gas system.

M_{wt}^{aw} mixture molecular weight of air and water vapor, $g/mole$.

M_{wt}^K molecular weight of mass component K, $g/mole$.

M_{wt}^{cw} defined in (B.2).

M^K amount of component K per unit porous medium volume; for $K \neq h$: kg/m^3; for $K=h$: J/m^3.

M_β mass of the β phase per unit porous medium volume, kg/m^3.

n outward unit normal vector.

N number of elements.

P pressure, Pa.

P_β pressure in the β phase, Pa.

P_{cgw} gas-water capillary pressure, Pa.

P_{cgn} gas-NAPL capillary pressure, Pa.

P_{cnw} NAPL-water capillary pressure, Pa.

P_{wb} wellbore pressure, Pa.

P_{crit} critical pressure, Pa

P_R reference pressure, Pa.

P_g^K partial pressure of mass component K in the gas phase, Pa.

P_{sat}^c saturated NAPL vapor pressure, Pa.

P_{sat}^w saturated water vapor pressure, Pa.

PI productivity index, m^3.

q^K rate of generation of component K per unit volume; for $K \neq h$: kg/m^3s; for $K=h$: J/m^3s.

q_β mass rate of generation of phase β in a source element, kg/s.

q^K rate of generation of component K in a source element; for $K \neq h$: kg/s; for $K=h$: J/s.

$R_l^{K(t+\Delta t)}$ residual of component K in element l at time level $t+\Delta t$; for $K \neq h$: kg/m^3; for $K=h$: J/m^3.

$\mathbf{R}$ vector of component residuals.

R universal gas constant, $mJ/mole\ K$.

R_g chemical gas phase retardation coefficient.

S_β β phase saturation.

$S_{\beta r}$ residual β phase saturation.

S_m empirical constant used in the calculation of capillary pressures.

S_g^* scaled gas phase saturation defined in (68).

S_n^* scaled NAPL saturation defined in (66).

S_w^* scaled water phase saturation defined in (67).

t time, s.

T temperature, K.

T_b chemical normal boiling temperature, K.

T_{br} chemical reduced boiling temperature.

T_b^w water normal boiling temperature, K.

T_{crit} critical temperature, K.

T_r reduced temperature.

T_{rR} reduced reference temperature.

T_R reference temperature, K.

T_{ref} temperature at which enthalpy is zero, K.

T^* defined by (B.5).

u specific internal energy, J/kg.

u_β specific internal energy of the β phase, J/kg.

u_g^K specific internal energy of mass component K in the gas phase, J/kg.

V_l volume of region l of porous medium, m^3.

V_{crit}^K critical molar volume for mass component K, $cm^3/mole$.

$\mathbf{X}$ vector of primary variables.

$\mathbf{Y}_{ll}$ diagonal submatrix of the Jacobian matrix.

$\mathbf{Y}_{lm}$ off-diagonal submatrix of the Jacobian matrix.

Z_{crit} critical compressibility.

Z_{RA} defined in (34).

α_{gn} constant used in the calculation of the gas-NAPL capillary pressure, $1/m$.

α_{gw} constant used in the calculation of the gas-water capillary pressure, $1/m$.

α_{nw} constant used in the calculation of the NAPL-water capillary pressure, $1/m$.

β phase index, β = g: gas phase; w: water phase; n: NAPL.

β_g defined in (65).

β_w defined in (64).

χ_β^K mole fraction of mass component K in the β phase.

χ_g^{aw} sum of air and water vapor mole fractions.

$\bar{\chi}_g^c$ saturated mole fraction of chemical vapor in the gas phase.

$\bar{\chi}_w^c$ chemical solubility in water (mole fraction).

Γ_l surface area, m^2.

Δt time step size, s.

$\Delta \mathbf{X}_l$ vector of unknown primary variable changes for element l.

ε_1 relative convergence criterion.

ε_P pore compressibility, $1/Pa$.

