

Appendix A
Thermodynamics Basics

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Thermodynamics Basics

A.1 Gibbs Free Energy and Chemical Potential

A solution to phase equilibrium thermodynamics was first described by Gibbs when he introduced the abstract concept of chemical potential (μ_i). As the name “potential” suggests, μ_i is an indicator of the potential of one molecule to move from one state to another (e.g., movement from one phase to another). The goal of phase equilibrium thermodynamics is to relate the concept of chemical potential of matter to physically measurable quantities, such as temperature, pressure, and composition (Prausnitz, Litchenthaler, and Azevedo 1985). The difficulty in working with chemical potential is that its components all depend on one another. Changes in chemical potential are calculated on arbitrary changes of the independent variables (e.g., temperature, pressure, and composition).

In order to be consistent with calculating these changes, the concept of a standard state must be introduced. A standard state is a particular state of species temperature at specified conditions of pressure, composition, and physical state. In thermodynamics, the standard state of 1 atm and 25°C is used (Smith, VanNess, and Abbott 1996). The standard state properties of specific compounds are marked by the superscript.

The concept of Gibbs free energy must be understood in order to mathematically explain the concept of phase equilibrium. Gibbs free energy is defined as the available energy within a bounded system. The fundamental equation of Gibbs free energy for a one-component system is shown in Equation A-1 (Prausnitz, Litchenthaler, and Azevedo 1985):

$$dG = -SdT + VdP \quad . \quad (A-1)$$

This equation states that a change in Gibbs free energy is a function of temperature and pressure ($G = f(T,P)$). For a single homogeneous phase composed of several components, the equation must be modified to reflect the fact that a change in the number of moles in the system will also change the Gibbs free energy of the system by making the following substitutions for V and $-S$. The equation becomes a partial differential equations (shown in Equations A-2 and A-3) (Valsaraj 1995):

$$V = \left(\frac{\partial G}{\partial P} \right)_{T, n_i} \quad (A-2)$$

$$-S = \left(\frac{\partial G}{\partial T} \right)_{p, n_i} \quad (A-3)$$

These relationships are derived from the basic laws of thermodynamics. A third term is added to the equation to account for changes in mass (moles) within a system (shown in Equation A-4) (Valsaraj 1995):

$$dG \equiv \left(\frac{\partial G}{\partial p} \right)_{T, n_i} dP + \left(\frac{\partial G}{\partial T} \right)_{p, n_i} dT + \sum_i \left(\frac{\partial G}{\partial n_i} \right)_{p, T, n_j} dn_i \quad . \quad (A-4)$$

The third partial differential on the right is commonly known as the chemical potential and is given the symbol, μ_i . Considering this new term, Gibbs energy is also a function of mass (in moles) of each species present in the system. According to Equation A-4, at constant pressure and temperature, chemical potential becomes a function of chemical composition. In other words, the partial molar Gibbs free energy is also a function of the chemical composition (Valsaraj 1995).

When the chemical potential of a molecule is equal in phases α and β , the system is said to be in equilibrium (shown in Equation A-5) (Smith, VanNess, and Abbott 1996):

$$\mu_i^\alpha = \mu_i^\beta \quad (A-5)$$

where

i = species of interest in the two phases.

Hence, $\Delta G = 0$. If the chemical potential is greater in state α than in state β , then a net transfer of species i to state β occurs until equilibrium is reached. It is important to remember that the equilibrium can be altered by temperature, pressure, and change in the mass (moles) of a compound.

A.2 Fugacity

Chemical potential is a difficult term to quantify, or, in other words, it “does not have an immediate equivalent in the physical world” (Prausnitz, Litchenthaler, and Azevedo 1985). Therefore, it is necessary to express the chemical potential in terms of some other function that can be more easily identified. This was accomplished by considering the chemical potential for a pure, ideal gas and then deriving Equation A-6 for isothermal changes (Prausnitz, Litchenthaler, and Azevedo 1985):

$$\mu_i - \mu_i^\circ = RT \ln \frac{P}{P^\circ} \quad (A-6)$$

This equation states that for an ideal gas, the change in chemical potential, in isothermally going from pressure P° to pressure P , is equal to the product of RT and the logarithm of the pressure ratio P/P° . Further analysis will reveal that this equation is actually derived from Equation A-1 by substituting in the ideal gas for V and integrating with respect to P . At constant temperature, the term including dT drops out in the integration. Hence, at constant temperature, the change in the abstract quantity of chemical potential is a simple logarithmic function of a physical quantity or pressure. The value of such an equation is that a simple mathematical expression has been used to define chemical potential; however, this works only for pure, ideal gases.

In the real world, intermolecular forces lead to nonidealities in the P/P° relationship. To define this nonideality, Lewis defined a new variable, f , called fugacity, by writing Equation A-7 for an isothermal change for any component in any system, whether it was solid, liquid, or gas; pure or mixed; or ideal or not (Prausnitz, Litchenthaler, and Azevedo 1985):

$$\mu_i - \mu_i^\circ = RT \ln \frac{f_i}{f_i^\circ} \quad (A-7)$$

where

f_i = fugacity at a specified state

f_i° = standard state fugacity.

