CHEMICAL SIMULATION MODELING OF
HEAT TRANSFER IN LMFBRs

MASTER

A Thesis Presented to
The Department of Chemical Engineering
Brigham Young University

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of the Requirements for the Degree
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by
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CHAPTER I

INTRODUCTION

The Nuclear Regulatory Commission (NRC) has identified three levels of safety which must be satisfied prior to the issuance of either a construction permit or an operating license for a nuclear reactor. The question of safety is addressed in the form of the Preliminary Safety Analysis Report (PSAR) which is submitted at the time a construction permit is applied for, and the Final Safety Analysis Report (FSAR), which is submitted in conjunction with obtaining an operating license.

The first level of safety involves the design of the plant for safe operation under normal conditions. This includes such things as instrumentation and control, operator protection, materials selection and environmental protection.

The second level of safety requires the design of the plant to provide for the protection of the environment, personnel and the public in the event that incidents do occur in spite of care in design, construction and operation. These include, for example, an emergency core cooling system in the event of a loss-of-coolant-flow accident, redundant capability for fast shutdown in the event that some control rods cannot be reinserted, independent offsite power and redundant, independent onsite power.

The third level of safety provides for additional systems as necessary to provide for hypothetical accidents which may occur

as a result of some safety systems failing together with the accident they are intended to prevent. Accidents of this nature are referred to as design basis accidents.

The NRC has determined that the likelihood of some accidents is so remote when considered in light of other safety measures that they need not be considered as design basis accidents.

Based on the precedence established in the licensing process of the Clinch River Breeder Reactor (CRBR) the NRC has chosen not to include the core disruptive accident (CDA) as a design basis accident for liquid metal fast breeder reactors (LMFBR). However, as an added safety measure the NRC did require in the preliminary evaluation that the containment in the CRBR maintain its integrity for at least 24 hours following a postulated CDA in which total core melt occurred within 1000 seconds (Nuc. News, July 1976).

The scenario which is generally analyzed in conjunction with a CDA because of the consequences is the loss-of-coolant-flow accident (LOF) which leads to a total core melt. In the case of the sodium-cooled reactor the first event in the LOF sequence involves the boiling off of the liquid sodium in the core at 882°C. As the core continues to heat the stainless steel cladding and containment begins to melt at 1400°C. Further heating causes the fuel to melt at approximately 2770°C and the steel to boil at 2800°C. The original core area would consist at this point of a boiling internally heated, molten pool.

To meet the thermal containment requirement previously mentioned requires that the heat transfer coefficients be determined

with a relatively high degree of accuracy. This poses several interesting problems. Since the molten pool in question is heated volumetrically the standard and proven heat transfer correlations may not provide an accurate representation of reality. A second problem is the development of a practical method of verification of proposed heat transfer correlations for the internally heated molten core system. Due to the prohibitive nature of creating a CDA in an actual nuclear reactor, alternative methods of verification are required.

A chemical reaction conducted in a wax cylinder was used in this study to simulate a CDA occurring in a reactor. The exothermic reaction of dimethyl sulfoxide (DMSO) with acetyl chloride (AC) was used as the chemical reaction to simulate the internally heated liquid pool. SUN-3420 wax was used to construct the cylindrical reaction vessel to simulate cladding and containment.

During a CDA, a question remains as to whether the containment would be miscible in the molten fuel. To allow for the possibility that either may be true, two cases were evaluated in this study. By using acetone as the solvent in the DMSO and AC solutions, the case in which the vessel was relatively insoluble in the reaction mixture was simulated. By using benzene as the solvent in the DMSO and AC solution, the case in which the molten vessel was more soluble in the reaction mixture was simulated.

Based on the findings of this work the proposed heat transfer correlations for volumetrically heated liquid pools may be used with greater confidence as to their accuracy and applicability.