ε_T matrix expansivity, $1/K$.

η_d dipole moment, *debyes*.

η_{dr} reduced dipole moment.

λ overall porous media thermal conductivity, $W/m\ K$.

λ_n NAPL thermal conductivity, $W/m\ K$.

λ_r rock grain thermal conductivity, $W/m\ K$.

λ_w liquid water thermal conductivity, $W/m\ K$.

μ_β β phase viscosity, kg/ms.

μ_{nR} reference NAPL viscosity, kg/ms.

μ_g^{aw} air-water vapor viscosity, kg/ms.

μ_g^c chemical vapor viscosity, kg/ms.

ρ density, kg/m^3.

ρ_β density of the β phase, kg/m^3.

ρ_b soil dry bulk density, kg/m^3.

ρ_{nsR} reference NAPL density, kg/m^3.

ρ_R soil grain density, kg/m^3.

σ_{ij} scale parameter defined in (B.3).

τ_g gas phase tortuosity.

θ_{ij} exponent for variation of D_g^{ij} with temperature.

ϕ porosity.

ϕ_R reference porosity.

$\Phi_{aw,c}$ interaction parameter.

$\Phi_{c,aw}$ interaction parameter.

ω Pitzer's acentric factor.

ω_β^K mass fraction of mass component K in the β phase.

Ω_d diffusion collision integral.

ACKNOWLEDGEMENTS

This work was supported in part by the Director, Office of Energy Research, Office of Basic Energy Sciences, Engineering and Geosciences Division of the U.S. Department of Energy, and in part pursuant to Interagency Agreement DW89931336-01-07 between the U.S. Environmental Protection Agency and the

U.S. Department of Energy under contract DE-AC03-76SF00098. The authors would like to thank C. H. Lai, H. W. Dorgarten, and C. F. Tsang for reviewing this manuscript.

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Table 1. Components and Phases

Components	Phases
air	gas
water	aqueous
organic chemical	NAPL
heat	

Table 2. Secondary Variables and Functional Dependence

Parameter	Phase		
	gas	aqueous	NAPL
Saturation	$S_g(S_w)$	-	$S_n(S_g,S_w)$
Relative Permeability	$k_{rg}(S_g,S_w)$	$k_{rw}(S_w)$	$k_{rn}(S_g,S_w)$
Viscosity	$\mu_g(P,\chi_g^c,T)$	$\mu_w(P,T)$	$\mu_n(T)$
Density	$\rho_g(P,\chi_g^c,T)$	$\rho_w(P,T)$	$\rho_n(P,T)$
Specific Enthalpy	$h_g(P,\chi_g^c,T)$	$h_w(P,T)$	$h_n(P,T)$
Capillary Pressure	-	$P_{cgw}(S_g,S_w)$	$P_{cgn}(S_g,S_w)$
Air Mass Fraction	$\omega_g^a(P,\chi_g^c,T)$	$\omega_w^a(P,\chi_g^c,T)$	$\omega_n^a(P,\chi_g^c,T)$
Water Mass Fraction	$\omega_g^w(P,\chi_g^c,T)$	$\omega_w^w(P,\chi_g^c,T)$	$\omega_n^w(P,\chi_g^c,T)$
Chemical Mass Fraction	$\omega_g^c(P,\chi_g^c,T)$	$\omega_w^c(P,\chi_g^c,T)$	$\omega_n^c(P,\chi_g^c,T)$
Water Molecular Diffusivity	$D_g^w(P,\chi_g^c,T)$	-	-
Chemical Molecular Diffusivity	$D_g^c(P,\chi_g^c,T)$	-	-
Tortuosity	$\tau_g(S_g,S_w)$	-	-
Chemical Henry's Constant	$H_{gw}^c(T)$		
Thermal Conductivity	$\lambda(S_g,S_w,T)$		