Neither fugacity nor chemical potential may be chosen independent of one another; when one is chosen, the other is fixed.

For a pure, ideal gas, the fugacity is equal to the pressure, and for a component i in a mixture of ideal gases, it is equal to its partial pressure, $y_i P$, where y_i is the gas phase mole fraction. Since all pure systems approach ideal-gas behavior at very low pressures (ambient pressures are considered to be low pressure), the definition of fugacity is completed by Equation A-8 (Prausnitz, Litchenthaler, and Azevedo 1985):

$$f_i/y_i P \rightarrow 0 \text{ as } P \rightarrow 0 \quad . \quad (\text{A-8})$$

Lewis called the ratio f/f° the “activity,” designated by the symbol a (not to be mistaken for activity coefficient). The activity of a substance gives an indication of how active a substance is relative to its standard state since it provides a measure of the difference between the substance’s chemical potential at the state of interest and its standard state during an isothermal change.

Since fugacity has been defined in terms of chemical potential, the fugacities in phases at equilibrium must be equal (shown in Equation A-9) (Prausnitz, Litchenthaler, and Azevedo 1985):

$$f_i^\alpha = f_i^\beta \quad . \quad (\text{A-9})$$

This equation is a more convenient method in equating chemical potentials. It states that fugacity (viewed also as escapability) must be equal in each phase for a system to reach equilibrium. In terms of vapor-liquid equilibria, Equation A-10 is stated as (Prausnitz, Litchenthaler, and Azevedo 1985):

$$f_i^V = f_i^L \quad . \quad (\text{A-10})$$

This expression simply restates that, at equilibrium, the chemical potential in each phase must be equal in terms of fugacity (escapability).

Another term that requires definition is the fugacity coefficient (ϕ) (shown in Equation A-11) (Smith, VanNess, and Abbott 1996):

$$\phi_i = \frac{f_i}{Y_i P} \quad (\text{A-11})$$

where

y_i = vapor mole fraction

P = system pressure.

A.3 Vapor-Liquid Equilibrium

With fugacity defined, the definition of an activity coefficient is expressed as Equation A-12 (Smith, VanNess, and Abbott 1996):

$$\gamma_i \equiv \frac{f_i}{x_i f_i^o} \quad . \quad (\text{A-12})$$

The activity coefficient is a function of the defined state fugacity divided by the standard state fugacity and liquid mole fraction. This expression is derived from nonideal properties of liquids and is similar to that of how activity is derived when discussing the nonidealities of gases. In other words, the value of the activity coefficient would be one in an ideal liquid. Equation A-13 is redefined in terms of fugacity of a liquid (Smith, VanNess, and Abbott 1996):

$$f_i^L = x_i \gamma_i f_i^o \quad . \quad (\text{A-13})$$

The last term in the equation, the standard state value of fugacity, is a derived expression given by Equation A-14:

$$f_i^o = f_i^{L,pure} \exp \left[\int_{P_{sat}}^P \frac{V_i}{RT} \right] \quad . \quad (\text{A-14})$$

At high pressures, the term in the brackets approaches zero (this can be mathematically proven through integration). Therefore, at ambient pressures (1 atm), the exponent has a value of one and is left out of the equation ($e^0 = 1$). With the pure-component fugacity, the first term on the right is defined in Equation A-15 (Smith, VanNess, and Abbott 1996):

$$f_i^{L,pure} = \phi_i^{sat} P^{sat} \quad . \quad (\text{A-15})$$

where

$$\phi_i^{sat} = f_i^{sat} / P_i^{sat} \quad .$$

This equation is substituted into the liquid fugacity equation and is now written as Equation A-16 (Smith, VanNess, and Abbott 1996):

$$f_i^L = x_i \gamma_i \phi_i^{sat} P_i^{sat} \quad . \quad (\text{A-16})$$

This equation is now redefined in terms of fugacity of a vapor (shown in Equation A-17) (Prausnitz, Litchenthaler, and Azevedo 1985):

$$f_{i,v} = \phi_i y_i P \quad . \quad (\text{A-17})$$

There are now two equations defining vapor- and liquid-phase fugacity. When discussing vapor-liquid equilibria, the fugacities must be set equal according to Equation A-18 (Smith, VanNess, and Abbott 1996):

$$y_i \phi_i P = x_i \gamma_i \phi_i^{\text{sat}} P_i^{\text{sat}} \quad (\text{A-18})$$

In low-pressure system, the fugacity coefficient approaches unity and can be left out of the equation. Under these conditions, the vapor-liquid equilibrium can be expressed as Equation A-19 (Smith, VanNess, and Abbott 1996):

$$y_i P = x_i \gamma_i P_i^{\text{sat}} \quad (\text{A-19})$$

(Note that Raoult's Law is a simplification of the vapor-liquid equilibrium equation with $\gamma_i = 1$.)

In attempting to describe activity coefficients, Figure A-1 will be analyzed in terms of activity. The figure gives total and partial pressure as a function of liquid composition. At the far left of the figure, the fraction of component x_A is at zero, in other words, pure B component. At this point, the indicated pressure is the pure-component vapor pressure of the B component. On the right side of the figure, the mole fraction of one indicates pure A component. This point is the pure-component vapor pressure of the A component.