CHAPTER II

MATERIALS SELECTION

The purpose of this study was to simulate a core disruptive accident (CDA) in which total core melt occurs. In previous studies the internally heated liquid pool was simulated by Farahat et al. (1976) using microwave heating, by Faradieh and Baker (1978) using resistive heating of electrolytic solutions, and by Wheeler (1978) using an exothermic chemical reaction. The exothermic chemical reaction of dimethyl sulfoxide (DMSO) and acetyl chloride (AC) used by Wheeler (1978) was used as the basis of the internally heated liquid pool in this study.

Wax was chosen as the substance to simulate containment material (e.g. stainless steel, concrete, etc.) because of the low melting point and ease with which it can be worked.

A question still exists as to whether the molten containment would be miscible with the molten fuel in the event that a CDA did occur in which the core was reduced to a molten state. Because of this unanswered question, it was desired to find waxes which would model the case in which the containment was soluble in the heat generating medium and other waxes which modeled the case in which the containment was relatively insoluble. An equally effective alternative was to find one wax which would model both the soluble and insoluble case by changing the solvent in the reaction system.

Solvent Comparison

In the work conducted by Wheeler (1978) using the DMSO-AC system, benzene was used as the solvent. In this study, acetone and toluene were compared with benzene on the basis of void fraction as a measure of the system ability to simulate a boiling regime and a non-boiling regime.

The comparison was made by using each solvent in a 4M, equimolar DMSO-AC open reaction. The solvents were compared on the basis of maximum void fraction and length of time above 50% void. Void fraction was determined as the difference between the boiled up height minus the liquid height divided by the boiled up height. The void fraction was converted to a void percent by multiplying the void fraction by 100. The results of this experiment are presented in Table 1.

To determine the void fraction and length of time above 50% void the reaction was run in a 250 ml graduated cylinder. AC together with sufficient solvent to provide 10 mls of AC solution was placed in the graduated cylinder. A small amount of ground bakelite was added to provide nucleation sites. 10 mls of equimolar DMSO solution using the same solvent was then introduced into the reaction vessel by means of a mechanical syringe pump at a rate of 24 mls/min. This experimental setup is illustrated in Figure 1.

The reaction was filmed using a super 8 movie camera. From the developed film the void fraction was determined. The length of time for which the void was above 50% was determined by counting the number of frames in which the void was above 50% and dividing this

TABLE 1
4 M Open DMSO-AC System

<u>Solvent</u>	<u>Acetone</u>	<u>Benzene</u>	<u>Toluene</u>
Max. void %	80%	60%	0%
Length of time above 50% void	8 sec.	4 sec.	0 sec.

Figure 1. Experimental Setup - Open System

number by the number of frames exposed per second. It was found that acetone as the solvent produced the greatest maximum void and longest sustained void followed by benzene and toluene in decreasing order.

Wax Comparison

It was desired that the wax or waxes chosen have both a melting point and a heat of melting low enough to allow substantial melting with the temperature and heat generated by the reaction system. It was also desired that the properties of the wax be such that the wax could be cast into forms free from such structural imperfections as cracks, fissures or granulation.

Seventeen waxes were compared. These waxes consisted of natural, micro-crystalline, paraffin and polyethylene glycol waxes. Two qualitative methods were employed as a preliminary elimination of those waxes which did not meet the requirements previously mentioned. To evaluate the molding characteristics of the waxes, each was cast into a cylindrical configuration and observed. The second method of comparison was to compare the solubility of each wax in the components of the reaction system. The results of these comparisons are tabulated in Table 2. It was found that SUN-3420 most closely matched the castability, low melting point and solubility requirements of this study.

The mold consisted of a 6-inch length of 2 1/2 inch inside diameter polypropylene tubing. The tubing was cut lengthwise into two equal sections. The two sections were placed together and held

