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ABSTRACT

THE DEVELOPMENT OF A SENIOR UNIT OPERATIONS LABORATORY ON THE SUPERCRITICAL EXTRACTION OF SOLID NAPHTHALENE WITH SUPERCRITICAL CARBON DIOXIDE

by
Ronald G. Gabbard

A Senior level Undergraduate Unit Operations Laboratory experiment was developed for the extraction of Naphthalene with supercritical Carbon Dioxide. A Supercritical Extraction Screening System purchased from Autoclave Engineers of Erie, Pennsylvania was modified slightly for use as the laboratory equipment. The experiment consists of extracting solid naphthalene from a sand bed in a fixed bed extractor and determining the mass transfer coefficient for the unit.

The lab has been designed to allow the students to develop their own experimental plan without much direct input. The experimental outline provided for the students primarily focuses on information needed for safe and proper operation of the equipment. The discussion questions the students are asked to consider, however, have been developed to provide some guidance on how the experimental plan should be developed. Additionally, these questions focus the students onto some of the other concerns of Supercritical Fluid Extraction like heat transfer and material handling.

Finally, the experiment allows the student to apply basic thermodynamic principles to real world problems like the prediction of unavailable physical properties near the critical point. These predictions are necessary to do calculations related to scale-up and equipment performance on Supercritical Fluid Extraction processes. A computer program written in BASIC that utilizes the Peng-Robinson equation of state with mixing rules that use a single binary interaction parameter is also included.

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SENIOR UNIT OPERATIONS LABORATORY
ON
THE SUPERCRITICAL EXTRACTION OF SOLID NAPHTHALENE
WITH SUPERCRITICAL CARBON DIOXIDE

by
Ronald G. Gabbard

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APPROVAL PAGE

THE DEVELOPMENT OF A
SENIOR UNIT OPERATIONS LABORATORY
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THE SUPERCRITICAL EXTRACTION OF SOLID NAPHTHALENE
WITH SUPERCRITICAL CARBON DIOXIDE

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This thesis is dedicated to
my parents, Dorothy J. and Billy A. Gabbard,
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LIST OF SYMBOLS

Variables:

$a,$	$(\text{ft}^2/\text{ft}^3)$	Surface area per unit volume of a packed bed
$a,$		Equation of state constant
$A,$	(ft^2)	Area
$b,$		Equation of state constant
$c_i,$	(lb/ft^3)	Concentration of component i in the bulk phase
$c_{li},$	(lb/ft^3)	Equilibrium concentration of component i at the solvent solute boundary or interface
$c_{lm},$	(lb/ft^3)	Log mean concentration driving force
$c_{\text{lsat}},$	(lb/ft^3)	Equilibrium saturation concentration that can be achieved in the exit stream of the extractor
$C_p,$	$(\text{Btu}/\text{lb } ^\circ\text{F})$	Heat capacity
$d,$	(ft)	Particle diameter
$D,$	(ft^2/sec)	Binary diffusion coefficient
$D,$	(ft)	Diameter
$f_i,$	(atm)	Fugacity of component i
$g,$	(ft/sec^2)	Acceleration due to gravity
$j,$	$(\text{lb}/\text{ft}^2\text{sec})$	One dimensional diffusion flux
$k,$	(ft/sec)	Mass transfer coefficient
$M,$	(lb/hr)	Mass flow rate
$N,$	$(\text{lb}/\text{ft}^2 \text{ sec})$	Mass flux (per unit time and interfacial area)

LIST OF SYMBOLS (Continued)

Variables (continued):

$p,$	(atm)	Vapor pressure
$P,$	(atm)	Total pressure
$P_c,$	(atm)	Critical pressure
$Q,$	(Btu/hr)	Heat input
$R_o,$	(ft)	Solute radius
$T,$	(K)	Temperature
$T_c,$	(K)	Critical temperature
$V,$	(ft ³)	Volume
$v^0,$	(ft/sec)	Empty column superficial velocity
$V_i,$	(ft ³)	Molar volume
$Y,$		Mole fraction of component i in either the vapor or supercritical fluid phase
$z,$	(ft)	Packed bed height
$Z,$		Compressibility factor
$\alpha,$		Equation of state constant
$\beta,$	(1/K)	Coefficient of thermal expansion
$\phi,$		Fugacity coefficient
$\rho,$	(lb/ft ³)	Density
$\mu,$	(cp or lb/ft sec)	Viscosity

LIST OF SYMBOLS (Continued)

Superscripts:

$\alpha, \beta,$	Identifies a general phase
F,	Identifies the supercritical fluid phase
S,	Identifies the solid or condensed phase
sb,	Property measured at sublimation for solid or saturation for liquid

Physical Constants:

K_B	Boltzmann constant, 1.380622×10^{-23} J/K
R	Gas constant, 0.08206 atm l/mol K

Dimensionless Numbers:

N_{Re}	$(dv^0 \rho / \mu)$	Reynolds Number
N_{Sc}	$(\mu / D \rho)$	Schmidt Number
N_{Gr}	$(D^3 \rho^2 g \beta \Delta T / \mu^2)$	Grashof Number
N_{Sh}	(kz / D)	Sherwood Number

CHAPTER 1
INTRODUCTION

Supercritical Fluid Extraction (SCFE) is quickly becoming a key unit operation in the chemical process industry (CPI). SCFE utilizes the unique properties of a fluid above its critical point (critical temperature and pressure) to enhance the ability of the fluid to carry out an extraction process. In many cases, fluids like carbon dioxide, which are normally gases at room temperature and low pressure, can become powerful solvents with solubility parameters as high as $14 \text{ (J/cm}^3\text{)}^{0.5}$ (Allada, 1984) where the solubility parameter is related to the cohesive-energy density (Prausnitz, et al., 1986). The unique properties of a supercritical solvent stem from its ability to behave like a liquid and a gas at the same time.

The fluid, once over its critical point, becomes a single homogeneous phase where liquid and vapor are indistinguishable. When this happens, the fluid maintains gas-like viscosity and diffusivity, with liquid-like density. The result is a fluid that has a low viscosity (even when heavily loaded with solute), a high diffusion coefficient which enhances mass transfer, and a relatively high liquid-like density. This high density allows the solvent to achieve very high solute loadings. The key advantage of a supercritical fluid, however, is not this

combination of liquid and gas properties but rather, the ease with which solute solubility in the supercritical phase can be altered. This makes for easy solute separation downstream of the extraction process by small changes in either temperature or pressure.

While the concept of SCFE has been known for over a century (Hannay and Hogarth, 1879), it has not been widely used in industry until recently for a variety of reasons. Foremost of these reasons is the high financial risk involved with SCFE; namely a relatively short track record of commercial scale success and high installation and operating costs. Another reason is that a conventional separation technique is usually already available. Add to this the difficulties caused by the lack of good theoretical models when doing scale-up, and it becomes obvious as to why there was no real incentive for SCFE development on a wide-scale industrial level. Even the early commercial applications: propane deasphalting in the 1930's, the SOLEXOL process of the 1940's, and the ROSE process in the 1950's (McHugh and Krukoni, 1986), were not enough to generate large-scale interest.

While these reasons remain true today, new motivating factors have paved the way for SCFE to become a viable extraction alternative. The modern chemical engineer is faced with environmental regulations that are constantly increasing in both complexity and number. These regulations

require stricter control of emissions and reductions in hazardous waste. The sharp rise in energy costs in the 1980's has lessened the historically large and favorable gap in operating costs which conventional high heat separation techniques such as distillation have had over high pressure SCFE systems. Additionally, increased performance demands, such as lower acceptable limits of residual solvents or other contaminants in the food and pharmaceutical industries, have made SCFE a popular choice. Finally, public pressures have put the CPI in the limelight to become responsible "good neighbors". One way to do this is by switching to an "environmentally friendly" solvent such as carbon dioxide.

As SCFE becomes more and more popular in industry, it is finding widespread application from the decaffeination of coffee to the removal of trace organic contaminants in waste water (Eckert, Van Alsten, Stoicos, 1986) and while these widely varying applications are using many different solvents, the one used most predominantly is still carbon dioxide. Additional work is going on in many other areas from coal liquefaction (Maddocks, Gibson, and Williams, 1979) to fractionation and purification of polymers (McHugh and Krukonis, 1986). Some of these processes, like coffee decaffeination, are vastly different from the original deasphalting and ROSE processes while others, like coal liquefaction, are very similar.

In some of these applications, SCFE has received high accolades for successfully dealing with complex separation problems while in others, it has received sharp criticism for being an overpriced, high risk technology. While Brennecke and Eckert (1989) point out that SCFE is neither a panacea nor a hazard, it is quickly becoming a unit operation chemical engineers will be able to utilize in the future.

With this in mind, the aim of this work is to develop a laboratory experiment that reinforces fundamental engineering principles and at the same time introduces one of the segments of this growing technology, specifically solid/SCFE, for an undergraduate senior level unit operations lab. The lab should provide the students the opportunity to explore this growing technology and utilize their engineering skills to deal with issues of scale-up and high pressure equipment design and operation. Additionally, from a theoretical thermodynamic point of view, it will allow them to explore physical property prediction at high pressures far away from ideal behavior when experimental data are not available.

CHAPTER 2

BACKGROUND

One of the fundamental problems facing the chemical engineer is scale-up. The existence of this problem is no different for the engineer who is working with a SCFE system. In fact, scale-up in this case may be considerably more difficult for three reasons. First, the industry lacks good theoretical models and empirical correlations for operations carried out near and beyond the critical point. Second, most published data are for model systems such as CO₂/Naphthalene and CO₂/Biphenyl. While these systems are valuable for needed fundamental research such as the development of correlations and models, they are not usually industrially significant. Finally, as with any new technology, problems are usually more difficult to solve because there is little or no past experience on which to build.

With all of the issues complicating SCFE system scale-up, the most effective method is one that comes directly from experimental or pilot plant data. This can usually be conveniently obtained through a fundamental mass transfer approach. It could be based on either Fick's law or the concept of a mass transfer coefficient.

Fick's law relates the diffusion flux, $-j_1$, to the concentration gradient, $\partial c_1/\partial z$,

$$-j_1 = D \frac{\partial c_1}{\partial z} \quad (1)$$

and requires accurate diffusion coefficient, D , data which are not always available.

The mass transfer coefficient approach relates the mass flux to a concentration difference, ΔC_{lm} ,

$$N = k \Delta C_{lm} \quad (2)$$

where k is defined as the mass transfer coefficient. This type of approach requires knowledge of physical and thermodynamic properties like viscosity, density and solubility. In many cases such as with the diffusion coefficient, solubility data may not be available. Both methods require knowledge of the system; operating conditions, mass transfer area, etc. The type of approach used will depend on the data available.

In many cases, it is likely that neither the diffusion coefficient nor the necessary solubility data will be known. In those instances, the more accurate analysis should result from predicting the solubility rather than from predicting the diffusion coefficient. The reason is that fairly accurate solubility predictions can be obtained using an

appropriate equation of state (EOS) to model equilibria in the supercritical region.

This is not the case with equations used to predict the diffusion coefficient. For example, while the Stokes-Einstein equation below can be used to predict diffusion coefficients in gases with good success (Reid, et al., 1977),

$$D = \frac{k_B T}{6 \pi \mu R_0} \quad (3)$$

it is only accurate to about 20% in liquids. These errors become significantly worse in supercritical fluids because the solute diffusion coefficients have been determined to be highly dependent on the supercritical solvents (Olesik and Woodruff, 1991). In Equation 3, k_B is the Boltzmann constant, μ is the viscosity, R_0 is the solute radius and T is the temperature. Other equations analogous to the Stokes-Einstein equation have similar problems in the critical region (Debenedetti and Reid, 1986).

The development of Equation 2 will be focused on here, since in the absence of diffusion coefficient data, it would be the most likely approach. Equation 2, as written, can be applied to any unit operation or system involving mass transfer. The use of a log mean driving force in the concentration term allows a weighted average to be taken across the entire process and alleviates the burden of

determining the solute concentration at the mass transfer interface. This makes the determination of k , the mass transfer coefficient, easily obtainable from operational data. The validity of using a log mean concentration difference will be demonstrated later, but first the equations will be developed using the concentration at the mass transfer interface.

Qualitatively, it is reasonable to assume that the total mass transferred in the system will be proportional to the mass transfer area and the concentration differences or driving force in the system,

$$\frac{\text{(TOTAL MASS TRANSFERRED)}}{\text{k(INTERFACIAL AREA) (CONCENTRATION DIFFERENCE)}} = \quad (4)$$

Dividing both sides of equation 4 by the area term one obtains,

$$\text{MASS FLUX} = \text{k(CONCENTRATION DRIVING FORCE)} \quad (5)$$

which is the same as Equation 2. Equation 5 is a typical flux equation where the flux is per unit time and interfacial area, and proportional to the driving force. Thus equation 5 can be re-written as follows,

$$N_1 = K(c_{1i} - c_1) \quad (6)$$

where N_1 is the mass flux of the solute at the interface having units of mass/time(area) and c_{1i} and c_1 are the concentrations of the solute at the interface and in the bulk fluid respectively.

If one views the SCFE column as a packed bed (as is the case in many industrial applications) and writes a mass balance on the solute over an infinitely small differential volume element (Figure 1), the following is obtained (Cussler, 1985):

$$0 = A(c_1 v^0|_z - c_1 v^0|_{z+\Delta z}) + A\Delta z a N_1 \quad (7)$$

The A in Equation 7 is the column cross sectional area and z is the length of the bed. After dividing Equation 7 by $A\Delta z$, assuming constant v^0 , and then taking the limit as Δz goes to zero, the following differential equation is obtained.

$$0 = -v^0 \frac{dc_1}{dz} + a N_1 \quad (8)$$

At this point, substituting equation 6 for N_1 and rearranging gives the following,

$$\frac{dc_1}{dz} = k \frac{a(c_{1_{sat}} - c_1)}{v^0} \quad (9)$$

In Equation 9, $c_{1_{sat}}$ has been substituted for c_{1i} because the saturation concentration is equal to the equilibrium concentration at the solute interface. This equation is subject to the following initial condition for the SCFE column:

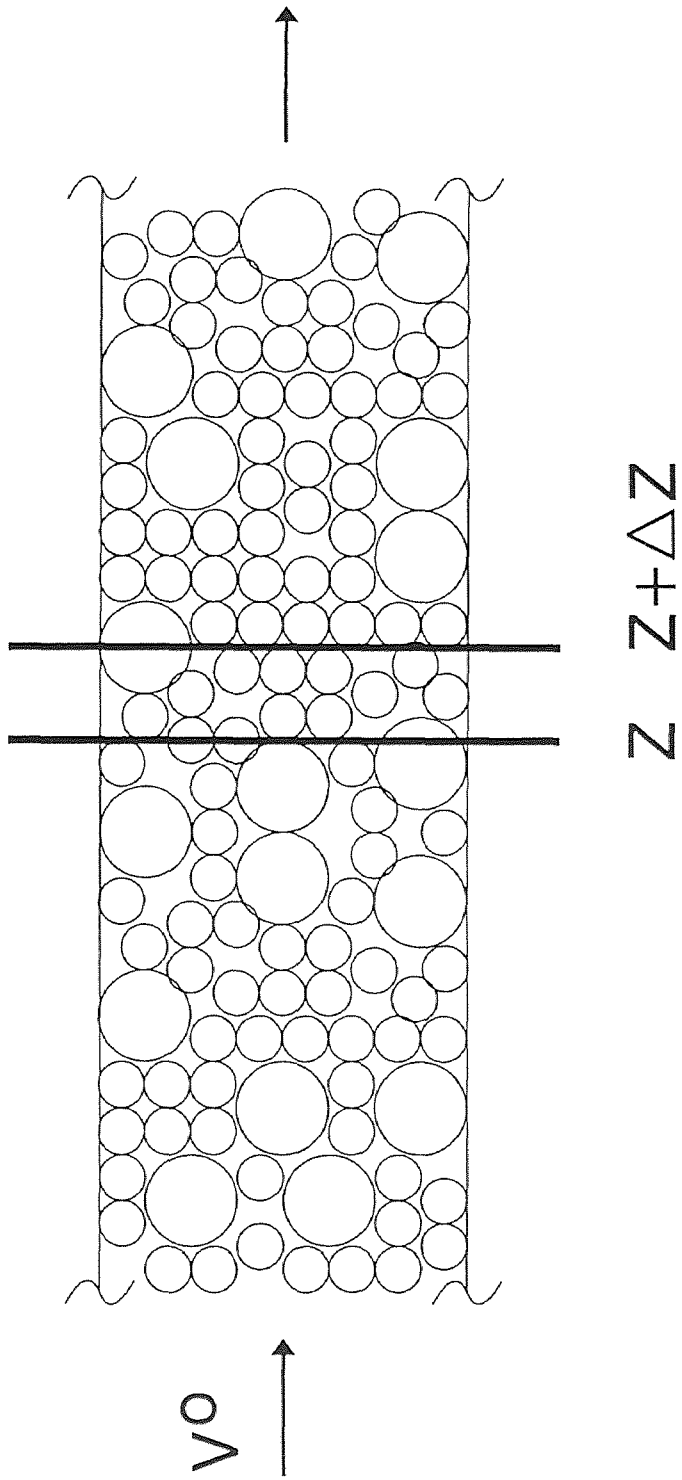


Figure 1
Differential Element in a
Packed Bed Extraction Column

$$c_1=0 \text{ @ } z=0 \quad (10)$$

Equation 10 assumes no recycle in the feed which is true for most laboratory cases but may not be true for all industrial applications. Integration and simplification yields the following expression, where C_{1sat} is the interfacial equilibrium concentration.

$$\frac{c_1}{C_{1sat}} = 1 - \exp\left(-\frac{kaz}{v^0}\right) \quad (11)$$

At this point, it is convenient to introduce the log mean concentration difference mentioned earlier. Most pilot scale operations will not be able to determine interfacial concentrations therefore engineers will have to rely on bulk concentrations in the inlet and outlet streams. The log mean concentration difference can be applied to the extraction column inlet and outlet streams analogously to the log mean temperature difference in a heat exchanger. It is defined as:

$$\Delta C_{lm} = \frac{(\Delta C_{1inlet} - \Delta C_{1outlet})}{\ln \frac{\Delta C_{1inlet}}{\Delta C_{1outlet}}} \quad (12)$$

where

$$\Delta C_{1inlet} = C_{1sat} - 0 \quad (13)$$

and

$$\Delta c_{1_{outlet}} = c_{1_{sat}} - c_1 \quad (14)$$

The validity of this approach can be demonstrated by expanding equation 11 back to its unsimplified form,

$$\frac{c_{1_{sat}} - c_1}{c_{1_{sat}} - 0} = \exp\left(\frac{-kaz}{v^0}\right) \quad (15)$$

Taking logs of both sides and rearranging again gives;

$$v^0 = \frac{kaz}{\ln \frac{c_{1_{sat}} - 0}{c_{1_{sat}} - c_1}} \quad (16)$$

If both sides of the equation are multiplied by c_1 , the result is,

$$c_1 v^0 = kaz \frac{(c_{1_{sat}} - 0) - (c_{1_{sat}} - c_1)}{\ln \frac{c_{1_{sat}} - 0}{c_{1_{sat}} - c_1}} \quad (17)$$

As defined earlier, the mass flux, N_1 is the mass transferred per unit time per unit transfer area. Thus equation 17 can be rewritten as follows,

$$N_1 = \frac{c_1 V^0}{az} = k \frac{(c_{1_{sat}} - 0) - (c_{1_{sat}} - c_1)}{\ln \frac{c_{1_{sat}} - 0}{c_{1_{sat}} - c_1}} \quad (18)$$

Note that equation 18 is the same as Equation 2 and can be viewed as an overall system flux. Equation 6 which was used to derive Equation 18 can be viewed as a local flux. The difference being the type of concentration difference used.

Thus, an engineer knowing only the solute solubility, solute concentrations of the incoming and outgoing streams, the total mass flux for a given period of time, and the system geometry (mass transfer area) can easily solve for k , the mass transfer coefficient in equation 2 or 18. In most cases, k can then be used to scale up the process accurately assuming variables of system geometry such as L/D , fluid space velocity, and bed porosity are kept constant. The solute solubility, if not known, can be estimated from basic thermodynamic principles as will be seen later in this chapter.

In many cases though, the actual mass transfer area for the column will not be known and will not be easily estimated because of void volumes in the packed bed and irregular shaped particles. In these cases, an alternative procedure would be to use an experimentally determined correlation to find k . In many of these cases, the correlation takes the following form.

$$N_{Sh} = f(N_{Re} N_{Sc}) \quad (19)$$

where N_{Re} is the Reynolds number, N_{Sc} is the Schmidt number, and N_{Sh} is the Sherwood number. Cussler (1985), gives the following specific correlation for packed beds which are often found in commercial scale SCFE columns:

$$\frac{k}{v^0} = 1.17 N_{Re}^{-0.42} N_{Sc}^{-0.67} \quad (20)$$

In this case the left hand side of the equation is a modified Sherwood number that relates k to the Reynolds and Schmidt numbers directly.