In ideal mixes where no interactions occur, the total pressure curve is a straight line from one pure component to the other ($\gamma_i = 1$). This is Raoult's Law behavior; however, chemical interactions lead to deviations from the ideal state. In the case of high activity ($\gamma_i > 1$), the total pressure is higher than the Raoult's Law line because of this increased activity or escaping potential. In the case of low activity ($\gamma_i < 1$), the liquid interaction leads to a lower total pressure.

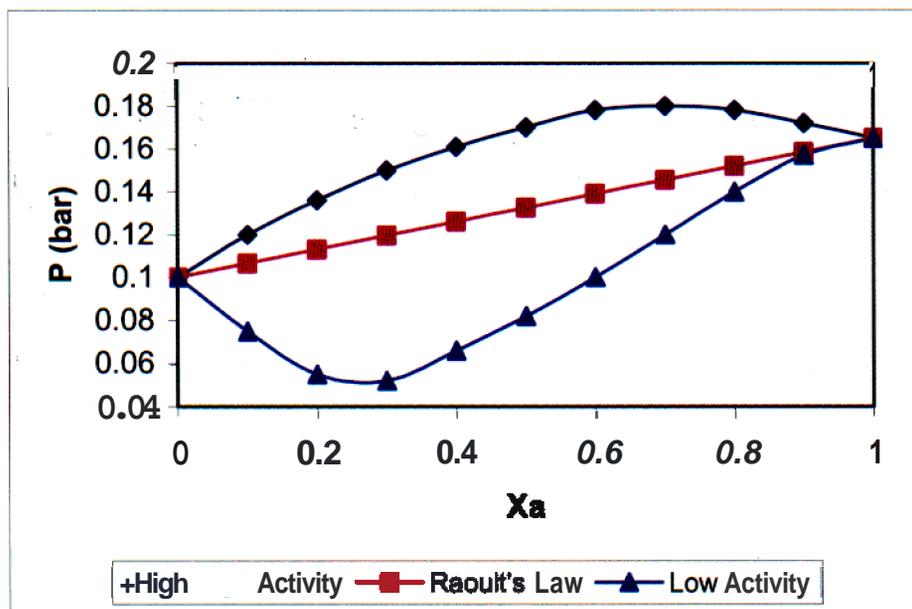


Figure A-1. Total and partial pressures of components x_a and x_b .

In terms of energy, high activity can be viewed as a type of repulsion, whereas low activity can be viewed as a form of attraction. There are no exact equations to represent these interactions in terms of activity as a function of composition. However, there are many accurate methods to estimate this functionality that include the NRTL, Van Laar, Margules, and Wilson equations.

Appendix B

Analytical Solution of Transient Diffusion

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B.1 Derivation of Mass Diffusion through a Liquid

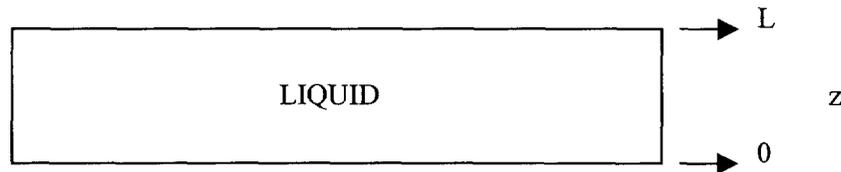


Figure B-1. Liquid layer configuration.

Transient diffusion:

$$\frac{\partial C}{\partial t} = D \cdot \frac{\partial^2 C}{\partial z^2}$$

Carslaw and Jaeger (1959) (heat transfer):

$$\frac{\partial T}{\partial t} = \kappa \cdot \frac{\partial^2 T}{\partial z^2}$$

Initial condition at $t = 0$: $C = C_0$

Boundary condition 1 at $z = 0$: $C = 0$

Boundary Condition 2 at $z = L$: $\frac{dC}{dz} = 0$

Find $C(t, z, D)$

Solution

$$C = Z(z) \cdot T(t)$$

$$z \cdot \frac{\partial T}{\partial t} = D \cdot T \cdot \frac{\partial^2 Z}{\partial z^2}$$

$$\frac{1}{D \cdot T} \cdot \frac{\partial T}{\partial t} = \frac{1}{Z} \cdot \frac{\partial^2 Z}{\partial z^2} = -\lambda^2$$

$$\frac{1}{D \cdot T} \cdot \frac{\partial T}{\partial t} = -\lambda^2$$

$$\frac{\partial^2 Z}{\partial z^2} = -\lambda^2 \cdot Z$$

$$\frac{d \ln T}{dt} = -\lambda D$$

$$\frac{d^2 Z}{dz^2} + \lambda^2 \cdot Z = 0$$

$$\ln T = -\lambda^2 \cdot D \cdot t + C_0$$

$$Z(z) = A \cdot \sin \lambda z + B \cdot \cosh z$$

$$T(t) = c_1 \cdot e^{-\lambda^2 \cdot D \cdot t}$$

T(t) and Z(z) are now defined, plug into C = Z(z)T(t):

$$C = e^{-\lambda^2 \cdot D \cdot t} \cdot [A' \cdot \sin \lambda z + B' \cdot \cos \lambda z] \quad \text{specific solution}$$