TABLE 2
Wax Comparison

Wax	Type	Casting	Hardness	M.P. (°C)	Solubility $\frac{\text{g wax added}}{\text{ml solvent}}$					
					Acetone	Acetyl Chloride	Benzene	Dimethyl Sulfoxide	Sulfuric Acid	Toluene
Polyethylene Glycol 600 Mono Stearate Petronauba W	Polyethylene Glycol	Good		33-38 ⁱ	--	0.02 ^f	0.02 ^f	0.02 ^a	--	--
		Good			--	0.03 ^{a,b}	0.03 ^{a,d,e}	0.03 ^a	0.03 ^{b,e}	--
Petrolite C-8500	Micro Crystalline	Fair			--	0.03 ^b	0.03 ^{c,d}	0.03 ^a	0.03 ^{b,e}	--
Be Square 190/195 Amberwax	Micro Crystalline	Good		88 ⁱ	--	0.03 ^a	0.03 ^d	0.03 ^a	0.03 ^{a,b}	--
Carnauba	Natural	Poor		83-86 ⁱ	--	0.03 ^a	0.03 ^a	0.03 ^a	0.03 ^{d,e}	--
ES-254	Micro Crystalline	Poor	1.3 ^h	35 ^h	0.01 ^a	0.01 ^f	--	0.01 ^a	--	0.01 ^f
TS-254A	Micro Crystalline	Poor	0.3 ^g	93 ^h	0.01 ^a	0.01 ^f	--	0.01 ^a	--	0.01 ^a
TS-970	Micro Crystalline	Poor	0.1 ^h	78 ^h	0.01 ^a	0.01 ^c	--	0.01 ^a	--	0.01 ^a
TS-254	Micro Crystalline	Poor	0.35 ^h	63 ^f	0.01 ^a	0.01 ^f	--	0.01 ^c	--	0.01 ^a
Sun 3420		Good	50 ^g	55 ^c	0.02 ^a	0.02 ^a	0.02 ^f	0.02 ^a	--	0.02 ^f

TABLE 2 (cont.)

Wax	Type	Casting	Hardness	M.P. (°C)	Solubility $\frac{\text{g wax added}}{\text{ml solvent}}$					
					Acetone	Acetyl Chloride	Benzene	Dimethyl Sulfoxide	Sulfuric Acid	Toluene
Sun P116		Fair	90 ^g	46 ^g	0.02 ^a	0.02 ^f	0.02 ^f	0.02 ^c	--	0.02 ^f
Sun P127		Good	60 ^g	55 ^g	0.02 ^a	0.02 ^a	0.02 ^f	0.02 ^a	--	0.02 ^f
Sun P137		Fair	20 ^g	60 ^g	0.02 ^a	0.02 ^a	0.02 ^c	0.02 ^a	--	0.02 ^f
Sun P-155		Good	20 ^g	67 ^g	0.02 ^a	0.02 ^a	0.02 ^f	0.02 ^a	--	0.02 ^c
Sun P-5512		Good	20 ^g	66 ^g	0.02 ^a	0.02 ^c	0.02 ^f	0.02 ^a	--	0.02 ^f
Sun 7717		Poor	50 ^g	76 ^g	0.02 ^a	0.02 ^c	0.02 ^c	0.02 ^a	--	0.02 ^{bc}

^aSmall amount of sample went into solution.

^bColor change occurred.

^cApproximately 1/2 of sample went into solution.

^dLoss of structural integrity (e.g. dispersed, flockulant, etc.)

^eCloudy solvent.

^fWax was completely dissolved in solvent.

^gPenetration at 100^oF (ASTM D-1321) Correspondence from Sun Petroleum Products Co. (Dec. 1, 1978).

^hPenetration with 100 g load, mm (ASTM D5-65) Technical Data Sheet, NP Series, TDS No. 3, IMC Chemical Group, Inc., Hillside, Ill.

ⁱBennett, Industrial Waxes, Vol. 1, Chemical Publishing Co., New York, (1963).

in place by four worm drive strap clamps. One end of the tube was stoppered with an aluminum foil covered rubber stopper. A test tube of 25 mm outside diameter was placed inside the mold in a concentric fashion, to a depth of approximately 3/4 inch above the rubber stopper. The test tube was stoppered with a two-hole rubber stopper with glass tubing inserted through the holes of the stopper. This arrangement is illustrated in Figure 2.