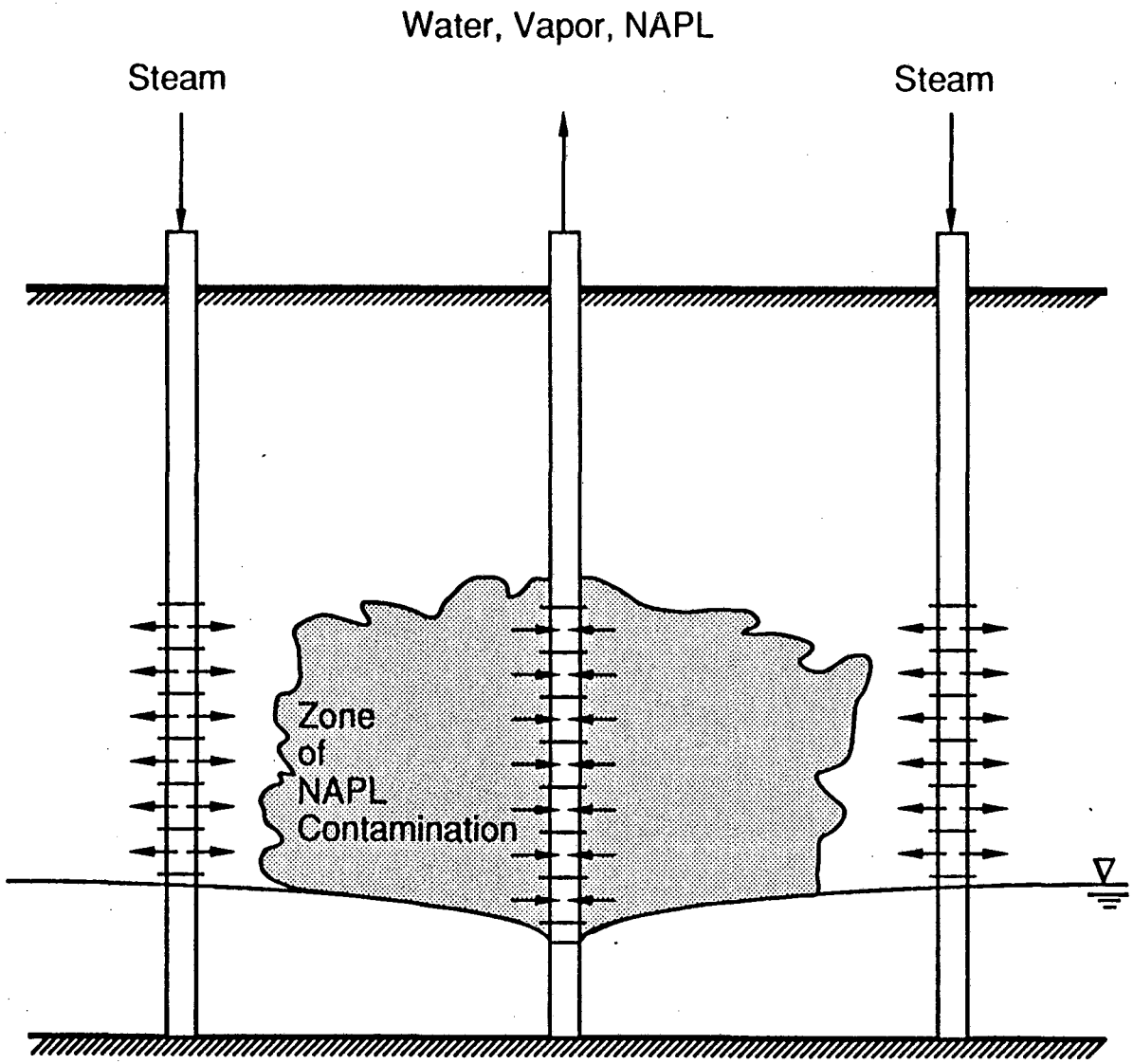

Figure 1. Diagram of a possible steam injection remediation system.