Use boundary conditions:

When z = 0,

$$C = 0 = e^{-\lambda^2 \cdot D \cdot t} \cdot [A' \cdot \sin 0 + B' \cdot \cos 0]$$

Therefore B' = 0, since cos(0) = 1

When z = L,

$$\frac{dC}{dz} = 0 = A' \cdot e^{-\lambda^2 \cdot D \cdot t} \cdot \lambda \cdot \cos \lambda L$$

Therefore cos λL = 0

$$hL = (2n+1)\pi/2 \quad n=0,1,2,\dots$$

Substitute in:

$$C = A' \cdot e^{-(2n+1)^2 \cdot \pi^2 \cdot D \cdot t} \cdot \sin \frac{(2n+1) \cdot \pi \cdot L}{2 \cdot L}$$

General solution:
$$C = \sum_n A'_n \cdot e^{-\left(\frac{(2n+1)\pi}{2L}\right)^2 \cdot D \cdot t} \cdot \sin\left(\frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}\right)$$

Initial condition: $C = C_0$, at $t = 0$

$$C_0 = \sum_n A'_n \cdot \sin\left(\frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}\right)$$

$$\int_0^L C_0 \cdot \sin\left(\frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}\right) dz = \sum_n \int_0^L A'_n \cdot \sin\left(\frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}\right) \cdot \sin\left(\frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}\right)$$

$$-\left(\left(\frac{2 \cdot L}{(2n+1) \cdot \pi}\right) \omega_0\right) \cdot \cos\left(\frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}\right) = A'_m \cdot \int_0^L \sin^2 \cdot \lambda \cdot n \cdot z \cdot dz$$

$$A'_m = \frac{4 \cdot C_0}{(2m+1) \cdot \pi}$$

Using $C = C_0$, solving for C_0 , the solution:

$$C = \sum_n \frac{4 \cdot C_0}{(2n+1) \cdot \pi} \cdot e^{-D \cdot t \cdot \left(\frac{(2n+1)\pi}{2L}\right)^2} \cdot \sin\left(\frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}\right)$$

This equation gives the mass fraction at point z . To solve for an average mass fraction of the liquid, the above equation is integrated with respect to z from 0 to L and divided by L :

$$C_{\text{avg}} = \frac{\int_0^L \frac{4 \cdot C_0}{\pi} \cdot \sum_{n=0}^{\infty} e^{-\frac{D \cdot (2n+1)^2 \cdot \pi^2}{(2L)^2} \cdot t} \cdot \sin\left(\frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}\right) dz}{L}$$

Use substitution rule:

$$\text{Let } u = \frac{(2n+1) \cdot \pi \cdot z}{2 \cdot L}, \text{ then } z = \frac{u \cdot 2 \cdot L}{(2n+1) \cdot \pi}$$

$$dz = \frac{2 \cdot L}{(2n+1) \cdot \pi} du \quad \text{at } z=L: \quad u = \frac{(2n+1) \cdot \pi}{2}$$

$$\text{at } z=0: u = 0$$

$$C_{\text{avg}} = \frac{\int_0^{(2n+1)\pi} \frac{4 \cdot C_o}{\pi} \cdot \sum_{n=0}^{\infty} e^{-\frac{D \cdot (2n+1)^2 \cdot \pi^2}{(2 \cdot L)^2}} \cdot \sin u \cdot \frac{2 \cdot L}{(2n+1) \cdot \pi} du}{L}$$

Once integrated, the equation becomes:

$$C_{\text{avg}} = \frac{8 \cdot \omega_o}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot e^{-\frac{D \cdot (2n+1)^2 \cdot \pi^2}{(2 \cdot L)^2}} \cdot \left[1 - \cos \frac{(2n+1) \cdot \pi}{2} \right]$$

For every whole integer, 1,2,3,... $-\cos \frac{(2n+1) \cdot \pi}{2} = 0$

The result is the analytical solution for calculating the average mass in the dish at time t (Section 2, Equation 2-10):

$$C_{\text{avg}} = \frac{8 \cdot C_o}{\pi^2} \cdot \sum_{n=0}^{\infty} \frac{1}{(2n+1)^2} \cdot e^{-\frac{D \cdot (2n+1)^2 \cdot \pi^2}{(2 \cdot L)^2}}$$

(The solution of analytical method of transient diffusion is compliments of Dr. &chard Rowley, Department of Chemical Engineering, Brigham Young University.)

B.2 Discussion of the Analytical Method

The first step in the use of the analytical method in calculating diffusion coefficients was to ensure that the equation fit the boundary conditions defined by the geometry of the petri dish experiments and was repeatable using different values of L.

An effective mass diffusion coefficient was calculated for carbon tetrachloride diffusing through TRO by fitting the analytical solution to experimental data. Equation 2-8 was used to predict the effective diffusion coefficient by minimizing error using the least squared difference method. Using the height of the liquid layer as the value for L, the calculated value of the effective diffusion coefficient was $1.27E-5 \text{ cm}^2/\text{second}$ with an error of 0.076. This answer was off by an order of magnitude compared those listed in previous work (Miller 1999).