The glass tubing in the test tube was connected to a temperature controlled water source in such a fashion that water could be circulated through the tube. This allowed the rate of heat removal from the wax to be controlled. Molten wax was placed inside the mold and allowed to cool to room temperature. Hot water was then circulated through the test tube. This caused a thin film of wax to melt around the test tube. The test tube was removed leaving a cavity in which the DMSO-AC reaction could then be conducted. Each casting was visually inspected for structural flaws such as fissures, granulation, etc.

To compare solubilities, a 0.1 g to 0.25 g sample of each wax was placed in an individual 20 ml, capped scintillation vial. 10 mls of a solvent at room temperature was then added. The vial was observed for any immediate results. The vial was observed approximately 24 hours later for any further results. It was observed at the conclusion of the 24 hour period that a color change had occurred in some waxes, some waxes had decomposed and others had turned the solvent cloudy.

Figure 2. Wax mold with temperature controlled center.

Materials Selection

Because of the casting quality, high solubility in benzene and toluene, and low solubility in acetone, DMSO and AC, SUN-3420 was selected as the wax to be used in this study. Benzene was chosen as the solvent to be used in the experiments simulating high containment solubility due to the availability of the work performed by Wheeler using the DMSO-AC-benzene system. Acetone was chosen as the solvent to be used in the experiments simulating low containment solubility because of the relative insolubility of SUN-3420 in acetone.

CHAPTER III

THEORETICAL DEVELOPMENT

The heat balance for an internally heated liquid pool contained in a vessel may be expressed as

$$Q_T = Q_V + Q_M + Q_1 + Q_W - Q_Z \quad (1)$$

where

Q_T = Total heat generated in pool per unit time.
 Q_V = Heat lost as latent heat of vaporization per unit time.
 Q_M = Heat lost as latent heat of melting per unit time.
 Q_1 = Heat lost as sensible heat to the liquid per unit time.
 Q_W = Heat lost as sensible heat to the wall per unit time.
 Q_Z = Viscous terms.

$$Q_V = -\lambda_V \rho_1 \left[\frac{dV_1}{dt} - \beta \frac{dV_W}{dt} \right] \quad (2)$$

where

λ_V = Heat of vaporization of the liquid
 ρ_1 = Density of the liquid
 V_1 = Volume of liquid
 V_W = Volume of wall
 t = Time
 β = Expansion factor ($\rho_{\text{melted wall}} / \rho_{\text{solid wall}}$)

$$Q_M = -\lambda_M \rho_W \frac{dV_W}{dt} \quad (3)$$

where

λ_m = Latent heat of melting of wall
 ρ_W = Density of solid wall

$$Q_1 = \rho_W \hat{c}_{p_W} (T_1 - T_M) \frac{dV_W}{dt} + \rho_1 \hat{c}_{p_1} \frac{\partial (V_1 T_1)}{\partial t} \quad (4)$$

where

$\hat{c}_{p_W}$ = Heat capacity of molten wax per unit mass
 T_1 = Bulk temperature of the liquid.
 T_M = Melting temperature of wall
 $\hat{c}_{p_1}$ = Heat capacity of liquid per unit mass

Using Fourier's law and written for cylindrical geometry

$$Q_W = -Ak_w \left. \frac{dT}{dr} \right|_{r=R} \quad (5)$$

where

T = Wall temperature
 R = Radius of interface
 k_w = Thermal conductivity of solid wall
 A = Area for heat transfer

From calculations based on the physical properties of the dimethyl sulfoxide (DMSO) acetyl chloride (AC) reaction conducted in a SUN-3420 wax cylinder, the sensible heat required to raise the boundary wall temperature from the initial temperature, T_0 , to the melting temperature, T_M , and the initial reaction mixture from the initial temperature, T_0 , to the boiling temperature, T_M , have been neglected based on the work of Wheeler (1978) with the same DMSO-AC reaction system. At boiling the temperature difference across the liquid vapor boundary is zero. Therefore, no heat is lost by conduction and all heat lost across this boundary is due to the escaping vapors.