The validity of Equation 19 has been questioned for supercritical fluids by Debenedetti and Reid (1986), who feel that a more accurate representation is obtained by accounting for the buoyant forces in the supercritical phase through an appropriate Grashof number, N_{Gr} :

$$N_{Sh} = f(N_{Re} N_{Sc} N_{Gr}) \quad (21)$$

While they demonstrated that the Grashof number is an important consideration due to natural convection and hydrodynamic effects, they did not propose a correlation for a packed bed. In the absence of other correlations, the one provided by Cussler can be used if necessary. It should be mentioned that this equation does not account for the fact that the packed bed is shrinking due to the loss of

extracted solute. This problem is not dealt with in this work.

As stated previously, unknown solubility data can be predicted from fundamental thermodynamic principles. The prediction comes directly from the solid/SCF phase equilibria which can be obtained from classical thermodynamics.

For any system with two phases in equilibrium, the following can be written,

$$f_i^\alpha = f_i^\beta \quad (22)$$

where f_i^α is the fugacity of component i in the α phase and f_i^β is the fugacity of the same component in the β phase. For a solid-supercritical fluid system, the solid can be considered pure in most cases. This is usually a good assumption because the diffusion of the supercritical fluid into the solid is much slower than the rate at which the solid dissolves into the supercritical fluid (McHugh and Krukoni, 1986). Refer to Figure 2. Thus, the equation for the fugacity of a pure solid is (McHugh and Krukoni, 1986),

$$f_i^s = P_i^{sb}(T) \phi_i^{sb}(T, P_i^{sb}) \exp \int_{P_i^{sb}}^P \frac{V_i^s}{RT} dP \quad (23)$$

where ϕ_i^{sb} is the fugacity coefficient of component i at its saturation (sublimation in the case of a solid) pressure and P_i^{sb} is the saturation (sublimation in the case of a solid) pressure and where the exponential is the Poynting

THE RATE OF DIFFUSION OF CARBON DIOXIDE INTO THE NAPHTHALENE IS MUCH SLOWER THAN THE RATE OF NAPHTHALENE DISSOLUTION INTO THE CARBON DIOXIDE. THEREFORE, THE PART OF THE NAPHTHALENE THAT WOULD HAVE CONTAINED DIFFUSED CARBON DIOXIDE HAS ALREADY DISSOLVED. HENCE, THE NAPHTHALENE CAN BE CONSIDERED A PURE SOLID.

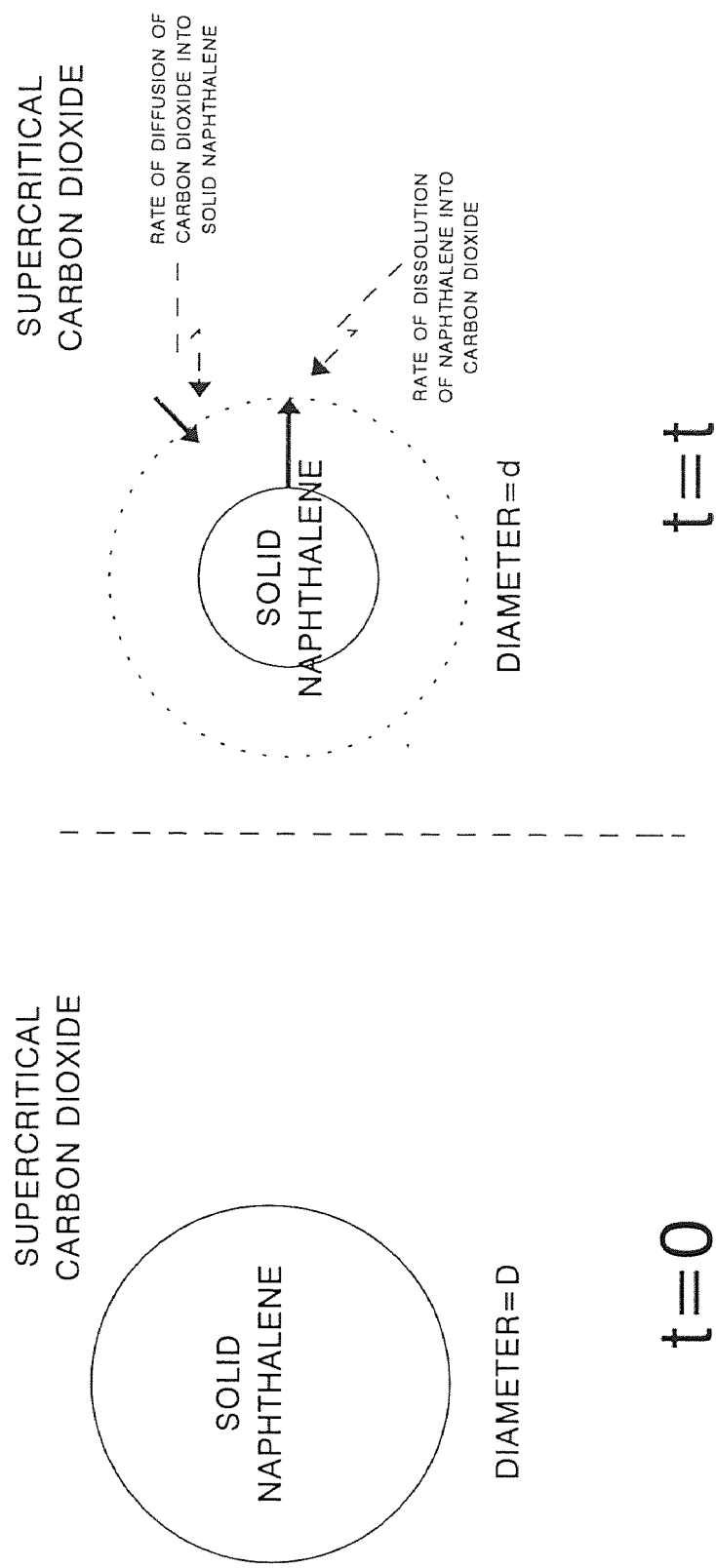


Figure 2
Diffusion/Dissolution Rate Comparison
of Naphthalene in Supercritical Carbon Dioxide

correction (PC). In the Poynting correction, V_i^s is the molar volume of the solid.

Prausnitz et. al. (1986) show that for an incompressible liquid or solid, the integral form of the Poynting correction in Equation 23 can be replaced with the following estimation:

$$PC = \exp \frac{V_i^s (P - P_i^{sb})}{RT} \quad (24)$$

This leads to a much simpler equation for the solid fugacity, f_i^s ,

$$f_i^s = P_i^{sb}(T) \phi_i^{sb}(T, P_i^{sb}) \exp \frac{V_i^s (P - P_i^{sb})}{RT} \quad (25)$$

The fugacity of the solid in the supercritical fluid phase is given by (Mart, Papadopoulos, Donohue, 1986),

$$f_i^F = y_i \phi_i^F P \quad (26)$$

where the supercritical fluid is treated as either a dense or highly compressed gas. Combining equations 21, 25, and 26 gives the solubility of the solid component in the supercritical phase as,

$$y_i = \frac{P_i^{sb}(T) \phi_i^{sb}(T, P_i^{sb})}{P \phi_i^F} \exp \frac{V_i^s (P - P_i^{sb})}{RT} \quad (27)$$

The value of $\phi_i^{sb}(T, P_i^{sb})$ in equation 27 will be unity if the solubility of the SCF can be shown to be negligible in the condensed phase and the solid can be considered non-

volatile. It has already been shown that the solid is pure in the development of the fugacity for the solid phase. The remaining constraint, that the solid must be non-volatile, is also usually true and can be easily confirmed if the vapor pressure of the solid is negligible compared to the system pressure (less than 1 %) at the system operating temperature. Hence, equation 27 reduces to,

$$y_i = \frac{P_i^{sb}(T)}{P\phi_i^F} \exp \frac{V_i^s(P - P_i^{sb})}{RT} \quad (28)$$

Since the system temperature and pressure will be known as well as the molar volume and vapor pressure of the solid, Equation 28 is fairly straightforward to solve with the exception of ϕ_i^F .

There are numerous ways to obtain the value of ϕ_i^F , however, only the Equation of State (EOS) method will be considered here. In general, the fugacity coefficient can be found from

$$\ln \phi_i = \frac{1}{RT} \int_v^\infty \left[\left(\frac{\partial P}{\partial n_i} \right)_{T, v, n_j} - \frac{RT}{V} \right] dV - \ln Z \quad (29)$$

where R is the gas constant, V is the volume, T is temperature, n indicates the various species, and Z is the compressibility factor. The three equations most widely cited in the literature (Trebble and Sigmond, 1990; Mart,

Papadopoulos and Donohue, 1986; Chou and Prausnitz, 1989; Brennecke and Eckert, 1987) for SCFE applications are:

Soave Redlich-Kwong (SRK)

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V(V+b)} \quad (30)$$

Peng-Robinson (P-R)

$$P = \frac{RT}{V-b} - \frac{a\alpha}{V^2 + 2bV - b^2} \quad (31)$$

Perturbed Hard Sphere (PHS)

$$P = \frac{RT}{V} \left[\frac{2V+b}{2V-b} \right] - \frac{Aa}{\sqrt{T}V(V+b)} \quad (32)$$

In Equations 30, 31, and 32, the constants a , b and α are dependent on the critical properties of the chemical species being evaluated. Additionally, when an EOS is used for systems of mixtures, mixing rules are employed. These mixing rules usually have at least one binary interaction parameter and in some cases more.

The P-R Equation with two binary interaction parameters seems to be the best suited for most supercritical fluid property predictions. Walas (1985), points out that the P-R EOS does a better job than the SRK at predicting liquid-like densities which are common in SCFE systems and it does a reasonably good job of representing critical point behavior. Alternatively, while the PHS equation may be more accurate than the P-R in some instances, the added level of

difficulty encountered in using it is seldom warranted for the added increase in accuracy.

Once ϕ_i^F has been determined, Equation 28 can be solved for the equilibrium solubility of the solute in the supercritical solvent. This equilibrium value can then be used to solve Equation 18 directly to obtain the mass transfer coefficient. This will provide a reliable means of scale-up.

CHAPTER 3

APPARATUS

A SCFE screening system was purchased from Autoclave Engineers of Erie, Pennsylvania. The pre-assembled, ASTM stamped and coded system included all of the necessary basic components; a feed pump, extraction column, extract receiver, instrumentation, and stand. See Figure 3 for a system flow diagram.

A standard CO₂ cylinder with a liquid dip tube is used as the feed tank. The CO₂ is cooled in an ice bath prior to entering a Milton Roy 1/4 Hp, variable speed positive displacement (PD) pump. The PD pump is capable of operating between 40-400 cc/hr and is protected from back flow by double ball check valves on the pump suction and discharge (See Figure 4). The pump discharge pressure is controlled by an adjustable back pressure control valve that can operate in the range of 100-7000 psig. Excess flow which causes a pressure higher than the target is recirculated back to the suction side of the pump. The pump discharge pressure is measured just upstream of this control valve. A vapor bleed valve, V1, is supplied downstream of the back pressure control valve. This allows any vaporized CO₂ caught in the pump feed line to be vented off during start-up. Without the vent, the feed pump would become vapor

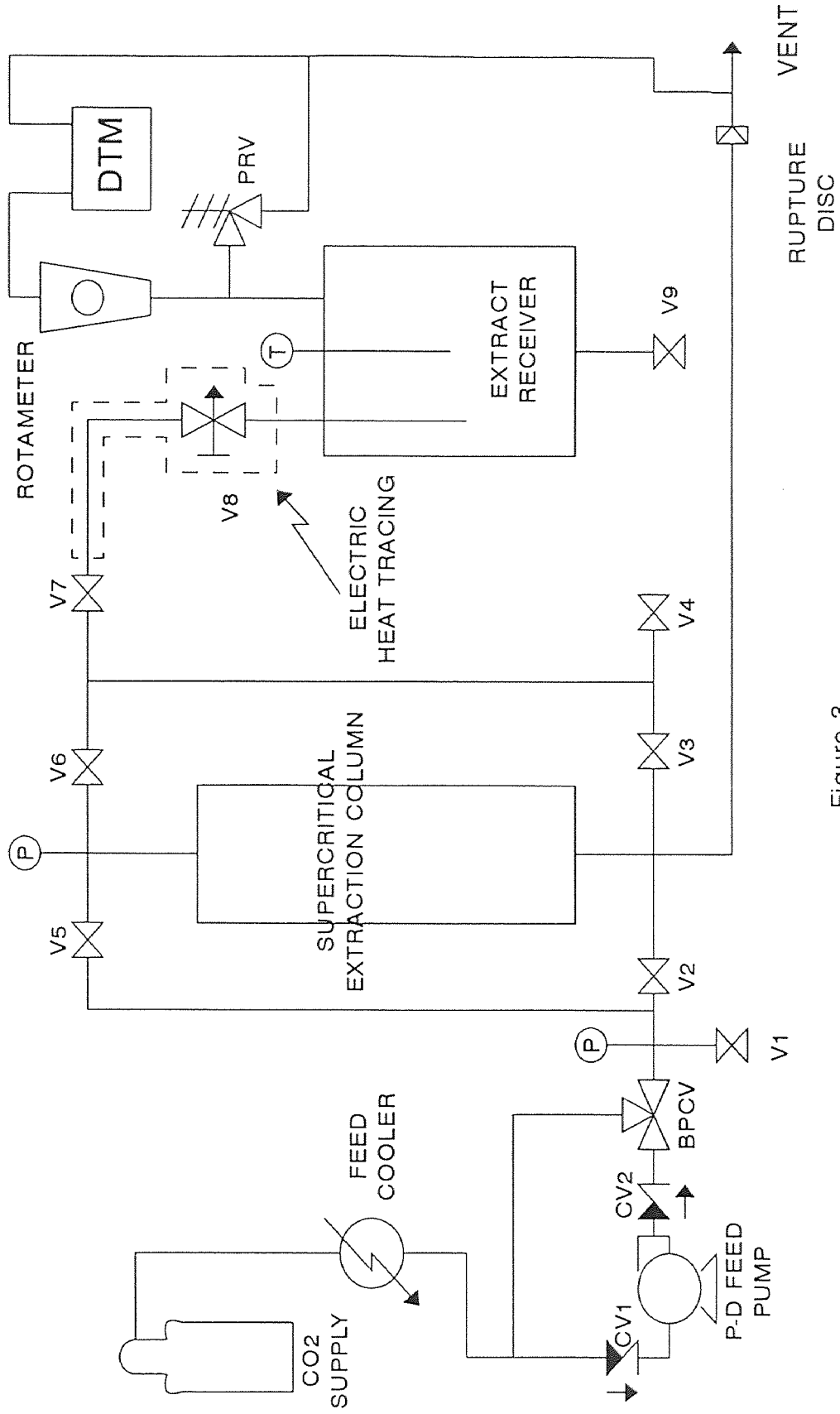


Figure 3
SCFE System Flow Diagram

DIRECTION
OF FLOW

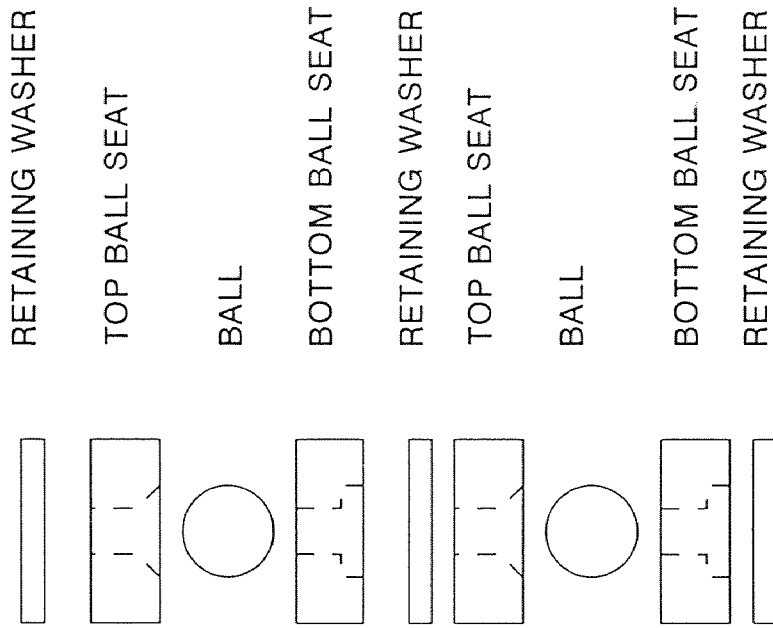


Figure 4
FEED PUMP CHECK VALVE DESIGN

bound and cavitate. Additional cooling is obtained by packing the pump head in ice.

Four valves around the extraction column, V2, V3, V5, and V6 isolate the column and provide the flexibility needed to operate it in either an upflow or downflow configuration. Upflow is obtained by opening valves V2 and V6, and closing V3 and V5. Downflow is obtained from the reverse, V2 and V6 closed, and V3 and V5 open.

The column is 12 inches long, has an inside diameter of 0.688 inches (nominal 1 inch OD), and is rated for approximately 10,000 psig @ 100 °C. It can be electrically heated with two external band heaters. A surface mounted thermocouple measures the outer column wall temperature and controls the band heaters in conjunction with a Watlow proportional/integral controller. Derivative control is not available on the controller. The column is protected from overpressurization by a 1/4 inch diameter rupture disc that is piped directly to the bottom of the column. The disc is nominally rated for 7000 psig @ 72 °F.

The pressure boundary on the downstream side of the column is maintained by a micro-metering needle valve, V8, also supplied by Autoclave Engineers. This valve, however, is not designed to provide a positive seal and it should never be used to isolate the column. The column should be isolated upstream of this valve with the blocking valve, V7. The line between V7 and V8, as well as the body of V8 is

electrically heat traced with a 110 volt heating tape. It is controlled by a Briskheat controller that can be set between 0-100% output but is typically at 15-40%. The heat tracing is in place to counteract the large Joule-Thomson cooling effect that results from the CO₂ as it flashes across the micro-metering valve and to prevent the line from freezing.

The extracted material was collected in the extract receiver. This vessel has a nominal volume of 99 cubic centimeters, and has a drain valve, V9, at the bottom. The vessel is protected by a pressure relief valve set to open at 5 psig and 72 °F. The extract and solvent enter the receiver from the top. The extract, which is no longer soluble in the non-supercritical solvent, separates from the solvent and is collected in the vessel while the solute-free CO₂ is discharged from the top of the vessel. It then passes through a small filter to a rotameter and then through the dry test meter. The filter is in place to protect the dry test meter from any possible entrained solids that could damage it. In addition, the temperature in the extract receiver is measured by a thermocouple that is displayed on channel two (2) of the Omega multi-point digital display.

The rotameter (calibrated for CO₂ at STP in units of SCFM) measures the instantaneous CO₂ flow rate. The CO₂ flow is then totalized by a dry test meter. This provides

total standard cubic feet of CO₂ used during an experiment.

Finally, there is also a small in-line carbon bed filter between the rotameter and the dry test meter. This is in place to remove any volatile organics that may not have been recovered in the extract receiver.

CHAPTER 4

DEVELOPMENT of the EXPERIMENT

4.1 SOLVENT/SOLUTE SYSTEM SELECTION

In order to develop the student experiment, three problems needed to be solved. First, what solvent would be used? Second, what solute or combination of solutes would be used? Third, what engineering principles would be demonstrated?

The solvent selection process was, by necessity, the first task since the results of the other work would depend on what solvent was chosen. In order to select the solvent, the following criteria were used. The fluid needed a reasonably low critical point. This is key in determining if the process will be economically (energy costs) and mechanically (pressure limitations) feasible when it is scaled up. The fluid also needed to be a good solvent for a wide variety of solutes. Additionally, since one of the key driving forces for the increase in industrial interest is low environmental impact, the solvent needed to have little effect on the environment and a low toxicity. This is also consistent with the needs of the solvent for the student laboratory which must emphasize safety. By necessity, it needed to have a very low toxicity. The goal was to identify a solvent that would possess the best balance of these key criteria. Solvent cost, although also very important, was not considered here.

Some typical fluids and their critical properties are summarized in Table 1 (McHugh and Krukonis, 1986; Smith and Van Ness, 1975).

Table 1

Typical SCFE Solvents and Their Critical Properties

FLUID	T_c (K)	P_c (atm)
Ammonia	405.6	111.3
Benzene	562.1	48.3
Chlorotrifluoromethane	302.0	38.7
Carbon Dioxide	304.2	72.8
Cyclohexane	553.4	40.2
Ethane	305.4	48.2
Ethylene	282.4	41.9
Isopropanol	508.3	47.0
Propane	369.8	41.9
Propylene	365.0	45.6
Trichlorofluoromethane	471.2	43.6
Water	647.1	217.6
p-Xylene	343.1	34.7

Upon examination of the critical properties, water is clearly the worst solvent choice among those listed in Table 1 because of its high critical pressure and temperature. These critical properties would require any process using water as the solvent to be run at very extreme temperatures and pressures. Determining the best choice is not as clear because many of the solvents listed have low critical

temperatures and pressures. Ethane, Ethylene, and Chlorotrifluoromethane could all be energy efficient solvents. All of these solvents, however, may have considerable toxicities, negative impacts on the environment, or could pose a significant safety problem.