Analysis of boundary conditions of the analytical solution reveals one significant flaw. In both the Carslaw and Jaeger (1959) method and in the equation derived by Dr. &chard Rowley, thickness of the dish is assumed to be a constant. This condition stems from the application of the heat and mass transfer analogy. Figure B-2 illustrates the boundary conditions of heat conduction through a slab.

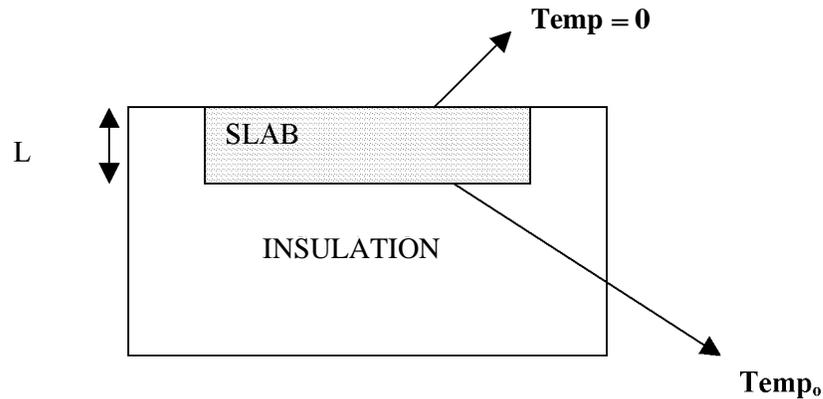


Figure B-2. Heat conduction through a slab of thickness L .

The slab is insulated on every side except at the top surface. A temperature of zero is assumed at the surface while the rest of the slab at time zero is considered to be a uniform constant temperature. The resulting temperature gradient initiates heat transfer. The rate of heat transfer through the slab is a function of conductivity (K). In the application of the heat and mass transfer analogy, effective diffusion is substituted for conductivity and concentration for temperature. Figure B-3 demonstrates change in parameters of the system when the heat and mass transfer analogy is applied:

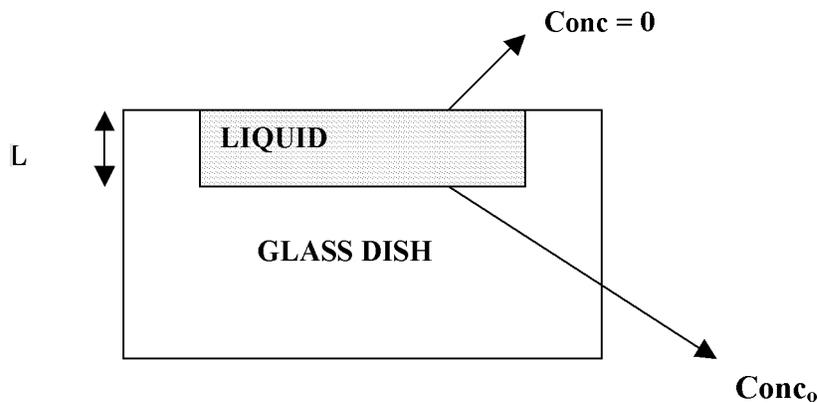


Figure B-3. Mass transfer through a liquid layer of thickness L .

Mass loss occurs by the same mechanism in which heat is lost. A concentration gradient, identical to that of the temperature gradient, results in mass loss through the surface of the liquid.

Unlike heat conduction where slab thickness remains constant, loss of mass (solvent) in the liquid results in a decrease in the height of the liquid layer (see Figure B-4). In this case, the assumption of a constant thickness does not hold true in the solution of diffusion. Application of the analogy has been successfully applied in situations where the thickness of the liquid layer was held constant (Anderson and Saddington 1949). However, in this study, the liquid thickness decreases because of the evaporation of the chlorinated solvent at the liquid surface.

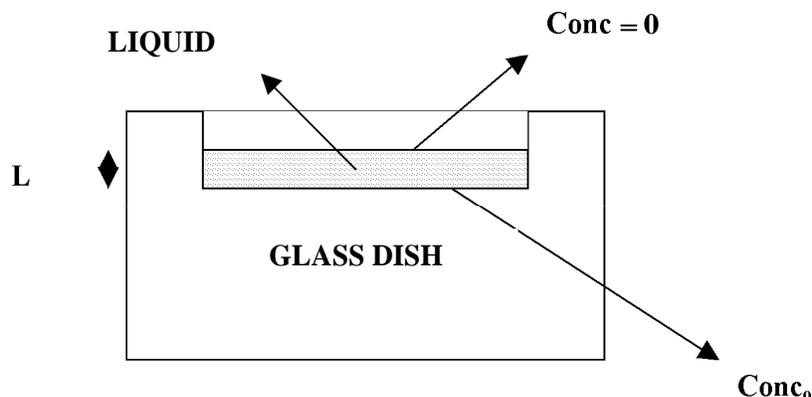


Figure B-4. Mass diffusion through a liquid layer of thickness L .