The amount of heat transferred to the wall, $Q_{W,T}$, may be written as

$$Q_{W,T} = Ah(T_l - T_w) \quad (6)$$

where

A = Area for heat transfer
 h = Heat transfer coefficient
 T_l = Bulk temperature of the liquid
 $Q_{W,T}$ = Total heat transferred to the wall (Energy/time)
 T_w = Wall temperature at the solid liquid interface

For the case of heat transfer to the sidewalls, (sideward heat transfer) several correlations have been proposed for calculating a Nusselt number and hence a heat transfer coefficient.

The first case to be considered is that of the non-boiling internally heated liquid pool. The predominant mechanism is natural convection. It was proposed by L. Baker et al. (1974) that the correlations for heat transfer from a vertical plate to a fluid could be used with the modification that the heat transfer coefficient obtained would be corrected to take into account that the heat was being transferred from an internally heated fluid to a plate.

The uncorrected equation for the Nusselt number as used by L. Baker et al. (1975) is

$$Nu_o = \frac{(4/3)(0.508)Pr^{1/2}Gr^{1/4}}{(0.952 + Pr)^{1/4}} \quad (7)$$

where

$$Nu_o = \frac{h_o L}{k} \quad \text{uncorrected Nusselt number}$$

$$Pr = \frac{C_p \mu}{k} \quad \text{Prandtl number}$$

$$Gr = \frac{g\beta\Delta T L^3 \rho^2}{\mu^2} \quad \text{Grashof number}$$

L = Pool height

h_o = Uncorrected heat transfer coefficient

β = Thermal coefficient of volumetric expansion

g = Gravitational constant

μ = Viscosity

Equation 7 works well for values of $GrPr < 10^9$. At greater values the flow becomes turbulent and the correlation breaks down. It is reported by W.H. McAdams (1954) that for the range $10^4 < GrPr < 10^9$ the correlation is described well by the equation

$$Nu_o = 0.59 (GrPr)^{1/4} \quad (8)$$

The corrected heat transfer coefficient is obtained as follows:

$$\frac{h}{h_o} = \frac{3.88}{3.88 - 12.91\phi + 46.5\phi^2} \quad (9)$$

where

h = Heat transfer coefficient for internal heat generation
 h_o = Heat transfer coefficient without internal heat generation

$$\phi = \frac{qL^{1/2}}{(g\beta)^{1/2}\Delta T^{3/2}(\rho C_p)} \quad (10)$$

q = Volumetric heat generation Energy/(Time)(Volume)

The correction h/h_o was found to be negligible (~3%) when $\phi < 0.01$.

The second case of sideward heat transfer to be treated is that of the boiling internally heated pool. Baker et al. (1975) calculated that as bubbles rise in the boiling pool, the fluid motion in the center is in the direction of the rising bubbles. At the walls, however, the fluid motion is downward. At the bottom of the pool the motion of the fluid is from the sidewalls toward the center with the converse being true at the top of the pool.

At low boiling rates the flow near the wall may be assumed to be laminar and correlations for tangential flow past a flat plate may be used. In the laminar region the following theoretically derived expression may be used as described by Bird, Stewart and Lightfoot (1960)

$$Nu_x = 0.332 Re_x^{1/2} Pr^{1/3} \quad (11)$$

where

$$Nu_x = \frac{h_x l}{k} = \text{Local Nusselt number}$$

h_x = Local heat transfer coefficient
 l = Position

$$Re_x = \frac{V_\infty \rho_f l}{\mu_f} = \text{Local Reynolds number}$$

V_∞ = Approach or bulk velocity

ρ_f = Density at film conditions
 μ_f = Viscosity at film conditions

$Pr = \left(\frac{C_p \mu}{k}\right)_f$ = Prandtl number (evaluated at film conditions)

An average Nusselt number may be also obtained from Bird, Stewart and Lightfoot (1960) as

$$Nu = 0.664 \left(\frac{L V_\infty \rho_f}{\mu_f}\right) Pr^{1/3} \quad (12)$$

where

L = Length of plate

Both Equations 11 and 12 are accurate to within 2% for $Pr > 0.6$. The correlations become inaccurate at lower Pr numbers.