Carbon dioxide has a critical temperature and pressure of 304.2 K and 72.8 atm respectively. While the critical point for CO₂ is not the most favorable of the various solvents listed, it is still only moderate, making supercritical CO₂ easy to handle in most commercial applications. A wide range of solutes are soluble in liquid CO₂ as shown in Table 2 (McHugh and Krukonis, 1986), which suggests that a wide range of solutes might be soluble in supercritical CO₂. Additionally, CO₂ is both environmentally friendly and non-toxic (with the exception of asphyxiation hazards), making it a clear choice for the student experiment.

Selection of the solute was a little more difficult. The solute-solvent system would determine the types of experiments that could be done, and ultimately, the engineering principles that could be demonstrated by the lab. Further, choosing the wrong solute could greatly complicate the analytical techniques required for successful completion of the assignment. For example, the extraction of caffeine from coffee was one possible choice for the lab

Table 2

Solubilities of Selected Compounds in

Liquid CO₂ at 298 K

Compound	Weight %	Compound	Weight %
Benzyl Benzoate	10	Aniline	3
Butyl Oxalate	M	o-Chloroaniline	5
Butyl phthalate	8	m-Chloroaniline	1
Butyl Stearate	3	N,N-Diethylaniline	17
Ethyl Acetate	M	N,N-Dimethylaniline	M
Ethyl Acetoacetate	M	Diphenylamine	1
Ethyl Benzoate	M	N-Ethylaniline	13
Ethyl Chloroformate	M	N-Methylaniline	20
Methyl Salicylate	M	Pyridine	M
Benzyl Alcohol	8	o-Cresol	2
Cyclohexanol	4	m-Cresol	4
Ethyl Alcohol	M	p-Cresol	2
Furfuryl Alcohol	4	2,4-Dichlorophenol	14
Heptyl Alcohol	6	0-Nitrophenol	M
Acetic Acid	M	Acetonitrile	M
Formic Acid	M	Acrylonitrile	M
Lactic Acid	0.5	Succinonitrile	2
Lauric Acid	1	Acetamide	1
Oleic Acid	2	N,N-Dimethylacetamide	M
Isocaproic Acid	M	Formamide	0.5

M=miscible

experiment. This, in fact, was the first choice for the lab because of its widespread commercial application.

Coffee is currently commercially decaffeinated by various supercritical CO₂ processes (Katz, et. al. 1981; Roselius, 1982; and Zosel, et. al. 1982) all over the world, and most noteworthy in the United States by Kraft General Foods in their Houston, Texas plant (Katz, et. al., 1990). The problem with having the students complete a lab experiment on the decaffeination of coffee (or tea) is that the results are not easily isolated. In either case (coffee or tea), there are many other compounds such as fatty acids and triglycerides (Roselius, et. al., 1982) that are extracted along with the caffeine. In order to determine information about the extraction column performance such as the mass transfer coefficient specific to caffeine, the caffeine would have to be isolated from the other compounds first. This requires a fair amount of organic chemistry and then, ultimately, some type of analytical instrument such as a spectrophotometer or a gas chromatograph (Broker and Sloman, 1965). While the students doing the lab should have the skills required to isolate and measure the caffeine, it turns the experiment more into an organic chemistry lab rather than a unit operations lab and greatly increases the chance of measurement errors. Other food stuff solutes such as spice extracts and vegetable oils (particularly soy and corn) were omitted for similar reasons.

In an effort to reduce the required data analysis, attention was focused on identifying a solute that had been part of a model system widely studied in the literature. One such system is carbon dioxide/naphthalene. Data for this system are available over a wide range of processing conditions. Further, naphthalene, which is commonly sold as moth balls, does not represent a significant health hazard to the students. Primarily for these reasons, the solute chosen was naphthalene. An additional benefit from using this system is that the solubility of naphthalene in supercritical carbon dioxide is high enough that experimental results can be obtained from a simple gravimetric analysis.

Enough naphthalene can be extracted from the column in a fairly short period of time so that weighing the column before and after the extraction provides a measurable weight difference. The difference is the amount of naphthalene that has been extracted directly. Experimentally, this was between 4-8 grams. Since the available weighing scale can accurately measure to tenths of a gram, this gave a minimum accuracy of 2% (one part in 40). More accurate weighing was not possible because of the heavy tare of the column (over 2000 grams when fully assembled). It should also be pointed out that there is little error introduced from dissolved CO_2 in the naphthalene because, as pointed out earlier, the solid naphthalene should be pure.

Some degree of accuracy is obviously sacrificed for this simple gravimetric analysis technique, however. Other methods of analysis such as collecting and analyzing the supercritical phase by gas or liquid chromatograph would be much more accurate but also much more difficult and time consuming. Further, sampling the supercritical phase can be fairly difficult and the very small samples obtained are very difficult to handle. Even small losses in material from the supercritical phase samples can create very large errors.

4.2 THE EXPERIMENTAL PLAN

The basic philosophy used in developing the student experiment was to allow the students to use their own technical ability and ingenuity to develop the specifics of the experimental plan they would follow. A format used by Barat and Armentante (1992) was followed for the experimental write-up. It gives the students only enough information to safely operate the equipment. The questions asked in the discussion section were designed to stimulate the students into properly planning their experiments; however, specific operating conditions are deliberately left out. Each lab group running the experiment is responsible for choosing the operating conditions for the experiment and justifying their choices. This philosophy becomes very important for the students as they prepare for life in

industry where they will inevitably be given an ill defined project to complete at some point early in their career.

The actual Student write-up for the experiment can be found in Appendix A. Additionally, Appendix C contains the details of the estimation of the surface to volume ratio needed for some of the student calculations. Following is a discussion of the development of the successful operation of the SCFE apparatus with carbon dioxide and naphthalene.

A gas cylinder with a liquid siphon tube was used to supply the SCFE unit with CO₂. The system valving was configured for upflow through the extraction column and the bleed valve was opened to ensure liquid carbon dioxide flow to the feed pump. A large portion of the CO₂ feed line was packed in an ice cooler in an attempt to prevent vapor from being generated in the feed line. Finally, the feed pump was set at the maximum rate of 400 cc/hr. These efforts were unsuccessful in developing supercritical pressures, however, because the pump was cavitating from vaporized CO₂ in the feed line.

This problem was solved by packing the pump head in ice. The cavitation was caused by the mechanical work put into the fluid by the pump. Since the feed to the pump is nearly saturated (See Figure 5), any small amount of heat input (thermal or mechanical) will first cause saturation

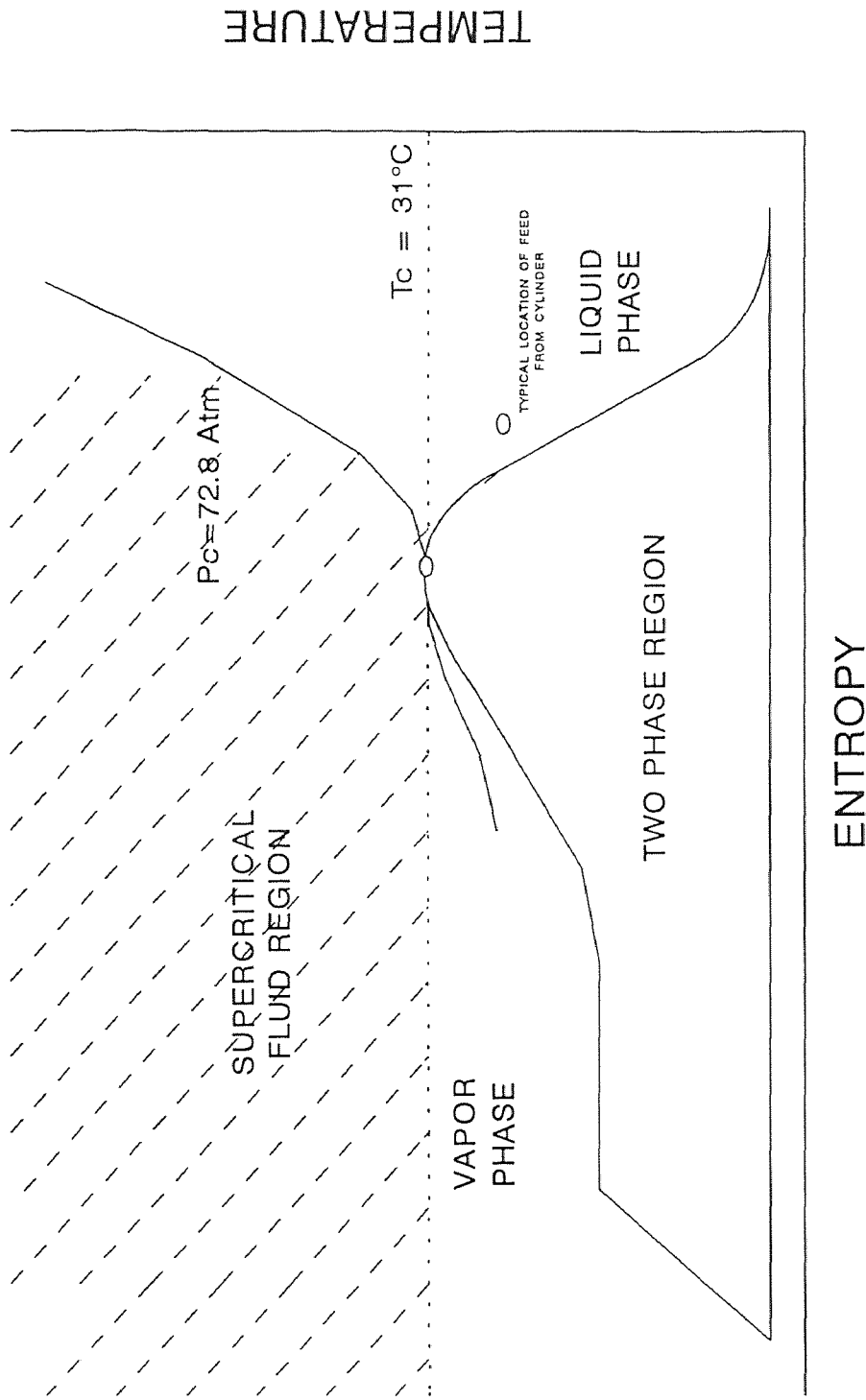


Figure 5
Temperature/Entropy Diagram
for Carbon Dioxide

and then some of the liquid to vaporize. Further, the amount of subcooling obtained from packing the feed line in ice was not sufficient to remove the additional heat added by the pump; this caused some of the CO₂ to vaporize. This vapor causes the feed pump to cavitate and in the worst case, to vapor lock. Once the pump head was packed in ice, the system was able to generate and maintain supercritical pressures. This was a clear indication that liquid was being supplied to the pump and that the pump was no longer cavitating.

Once these pressures were obtained, it became evident that pressurizing the entire system would take a fairly long time, 20 minutes or more. This meant that it would also take a long time to determine if the pump was pumping properly or cavitating. In order to reduce this time, the extraction column was isolated from the system by shutting the appropriate valves. This greatly reduced the volume of the system that needed to be pressurized by the feed pump which in turn reduced the time it took to generate high pressures in that part of the system. If liquid CO₂ was being properly supplied to the pump, then it just took a few minutes to pressurize the isolated part of the system. Once proper pump operation was confirmed, the extraction column was re-opened to the system in the desired configuration (upflow or downflow) for full system pressurization.

If pressure significantly above tank pressure was not achieved in the isolated part of the system in the first few minutes, then the bleed valve was opened again to vent off any vapor that had formed in the feed line. This was repeated until the desired pressure was obtained in a reasonable period of time. If venting off the vapor did not correct the problem, then more ice was added to the pump head and the procedure was again repeated.

Initial runs were conducted on the apparatus in the upflow configuration. Each of these runs were completed with the extraction column completely loaded with naphthalene (Aldrich Chemical Company, Cat. # 91-20-3, 99+% pure, scintillation grade), about 30-40 grams. The actual column charge weight varied a little with each experiment because of the widely varying naphthalene particle size. This created a slightly different void fraction each time which was responsible for the differing column load weights. In all cases however, the column load weight was between the 30-40 gram range. The column was weighed before and after each experiment and the weight difference was used as the total naphthalene extracted. The total CO_2 used in the experiments was obtained from the totalizing dry test meter. In some cases, estimates of CO_2 losses from the pressure relief valve on the extract receiver also had to be made. The naphthalene concentration in the fluid phase was obtained by converting both quantities to moles and then

dividing the number of pounds of naphthalene by the total number of moles (naphthalene and carbon dioxide). From this point, assuming ideal gas for the carbon dioxide, and using standard conversions, any concentration units can be obtained (i.e., lb_m/ft^3).

In doing these initial runs, it became clear that the micro-metering valve used to maintain pressure and control flow through the extraction column would need to be relocated. The original location for this valve was about 18 inches upstream of the extract receiver. As the CO_2 and naphthalene mixture passed through the valve, the pressure was reduced to just slightly above atmospheric. The sudden reduction in pressure caused a subsequent reduction in naphthalene solubility and continuously caused now insoluble naphthalene to plug the line. This plug would isolate the extraction column from the dry test meter making it impossible to accurately measure the amount of carbon dioxide used in the experiment. The problem was resolved by relocating the micro-metering valve further downstream so that it discharged almost directly into the extract receiver.

Once this was corrected, experiments were run at various pressures from 700 psig to 4500 psig ($P_c=1085$ psig). The results of these experiments were difficult to interpret because the discharge tubing from the extraction column to the micro-metering valve would plug periodically during

shutdowns. The reason for this is very similar to the reason why the line was plugging before the metering valve was relocated. As the system was being shut down, the pressure in the system would begin to decrease. This decrease in pressure would result in some amount of previously soluble naphthalene to become insoluble and precipitate out in the discharge line. This problem can be overcome by carefully monitoring the experiment shutdown but may make student-run experiments more difficult. One recommendation will be to include a way of depressurizing the system during shut down that does not utilize the micro-metering valve but still passes the CO_2 through the dry test meter.

Another problem which occurred was that the data indicated that the column discharge stream was saturated with naphthalene. This being the case, a mass transfer analysis approach would be of little use; i.e., $c_2 = c_{1\text{sat}}$ in Equation 18.

The most likely reason the column discharge was saturated with naphthalene was the very low CO_2 space velocity in the column. Even with the feed pump set at the maximum rate of 400 cc/hr, the empty column superficial velocity was only 1.09 in/min (2.78 cm/min). With such a slow superficial velocity, it appears that the CO_2 contact time in the column was long enough for the system to reach phase equilibrium. Since the feed pump was already set to

deliver the maximum rate, the only other way to reduce the CO_2 contact time was to reduce the naphthalene bed height.

This can be accomplished by loading the column with less naphthalene and then filling the rest of it with sand or some other inert material. As a reasonable first guess, the bed height should be reduced to about 4 inches or roughly 25% of the previously tested bed heights (about 10 grams of naphthalene). This should ensure that the students do not obtain results that indicate that the exit stream is saturated and still provide enough naphthalene mass for the gravimetric analysis used in the experiment to be reasonable.

Finally, the questions at the end of the experiment were designed to prompt the students to think about column performance characteristics and scale-up, the mechanical issues of design, and how thermodynamics and property prediction are necessary parts of practical chemical engineering applications. In order for the students to properly answer all of the questions, they will have to formulate an experimental plan prior to starting their work. In doing so, the students need to recognize that these experiments cannot be done haphazardly because of the time constraints they are under. They will need to generate, at a very minimum, three quality sets of experimental data, and preferably more than the three sets. It should be pointed out that with fewer than three data sets, some of the

questions cannot be answered. Further, since the column pressure control fluctuates widely (± 300 psig), the students will have to account for this in the experiments they choose to run.

For example, little data may be obtained from experiments run at 1300 psig and 1800 psig. The 1300 psig target could easily drift up to 1500 psig or 1600 psig and the 1800 psig target could just as easily drift down to 1500 or 1600 psig. To avoid this problem, it is recommended that the students choose pressure targets at least 1000 psig apart but not more than 1500 psig.

If the targets are too far apart, this will cause a problem in not having a large enough operating window to get the necessary data. For example, if the students choose 2500 psig as a starting point and want to increment by 2500 psig, they will only be able to achieve one additional run at 5000 psig. They will not be able to achieve the third run at 7500 psig because it exceeds the upper operating limit of the unit (nominally, 7000 psig because of the rupture disc).

In order to avoid this problem, two experimental plans are outlined below. These can be given to the students if necessary but the students should be encouraged to devise the experimental plans for themselves. In both, the temperature, as long as it is below 55 °C, is not important and can be chosen arbitrarily by the students. Temperatures

above 55 °C may ultimately result in column operating pressures higher than desired. It should also be noted that temperatures below 31 °C can be chosen but will result only in near critical conditions and not supercritical conditions. Table 3 summarizes the first set of possible experiments and Table 4 summarizes the second set.

Ambient temperature has been chosen as one of the operating temperatures in these Tables only as a matter of convenience. By doing so, the necessity to control one of the operating parameters, specifically temperature, has been removed which might make operating the lab easier to handle during the first few experimental runs. In the case of either experimental plan if time permits, additional runs at 35 °C should be completed.

Table 3

Experimental Plan A

Pressure Incremented by 1000 psig Intervals

Run #	Column Pressure (psig)	Column Temperature (°C)
1	1000	Ambient
2	2000	Ambient
3	3000	Ambient
4	4000	Ambient
5	1000	35
6	3000	35

Table 4

Experimental Plan B

Pressure Incremented by Factors of the Critical Pressure

Run #	Column Pressure (psig)	Column Temperature (°C)
1	P_c	Ambient
2	$2 \times P_c$	Ambient
3	$3 \times P_c$	Ambient
4	$4 \times P_c$	Ambient
5	P_c	35
6	$3 \times P_c$	35

Detailed answers to the questions that the students have been asked to answer along with sample calculations can be found in Appendix B. The data used in Appendix B to illustrate the sample calculations were estimated only, not truly measured since much of the experimental data indicated that the column discharge stream was saturated with naphthalene. It should not be taken as rigorous experimental data. Appendix B also has a sample data sheet for an experimental run.

4.3 STUDENT PROBLEMS

Some comments on the parts of the experimental procedure that could be most troublesome to the students are noteworthy (refer to Figure 3). In addition, an

Instructors's troubleshooting guide is contained in Appendix D.

First, obtaining critical pressures will be very difficult if there is not enough cooling supplied at the pump head or the vaporized CO₂ in the feed line is not properly vented off. If this happens, attempt to vent the feed line or add more cooling to the pump head as discussed earlier. It is important to note that it is not necessary to get liquid CO₂ out of the vent valve, V1. As long as whitish haze and some "snow" is discharged, the system should be properly vented. If this does not correct the problem, check to make sure that the gas supply cylinder is not empty. Additionally, make sure the cylinder is fitted with a siphon or bottom discharge tube to supply liquid to the pump.

Second, once flow is established in the extraction column, the discharge rate must be kept below 0.05 SCFM in the rotameter. Higher rates than this will reduce the column pressure because the feed pump can not maintain a sufficient supply of CO₂ to maintain the pressure. Higher rates will also lead to possible solids entrainment in the piping downstream of the extract receiver.

Third, some solids entrainment in the piping downstream of the extract receiver is inevitable. There is a pressure relief valve and a filter between the receiver and the rotameter. If this filter is allowed to plug, the pressure

relief valve will open, venting CO₂ to the atmosphere before it goes through the rotameter and the totalizing dry test meter. The result is an erroneously high calculated naphthalene concentration in the extraction column discharge. This leads to erroneously high mass transfer coefficients and thermodynamic inconsistencies in the experimentally determined concentration and the predicted equilibrium solubility of the naphthalene. In the worst cases, the experimentally determined value will exceed the predicted equilibrium solubility rendering a mass transfer coefficient calculation useless in characterizing column performance.

Fourth, any evidence of CO₂ leaking from the weep holes in any of the fittings will also lead to inaccuracies in measuring the total CO₂ used. The most likely place for these weep holes to leak is on the extraction column. If the students are not careful when re-assembling the column (as also indicated in Appendix A), the threaded ferrules on the column will be moved and will not properly seal the weep holes. This may also result in a problem with reaching the desired experimental pressure. If the weep hole leak is large enough, the feed pump will not be able to maintain pressure in the column.

Finally, the students should be told **never** to close the micro-metering valve, V8, past the zero mark on the side vernier of the valve body. This valve is a precise metering

valve and is not intended to act as an isolation (on-off) valve for the column; it does not completely seal. It is a needle valve with a tapered stem and seat. Closing the valve past the zero mark on the vernier forces the tapered stem into the seat further than it is designed to go. This will widen the seat taper and ruin the valve. If the students need to isolate the column, the blocking valve, V7, must be used.

4.4 SAFETY

The unit, as a whole, has been designed to be safe. The extraction column is protected by a rupture disc and the downstream equipment after the extract receiver is protected by a safety relief valve. There are a few areas, however, in which the students must be cautioned in. The gas supply cylinder is unregulated and therefore must be handled with extreme care. The critical sample valve (V4) on the high pressure side of the column discharges to the surroundings. If this valve is inadvertently opened, it will discharge the high pressure critical phase to the room.