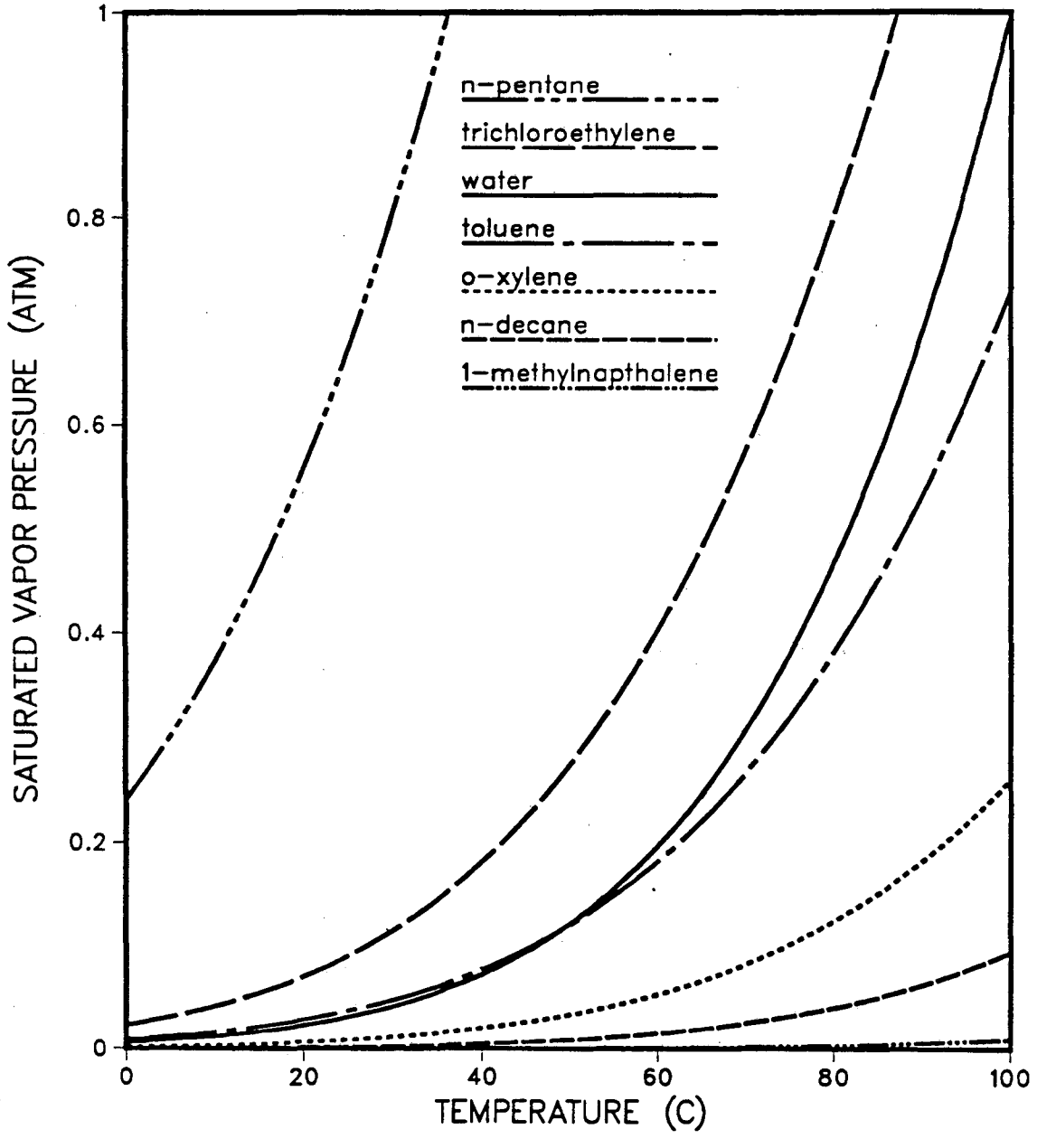

Figure 2. Variation of saturated vapor pressure with temperature.