Based on the work of Fair, Lambricht and Anderson (1962), Baker et al. (1975) suggested that V_∞ would be proportional to the superficial vapor velocity U_V . On this basis V_∞ in Equations 11 and 12 may be replaced by U_V and a proportionality constant c . Equation 12 becomes

$$Nu = c \left(\frac{L U_V \rho_f}{\mu_f}\right)^{1/2} Pr^{1/3} = c Re^{1/2} Pr^{1/3} \quad (13)$$

where c = proportionality constant.

As the bubbling rate increases, the flow near the wall becomes more turbulent. This process may be thought of as turbulent diffusion of packets of fluid from the pool interior to the side wall.

For an average packet residence time at the wall of θ , Baker et al. (1975) describe the heat transfer coefficient as

$$h = \frac{\sqrt{4 C_p \rho k}}{\pi \theta} \quad (14)$$

where θ = mean packet residence time at the wall.

In order to estimate θ , Baker et al. make several assumptions:

1) Bubble size is independent of boiling rate. Since the distribution of bubble diameters is in a narrow range, the bubble rise velocity or terminal velocity will be essentially the same. On this basis, increasing the vaporization rate will increase the frequency of bubble formation.

$$f = c' \left(\frac{W}{AL} \right) = c' \left(\frac{U_V}{L} \right) \quad (15)$$

where

- f = Frequency of bubble formation
- c' = Constant
- W = Volumetric vapor generation rate
- A = Base area of pool
- L = Height of pool
- U_V = Superficial vapor velocity

2) The frequency of local bubble disturbance of the fluid at the wall is proportional to the frequency of bubble formation. On the basis of assumption 1, the disturbance of each bubble and the length of time of each disturbance would be the same. This results in a residence time at the wall of a packet of fluid between bubble disturbances of

$$\theta = \frac{c''}{f} = c''' \frac{L}{U_V} \quad (16)$$

where c'' and c''' are constants.

Substituting Equation 16 into Equation 14, the heat transfer coefficient in terms of the superficial vapor velocity becomes

$$h = c^{IV} \sqrt{\frac{C_p \rho k U_V}{L}} \quad (17)$$

where c^{IV} is a constant.

Equation 17 may be arranged in terms of a Nusselt number as

$$Nu = \frac{hL}{k} = c^{IV} [Re]^{1/2} [Pr]^{1/2} \quad (18)$$

where $Re = \frac{LU_V \rho}{\mu}$.

It may be noted that in the laminar flow model, the Prandtl number is raised to the 1/3 power, where in the turbulent flow model it is raised to the 1/2 power.

Baker et al. (1975) found using a boiling pool of $Zn SO_4-H_2O$ with resistive internal heat generation that the constants c and c^{IV} for use in Equations 13 and 18 respectively to be

$$c = 2.131 \pm 0.121 = 2.131 (1 \pm 0.0568)$$

$$c^{IV} = 1.76 \pm 0.101 = 1.76 (1 \pm 0.0572)$$

For the case of laminar flow, Equation 13 becomes

$$Nu = 2.131 (1 \pm 0.0568) Re^{1/2} Pr^{1/3} \quad (19)$$

For the case of turbulent penetration Equation 18 becomes

$$Nu = 1.76 (1 \pm 0.0572) (Re)^{1/2} (Pr)^{1/2} \quad (20)$$

Baker et al. (1975) further generalized the correlation for sideward heat transfer by introducing a velocity term referred to as a thermal convection reference velocity.

$$V_{TC} = (g\beta\Delta TL)^{1/2} = \left[\frac{g(\rho_w - \rho_p)}{\rho_{AV}} L \right]^{1/2} \quad (21)$$

where

$$\begin{aligned} V_{TC} &= \text{Thermal convection velocity} \\ \rho_w &= \text{Fluid density at the wall} \\ \rho_p &= \text{Bulk fluid density} \\ \rho_{AV} &= \text{Average fluid density} \end{aligned}$$

Using the thermal convection velocity the Nusselt number may be expressed as

$$Nu = 2.131 \left(\frac{LV_{TC}\rho_{AV}}{\mu} \right)^{1/2} Pr^{1/3} \quad (22)$$

where

$$\begin{aligned} V &= U_V \text{ (superficial vapor velocity) for boiling pools} \\ V &= 0.078 V_{TC} \text{ for non-boiling pools} \end{aligned}$$

The prediction of downward heat transfer must also be considered in terms of a boiling case.