When operating the apparatus, the feed pump discharge pressure must be closely monitored. While the maximum intended discharge pressure for this pump is less than 6000 psig when pumping water, lower than the nominal rupture disc burst pressure of 7000 psig, the pump is capable of reaching the burst pressure with CO₂. Further, even if the pump

discharge pressure is set lower than the burst pressure, if the column is heated at high pressure, the increase in temperature may be enough to cause the pressure in the column to exceed the burst pressure.

Students should exercise extreme caution when tightening up any loose fittings as indicated by leaks from the fitting weep holes when the system is under pressure. Under no circumstances should the students try to tighten the large nuts at the ends of the column while it is under pressure. A good rule of thumb is to allow the students to only tighten up fittings that are 5/8 inch or smaller while the system is pressurized. Fittings larger than that would likely result in a student twisting the fitting and possibly breaking it while the unit is under pressure.

Finally, Material Safety Data Sheets (MSDS) for carbon dioxide and naphthalene have been included in Appendix F for easy reference.

Chapter 5

RECOMMENDED FUTURE WORK

1. Construct a new extract receiver that has the following changes (Refer to Figure 6):
 - a. Increase the length from 12 to 24 cm.
 - b. Increase the diameter from 6 to 12 cm.
 - c. Make the vessel out of a clear acrylic material.
 - d. Add two additional nozzles making a total of four.

The new design would decrease the superficial gas velocity entering the extract receiver. This should reduce the amount of solids that are entrained in the exit stream and reduce the frequency of cleaning the filter protecting the rotameter and dry test meter. The added nozzles will allow for a pressure relief valve to be installed directly onto the vessel and for a new line to be piped up from the column to the vessel (via the critical phase sample valve, V4, which is a on-off isolation type valve). This line from the critical phase sample valve to the extract receiver will allow the students to bypass the micro-metering valve on shut down and still measure the CO₂ in the column (See Figure 7). This should eliminate the

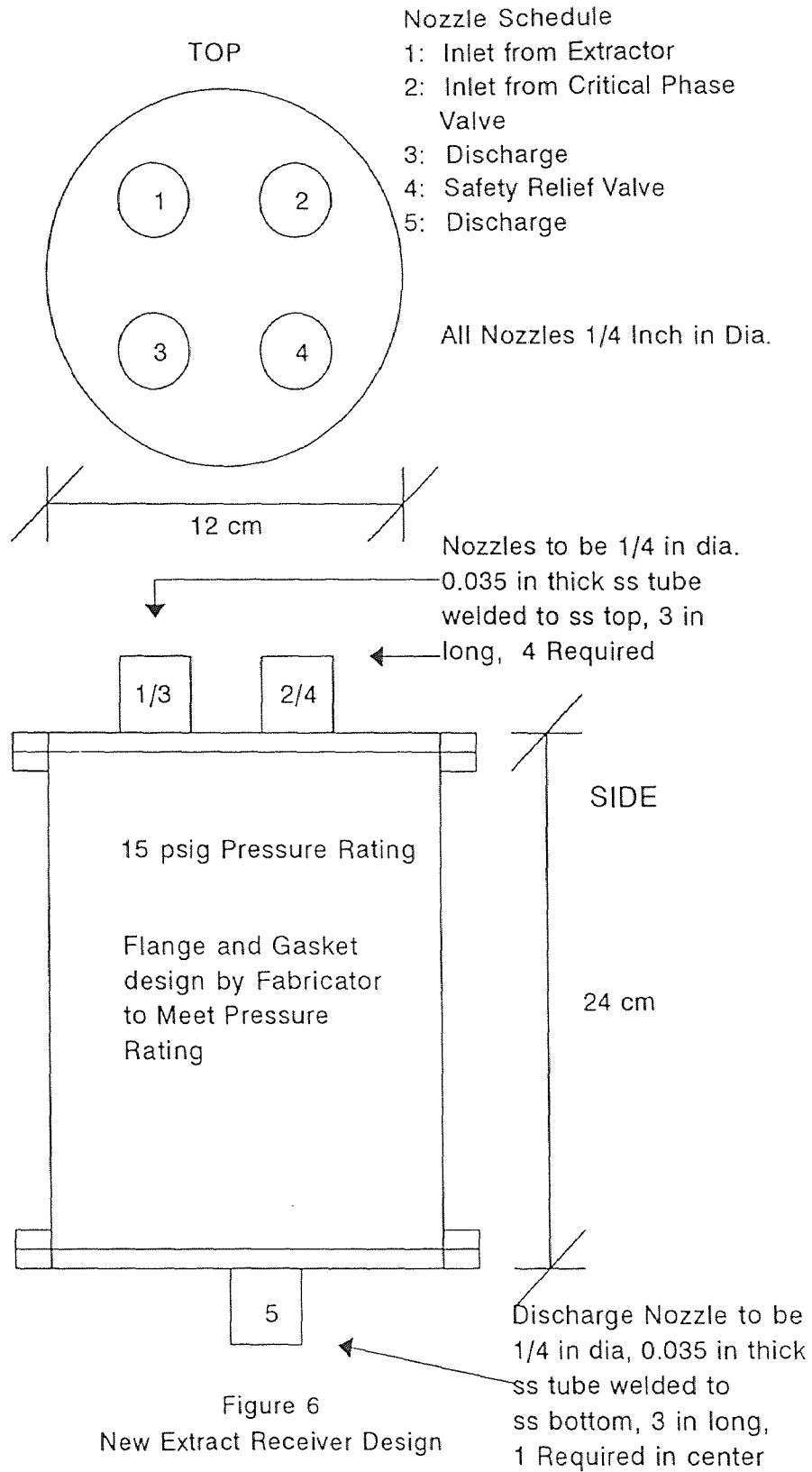


Figure 6
New Extract Receiver Design

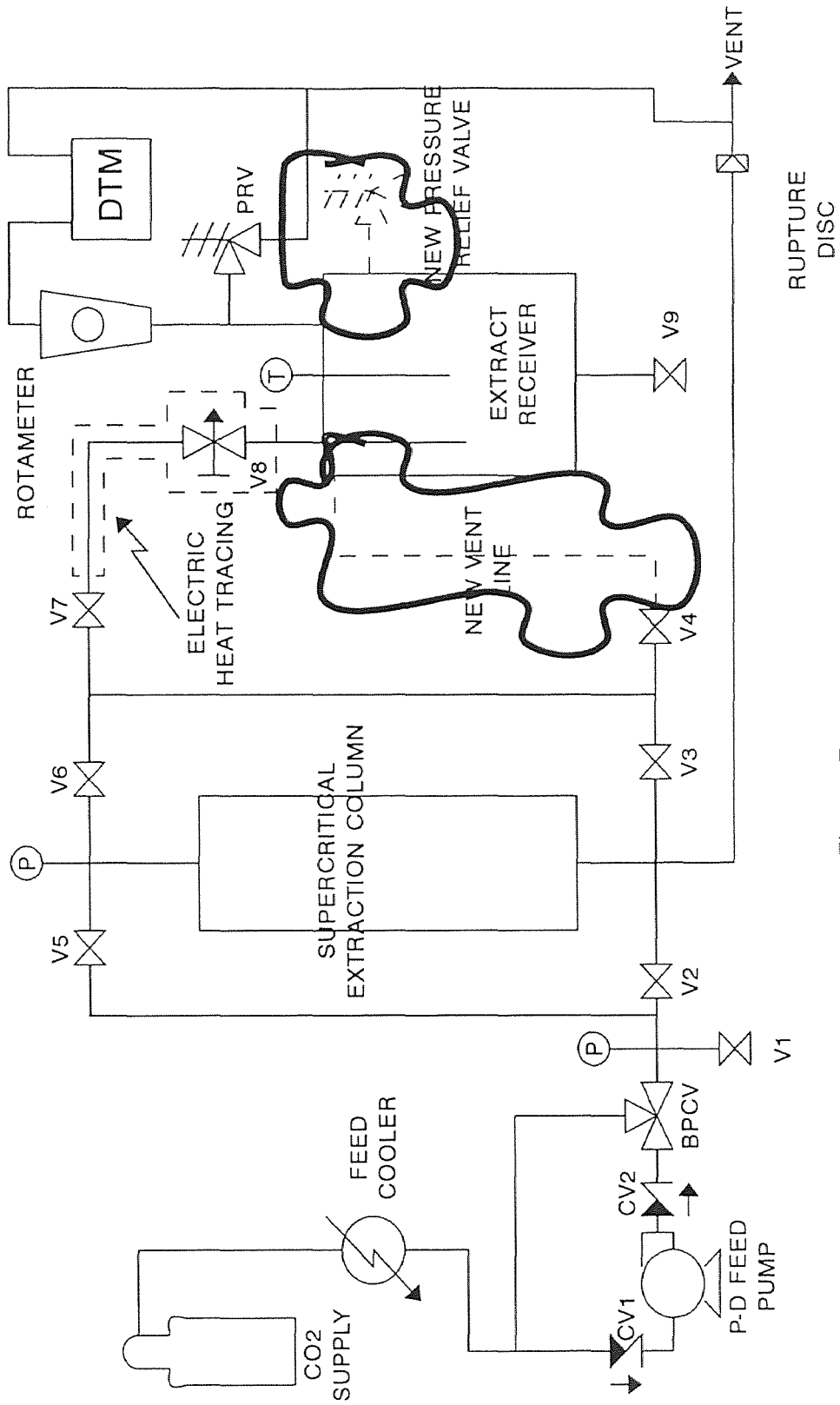


Figure 7
Modified Process Flow Diagram
Includes Bypass for System Shut Down

problem of the discharge line plugging up with naphthalene on shut down because this outlet through the critical phase sample valve will not be restricted by a very small orifice like the metering valve. Installing the pressure relief valve on one of the spare nozzles of the extract receiver will help insure that it is properly protected from overpressurization. If the pressure relief valve is left downstream of the extract receiver in the discharge line and it plugs, then the receiver will no longer have pressure relief protection. Placing it directly on the receiver minimizes the chance of the relief valve being made inoperable from a plug. Finally, if a suitable clear acrylic material can be identified, then the students will be able to visually observe the naphthalene precipitate out into the extract receiver.

2. Install a large high pressure reservoir after the feed pump and in parallel with the extraction column. This could be filled and pressurized with CO₂ prior to starting flow to the extraction column. Once the pump was running and liquid feed was confirmed, this reservoir could be used in conjunction with the feed pump to pressurize the extraction column to the desired operating pressure. This would greatly reduce the time necessary to get to steady state in the column and

speed up the experiments. Additionally, it would minimize the error that results from the CO₂ becoming saturated on start-up while the column pressure is slowly increasing to the desired operating target.

This reservoir would have to be a pressure vessel that was rated for the same pressures as the extraction column. This could possibly be supplied by a vendor such as Autoclave Engineers or Hoke, or costume built by an ASME coded pipe shop. The design of the vessel would be fairly straight forward. It would only need two nozzles, an inlet and an outlet. All necessary instrumentation (pressure and temperature) could be added to the inlet or discharge piping.

3. Have students confirm the surface to volume ratio of the naphthalene packed bed by giving the students the correlation for a modified Sherwood number and have them solve for the ratio.
4. Granulate and sieve the naphthalene crystals. The current experimental plan does not require any size reduction/classification. The result is a very widely varying surface to volume ratio for the naphthalene packed bed. This size reduction could be accomplished by simply crushing the material through a fixed screen size, possibly about 100 mesh. This would reduce the

average particle size in the bed and also decrease the particle size distribution. Both of these will reduce the variability of the surface to volume ratio in the packed bed.

5. Students could be asked to perform the experiment on a variety of different solutes over the period of a year. Each lab group could use a different solute. At the end of the year the students could pool the data together and look for trends in the data that might lead to possible experimental correlations.

6. A two parameter Peng-Robinson EOS could be developed and given to the students for use as a canned program. This would greatly reduce the resulting error obtained in calculating the equilibrium solubility of naphthalene or other solute when using the single parameter Peng-Robinson EOS given in Appendix E and could improve the overall results of the laboratory.

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APPENDIX A

STUDENT OUTLINE FOR
THE SUPERCRITICAL FLUID EXTRACTION OF SOLID NAPHTHALENE
WITH SUPERCRITICAL CARBON DIOXIDE

INTRODUCTION

In this experiment, a packed bed extraction column is used to study the solubility of solid naphthalene in supercritical carbon dioxide. The key objective of the experiment is to determine the mass transfer coefficient for the extraction. Additionally, the measured naphthalene solubility is compared to theoretically determined values. One acceptable method of determining these theoretical values is to use the Peng-Robinson equation of state (EOS).

SUGGESTED PROCEDURE

1. Load extraction column with 8-10 grams of solid naphthalene. Measure the bed height of the naphthalene and then fill the remainder of the column with sand. Refer to Appendix 1 for loading instructions.
2. Check to make sure valves V1, V2, V5, V7, and V9 are shut then connect the CO₂ gas cylinder to the suction side of the feed pump. Refer to Figure 1.

3. Power up the control panel and the electric heat tracing on the metering valve, V8. This heat tracing is controlled by the Briskheat controller and should be set between 15-40% output.
4. Fill the feed cooler with ice water and pack the pump head in ice.
5. Slowly open the gas cylinder valve and then start the pump. NEVER START THE PUMP UP AGAINST A BACK PRESSURE GREATER THAN 800 PSIG (the pump motor is not large enough to start against high back pressures and anything over 800 psig will cause an electrical overload and the fuses to blow). Adjust the pump to 100% output if it is not already there. Open valve V1 very slightly and bleed off any vapor that has formed in the feed line.
6. Once the pump starts to pump liquid and pressure begins to build, shut valve, V1 and either open valves V2 and V6 for upflow or valves V3 and V5 for downflow. Also make sure V8 is closed. **NEVER CLOSE THE METERING VALVE PAST ZERO ON THE VERNIER SCALE - PERMANENT DAMAGE TO THE VALVE SEAT WILL RESULT.**

7. Adjust the column heater to the desired temperature.
This should never be set greater than 55 °C.

8. Once the column is at the desired extraction temperature and pressure, open valve V7 and then adjust the metering valve, V8 so that the flow rate through the rotameter is less than 0.05 SCFM. **NEVER CLOSE THE METERING VALVE PAST ZERO ON THE VERNIER SCALE - PERMANENT DAMAGE TO THE VALVE SEAT WILL RESULT.** This valve (V8) will have to be adjusted continuously in order to maintain a relatively constant pressure in the extraction column. (Why?) Pressure should try to be held to within +/- 300 psig of the desired set point.

9. Operate the column until a minimum of 0.8 standard cubic feet (SCF) of CO₂ have passed through the column (the equivalent of sixteen residence times) as measured by the dry test meter (DTM) to insure good data collection. Sixteen residence times should allow enough steady state operating time to reduce the errors caused by the unsteady state operations of start-up and shut down.

10. Shut either V2 or V5 depending on which flow pattern was chosen, shut off the feed pump, and let the column depressurize.

11. Depressurize the feed section of the system (the section upstream of V2/V5) by slowly opening V1.
12. After the column has been completely depressurized, shut off all electric power to the unit and remove the column. Weigh the column to determine how much naphthalene has been lost after the column cools down to room temperature. Also record the total SCF of CO₂ gas that was used. There is no need to remove and clean the extract receiver until all of the experiments have been completed.
13. Repeat steps 2-12 for each pressure and temperature combination studied. TEMPERATURE SHOULD BE KEPT CONSTANT WHILE PRESSURE IS VARIED FROM JUST BELOW CRITICAL TO AS MUCH AS 4X CRITICAL. A MINIMUM OF THREE RUNS WILL BE NECESSARY TO ANSWER ALL THE QUESTIONS. A second temperature can be studied if time remains after the first three experiments.
14. After all experiments are complete, remove the extract receiver, clean it out, and replace it so it will be ready for the next lab session.

USEFUL DATA:

EXTRACTION COLUMN:

Nominal Length:	12 inches
Nominal Diameter:	1 inch
Pressure Rating @ 72 °F:	10,000 psig
Pressure Relief Device:	Rupture Disc Set @ 7000 psig @ 72 °F

USEFUL DATA (Continued):

EXTRACT RECEIVER:

Nominal Length:	4 inches
Nominal Diameter:	2 inches
Pressure Rating @ 72 °F:	15 psig
Pressure Relief Device:	Pressure Relief Valve set @ 5 psig @ 72 °F

FEED PUMP:

Type:	Positive Displacement
Motor Size:	0.25 Hp
Capacity:	40-400 cc/hr
Backflow Protection:	Double Ball Valves on Suction and Discharge Sides of Pump

DISCUSSION TOPICS

1. Is the column exit stream saturated with naphthalene?
2. Determine the mass transfer coefficient, k .
3. For packed beds, the mass transfer coefficient can be represented as a function of the N_{Re} and the N_{Sc} numbers. If that function takes the form of:

$$k/v^0 = a(N_{Re})^b(N_{Sc})^c$$

where V^0 is the empty column superficial velocity, then determine the values of the constants a , b , and c .

4. What is the fugacity coefficient of the solute in the condensed phase at its sublimation pressure?
5. Use the Peng-Robinson or other suitable EOS to predict the solubility of the solute in the supercritical solvent. How well does the EOS predictions compare to solubilities reported in the literature?
6. How much energy input is required to maintain isothermal conditions across the metering valve, V8?

DISCUSSION TOPICS (Continued)

7. Support your decision to operate the column in either the upflow or downflow configuration. (While at this scale, this decision is not very important, it becomes critical as the scale is increased.)

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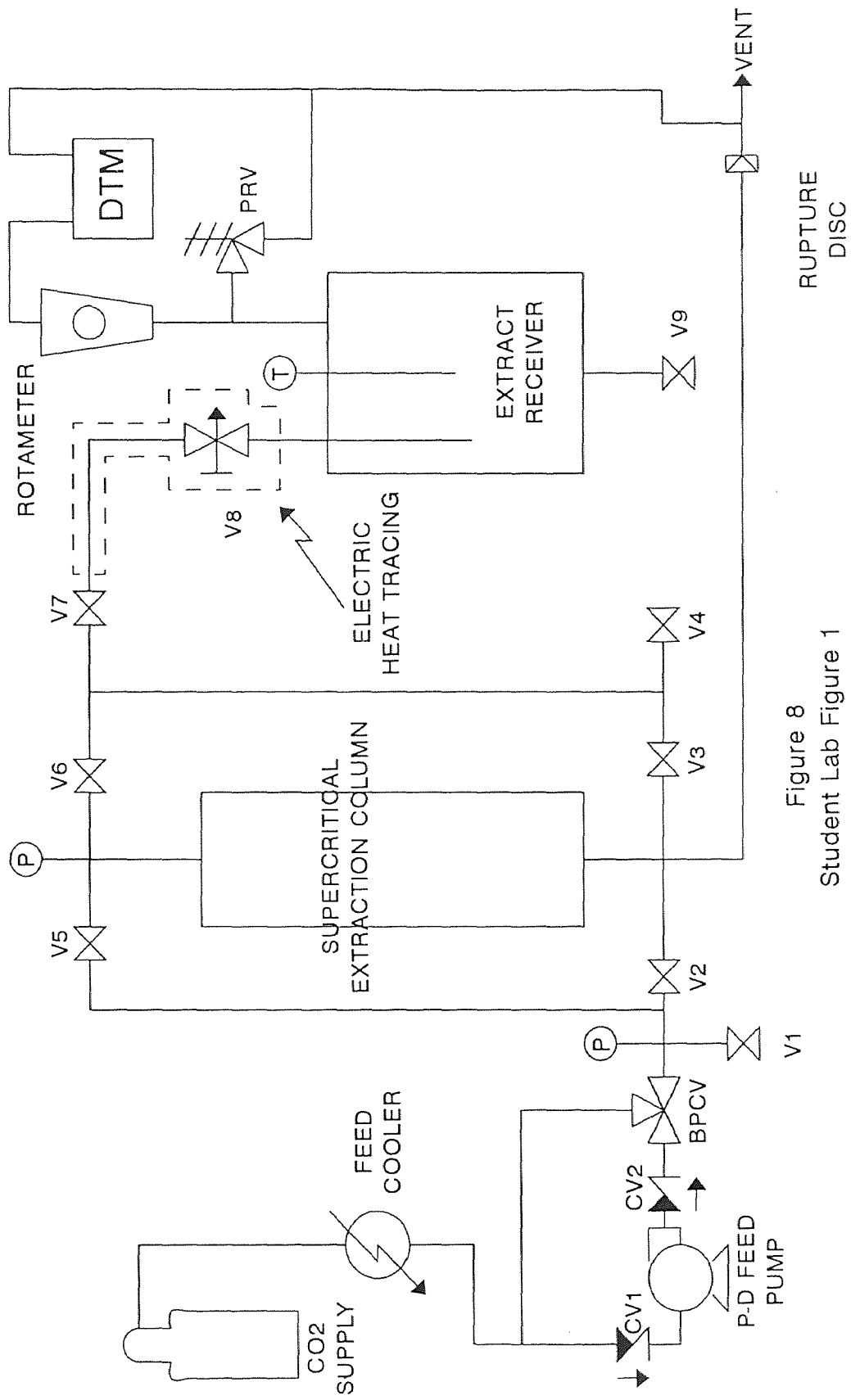


Figure 8
 Student Lab Figure 1
 Process Flow Diagram

STUDENT EXPERIMENT APPENDIX 1
SUPERCRITICAL FLUID EXTRACTION
COLUMN LOADING/UNLOADING

SAFETY:

-NEVER REMOVE COLUMN WHILE GAS SUPPLY CYLINDER IS CONNECTED
TO THE UNIT.