According to the analytical equation, thickness of the dish is held at a constant of thickness L . However, thickness of the liquid layer is reduced by 67% when the chlorinated solvent has completely evaporated out of the mixture, leaving behind a liquid that is almost pure TRO with traces of carbon tetrachloride remaining in the liquid phase. At this point, thickness of the liquid layer is 33% of the starting thickness of 1.35 cm or 0.45 cm. This inconsistency can be addressed in several ways.

One solution to the problem is to view the diffusion of carbon tetrachloride through a constant 0.45-cm layer of oil. This simplistic approach assumes that carbon tetrachloride diffuses only through the TRO. In reality, the carbon tetrachloride not only diffuses through the TRO, but it also dissolves through itself. In other words, the carbon tetrachloride must diffuse through a mixture of components before it reaches the surface and evaporates.

A more practical solution is to view the thickness of the liquid layer as an average of the height of the mixture at time zero and the height of the oil at the point of complete evaporation. This simple approach accounts for both the extremes in thickness. It is important to note that this method derives an average diffusion coefficient and is an approximation. In following this reasoning, it is assumed that using an average thickness will actually produce a more reasonable value for the thickness of the liquid layer. Therefore, a uniform thickness of $(1.35 \text{ cm} + 0.45 \text{ cm})/2$, or 0.90 cm, will be used for L in the analytical solution.

To confirm this approach, carbon tetrachloride, TRO evaporation experiments were completed in three petri dishes with varying height and the same surface area. The results are listed in Table B-1.

Table B-1. Comparison of varying L in the analytical solution with carbon tetrachloride and Texaco Regal Oil.

Height (cm)	L (cm)	Effective Diffusion Coefficient (cm ² /second)	Mean Squared Difference
0.5	0.333	6.2E-6	3.402E-4
1.35	0.90	5.5E-6	1.807E-4
2.0	1.333	4.7E-6	9.152E-5

As Table B-1 demonstrates, the values of effective diffusion are within 15% of each other. The use of any other value of L resulted in substantial differences in the values of the fitted effective diffusion coefficient (greater than order of magnitude). Therefore, two-thirds of the petri dish height for L are used in the analytical solution.

A noted trend of improved fit is seen as the height of the dish increases. At the time of this research, the petri dish with the height of 1.35 cm was the only dish available in sufficient quantity to perform the experiments and was used throughout the study.

Appendix C

Permeability Calculation through Polyethylene Bagging

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Permeability Calculation through Polyethylene Bagging

Table C-1. Dimensions of a 55-gallon drum and polyethylene bag.

Length	85.09 cm
Radius	27.94 cm
Circumference	175.51 cm
Polyethylene bag (10-mil poly) thickness	0.02286 cm

Schematic of the surface area of polyethylene bagging is available to VOC vapor escape while the drums are in the vertical and horizontal positions.

Vertical Position:

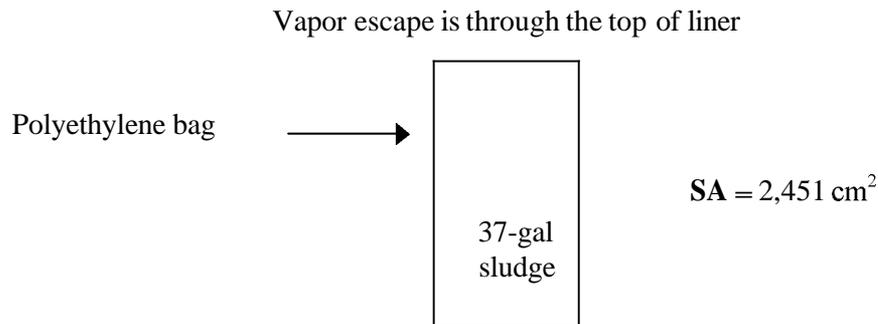


Figure C-1. Volatile organic compound vapor escape from polyethylene bagging in the vertical position.

Horizontal Position:

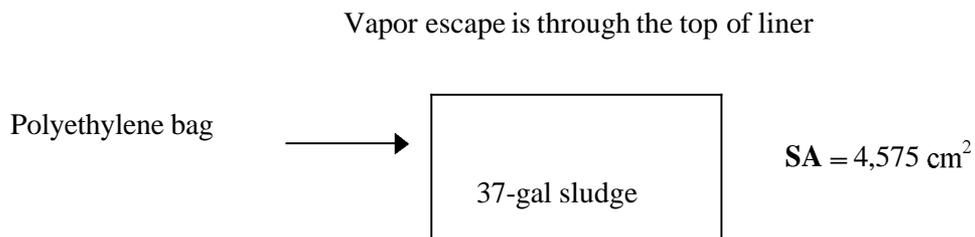


Figure C-2. Volatile organic compound vapor escape from polyethylene bagging in the horizontal position.