Based on the work of Kulachi and Goldstein (1972), and Jahn and Reineke (1974), Baker et al. (1975) suggest that the predominant heat transfer mechanism for the non-boiling case is conduction.

As a preliminary step to characterizing the upward and downward heat transfer, thermal layers may be considered to exist with upper and lower horizontal thermal boundaries of a uniform temperature. ($T_1 = T_0$ where T_1 = upper thermal boundary temperature, T_0 = lower thermal boundary temperature.) The thermal layer may then be divided at the plane of maximum horizontally averaged temperature, $\hat{T}$, into an upper and lower sublayer. All of the heat generated in the lower sublayer is then assumed to transfer down and all the heat generated in the upper sublayer is assumed to transfer upward. Based on this model Kulachi and Goldstein defined an internal Rayleigh number and two Nusselt numbers as

$$Ra_{KG} = \frac{g\beta qL^5}{64\alpha\nu k} \quad (23)$$

$$Nu_1 = \frac{Q_1 L}{(\hat{T} - T_1)k} \quad (24)$$

$$Nu_0 = \frac{Q_0 L}{(\hat{T} - T_0)k} \quad (25)$$

where

$$\begin{aligned} Ra_{KG} &= \text{Internal Rayleigh number as defined by Kulachi and Goldstein} \\ \alpha &= \text{Thermal diffusivity} \\ \nu &= \text{Kinematic viscosity} \end{aligned}$$

Q_1 = Upward heat flux
 Q_0 = Downward heat flux
 $\hat{T}$ = Maximum horizontally averaged layer temperature
 T_1 = Upper boundary temperature
 T_0 = Lower boundary temperature
 Nu_1 = Upper sublayer Nusselt number
 Nu_0 = Lower sublayer Nusselt number
 L = Total layer depth

To extend the applicability of the work of Kulachi and Goldstein (1972) to systems where the boundary temperatures were not equal, Baker et al. (1975) introduced an external Rayleigh number and the fraction of heat generated which is transferred downward; η .

$$Ra_E = \frac{g\beta L^3}{\alpha\nu} (T_1 - T_0) \quad (26)$$

where Ra_E = External Rayleigh number.

Dividing Ra_E by Ra_{KG} produces

$$\frac{Ra_E}{Ra_{KG}} = \frac{64 k (T_1 - T_0)}{qL^2} \quad (27)$$

Assuming uniform heat production, η may be written as

$$\eta = \frac{L_0}{L} \quad (28)$$

where

η = Fraction of heat transferred downward
 L_0 = Lower sublayer height
 L = Total layer height

Written in terms of η the sublayer Nusselt numbers become

$$Nu_1 = \frac{0.403 Ra_{KG}^{0.226} [32(1-\eta)^5]^{0.226}}{(1-\eta)} \quad (29)$$

$$Nu_0 = \frac{2}{\eta} \quad (30)$$

η may be found numerically from

$$\frac{(1-\eta)^{0.870}}{32 \eta^2 - Ra_E / Ra_{KG}} = 0.138 Ra_{KG}^{0.226} \quad (31)$$

From Equation 26 it can be seen that Ra_E may be negative, positive or zero.