-NEVER ATTEMPT TO DO ANY WORK ON COLUMN UNTIL YOU HAVE
VERIFIED THAT IT IS NOT UNDER ANY PRESSURE. ALWAYS
OPEN V1, V2, V3, AND V4.

-NEVER ATTEMPT TO REMOVE THE COLUMN CAP NUTS WHILE COLUMN IS
STILL UNDER PRESSURE OR IN PLACE ON THE SKID.

REFER TO FIGURE 2.

1. Verify gas supply cylinder is not connected to the process and that V1, V2, V3, and V4 are all open. This insures the column is not under any pressure and is vented.
2. Disconnect the heat tracing wire and the thermocouple wire (on the column).

3. Loosen the 1/4 inch tube nut connections at the top and bottom of the column. Remove the tubing from the top and bottom of the column.
4. Remove the "U"-bolt supporting the column on the stand. The column can now be lifted off the stand and brought to a bench to be worked on.
5. Loosen the top and bottom cap nuts on the column with large crescent or open end wrenches. DO NOT MOVE THE THREADED FERRULES ON EITHER END OF THE COLUMN OR IT WILL LEAK ON RE-ASSEMBLY. Be careful not to strip the nuts.
6. Inspect the column for cleanliness. Clean if necessary, especially the sealing surfaces, refer to Figure 2.
7. In the bottom of one cap nut place a small wad of glass wool and re-install and tighten the cap nut onto the end of the column. The glass wool will prevent solids from falling down into the piping.
8. Load 8-10 grams of naphthalene into the column and measure the bed height of the naphthalene.

9. Finish filling the column with sand or some other known inert solid to complete the packed bed.
10. Place another small wad of glass wool into the other cap nut and re-install and tighten it. The column is ready for installation back on the SCFE unit.
11. While holding the column in one hand, start the 1/4 inch tubing nuts into the column cap nuts on top and bottom. Tighten these nuts until they are hand tight.
12. Hang the column off the supports with the "U"-bolt and tighten.
13. Tighten the 1/4 inch tubing nuts and re-connect the heat tracing and thermocouple leads.
14. Close valves V1, V2, V3, and V4.
15. Connect the gas supply and check the column for leaks while starting up. If leaks are found on any small fittings (5/8 inch or less) while the column is being pressurized, try to gently tighten them in place. If this fails, the unit must be taken back apart and re-assembled taking special care to check the alignment of

the threaded ferrules and the cleanliness of all sealing surfaces.

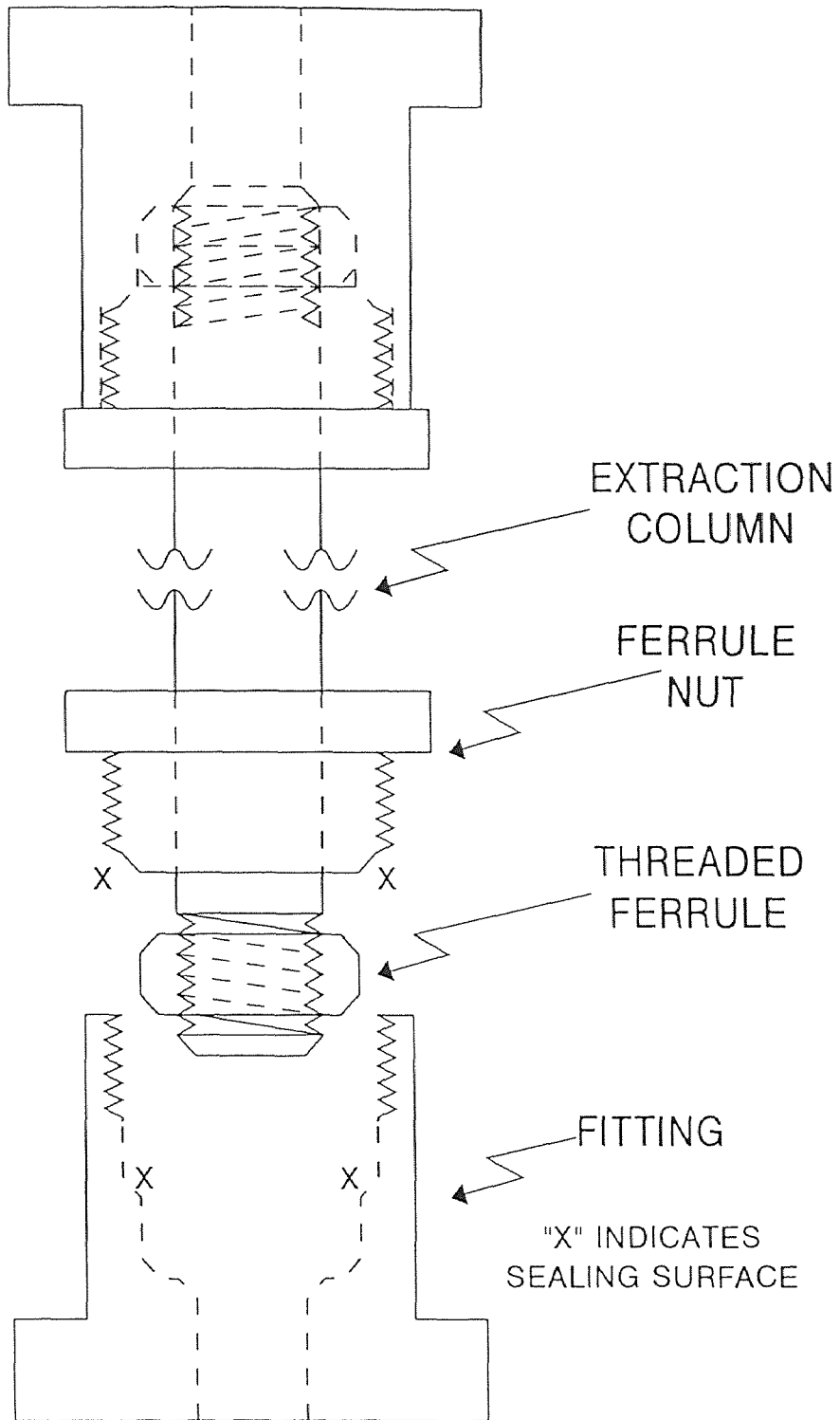


Figure 9
Student Lab Figure 2
Column Assembly Detail

APPENDIX B

SAMPLE
DATA SHEETS, CALCULATIONS,
AND
ANSWERS TO QUESTIONS

NOTE: THE DATA CONTAINED IN THIS APPENDIX HAS BEEN
ESTIMATED. IT SHOULD ONLY BE USED FOR
ILLUSTRATIVE PURPOSES.

TABLE 5
SAMPLE EXPERIMENTAL DATA SHEET

COLUMN WT, INITIAL (GRAMS): 2676.2 DRY TEST METER INITIAL READING (SCF): 222.770
 COLUMN WT, FINAL (GRAMS): 2674.3 DRY TEST METER FINAL READING (SCF): 225.426
 BED HEIGHT, (INCHES): 3.5 AMBIENT TEMPERATURE (°F): 72

TIME HR/MIN	P1 PSIG	P2 PSIG	FLOW RATE SCFM	DTM SCF	COMMENTS
00:00	4500	4500	0.03	222.770	
00:05	4600	4600	0.04	222.95	
00:10	4500	4500	0.05	223.09	
00:15	4300	4300	0.04	223.27	ADJUSTED V8
00:20	4500	4500	0.04	223.49	
00:25	4500	4500	0.05	223.73	
00:30	4800	4800	0.04	223.93	ADJUSTED V8
00:35	4700	4700	0.05	224.18	
00:40	4500	4500	0.03	224.26	
00:45	4500	4500	0.03	224.45	
00:50	4600	4600	0.05	224.62	
00:55	4300	4300	0.04	224.78	ADJUSTED V8
01:00	4400	4400	0.05	225.01	
01:05	4600	4600	0.05	225.28	
01:10	4300	4300	0.03	225.426	

P1: UPSTREAM EXTRACTION COLUMN PRESSURE, P2: DOWNSTREAM EXTRACTION COLUMN PRESSURE
 DTM: DRY TEST METER; INTERMEDIATE VALUES ONLY READ TO TWO PLACES

SAMPLE CALCULATIONS AND
ANSWERS TO THE QUESTIONS IN THE DISCUSSION TOPIC

Question 1: Is the exit stream saturated with naphthalene?

The answer should be no. The result could be presented in a Table of naphthalene concentration in the exit stream vs the naphthalene solubility at equilibrium as predicted by the student's EOS program. The method for doing this type of calculation is outlined in Appendix E along with an example program coded in Basic.

Table 6

**Naphthalene Concentration in Column Discharge vs
Predicted Equilibrium Solubility from an EOS Model**

Pressure	Measured Conc'n.*	Predicted Equilibrium Sol.
psig	mol fraction	mol fraction
700	0.000107	0.00005658
2000	0.005483	0.01070
2300	0.005790	0.01210
3000	0.007378	0.01439
4500	0.007591	0.01670

* These measured values are only estimates because some CO₂ was lost from the pressure relief valve in some experiments and this had to be estimated. Additional errors may have occurred because the exit stream may have been saturated but this could not be determined with the CO₂ losses.

If the student results indicate a saturated exit stream, then they should discuss the following points. First, the concept of a mass transfer approach is not really valid because it is impossible to determine at what point in the column saturation occurred. Second, if saturation did in fact occur, then that implies that column performance can be increased because some of the fixed bed in the column was not being fully utilized (the supercritical carbon dioxide became saturated in some nominal bed depth that was less than the actual bed depth). On commercial scale equipment, the most likely way to increase column performance would be to increase the feed rate providing higher throughputs to better utilize the extraction bed. Lastly, the students should discuss what possible experimental errors led to the saturated result. These could include but are not limited to:

1. Poor column weighing before or after extraction.
2. A misread Dry Test Meter.
3. A loss of CO₂ from a leak or from the pressure relief valve opening.
4. Computational error.

Even if the students have determined that the column discharge was saturated, they should still proceed with the rest of the questions to demonstrate they can do the analysis.

Question 2: Determine the mass transfer coefficient, k .

The solution to this problem is straight-forward once the equilibrium solubility of the naphthalene in the CO_2 at the various pressures and temperatures is known.

Equation 18, after rearrangement provides the desired result directly.

A sample calculation follows.

First, the empty column superficial velocity, V^o , needs to be calculated. The cross sectional area of the column is:

$$A = \frac{\pi (D^2/144)}{4}; D = 0.688 \text{ inches}$$

$$A = 0.0026 \text{ ft}^2$$

The volumetric throughput of the feed pump is 400 cc/hr (the pump is set for maximum rate), therefore,

$$V^o = 400 \frac{\text{cm}^3}{\text{hr}} * \frac{\text{inches}^3}{2.54^3 \text{cm}^3} * \frac{\text{ft}^3}{12^3 \text{inches}^3} * \frac{1}{0.0026 \text{ ft}^2} * \frac{\text{hr}}{3600 \text{ sec}}$$

$$V^o = 0.0015 \text{ ft/sec}$$

The following other data are known or have been measured:

$$a = 2.6 \text{ ft}^2/\text{ft}_3$$

$$c_{\text{isat}} = 0.0039 \text{ lb}_m/\text{ft}^3$$

$$c_1 = 0.0020 \text{ lb}_m/\text{ft}^3$$

The log mean concentration difference can be determined as follows:

$$\Delta C_{LM} = \frac{(C_{1sat} - 0) - (C_{1sat} - C_1)}{\ln \frac{(C_{1sat} - 0)}{(C_{1sat} - C_1)}}$$

$$= \frac{0.0039 - (0.0039 - 0.0020)}{\ln \frac{0.0039}{(0.0039 - 0.0020)}}$$

$$\Delta C_{LM} = 0.0028 \text{ lb}_m / \text{ft}^3$$

Then the mass transfer coefficient, k , can be obtained directly from Equation 18:

$$\frac{C_1 V^0}{az} = k \Delta C_{LM}$$

where z is the length of the fixed bed.

Rearranging and solving for k ,

$$k = \frac{C_1 V^0}{az \Delta C_{LM}}$$

Plugging in, $k = 4.121 \times 10^{-4} \text{ ft/sec}$

Question 3: For packed bed, the mass transfer coefficient can be represented as a function of the N_{Re} and the N_{Sc} numbers. If that function takes the form of:

$$k/V^0 = a (N_{Re})^b (N_{Sc})^c \quad A1$$

where V^0 is the empty column superficial velocity, then determine the values of the constants a , b , and c .

The answer to this question requires that k be determined for at least three different experimental conditions.

The Reynolds and Schmidt numbers also need to be calculated for each set of conditions. The diameter used in the Reynolds number should be the mean particle diameter. The diffusion coefficient used in the Schmidt number was taken as the average of the values reported by Funazukuri and Ishiwata (1992) and assumed to be independent of temperature and pressure. The viscosity of the CO_2 was estimated by the method presented by Jossi, Stiel, and Thodos (1962).

For example, once k , N_{Re} , and N_{Sc} were determined for the three sets of experimental conditions, then Equation A1 can be rearranged as follows:

$$\ln(k/V^0) = \ln a + b \ln(N_{Re}) + c \ln(N_{Sc}) \quad A2$$

The results for k , N_{Re} , and N_{Sc} from each experiment can then be plugged into Equation A2. This generates a

system of three equations with three unknowns, a , b , and c . These can be solved in any number of convenient ways to determine the values for the coefficients. The literature values are respectively, 1.17, -0.42, and -0.67 (Cussler, 1984). Additionally, if the students are able to get more than three sets of experimental data, rather than solving a simple set of three equations with three unknowns, they could employ a regression technique to determine the constants.

Question 4: What is the fugacity coefficient of the solute in the condensed phase at its sublimation pressure?

The partial fugacity coefficient of the solid in the condensed phase must be equal to 1. This is a result of the low vapor pressure of the solid at the conditions of interest. Further, if the partial fugacity coefficient was equal to anything other than 1, then that would indicate that the condensed phase was not a pure solid and some of the basic assumptions made in determining the equilibrium solubility of the solid on the solvent would no longer be valid.

Question 5: Use the Peng-Robinson or other suitable EOS to predict the solubility of the solute in the supercritical solvent. How well does the EOS prediction compare to values reported in the literature?

A Computer Program written in BASIC for a Peng-Robinson EOS using a single binary interaction parameter has been provided in Appendix E along with flow sheets on how to solve the problem.

Question 6: How much energy input is required to maintain isothermal conditions across the metering valve, V8?

This is a classic Joule-Thomson (J-T) isenthalpic throttling problem. The students should be encouraged to measure the temperature decrease across the micro-metering valve experimentally with pure CO₂ to get a physical feel for how significant this effect can be. This should not be done with a CO₂/naphthalene mixture because the mixture is likely to plug up the discharge system without the necessary heating on the valve. While measuring this effect with pure CO₂ will only be an estimate, it will be a fairly good one because the naphthalene concentration expected in the exit stream during an experiment is very low, much less than 1 wt%.

Alternatively, the students could use the J-T coefficient for carbon dioxide to estimate the

temperature drop theoretically. In either case, once the temperature drop is known, a straight-forward energy balance will provide the necessary heat input information. A sample calculation follows for a case with a 700 psig pressure drop. In it, the temperature loss across the valve was estimated; the J-T coefficient was obtained from Bromberg (1985) and assumed to be independent of pressure.

Since the CO₂ mass flow rate is being measured downstream of the micro-metering valve on the low pressure side, the gas can be assumed to be ideal. The discharge rate is 0.05 standard ft³/min.

$$\dot{m} = 14.7 \text{ psia} * \frac{0.05 \text{ ft}^3}{\text{min}} * \frac{1}{459 + 70 R} * \frac{1 \text{ lbmol} R}{10.73 \text{ psia ft}^3} * \frac{44 \text{ lbs}}{\text{lbmol}}$$

$$\dot{m} = 0.0057 \text{ lb/min}$$

The J-T coefficient for CO₂ at 21°C (70°F) is 1.1232 °C/atm so

$$\Delta T = 1.1232 \Delta P$$

$$= 1.1232 (1 - 47.6); T \text{ is } ^\circ\text{C}, P \text{ is atm}$$

$$\Delta T = -52.3^\circ\text{C}$$

Knowing the total mass flow rate of the CO₂ and the temperature change, a simple energy balance can be done around the metering valve:

$$Q = \dot{m} C_p \Delta T$$

$$Q = 0.0057 \text{ lbs/min} * \frac{0.201 \text{ BTU}}{(\text{lb}^\circ \text{F})} * 126.14^\circ \text{F}$$

$$Q = 0.1445 \text{ BTU/min}; 9 \text{ BTU/hr}$$

A more accurate alternative solution may be obtained if a Temperature/Enthalpy or other similar thermodynamic data chart is used. The students could identify the point before the metering valve on the chart, follow a constant enthalpy line to the reduced pressure and obtain the specific enthalpy (BTU/lb) change directly. This could then be multiplied by the mass flow rate to provide the desired result.

Question 7: Support your decision to operate the column in either the upflow or downflow configuration.

Most liquid/solid extraction processes are run in an upflow configuration. Usually the only deviation from this is on the rare occasion when the solute happens to be lighter than the solvent. In that case, the column would most likely be run in a downflow configuration. There is no real difference in terms of the mechanics of operation between a normal liquid/solid extraction and a SCF/solid extraction so the same logic should apply.

APPENDIX C
DETERMINATION OF THE SURFACE TO VOLUME RATIO
FOR THE NAPHTHALENE PACKED BED

Test runs were conducted on the unit to estimate the value of a , the surface area to volume ratio for the naphthalene in the column.

The surface to volume ratio for the naphthalene packed bed was estimated to be $2.6 \text{ ft}^2/\text{ft}^3$ by solving equation 18. In order to use equation 18, first the mass transfer coefficient needed to be calculated from equation 20. Then the equilibrium solubility of naphthalene in supercritical CO_2 needed to be estimated.

The viscosity, density, and diffusion coefficient were all necessary to solve equation 20. The viscosity was estimated from the method described by Jossi, Stiel, and Thodos (1962). The supercritical CO_2 density was obtained from a Pressure-Entropy Diagram (Perry and Chilton, 1973). In solving for the Reynolds number in Equation 20, the diameter used was the average particle size diameter in the packed bed and the supercritical fluid in the column was assumed to be pure CO_2 . This assumption is based on the fact that the naphthalene mole fraction was less than 0.02 at the conditions the experiments were run at. Additionally, as with most diffusion problems, the diffusion coefficient was assumed independent of pressure and temperature. The diffusion

coefficient was obtained by averaging the values reported by Funazukuri and Ishiwata (1992).

The naphthalene solubility was estimated from a computer program that utilizes the P-R EOS with a single binary interaction parameter (Appendix E).

The estimated surface to volume ratio is an order of magnitude estimate only as a result of the error in predicting the equilibrium solubility of naphthalene with the P-R EOS. The error is also partially due to the physical state of the naphthalene being used in the experiment. The material was in the crystalline form and varied greatly in size and shape, everything from fine dust to 0.25 inch long thin sheets). This error could be reduced by processing the naphthalene through a size reduction/classification process such as grinding and screening. This would result in naphthalene particles with a much more normal (and narrow) size distribution that a surface to volume ratio could better represent. This was one of the recommendations for improving the laboratory in the future.

APPENDIX D
EXPERIMENTAL TROUBLESHOOTING GUIDE

This troubleshooting guide is intended to be used by the student, lab assistant, and the instructor. It will focus only on mechanical issues and will not aide the students in answering any of the questions at the end of the lab. The guide has been set up in tabular form with columns for symptom, most likely causes, and, finally, corrective actions. In the case of more than one listed symptom, the first one given may not necessarily be the most likely. The situation at hand will determine which corrective actions are tried first, second, and so on until the problem is corrected. Additionally, a second Table, Table 8 covers key safety and mechanical "DO's and DO NOT's".

One additional helpful note is that if anything (lines or equipment) becomes plugged or coated with solid naphthalene, then a carbon tetrachloride solvent wash (done in a fume hood) should work well in removing the naphthalene.

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
1. Can not generate pressure above the cylinder pressure in the system.	1.1. CO ₂ cylinder is empty of liquid.	1.1. Replace cylinder.
	1.2. CO ₂ cylinder is not equipped with a siphon tube.	1.2. Replace cylinder.
	1.3. Feed line has not been properly vented.	1.3. Open valve V1 until the feed line is properly vented.
	1.4. Pump head is not packed sufficiently in ice.	1.4. Add ice to pump head and vent feed line through V1.
	1.5. System has a leak in it or rupture disc is blown.	1.5. Fix leak or replace disc.
	1.6. CO ₂ valve is not open.	1.6. Open valve.
	1.7. Feed pump is broken.	1.7. Refer to manual on feed pump.