The permeability values p , of VOCs passing through polyethylene bagging at 25°C are provided by Liekhus and Peterson (1995). The permeability value for PCE was not determined by Liekhus and Peterson (1995) and has been assumed to be the same as the value for TCE because of similar stereochemistry.

carbon tetrachloride	1.81×10^{-8}	$\text{cm}^3 \text{ (STP) cm}^{-1} \text{ s}^{-1} \text{ (cm Hg)}^{-1}$
TCA	1.18×10^{-8}	
TCE	4.96×10^{-8}	
PCE	4.96×10^{-8}	

The vapor fractions, y_i , for chlorinated solvents in the field mixture are determined by the percent by volume of solvents in the field mixture. The following are y_i corresponding to the percentage by volume.

carbon tetrachloride	68.9%	$y_i = 0.0565$
TCA	14.1%	$y_i = 0.0022$
TCE	10.9%	$y_i = 0.0005628$
PCE	6.1%	$y_i = 0.000707$

Equation C-1 is the formula for calculating the rate of volume of displaced VOC across the polyethylene bagging.

$$p, \times (y_i \times P) \times SA/th \times p, = \text{cm}^3/\text{second} \quad (\text{C-1})$$

where

- y_i = vapor fraction of i^{th} VOC in vapor phase, $\text{cm}^3 \text{ VOC}/\text{cm}^3 \text{ gas}$
- P = pressure surrounding vapor, cm Hg (76cm)
- SA = surface area of the bagging, cm^2
- th = thickness of the bagging, cm
- $p,$ = permeability of i^{th} VOC, $\text{cm}^3 \text{ (standard temperature and pressure) cm}^{-1} \text{ s}^{-1} \text{ (cm Hg)}^{-1}$

Appendix D
Chemical Properties

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Chemical Properties

Table D-1. Chemical properties of Texaco Regal Oil 32.

Parameter	Texaco Regal Oil 32
Appearance ^a	Very light, pale yellow
Structure ^c	Paraffinic hydrocarbon (alkane)
Average gram molecular weight ^b	360 (American Society for Testing and Materials Manual 2502)
Specific gravity ^c	0.8665
Pour point ^c	-25°F
Kinematic viscosity ^b	77.037 at 21°C

a. Texaco Regal Oil 32 product sheet

b. Verbal communication with Texaco Oil, Inc

c. Texaco material safety data sheet

Table D-2. Chemical properties of carbon tetrachloride and trichloroethene

Parameter	Carbon tetrachloride	Trichloroethene
Chemical formula ^c	CCl ₄	C ₂ HCl ₃
Appearance ^c	Clear, colorless liquid	Clear, colorless liquid
Gram molecular weight (g/mol) ^a	153.82	131.39
Density (g/cm ³) ^a	1.59472 @ 20°C	1.461 @ 20°C
Relative vapor density ^c	5.31	4.54
Boiling point (“C”) ^c	76.54	87.2
Melting point (“C”) ^c	-22.99	-87.1
Vapor pressure (mmHg) ^a	90 @ 25°C	56.8 @ 25°C
Diffusivity in water (10 ⁵ cm ² /second) ^a	0.90 @ 20°C	0.94 @ 20°C
Solubility ^c	785 mg/L @ 20°C	1,080 mg/L @ 20°C
Log K _{oc} ^a	2.83	2.025
Henry's Constant (10 ² atm*m ³ /mol) ^a	3.02 @ 25°C	9.9 @ 20°C
Dynamic viscosity (cP) ^b	0.97	0.57
Kinematic viscosity (cS) ^b	0.61	0.39

a. Montegomery 1996

b. Pankow and Cherry 1996

Table D-3. Chemical properties of 1,1,1-trichloroethane and tetrachloroethene

Parameter	1,1,1-trichloroethane	Tetrachloroethene
Chemical formula [”]	C ₂ H ₃ Cl ₃	C ₂ Cl ₄
Appearance [“]	Clear, colorless liquid	Clear, colorless liquid
Gram molecular weight (g/mol) ^a	133.40	165.83
Density (g/cm ³) ^a	1.339 @ 20°C	1.623 @ 20°C
Relative vapor density [”]	4.60	5.72
Boiling point (“C”)	76.54	121.2
Melting point (“C”)	-30.6	-19
Vapor pressure (mmHg) ^a	100 @ 25°C	14 @ 25°C
Diffusivity in water (10 ⁵ cm ² /second) ^a	0.89 @ 20°C	0.87 @ 20°C
Solubility [”]	480 mg/L @ 20°C	149 mg/L @ 20°C
Log K _{oc} ^a	2.50	2.53
Henry's Constant (10 ² atm*m ³ /mol) ^a	1.5 @ 20°C	15.3 @ 20°C
Dynamic viscosity (cP) ^b	0.84	0.9
Kinematic viscosity (cS) ^b	0.62	0.61