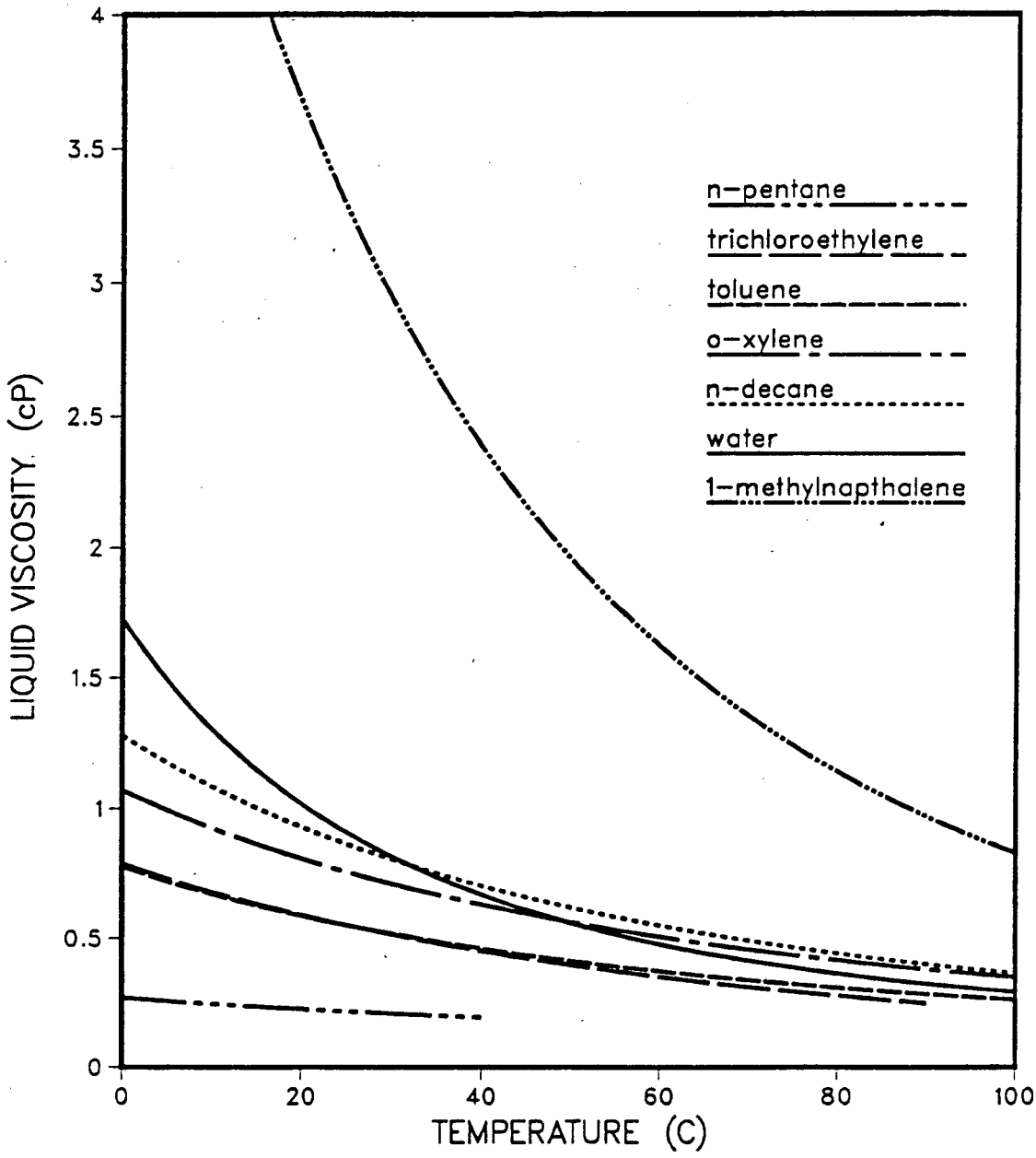

Figure 3. Variation of liquid viscosity with temperature (1cP = $10^{-3} Pa \cdot s$).