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
2. System up to column is pressurized when isolated but when opened to column the system can not maintain or generate pressure.	2.1. Column has a leak.	2.1 Shut system down and fix leak.
	2.2. Improper valve is opened. Either a valve that needs to be opened is not or a valve that should be closed is open.	2.2. Check to make sure that the valves are lined up properly and that the valves that need to be open are and the ones that need to be closed are.
	2.3. System has not been given enough time to repressurize after the large volume associated with the column was added to the system.	2.3. Allow enough time for feed pump to repressurize the system. This could take 20 minutes or more.
	2.4. Line between feed pump and column has plugged.	2.4. This is a very unlikely possibility. If it is expected, disconnect the column and try to blow CO ₂ through the system.

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
2.	<p>System up to column is pressurized when isolated but when column is put in line the system can not maintain or generate pressure.</p> <p>2.5. Back pressure control valve is not properly adjusted.</p>	<p>2.5. Check the adjustment of the back pressure control valve. Turning it clockwise will increase the pressure the extraction column sees.</p>
3.	<p>System has been working well and then starts to loose pressure.</p> <p>3.1. The feed pump is cavitating because it no longer has enough cooling.</p> <p>3.2. The system has developed a leak. Most likely, one of the fittings was leaking to begin with but some foreign material or solid CO₂ was plugging up the weep hole. The material finally blew free and the leak re-started.</p>	<p>3.1. Replace the ice around the feed pump and vent the system through V1.</p> <p>3.2. If it is a small leak not on the column, try to tighten it up. If the leak is on the column, shut the system down and tighten it per the column installation instructions.</p>

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
3.	System has been working well and then starts to loose pressure.	3.3. The CO ₂ tank has gone empty. (It may still have pressure but there is no liquid, only vapor in it.) 3.4. While adjusting the micro-metering valve, it was opened too much and left open.
3.3.	Take all possible data in an attempt to save the experiment then shut down the system and replace the CO ₂ tank.	
3.4.	Readjust the micro-metering valve. The flow may have to be reduced to even below the 0.05 SCFM maximum rate in order for the column to repressurize.	
4.	Rotameter is indicating loss of flow control from the desired specification of 0.05 SCFM.	3.5. Rupture disc has blown 4.1. Micro-metering valve is improperly adjusted.
3.5.	Replace rupture disc.	
4.1.	Readjust micro-metering valve. If it has plugged with solid material, it may have to be cycled full open and then shut again to remove the solid material.	

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
4. Rotameter is indicating loss of flow control from the desired specification of 0.05 SCFM.	<p>4.2. Line between extraction column and micro-metering valve is partially plugged.</p> <p>4.3 Line between micro-metering valve and extract receiver has partially plugged.</p>	<p>4.2. Shut unit down and clean lines.</p> <p>4.3. Increase heat input from heating tape on metering valve. If this does not correct the problem, isolate column with block valve, V7 and then remove line between metering valve and receiver and replace with a new line that should already be available. Resume experiment if this is done expediently (a few minutes or less).</p>

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
5. Rotameter does not indicate any flow.	5.1. Line between extraction column and micro-metering valve has plugged completely.	5.1. Try establishing flow in opposite direction of original experimental plan (i.e., if system was set up for upflow, then switch to downflow. If this does not work, shut down and clean out line.
	5.2. Line between micro-metering valve and extract receiver has plugged.	5.2. Increase amount of heat input from heating tape and see if line has frozen. If not, isolate column with block valve, V7 and then remove line between metering valve and receiver and replace with a new line. Resume experiment if this is done expeditiously (a few minutes or less).

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
5. Rotameter does not indicate any flow.	5.3. Extract receiver is full.	5.3. Shut block valve V7 to isolate column and quickly clean extract receiver. Continue experiment is this is done expediently (a few minutes or less).
6. Column pressure is not controllable to within specified limit of +/- 300 psig.	6.1. Feed pump is not properly performing.	6.1 See item #2.
	6.2. Micro-metering valve is plugged or partially plugged.	6.2. See items #4 and #5.

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
6. Column pressure is not controllable to within specified limit of +/- 300 psig.	6.3. Column temperature control is not steady (ie. a problem with the band heater or associated control loop).	6.3. Check column temperature carefully. If it is widely fluctuating or far off of set point, first check power cord and thermocouple (TC) connections. If these are ok and problem persists, shut unit down and check TC calibration by immersing it in a water bath of known temperature (i.e., ice bath: 32°F and boiling water: 212°F). If a problem with the TC calibration is found, replace it with a J type. If TC is ok, then there is a problem with the controller. Seek manufacturers support.

TABLE 7
EXPERIMENTAL TROUBLESHOOTING GUIDE FOR MECHANICAL PROBLEMS

PROBLEM	CAUSE	SOLUTION
7. Dry test meter is not indicating flow but rotameter is.	7.1. In-line filter between extract receiver and dry test meter is plugged.	7.1. Shut block valve, V7 to isolate column and then remove filter and clean. Use extreme caution when removing filter housing so it does not break, it is only plastic.
	7.2. Line between extract receiver and dry test meter has plugged.	7.2. Shut unit down and clean line.
	7.3 The pressure relief valve in line between the extract receiver and the dry test meter is stuck open.	7.3. Shut the system down and clean out the safety relief valve. If the valve needs to be dis-assembled for cleaning, it may require special skills to make sure the relief pressure is not altered after it is re-assembled.

TABLE 8
SCFE LABORATORY DO'S AND DO NOT'S

DO'S

1. DO VENT DOWN THE ENTIRE SYSTEM BEFORE REMOVING THE EXTRACTION COLUMN
2. DO HANDLE THE CO₂ SUPPLY CYLINDER WITH EXTREME CAUTION SINCE IT IS NOT REGULATED
3. DO BECOME FAMILIAR WITH THE MSDS FOR NAPHTHALENE
4. DO CHECK THE FILTER ON THE EXTRACT RECEIVER PERIODICALLY TO PREVENT IT FROM PLUGGING
5. DO USE EXTREME CAUTION WHEN TIGHTENING UP SMALL LEAKS IN THE SMALLER FITTINGS IF THE SYSTEM IS UNDER PRESSURE
6. DO USE EXTREME CAUTION WHEN HANDLING THE PLASTIC HOUSING OF THE IN-LINE FILTER HOUSING FOR THE FILTER BETWEEN THE EXTRACT RECEIVER AND THE DRY TEST METER

DO NOT'S

1. DO NOT EVER TURN MICRO-METERING VALVE PAST THE ZERO MARK ON THE VERNIER ON THE SIDE OF THE VALVE BODY
2. DO NOT EVER TRY TO TIGHTEN THE LARGE FITTINGS ON THE EXTRACTION COLUMN WHILE THE SYSTEM IS UNDER PRESSURE
3. DO NOT OPEN THE CRITICAL PHASE SAMPLE VALVE UNLESS THE DISCHARGE AREA HAS BEEN SECURED
4. DO NOT LET THE PRESSURE DOWNSTREAM OF THE DRY TEST METER EXCEED 5 PSIG
5. DO NOT TAMPER WITH THE RUPTURE DISC ON THE COLUMN
6. DO NOT OVER TIGHTEN FITTINGS
7. DO NOT ALLOW THE PUMP DISCHARGE PRESSURE TO EXCEED 6000 PSIG
8. DO NOT ALLOW THE EXTRACTION COLUMN TEMPERATURE TO EXCEED 55°C
9. DO NOT START THE PUMP AGAINST A BACK PRESSURE GREATER THAN 500 PSIG

APPENDIX E

COMPUTER PROGRAM FOR THE PENG-ROBINSON EQUATION OF STATE USING ONE BINARY INTERACTION PARAMETER

The program was checked against the equilibrium data of McHugh and Paulaitis and found to have only fair predictive capabilities, see Table 9. The binary interaction parameter was optimized by trial and error to best fit the experimental data and was determined to be 0.103. With this value of k_{ij} , the resulting errors in the prediction of the equilibrium solubilities were typically between 15-50% low when compared to the experimental values. The largest errors occurred at the lowest solubilities (ie 0.0044 vs experimental value of 0.0075 for 35 °C and 85.7 Atm.).

In order to check the single parameter P-R EOS presented here, the following was done. The values of Z , the compressibility factor that it calculated were compared to the values of Z calculated by a program in the literature (Walas, 1980) that uses a single parameter SRK EOS (see Table 10). The predicted values of Z from the P-R EOS were almost always lower than those predicted by the SRK EOS. This was expected because the predicted values of Z_c from the P-R EOS, 0.307, is lower than the predicted value of 0.333 that the SRK EOS predicts (Walas, 1980).

These results can be significantly improved by adding a second interaction parameter to the EOS as indicated by Chai

(1981), Paulaitis, McHugh, and Chai (1983), and Deiters and Schneider (1976); however, this was not done in this work for the following reason. It is desirable for the calculations and methods used here to be as representative as possible of what the students will do and it is not anticipated that they will add the second interaction parameter.

Table 9

Comparison of Naphthalene Solubility in Supercritical CO₂:
Experimental (McHugh and Paulaitis) vs Predicted from P-R EOS Program

PRESSURE psig	TEMPERATURE K	MEASURED SOLUBILITY mol naphthalene/mol	PREDICTED SOLUBILITY mol naphthalene/mol	% DIFFERENCE
1260	308	0.00750	0.00442	(41)
1545	308	0.01066	0.00768	(28)
2552	308	0.01605	0.01271	(21)
3227	308	0.01830	0.01492	(18)
3704	308	0.01922	0.01579	(18)
1192	328	0.00131	0.00064	(51)
1485	328	0.00292	0.00203	(30)
1765	328	0.01229	0.00665	(46)
2084	328	0.02544	0.01354	(46)
2537	328	0.03473	0.02221	(36)
3243	328	0.04366	0.03321	(24)
4175	328	0.05382	0.04439	(18)
1573	335	0.00524	0.00261	(50)
2383	335	0.03401	0.02154	(37)
2795	335	0.05386	0.03454	(36)
3155	335	0.06990	0.04823	(31)
3600	335	0.09064	0.42881	373
4228	335	0.09802	0.40152	310
2202	338	0.02427	0.01601	(34)
2790	338	0.05015	0.04312	(14)
3090	338	0.06440	0.52555	716
3369	338	0.07907	0.51622	552

TABLE 10

Comparison of Z Calculated Using Peng-Robinson EOS Program Provided Here
and Soave-Redlich Kwong EOS Program Provided in Walas (1985)

PRESSURE psig	TEMPERATURE K	Z (P-R)	Z (SRK)	ϕ_1^F (P-R)	ϕ_1^F (SRK)
1260	308	0.2471	0.2961	0.00106	0.18527
1545	308	0.2591	0.3573	0.00054	0.16364
2552	308	0.3511	0.5444	0.00027	0.12979
3227	308	0.4337	0.6977	0.00022	0.11826
3704	308	0.4840	0.7900	0.00021	0.114746
1192	328	0.6018	0.28664	0.04174	0.26795
1485	328	0.4699	0.34833	0.01420	0.23195
1765	328	0.3812	0.40544	0.00316	0.21522
2084	328	0.3685	0.46818	0.00144	0.20551
2537	328	0.3959	0.55509	0.00082	0.19342
3243	328	0.4620	0.68619	0.00052	0.18278
4175	328	0.5601	0.85260	0.00040	0.18014
1573	335	0.5019	0.36888	0.01418	0.24937
2383	335	0.4016	0.42612	0.00141	0.21855
2795	335	0.4277	0.60096	0.00084	0.21870
3155	335	0.4604	0.66438	0.00059	0.22169
3600	335	0.7243	0.74004	0.00066	0.22981
4228	335	0.8218	0.84724	0.00071	0.23022
2202	338	0.4144	0.49320	0.00257	0.23104
2790	338	0.4304	0.60072	0.00088	0.22683
3090	338	0.6821	0.65324	0.00071	0.22956
3369	338	0.7355	0.70071	0.00072	0.23506

NOMENCLATURE FOR SINGLE PARAMETER PENG-ROBINSON EOS

(Consistent with Walas, 1985)

TC(I): Critical temperature of component i
 PC(I): Critical pressure of component i
 W(I): Acentric factor for component i
 A(I): PR constant, a, for component i
 B(I): PR constant, b, for component i
 AA(I): PR constant, A, for component i
 BB(I): PR constant, B, for component i
 TR(I): Reduced temperature for component i
 ALPHA(I): PR constant, α , for component i
 AALPHA(I): PR constants $a\alpha$ for component i
 Y(I): Mole fraction of component i in vapor or
 supercritical phase
 SUM(I): Summation that appears in the PR equation for ϕ_i
 TERM1(I): Program holding variable
 TERM2(I): Program holding variable
 TERM3(I): Program holding variable
 LNPHI(I): Natural log of fugacity coefficient of component i
 PHI(I): Fugacity coefficient of component i
 T: System temperature
 P: System pressure
 MV: Molar volume of solute
 P2SAT: Vapor pressure of solute
 YCALC: Dummy variable for Y(2)
 R: Gas constant
 KIJ: Binary interaction parameter
 PF: Poynting correction
 YNEW: Dummy variable for Y(2)
 DELTA: Convergence interval
 AALPHA1: Same as AALPHA(I), but component specific for
 component 1
 AALPHA2: Same as AALPHA(I), but component specific for
 component 2
 AALPHA12: PR constant, $a\alpha_{12}$ needed for mixing rules
 A12: PR constant, A_{12} needed for mixing rules
 BM: PR constant, B, for mixture
 AM: PR constant, A, for mixture
 AALPHAM: PR constant, $a\alpha$ for mixture
 Z: Compressibility factor
 SQ2: Square root of 2
 Q1: Constant in Peng-Robinson EOS
 Q2: Constant in Peng-Robinson EOS
 Q3: Constant in Peng-Robinson EOS
 F: Defined function of the cubic form of the Peng-
 Robinson EOS
 F1: Derivative of F
 H: Convergence increment

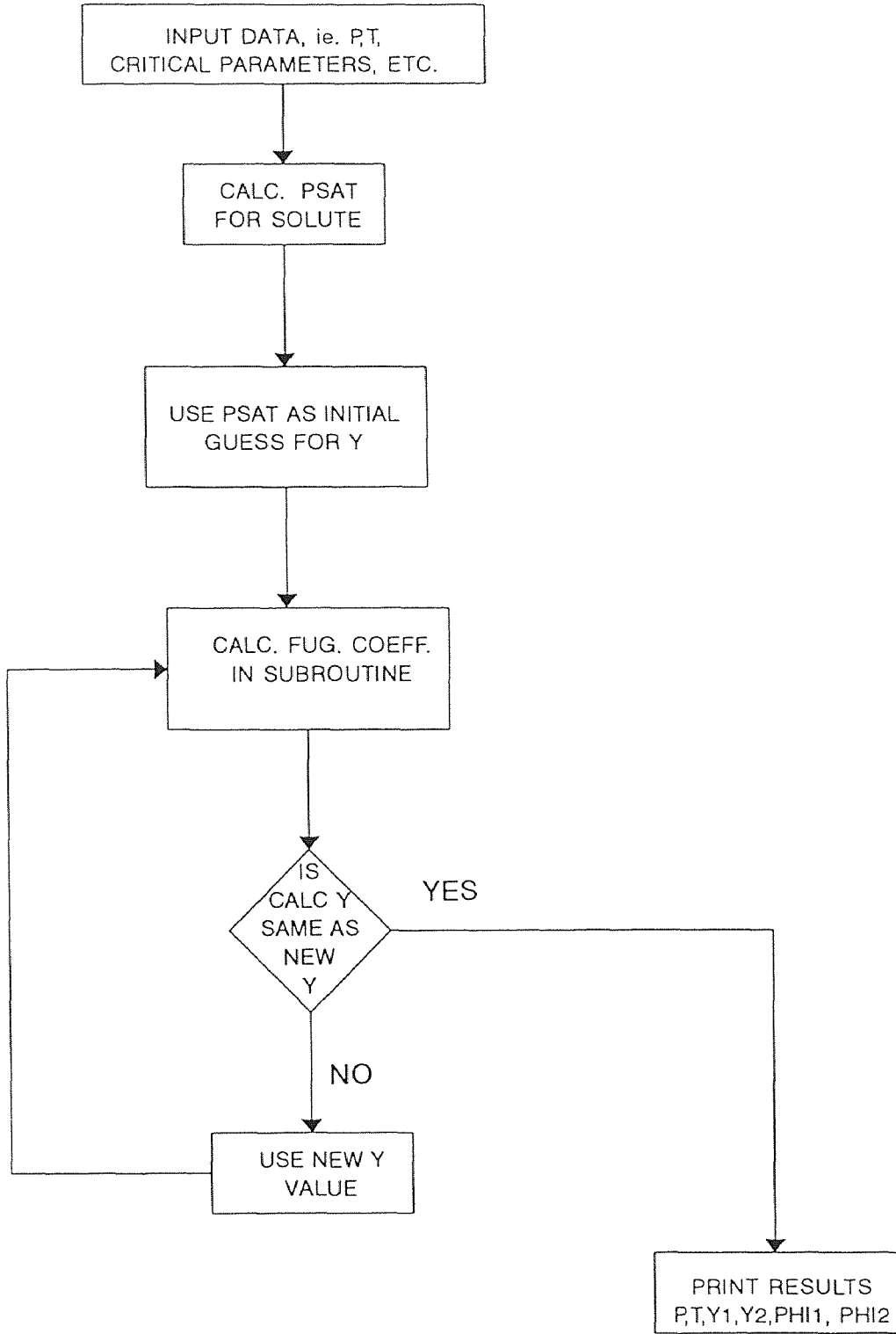


Figure 10
Flow Chart for P-R EOS

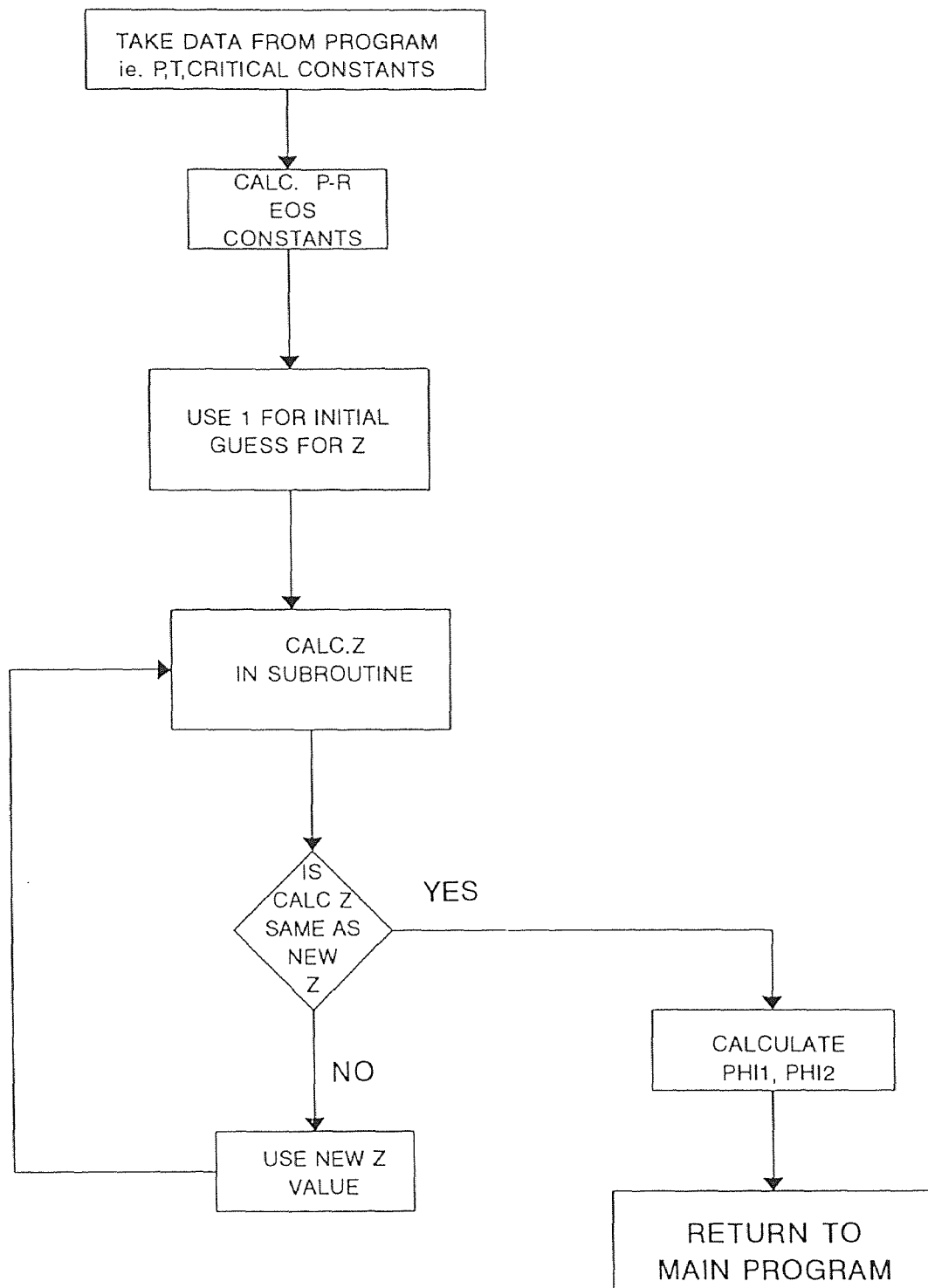


Figure 11
Flow Chart for Subroutine in P-R EOS

BASIC PROGRAM LISTING FOR SINGLE PARAMETER PENG-ROBINSON EOS

```

10  DIM TC(2), PC(2), W(2), A(2), B(2), AA(2), BB(2), TR(2)
20  DIM ALPHA(2), AALPHA(2), Y(2), SUM(2)
30  DIM TERM1(2), TERM2(2), TERM3(2), LNPHI(2), PHI(2)
40  T=308.15
50  INPUT P
60  MV=.11194
70  P2SAT=EXP(26.708-8712/T)/760
80  YCALC=P2SAT
90  Y(2)=YCALC
100 PRINT "P(ATM)=", P, "T(K)=", T, "Y(2)=", Y(2)
110 Y(1)=1-Y(2)
120 PRINT "Y(1)=", Y(1)
130 R=.08206
140 KIJ=.103
150 TC(1)=304.2
160 PC(1)=72.8
170 W(1)=.225
180 TC(2)=748.4
190 PC(2)=40
200 W(2)=.302
210 PF=EXP(MV*(P-P2SAT)/R/T)
220 GOSUB 330
230 YNEW=P2SAT/P/PHI(2)*PF
240 DELTA=Y(2)-YNEW
250 IF ABS(DELTA/Y(2))<=.01 THEN 280
260 YCALC=YNEW
270 GOTO 90
280 Y(1)=1-Y(2)
290 PRINT "Y1=", Y(1), "Y2=", Y(2)
300 PRINT "PHI1=", PHI(1), "PHI2=", PHI(2)
310 PRINT "P=", P, "T=", T, "Z=", Z
320 END
330 FOR I=1 TO 2
340     TR(I)=T/TC(I)
350     ALPHA(I)=(1-(.37464+1.54226*W(I)-.26992*W(I)^2)*(1-
        TR(I)^.5))^2
360     A(I)=.45724*R^2*TC(I)^2/PC(I)
370     B(I)=.0778*R*TC(I)/PC(I)
380     AA(I)=A(I)*ALPHA(I)*P/R^2/T^2
390     BB(I)=B(I)*P/R/T
400 NEXT I
410 AALPHA1=A(1)*AALPHA(1)
420 AALPHA2=A(2)*AALPHA(2)
430 AALPHA12=(1-KIJ)*(AALPHA1*AALPHA2)^.5
440 AA12=(1-KIJ)*(AA(1)*AA(2))^.5
450 BM=Y(1)*BB(1)+Y(2)*BB(2)
460 AM=Y(1)^2*AA(1)+Y(2)^2*AA(2)+2*Y(1)*Y(2)*AA12
470
AALPHAM=Y(1)^2*AALPHA1+Y(2)^2*AALPHA2+2*Y(1)*Y(2)*AALPHA12
480 Z=1