a. Montgomery 1996

b. Pankow and Cherry 1996

Appendix E
HYSYS Data Sheet

Appendix E

HYSYS Data Sheet

1	HYSYS Fluid Package Specs sheet					NoName.hsc	
2							
3	Name : Basis-1						
4	Property Package: NRTL						
5							
6	Activity Model Specifications						
7	Vapour Model		UNIFAC Estimation Temp		Use Poynting Correction		
8	Ideal		77.00 F		Yes		
9							
10	Current Component List						
11	n-C25		111-C1C2		C13-C2=		
12	C14-C2=		CC14				
13							
14	Activity Model Interaction Parameters						
15							
16	Aij Coefficient Matrix						
17							
18	Components	n-C25	111-C1C2	C13-C2=	C14-C2=	CC14	
19	n-C25	---	760.8	821.0	-381.3	1235.	
20	111-C1C2	-804.8	---	-319.6	-565.6	882.9	
21	C13-C2=	-853.9	72.53	---	54.47	877.9	
22	C14-C2=	291.0	389.0	-55.97	---	1252.	
23	CC14	-1852.	-692.8	501.0	585.4	---	
24							
25	Bij Coefficient Matrix						
26	Components	n-C25	111-C1C2	C13-C2=	C14-C2=	CC14	
27	n-C25	---	1.000e-29	1.000e-29	1.000e-29	1.000e-29	
28	111-C1C2	1.000e-29	---	1.000e-29	1.000e-29	1.000e-29	
29	C13-C2=	1.000e-29	1.000e-29	---	1.000e-29	1.000e-29	
30	C14-C2=	1.000e-29	1.000e-29	1.000e-29	---	1.000e-29	
31	CC14	1.000e-29	1.000e-29	1.000e-29	1.000e-29	---	
32							
33	Alpha_{ij}/C_{ij} Coefficient Matrix						
34	Components	n-C25	111-C1C2	C13-C2=	C14-C2=	CC14	
35	n-C25	---	0.3000	0.3000	0.3000	0.3000	
36	111-C1C2	0.3000	---	0.3000	0.3000	0.3000	
37	C13-C2=	0.3000	0.3000	---	0.3000	0.3000	
38	C14-C2=	0.3000	0.3000	0.3000	---	0.3000	
39	CC14	0.3000	0.3000	0.3000	0.3000	---	
40							
41	Stability Test Information						
42	Stability Test Parameters			Phase(s) To Initiate Test			
43	Maximum Phases Allowed	3.000		Deleted:	Enabled	Ideal Gas:	Disabled
44	Test Method	Low		Average of Existing:	Disabled	Wilson's Equation:	Enabled
45							
46	Components To Initiate Test						
47	Component		Status				
48	n-C25		Not Initiated				
49	111-C1C2		Not Initiated				
50	C13-C2=		Not Initiated				
51	C14-C2=		Not Initiated				
52	CC14		Not Initiated				
53							
54	Attached Reaction Sets						
55							
56	Active Properties Selection						
57							
58	K Value (V/L1)	Not Selected		Vapour Thermal Conductivity		Not Selected	
59	K2	Not Selected		Liquid Thermal Conductivity		Not Selected	
60	Enthalpy Model	Not Selected		Surface Tension		Not Selected	
61	Vapour Viscosity	Not Selected		Liquid Density		Not Selected	
62	Liquid Viscosity	Not Selected					
63							
64	Remarks:						
65							
66	Date:	Fri Jan 28 10:38:28 2000	Version:	HYSYS v1.1.1 (Build 1403)	Page No:	1	Of:
						2	

* Specified by user.

Appendix F

Schroeder Method of Estimating Molar Volumes

Appendix F

Schroeder Method of Estimating Molar Volumes

The Schroeder method is generally accurate to within 3 - 4%. Carbon tetrachloride is listed in "The Properties of Gases and Liquids" and from this information, it is used to verify the validity of the Schroeder method. The molar volumes are calculated using table 3-8 (pg. 53) in "The Properties of Gases and Liquids".

This is the known molar volume of Carbon tetrachloride: $V_{CT_known} = 102 \frac{\text{cm}^3}{\text{mol}}$

These are the molar volumes for each atom (Table 3-8):

$$C = 7 \frac{\text{cm}^3}{\text{mol}} \quad Cl = 24.5 \frac{\text{cm}^3}{\text{mol}}$$
$$H = 7 \frac{\text{cm}^3}{\text{mol}} \quad \text{bond double} = 7 \frac{\text{cm}^3}{\text{mol}}$$

Calculate error using known value of carbon tetrachloride.

$$V_{CT} = (1 \cdot C + 4 \cdot Cl) \quad V_{CT} = 105 \frac{\text{cm}^3}{\text{mol}}$$

$$\text{error} = \frac{V_{CT} - V_{CT_known}}{V_{CT_known}} \quad \text{error} = 2.941\%$$

As can be seen, the error is relatively small. Calculate values for remaining components.

$$V_{TCE} := (2 \cdot C + 3 \cdot Cl + 1 \cdot H + 1 \cdot \text{bond double}) \quad V_{TCE} = 101.5 \frac{\text{cm}^3}{\text{mol}}$$

$$V_{TCA} := (2 \cdot C + 3 \cdot Cl + 3 \cdot H) \quad V_{TCA} = 108.5 \frac{\text{cm}^3}{\text{mol}}$$

$$V_{PCE} := (2 \cdot C + 4 \cdot Cl + 1 \cdot \text{bond double}) \quad V_{PCE} = 119 \frac{\text{cm}^3}{\text{mol}}$$

$$V_{TRO} := (25 \cdot C + 56 \cdot H) \quad V_{TRO} = 567 \frac{\text{cm}^3}{\text{mol}}$$

$$V_{\text{hex}} := (6 \cdot C + 14 \cdot H) \quad V_{\text{hex}} = 140 \frac{\text{cm}^3}{\text{mol}}$$