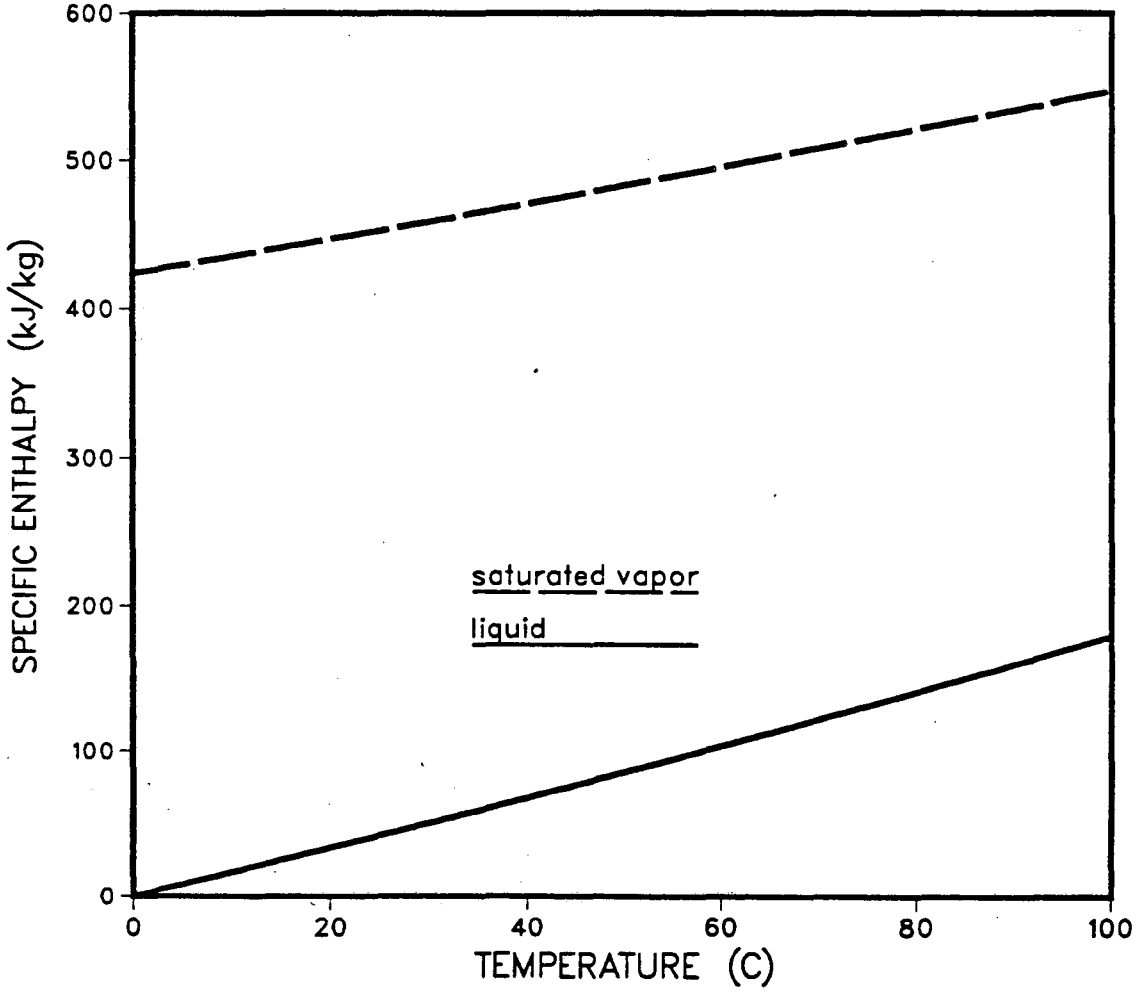

Figure 4. Variation of toluene specific enthalpy with temperature.

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