```

```
490 GOSUB 650
500 SQ2=2^.5
510 Q1=1+SQ2
520 Q2=SQ2-1
530 Q3=2*SQ2
540 SUM(1)=Y(1)*AALPHA1+Y(2)*AALPHA12
550 SUM(2)=Y(1)*AALPHA12+Y(2)*AALPHA2
560 FOR I=1 TO 2
570     TERM1(I)=BB(I)/BM*(Z-1)-LOG(Z-BM)
580     TERM2(I)=AM/Q3/BM*((BB(I)/BM)-(2*SUM(I)/AALPHAM))
590     TERM3(I)=LOG((Z+BM*Q1)/(Z-Q2*BM))
600     LNPHI(I)=TERM1(I)+TERM2(I)*TERM3(I)
610     PHI(I)=EXP(LNPHI(I))
620 NEXT I
630 PRINT "Z=", Z
640 RETURN
650 F=Z^3-(1-BM)*Z^2+(AM-3*BM^2-2*BM)*Z-(AM*BM-BM^2-BM^3)
660 F1=3*Z^2-2*(1-BM)*Z+(AM-3*BM^2-2*BM)
670 H=F/F1
680 Z=Z-H
690 IF ABS(H/Z)<=.0001 THEN 500
700 GOTO 650
710 RETURN
```

APPENDIX F

CARBON DIOXIDE and NAPHTHALENE MATERIAL SAFETY DATA SHEET



chemists helping chemists in research & industry

aldrich chemical co., inc.

P.O. Box 355, Milwaukee, Wisconsin 53201 USA

 Telephone: (414) 273-3850
 TWX: (910) 262-3052 Aldrichem
 Telex: 26 843 Aldrich MI
 FAX: (414) 273-4979

 ATTN: SAFETY DIRECTOR
 RON GAUBERT
 BASF CORPORATION POLYMERS DIVISION
 1065 CRANSBURY & SOUTH RIVER ROAD
 JAMESBURG NJ 08831-9721

 DATE: 07/23/93
 CUST#: 921215
 PD#:

MATERIAL SAFETY DATA SHEET PAGE 1

IDENTIFICATION

 PRODUCT #: 13450-0
 CAS #: 91-20-3
 MF: C10H8

NAME: NAPHTHALENE, 99+%, SCINTILLATION GRADE

SYNONYMS

 CAMPHOR TAR * MIGHTY 150 * MIGHTY R01 * MOTH BALLS * MOTH BALLS (DOT)
 * MOTH FLAKES * NAFTALEN (POLISH) * NAPHTHALENE (ACGIH, DOT, OSHA) *
 NAPHTHALIN * NAPHTHALIN (DOT) * NAPHTHALINE * NAPHTHENE * NAPHTHALENE
 (DOT) * NCI-C52904 * RCRA WASTE NUMBER U165 * TAR CAMPHOR * UN 1334
 (DOT) * WHITE TAR *

TOXICITY HAZARDS

 RTECS #: QJ0525000
 NAPHTHALENE

IRRITATION DATA

 SKN-RBT 495 MG OPEN MLD
 EYE-RBT 100 MG MLD

 UCDS** 1/11/68
 BIODFX* 16-4/70

TOXICITY DATA

 ORL-CHO LD50:100 MG/KG
 UNR-HMN LD50:29 MG/KG
 UNR-HAN LD50:74 MG/KG
 ORL-RAT LD50:490 MG/KG
 SKN-RAT LD50:>2500 MG/KG
 ORL-MUS LD50:533 MG/KG
 IPR-MUS LD50:150 MG/KG
 SCU-MUS LD50:967 MG/KG
 IVN-MUS LD50:100 MG/KG
 SKN-RBT LD50:>20 GM/KG
 ORL-SPG LD50:1200 MG/KG

 28ZRAQ -,228,60
 YKYUA6 31,1499,80
 A5DCAI 2,73,70
 B5GHAT -,99,82
 TXAPA9 14,515,69
 FAATDF 4,406,84
 NTIS** A0691-490
 TOIZAG 20,772,73
 CSLNX* NX#00203
 NTIS** A0-A062-138
 GISAAA 47(11),78,82

REVIEWS, STANDARDS, AND REGULATIONS

 ACGIH TLV-TWA 10 PPM; STEL 15 PPM 85INAB 5,420,86
 EPA FIFRA 1988 PESTICIDE SUBJECT TO REGISTRATION OR RE-REGISTRATION
 FEREAC 54,7740,89
 OSHA STANDARD-AIR:TWA 10 PPM (50 MG/M3) DTLVS* 3,177,71
 OSHA PEL:8H TWA 10 PPM (50 MG/M3) FEREAC 54,2923,89
 OSHA PEL FINAL:8H TWA 10 PPM (50 MG/M3); STEL 15 PPM (75 MG/M3) FEREAC
 54,2923,89
 OEL-ARAB REPUBLIC OF EGYPT:TWA 10 PPM (50 MG/M3) JANUARY 1993
 OEL-AUSTRALIA:TWA 10 PPM (50 MG/M3); STEL 15 PPM (75 MG/M3) JANUARY
 1993
 OEL-BELGIUM:TWA 10 PPM (52 MG/M3); STEL 15 PPM (79 MG/M3) JANUARY 1993

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MATERIAL SAFETY DATA SHEET PAGE 2

PRODUCT #:

CUST#: 921215

MF: C10H8

NAME: NAPHTHALENE, 99+%, SCINTILLATION GRADE

- - - - TOXICITY HAZARDS - - - -

OEL-DENMARK:TWA 10 PPM (50 MG/M3) JANUARY 1993
 OEL-FINLAND:TWA 10 PPM (50 MG/M3);STEL 20 PPM (100 MG/M3) JANUARY 1993
 OEL-FRANCE:TWA 10 PPM (50 MG/M3) JANUARY 1993
 OEL-GERMANY:TWA 10 PPM (50 MG/M3) JANUARY 1993
 OEL-HUNGARY:TWA 40 MG/M3;STEL 80 MG/M3;SKIN JANUARY 1993
 OEL-THE NETHERLANDS:TWA 10 PPM (50 MG/M3) JANUARY 1993
 OEL-THE PHILIPPINES:TWA 10 PPM (50 MG/M3) JANUARY 1993
 OEL-POLAND:TWA 20 MG/M3 JANUARY 1993
 OEL-RUSSIA:STEL 20 MG/M3 JANUARY 1993
 OEL-SWITZERLAND:TWA 10 PPM (50 MG/M3) JANUARY 1993
 OEL-UNITED KINGDOM:TWA 10 PPM (50 MG/M3);STEL 15 PPM (75 MG/M3)
 JANUARY 1993
 OEL IN BULGARIA, COLOMBIA, JORDAN, KOREA, NEW ZEALAND, SINGAPORE,
 VIETNAM CHECK ACCGIH TLV
 NIOSH REL TO NAPHTHALENE-AIR:10H TWA 10 PPM;STEL 15 PPM NIOSH* DHHS
 #92-100,92
 NIOSH 1974: HZD 49600; NIS 71; TNF 4341; NOS 68; TNE 44297
 NIOSH 1983: HZD 49600; NIS 83; TNF 7209; NOS 97; TNE 112696; TFE 5220
 EPA GENETOX PROGRAM 1988, NEGATIVE: CELL TRANSFORM.-MOUSE EMBRYO
 EPA GENETOX PROGRAM 1988, NEGATIVE: CELL TRANSFORM.-RLV F344 RAT
 EMBRYO
 EPA GENETOX PROGRAM 1988, NEGATIVE: HISTIDINE REVERSION-AMES TEST
 EPA TSCA CHEMICAL INVENTORY, JUNE 1990
 ON EPA IRIS DATABASE
 EPA TSCA TEST SUBMISSION (TSCATS) DATA BASE, JANUARY 1993
 NIOSH ANALYTICAL METHODS: SEE HYDROCARBONS, AROMATIC, 1501;
 NIOSH ANALYTICAL METHODS: SEE POLYNUCLEAR AROMATIC HYDROCARBONS (HPLC)
 , 5506; (GC), 5515
 NTP CARCINOGENESIS STUDIES (INHALATION);SOME EVIDENCE:MOUSE NTPTR*
 NTP-TR-410,92
 OSHA ANALYTICAL METHOD #35

TARGET ORGAN DATA

SENSE ORGANS AND SPECIAL SENSES (PTOSIS)
 BEHAVIORAL (SOMNOLENCE)
 BEHAVIORAL (TREMOR)
 BEHAVIORAL (CHANGE IN MOTOR ACTIVITY)
 BEHAVIORAL (ATAXIA)
 LUNGS, THORAX OR RESPIRATION (RESPIRATORY DEPRESSION)

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M A T E R I A L S A F E T Y D A T A S H E E T

PAGE 3

PRODUCT #:

CUST#: 921215

MF: C10H8

NAME: NAPHTHALENE, 99+2, SCINTILLATION GRADE

- - - - TOXICITY HAZARDS - - - -

LUNGS, THORAX OR RESPIRATION (TUMORS)
 TUMORIGENIC (NEOPLASTIC BY RTECS CRITERIA)
 ONLY SELECTED REGISTRY OF TOXIC EFFECTS OF CHEMICAL SUBSTANCES
 (RTECS) DATA IS PRESENTED HERE. SEE ACTUAL ENTRY IN RTECS FOR
 COMPLETE INFORMATION.

- - - - HEALTH HAZARD DATA - - - -

ACUTE EFFECTS

HARMFUL IF SWALLOWED, INHALED, OR ABSORBED THROUGH SKIN.
 CAUSES EYE AND SKIN IRRITATION.
 MATERIAL IS IRRITATING TO MUCOUS MEMBRANES AND UPPER
 RESPIRATORY TRACT.
 SYMPTOMS OF EXPOSURE MAY INCLUDE BURNING SENSATION, COUGHING,
 WHEEZING, LARYNGITIS, SHORTNESS OF BREATH, HEADACHE, NAUSEA AND
 VOMITING.
 ABSORPTION INTO THE BODY LEADS TO THE FORMATION OF METHEMOGLOBIN
 WHICH IN SUFFICIENT CONCENTRATION CAUSES CYANOSIS. ONSET MAY BE
 DELAYED 2 TO 4 HOURS OR LONGER.
 MAY CAUSE ALLERGIC SKIN REACTION.
 NAPHTHALENE IS RETINOTOXIC AND SYSTEMIC ABSORPTION OF ITS VAPORS ABOVE
 15PPM, MAY RESULT IN CATARACTS, OPTICAL NEURITIS, INJURIES TO THE
 CORNEA AND MARKED EYE IRRITATION. INGESTION OF LARGE QUANTITIES HAVE
 BEEN REPORTED TO CAUSE SEVERE HEMOLYTIC ANEMIA AND HEMOGLOBINURIA.

CHRONIC EFFECTS

CARCINOGEN.
 TARGET ORGAN(S):
 EYES
 BLOOD
 KIDNEYS
 LUNGS

FIRST AID

IN CASE OF CONTACT, IMMEDIATELY FLUSH EYES OR SKIN WITH COPIOUS
 AMOUNTS OF WATER FOR AT LEAST 15 MINUTES WHILE REMOVING CONTAMINATED
 CLOTHING AND SHOES.
 ASSURE ADEQUATE FLUSHING OF THE EYES BY SEPARATING THE EYELIDS
 WITH FINGERS.
 IF INHALED, REMOVE TO FRESH AIR. IF NOT BREATHING GIVE ARTIFICIAL
 RESPIRATION. IF BREATHING IS DIFFICULT, GIVE OXYGEN.

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M A T E R I A L S A F E T Y D A T A S H E E T

PAGE 4

PRODUCT #:

CUST#: 921215

MF: C10H8

NAME: NAPHTHALENE, 99+%, SCINTILLATION GRADE

- - - - HEALTH HAZARD DATA - - - -

 IF SWALLOWED, WASH OUT MOUTH WITH WATER PROVIDED PERSON IS CONSCIOUS.
 CALL A PHYSICIAN.
 DISCARD CONTAMINATED CLOTHING AND SHOES.

- - - - PHYSICAL DATA - - - -

 BOILING POINT: 217.7 C
 MELTING POINT: 80 C TO 82 C
 VAPOR DENSITY: 4.4
 VAPOR PRESSURE: .03 MM @ 25 C
 1 MM @ 53 C

 APPEARANCE AND ODOR
 WHITE CRYSTALS

- - - - FIRE AND EXPLOSION HAZARD DATA - - - -

 FLASHPOINT: 174 F
 AUTOIGNITION TEMPERATURE: 978 F
 LOWER EXPLOSION LEVEL: .9%
 UPPER EXPLOSION LEVEL: 5.9%

EXTINGUISHING MEDIA

 CARBON DIOXIDE.
 DRY CHEMICAL POWDER.
 FOAM AND WATER SPRAY ARE EFFECTIVE BUT MAY CAUSE FROTHING.

SPECIAL FIREFIGHTING PROCEDURES

 WEAR SELF-CONTAINED BREATHING APPARATUS AND PROTECTIVE CLOTHING TO
 PREVENT CONTACT WITH SKIN AND EYES.
 FLAMMABLE SOLID.

UNUSUAL FIRE AND EXPLOSION HAZARDS

 THIS MATERIAL, LIKE MOST MATERIALS IN POWDER FORM, IS CAPABLE OF
 CREATING A DUST EXPLOSION.

- - - - REACTIVITY DATA - - - -

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M A T E R I A L S A F E T Y D A T A S H E E T P A G E 5

PRODUCT #: MF: C10H8

CUST#: 921215

NAME: NAPHTHALENE, 99+%, SCINTILLATION GRADE

- - - - REACTIVITY DATA - - - -

OXIDIZING AGENTS

HAZARDOUS COMBUSTION OR DECOMPOSITION PRODUCTS

 TOXIC FUMES OF:
 CARBON MONOXIDE, CARBON DIOXIDE

- - - - SPILL OR LEAK PROCEDURES - - - -

STEPS TO BE TAKEN IF MATERIAL IS RELEASED OR SPILLED

 EVACUATE AREA.
 WEAR SELF-CONTAINED BREATHING APPARATUS, RUBBER BOOTS AND HEAVY RUBBER GLOVES.
 SWEEP UP, PLACE IN A BAG AND HOLD FOR WASTE DISPOSAL.
 AVOID RAISING DUST.
 VENTILATE AREA AND WASH SPILL SITE AFTER MATERIAL PICKUP IS COMPLETE.

WASTE DISPOSAL METHOD

 DISSOLVE OR MIX THE MATERIAL WITH A COMBUSTIBLE SOLVENT AND BURN IN A CHEMICAL INCINERATOR EQUIPPED WITH AN AFTERBURNER AND SCRUBBER.
 OBSERVE ALL FEDERAL, STATE AND LOCAL ENVIRONMENTAL REGULATIONS.

- - - - PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE - - - -

 WEAR APPROPRIATE NIOSH/MSHA-APPROVED RESPIRATOR, CHEMICAL-RESISTANT GLOVES, SAFETY GOGGLES, OTHER PROTECTIVE CLOTHING.
 USE ONLY IN A CHEMICAL FUME HOOD.
 SAFETY SHOWER AND EYE BATH.
 DO NOT BREATHE DUST.
 AVOID CONTACT WITH FUMES.
 DO NOT GET IN EYES, ON SKIN, ON CLOTHING.
 AVOID PROLONGED OR REPEATED EXPOSURE.
 WASH THOROUGHLY AFTER HANDLING.
 CARCINOGEN.

 TOXIC.
 IRRITANT.
 SENSITIZER.
 KEEP TIGHTLY CLOSED.
 KEEP AWAY FROM HEAT, SPARKS, AND OPEN FLAME.
 HYGROSCOPIC

LABEL PRECAUTIONARY STATEMENTS

 FLAMMABLE (USA DEFINITION)
 HIGHLY FLAMMABLE (EUROPEAN DEFINITION)

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M A T E R I A L S A F E T Y D A T A S H E E T

PAGE 6

PRODUCT #:

CUST#: 921215

NAME: NAPHTHALENE, 99+%, SCINTILLATION GRADE

MF: C10H8

- - - - PRECAUTIONS TO BE TAKEN IN HANDLING AND STORAGE - - - -

TOXIC

MAY CAUSE CANCER.

HARMFUL BY INHALATION, IN CONTACT WITH SKIN AND IF SWALLOWED.

IRRITATING TO EYES, RESPIRATORY SYSTEM AND SKIN.

MAY CAUSE SENSITIZATION BY SKIN CONTACT.

TARGET ORGAN(S):

BLOOD

EYES

KIDNEYS

LUNGS

HYGROSCOPIC

KEEP AWAY FROM SOURCES OF IGNITION. NO SMOKING.

IF YOU FEEL UNWELL, SEEK MEDICAL ADVICE (SHOW THE LABEL WHERE POSSIBLE).

IN CASE OF CONTACT WITH EYES, RINSE IMMEDIATELY WITH PLENTY OF WATER AND SEEK MEDICAL ADVICE.

WEAR SUITABLE PROTECTIVE CLOTHING, GLOVES AND EYE/FACE PROTECTION.

REGULATORY INFORMATION

THIS PRODUCT IS SUBJECT TO SARA SECTION 313 REPORTING REQUIREMENTS.

THE ABOVE INFORMATION IS BELIEVED TO BE CORRECT BUT DOES NOT PURPORT TO BE ALL INCLUSIVE AND SHALL BE USED ONLY AS A GUIDE. ALDRICH SHALL NOT BE HELD LIABLE FOR ANY DAMAGE RESULTING FROM HANDLING OR FROM CONTACT WITH THE ABOVE PRODUCT. SEE REVERSE SIDE OF INVOICE OR PACKING SLIP FOR ADDITIONAL TERMS AND CONDITIONS OF SALE.

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SUBSTANCE IDENTIFICATION

SUBSTANCE: CARBON DIOXIDE, GAS CAS-NUMBER 124-38-9

TRADE NAMES/SYNONYMS:
CARBONIC ACID GAS; CARBONIC ANHYDRIDE; CARBON DIOXIDE; CARBON OXIDE;
STCC 4904535; UN 1013; CO2; MG104260

CHEMICAL FAMILY:
OXIDE OF CARBON

MOLECULAR FORMULA: C-O2

MOLECULAR WEIGHT: 44.01

CERCLA RATINGS (SCALE 0-3): HEALTH=3 FIRE=0 REACTIVITY=0 PERSISTENCE=0
NFPA RATINGS (SCALE 0-4): HEALTH=U FIRE=0 REACTIVITY=0

COMPONENTS AND CONTAMINANTS
COMPONENT: CARBON DIOXIDE, GAS PERCENT: 100
CAS# 124-38-9

OTHER CONTAMINANTS: NONE

EXPOSURE LIMITS:

CARBON DIOXIDE:
10,000 PPM (18,000 MG/M3) OSHA TWA; 30,000 PPM (54,000 MG/M3) OSHA STEL
5,000 PPM (9,000 MG/M3) ACGIH TWA; 30,000 PPM (54,000 MG/M3) ACGIH STEL
5,000 PPM (9,000 MG/M3) NIOSH RECOMMENDED TWA;
30,000 PPM (54,000 MG/M3) NIOSH RECOMMENDED STEL
5,000 PPM (9,000 MG/M3) DFG MAK TWA;
10,000 PPM (18,000 MG/M3) DFG MAK 60 MINUTE PEAK, MOMENTARY VALUE,
3 TIMES/SHIFT

MEASUREMENT METHOD: GAS COLLECTION BAG; GAS CHROMATOGRAPHY WITH FLAME
IONIZATION DETECTION; (NIOSH VOL. II(3) # S249).

PHYSICAL DATA

DESCRIPTION: COLORLESS, ODORLESS GAS, WITH A SLIGHT ACIDIC TASTE.

BOILING POINT: -109 F (-79 C) (SUBLIMES)

MELTING POINT: -70.6 F (-57 C) @ 4000 MMHG SPECIFIC GRAVITY: 1.522 @ 21 C

VAPOR PRESSURE: 43700 MMHG @ 21 C PH: ACIDIC IN SOLUTION

SOLUBILITY IN WATER: SOLUBLE VAPOR DENSITY: 1.5 MG104260 PAGE 02 OF 07

SOLVENT SOLUBILITY: SOLUBLE IN ALCOHOL, ACETONE, HYDROCARBONS, MOST
ORGANIC LIQUIDS

VAPOR DENSITY: 1.977 G/L @ 750 MMHG AND 0 C.

FIRE AND EXPLOSION DATA

FIRE AND EXPLOSION HAZARD:
NEGLECTIBLE FIRE HAZARD WHEN EXPOSED TO HEAT OR FLAME.

FIREFIGHTING MEDIA:
DRY CHEMICAL OR CARBON DIOXIDE
(1990 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.5).

FOR LARGER FIRES, USE WATER SPRAY, FOG OR REGULAR FOAM
(1990 EMERGENCY RESPONSE GUIDEBOOK, DOT P 5800.5).

FIREFIGHTING:
MOVE CONTAINER FROM FIRE AREA IF YOU CAN DO IT WITHOUT RISK. APPLY COOLING
WATER TO SIDES OF CONTAINERS THAT ARE EXPOSED TO FLAMES UNTIL WELL AFTER FIRE
IS OUT. STAY AWAY FROM ENDS OF TANKS. ISOLATE FOR 1/2 MILE IN ALL DIRECTIONS
IF TANK, RAIL CAR OR TANK TRUCK IS INVOLVED IN FIRE (1990 EMERGENCY RESPONSE
GUIDEBOOK, DOT P 5800.5, GUIDE PAGE 21).

USE AGENT SUITABLE FOR TYPE OF FIRE. COOL CONTAINERS WITH FLOODING AMOUNTS OF
WATER. APPLY FROM AS FAR A DISTANCE AS POSSIBLE.

EXTINGUISH USING AGENT INDICATED. COOL CYLINDERS WITH FLOODING AMOUNTS OF
WATER FROM AS FAR A DISTANCE AS POSSIBLE. DO NOT USE WATER DIRECTLY ON
MATERIAL. USE WATER SPRAY TO ABSORB VAPORS. AVOID BREATHING VAPORS. KEEP
UPWIND. CONSIDER EVACUATION OF DOWNWIND AREA IF MATERIAL IS LEAKING.

TRANSPORTATION DATA

DEPARTMENT OF TRANSPORTATION HAZARD CLASSIFICATION 49 CFR 172.101:
NONFLAMMABLE GAS

DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS 49 CFR 172.101 AND
SUBPART E:
NONFLAMMABLE GAS

DEPARTMENT OF TRANSPORTATION PACKAGING REQUIREMENTS: 49 CFR 173.302 AND
49 CFR 173.304
EXCEPTIONS: 49 CFR 173.306

FINAL RULE ON HAZARDOUS MATERIALS REGULATIONS (HMR, 49 CFR PARTS 171-180).
DOCKET NUMBERS HM-181, HM-181A, HM-181B, HM-181C, HM-181D AND HM-204
EFFECTIVE DATE OCTOBER 1, 1991. HOWEVER, COMPLIANCE WITH THE REGULATIONS IS
AUTHORIZED ON AND AFTER JANUARY 1, 1991.
(55 FR 52402, 12/21/90).

U.S. DEPARTMENT OF TRANSPORTATION SHIPPING NAME-ID NUMBER, 49 CFR 172.101:

U.S. DEPARTMENT OF TRANSPORTATION HAZARD CLASS OR DIVISION, 49 CFR 172.101:
2.2 - NON-FLAMMABLE COMPRESSED GAS

U.S. DEPARTMENT OF TRANSPORTATION LABELING REQUIREMENTS, 49 CFR 172.101
AND SUBPART E:
NONFLAMMABLE GAS

U.S. DEPARTMENT OF TRANSPORTATION PACKAGING REQUIREMENTS:
EXCEPTIONS: 49 CFR 173.306
NON-BULK PACKAGING: 49 CFR 173.302 AND 49 CFR 173.304
BULK PACKAGING: 49 CFR 173.302; 49 CFR 173.314 AND 49 CFR 173.315

U.S. DEPARTMENT OF TRANSPORTATION QUANTITY LIMITATIONS 49 CFR 172.101:
PASSENGER AIRCRAFT OR RAILCAR: 75 KG
CARGO AIRCRAFT ONLY: 150 KG

TOXICITY

CARBON DIOXIDE:
TOXICITY DATA: 9 PPH/5 MINUTES INHALATION-HUMAN LCLO; 90000 PPM/5 MINUTES
INHALATION-MAMMAL LCLO; REPRODUCTIVE EFFECTS DATA (RTECS).
CARCINOGEN STATUS: NONE
ACUTE TOXICITY LEVEL: INSUFFICIENT DATA
TARGET EFFECTS: SIMPLE ASPHYXIANT. POISONING MAY AFFECT THE RESPIRATORY AND
NERVOUS SYSTEMS AND HEART
AT INCREASED RISK FROM EXPOSURE: PERSONS WITH A HISTORY OF CARDIOVASCULAR
OR PULMONARY IMPAIRMENT.

HEALTH EFFECTS AND FIRST AID

INHALATION:
CARBON DIOXIDE:
SIMPLE ASPHYXIANT. 50,000 PPM IMMEDIATELY DANGEROUS TO LIFE OR HEALTH.
ACUTE EXPOSURE- IN THE SOLID OR LIQUID FORM CARBON DIOXIDE IS VERY VOLATILE,
READILY RELEASING THE GAS AT CONCENTRATIONS FROM 2-10%. IT MAY CAUSE
ACIDIC ASTHMA, HEADACHE, VERTIGO, NAUSEA, LABORED BREATHING,
WEAKNESS, DROWSINESS, MENTAL CONFUSION, AND INCREASE IN BLOOD PRESSURE,
PULSE AND RESPIRATORY RATE. EXPOSURE TO 10% FOR A FEW MINUTES HAS BEEN
REPORTED TO CAUSE VISUAL DISTURBANCES, TINNITUS, TREMORS, PROFUSE
PERSPIRATION, RESTLESSNESS, PARESTHESIAS, GENERAL FEELING OF DISCOMFORT,
LOSS OF CONSCIOUSNESS, AND COMA. CONCENTRATIONS OF 25-30% MAY CAUSE
COMA AND CONVULSIONS WITHIN ONE MINUTE. TACHYCARDIA AND ARRHYTHMIAS ARE
POSSIBLE. CONCENTRATIONS OF 50% MAY CAUSE SYMPTOMS OF HYPOCALCEMIA
INCLUDING CARPOPELAL SPASMS. EXCESSIVE CARBON DIOXIDE FOR A TIME PERIOD OF
NOT MORE THAN 5 MINUTES WAS REPORTED TO CAUSE EFFECTS ON VISION WITH
CONSTRICTION OF VISUAL FIELDS, ENLARGEMENT OF BLIND SPOTS, PHOTOPHOBIA,
LOSS OF CONVERGENCE AND ACCOMMODATION, AND DEFICIENT DARK ADAPTATION AS
WELL AS HEADACHE, INSOMNIA, AND PERSONALITY CHANGES. LARGELY DEPRESSION
AND IRRITABILITY, EVEN WHEN THERE IS SUFFICIENT OXYGEN PRESENT TO PREVENT
SIMPLE ASPHYXIATION BY CARBON DIOXIDE. HIGH CONCENTRATIONS MAY CAUSE
ADVERSE EFFECTS BY INTERFERING WITH ITS NORMAL ELIMINATION FROM THE BODY.
INITIALLY EXPOSURE TO INCREASED CARBON DIOXIDE CONCENTRATIONS RESULTS IN
A COMPENSATORY INCREASE IN BOTH RATE AND DEPTH OF VENTILATION. BEYOND A
CERTAIN POINT, HOWEVER, THIS MAY REVERSE TO HYPOVENTILATION RESULTING IN

RESPIRATORY ACIDOSIS. DEATH FROM ASPHYXIA MAY OCCUR IF THE CONCENTRATION
AND DURATION OF EXPOSURE ARE SUFFICIENT. REPRODUCTIVE EFFECTS HAVE BEEN
REPORTED IN ANIMALS.

CHRONIC EXPOSURE- IT HAS BEEN REPORTED THAT PERSONS MAY TOLERATE 1.5% IN
INHALED AIR FOR PROLONGED PERIODS WITHOUT ADVERSE EFFECTS, BUT CALCIUM/
PHOSPHORUS METABOLISM MAY BE AFFECTED WITH SERUM LEVELS OF CALCIUM AND
URINARY PHOSPHORUS PROGRESSIVELY FALLING AT 2% CONCENTRATION. DEEPENED
RESPIRATION MAY OCCUR AT 3% IMPAIRMENT OF PERFORMANCE HAS BEEN NOTED. IT
HAS HOWEVER BEEN DEMONSTRATED THAT THE DEVELOPMENT OF TOLERANCE MAY
OCCUR DURING PROLONGED EXPOSURE TO LOW LEVELS. REPRODUCTIVE EFFECTS HAVE
BEEN REPORTED IN ANIMALS.

FIRST AID- REMOVE FROM EXPOSURE AREA TO FRESH AIR IMMEDIATELY. IF BREATHING
HAS STOPPED, GIVE ARTIFICIAL RESPIRATION. MAINTAIN AIRWAY AND BLOOD
PRESSURE AND ADMINISTER OXYGEN IF AVAILABLE. KEEP AFFECTED PERSON WARM AND
AT REST. TREAT SYMPTOMATICALLY AND SUPPORTIVELY. ADMINISTRATION OF OXYGEN
SHOULD BE PERFORMED BY QUALIFIED PERSONNEL. GET MEDICAL ATTENTION
IMMEDIATELY.

SKIN CONTACT:

CARBON DIOXIDE:
ACUTE EXPOSURE- NO ADVERSE EFFECTS HAVE BEEN REPORTED FROM EXPOSURE TO THE
GAS. DUE TO RAPID EVAPORATION, THE LIQUID OR SOLID MAY CAUSE FROSTBITE
WITH REDNESS, TINGLING AND PAIN OR NUMBNESS. IN MORE SEVERE CASES
THE SKIN MAY BECOME HARD AND WHITE AND DEVELOP BLISTERS.
CHRONIC EXPOSURE- NO ADVERSE EFFECTS ARE EXPECTED FROM EXPOSURE AT LOW
LEVELS.

FIRST AID- IT IS UNLIKELY THAT EMERGENCY TREATMENT WILL BE REQUIRED. IF
ADVERSE EFFECTS OCCUR, GET MEDICAL ATTENTION.
IN CASE OF FROSTBITE, WARM AFFECTED SKIN IN WARM WATER AT A TEMPERATURE OF
107 F. IF WARM WATER IS NOT AVAILABLE OR IMPRACTICAL TO USE, GENTLY WRAP
AFFECTED PART IN BLANKETS. ENCOURAGE VICTIM TO EXERCISE AFFECTED PART WHILE
IT IS BEING WARMED. ALLOW CIRCULATION TO RETURN NATURALLY (MATHESON GAS,
6TH ED.). GET MEDICAL ATTENTION IMMEDIATELY.

EYE CONTACT:

CARBON DIOXIDE:
ACUTE EXPOSURE- AT HIGH CONCENTRATIONS IN AIR, CARBON DIOXIDE MAY CAUSE A
STINGING SENSATION OF THE EYES. 200,000 PPM OF THE GAS MAY CAUSE
IRRITATION, DUE TO RAPID EVAPORATION, THE LIQUID OR SOLID MAY CAUSE
FROSTBITE WITH REDNESS, PAIN, AND BLURRED VISION.
CHRONIC EXPOSURE- NO ADVERSE EFFECTS ARE EXPECTED FROM EXPOSURE TO LOW
LEVELS.

FIRST AID- IT IS UNLIKELY THAT CONTACT WITH THE GAS FORM WILL REQUIRE
EMERGENCY TREATMENT. IF CONTACT WITH LIQUIDIFIED OR COMPRESSED GAS OCCURS,
WASH WITH LARGE AMOUNTS OF WARM WATER UNTIL NO EVIDENCE OF CHEMICAL REMAINS
(APPROXIMATELY 15-20 MINUTES). GET MEDICAL ATTENTION IMMEDIATELY.

INGESTION:

CARBON DIOXIDE:
ACUTE EXPOSURE- INGESTION OF A GAS IS UNLIKELY. IF THE LIQUID OR SOLID IS
SWALLOWED, FROSTBITE DAMAGE OF THE LIPS, MOUTH AND MUCOUS MEMBRANES MAY
OCCUR.
CHRONIC EXPOSURE- NO DATA AVAILABLE.

FIRST AID- IT IS UNLIKELY THAT EMERGENCY TREATMENT WILL BE REQUIRED. IF ADVERSE EFFECTS OCCUR, TREAT SYMPTOMATICALLY AND SUPPORTIVELY AND GET MEDICAL ATTENTION.

 REACTIVITY

REACTIVITY:
 STABLE UNDER NORMAL TEMPERATURES AND PRESSURES.

INCOMPATIBILITIES:

CARBON DIOXIDE:
 ACRYLALDEHYDE: EXOTHERMIC POLYMERIZATION.
 BARIUM PEROXIDE: INCANDESCENT REACTION.
 CESIUM OXIDE: IGNITION.
 DIETHYL MAGNESIUM: IGNITION.
 ETHYLENEIMINE: EXPLOSIVE POLYMERIZATION.
 HYDRAZINE: DECOMPOSITION.
 METAL ACETYLIDES: IGNITION OR INCANDESCENCE.
 METAL HYDRIDES: REDUCTION REACTION.
 METALS: DUSTS OF MANY METALS SUSPENDED IN CARBON DIOXIDE ATMOSPHERES ARE IGNITABLE AND EXPLOSIVE; SOME BULK METALS WILL BURN IN THE GAS AT ELEVATED TEMPERATURES.
 POTASSIUM: MIXTURES OF THE SOLIDS ARE IMPACT-SENSITIVE.
 POTASSIUM-SODIUM ALLOY: MIXTURES OF THE SOLIDS ARE IMPACT-SENSITIVE.
 SODIUM: MIXTURES OF THE SOLIDS ARE IMPACT-SENSITIVE.
 SODIUM PEROXIDE: HIGHLY EXOTHERMIC REACTION; MAY BE EXPLOSIVE IN THE PRESENCE OF METALS.

DECOMPOSITION:
 TEMPERATURES ABOVE 1700 C MAY CAUSE DECOMPOSITION AND THE RELEASE OF OXYGEN AND HIGHLY TOXIC CARBON MONOXIDE.

POLYMERIZATION:
 HAZARDOUS POLYMERIZATION HAS NOT BEEN REPORTED TO OCCUR UNDER NORMAL TEMPERATURES AND PRESSURES.

 STORAGE AND DISPOSAL

OBSERVE ALL FEDERAL, STATE AND LOCAL REGULATIONS WHEN STORING OR DISPOSING OF THIS SUBSTANCE. FOR ASSISTANCE, CONTACT THE DISTRICT DIRECTOR OF THE ENVIRONMENTAL PROTECTION AGENCY.

--STORAGE--

STORE AWAY FROM INCOMPATIBLE SUBSTANCES.
 STORE IN ACCORDANCE WITH 29 CFR 1910.101.

 CONDITIONS TO AVOID

DO NOT PERMIT PHYSICAL DAMAGE OR OVERHEATING OF CONTAINERS. CONTENTS ARE UNDER PRESSURE. CONTAINERS MAY RUPTURE VIOLENTLY AND TRAVEL A CONSIDERABLE DISTANCE. CONTACT OF LIQUEFIED GASES WITH WATER MAY CAUSE VIOLENT EXPLOSIONS DUE TO

RAPID TEMPERATURE FLUCTUATIONS.

 SPILL AND LEAK PROCEDURES

OCCUPATIONAL SPILL:
 DO NOT TOUCH SPILLED MATERIAL. STOP LEAK IF YOU CAN DO SO WITHOUT RISK. KEEP UNNECESSARY PEOPLE AWAY. ISOLATE HAZARD AREA AND DENY ENTRY. VENTILATE CLOSED SPACES BEFORE ENTERING.

 PROTECTIVE EQUIPMENT

VENTILATION:
 PROVIDE GENERAL DILUTION VENTILATION TO MEET PUBLISHED EXPOSURE LIMITS.

RESPIRATOR:
 THE FOLLOWING RESPIRATORS AND MAXIMUM USE CONCENTRATIONS ARE RECOMMENDATIONS BY THE U.S. DEPARTMENT OF HEALTH AND HUMAN SERVICES, NIOSH POCKET GUIDE TO CHEMICAL HAZARDS, NIOSH CRITERIA DOCUMENTS OR BY THE U.S. DEPARTMENT OF LABOR, 29 CFR 1910 SUBPART Z.
 THE SPECIFIC RESPIRATOR SELECTED MUST BE BASED ON CONTAMINATION LEVELS FOUND IN THE WORK PLACE. MUST NOT EXCEED THE WORKING LIMITS OF THE RESPIRATOR AND BE JOINTLY APPROVED BY THE NATIONAL INSTITUTE FOR OCCUPATIONAL SAFETY AND HEALTH AND THE MINE SAFETY AND HEALTH ADMINISTRATION (NIOSH-MSHA).

CARBON DIOXIDE:

50,000 PPM- ANY SUPPLIED-AIR RESPIRATOR.
 ANY SELF-CONTAINED BREATHING APPARATUS.

ESCAPE- ANY APPROPRIATE ESCAPE-TYPE, SELF-CONTAINED BREATHING APPARATUS.
 FOR FIREFIGHTING AND OTHER IMMEDIATELY DANGEROUS TO LIFE OR HEALTH CONDITIONS:
 ANY SELF-CONTAINED BREATHING APPARATUS THAT HAS A FULL FACEPIECE AND IS OPERATED IN A PRESSURE-DEMAND OR OTHER POSITIVE-PRESSURE MODE.

ANY SUPPLIED-AIR RESPIRATOR THAT HAS A FULL FACEPIECE AND IS OPERATED IN A PRESSURE-DEMAND OR OTHER POSITIVE-PRESSURE MODE IN COMBINATION WITH AN AUXILIARY SELF-CONTAINED BREATHING APPARATUS OPERATED IN PRESSURE-DEMAND OR OTHER POSITIVE-PRESSURE MODE.

CLOTHING:
 FOR THE GAS FORM, PROTECTIVE CLOTHING NOT REQUIRED.
 IF CONTACT WITH THE LIQUID FORM IS POSSIBLE, EMPLOYEE MUST WEAR APPROPRIATE PROTECTIVE CLOTHING AND EQUIPMENT TO PREVENT SKIN FROM FREEZING.

GLOVES:
 PROTECTIVE GLOVES ARE NOT REQUIRED BUT RECOMMENDED.

EYE PROTECTION:
 EYE PROTECTION NOT REQUIRED, BUT ADVISABLE.

-ADDITIONAL INFORMATION-
THIS MSDS IS SUPPLIED PURSUANT TO OSHA REGULATIONS. OTHER GOVERNMENT REGULATIONS MUST BE REVIEWED FOR APPLICABILITY TO THIS PRODUCT. WE BELIEVE THE INFORMATION SOURCE IS RELIABLE AND THE INFORMATION IS ACCURATE AS OF THE DATE HEREOF. HOWEVER, ACCURACY OR COMPLETENESS IS NOT GUARANTEED AND NO WARRANTY OF ANY TYPE IS GRANTED. THE INFORMATION RELATES ONLY TO THIS SPECIFIC PRODUCT. IF COMBINED WITH OTHER MATERIALS, ALL COMPONENT PROPERTIES MUST BE CONSIDERED.