Negative values of Ra_E correspond to the lower boundary temperature being greater than the upper boundary temperature. The limit of this case is when all of the heat generated is transferred upward and $\eta \rightarrow 0$. This limit occurs at

$$Ra_E \geq 72.6 Ra_{KG}^{0.774} \quad (32)$$

For the converse where the upper boundary temperature is greater than the lower boundary temperature the limit of applicability of Equation 31 occurs when the stability limit of the upper sublayer is reached. This condition exists when the Nusselt number defined in terms of the actual sublayer height, Nu' , is equal to two.

$$Nu_1' = \frac{q L_1}{(\hat{T} - T_1)k} \quad (33)$$

where

Nu_1' = Nusselt number for upper sublayer defined in terms of actual sublayer height
 L_1 = Upper sublayer height

Based on the work of Kulacki and Emara (1975) and modified by Baker et al. (1975)

$$Nu_1' = 0.403 [32 Ra_{KG} \left(\frac{Nu_1}{Nu_1 + Nu_0} \right)^5]^{0.226} \quad (34)$$

When $Nu_1' \geq 2$ the heat transfer mechanism throughout the layer is that of conduction. When this occurs the sublayer Nusselt numbers become

$$Nu_1 = \frac{e}{1-\eta} \quad (35)$$

$$Nu_0 = \frac{2}{\eta} \quad (36)$$

When $Nu_1' \geq 2$, equation 37 is employed in the calculation of η rather than equation 31.

$$\eta = 0.5 + \frac{Ra_E}{64 Ra_{KG}} \quad (37)$$

The boundary between the total conduction regime and the conduction-convection regime is calculated by substituting equation 37 into equation 31 to obtain

$$\eta = 1 - 2.064 Ra_{KG}^{-0.200} \quad (38)$$

which defines the boundary between the regimes.

Since η is bounded between 0 and 1 an additional limit exists as $\eta \rightarrow 1$. At this limit all the heat generated is transferred downward.

For the case of boiling downward heat transfer, Baker et al. (1975) found the ratio of the sideward heat flux to the downward heat flux to vary as a function of the boiling heat flux. As the boiling flux increased, the ratio of the sideward heat flux approached a fairly constant value of 3.8. Stein et al. (1974) found this ratio to reach an equilibrium value of approximately 5.0. This finding indicates that as the boiling rate is increased, the disturbance created by the vapor bubbles predominates. This results in a uniform effect on both the sideward and downward heat transfer.

Baker et al. (1975) also compared the downward heat transfer from a boiling pool to that predicted by the conduction model alone.

They found that at the lower values of the boiling heat flux, the downward heat flux was less than that predicted from conduction alone. At larger values of the boiling heat flux they found that the ratio of downward heat transfer to that predicted by conduction only levels out in a range of 2 to 4.

Using resistive heating of a salt water pool, Hesson and Gunther (1972) correlated the downward heat flux from a boiling pool to be

$$Q_D = 0.45 S^{1/3} k(\rho/\mu)^{2/3} (\mu C_p/k)^{0.25} \Delta T$$

where

- k = Thermal conductivity of the liquid (erg/cm sec°K)
- S = Ratio of vapor fractions in rising and descending circulation paths (S goes to 1 as the heat input increases)
- ρ = Density of fluid (g/cm³)
- μ = Viscosity of liquid (g/cm sec)
- C_p = Specific heat of liquid (erg/cm°K)

All of the correlations previously described were derived in the absence of mass transfer. To correct for the presence of mass transfer, the heat transfer coefficients are corrected using a film theory convection factor as outlined by Bird, Stewart and Lightfoot (1960).

$$h_{cor} = h \frac{\phi_T}{R_T} \quad (39)$$

where h_{cor} = heat transfer coefficient corrected for mass transfer.

$$\phi_T = \frac{(\tilde{N}_{ao} \tilde{C}_{pa} + \tilde{N}_{bo} \tilde{C}_{pb})}{\tilde{N}_{ao} \lambda_M - k_W \left. \frac{dT}{dr} \right|_{r=R}} (T_1 - T_w) \quad (40)$$

where

- $\tilde{N}_{ao}$ = Molar flux of component a at the interface
- $\tilde{N}_{bo}$ = Molar flux of component b at the interface
- $\tilde{C}_{pa}$ = Molar heat capacity of component a
- $\tilde{C}_{pb}$ = Molar heat capacity of component b

$$R_T = \exp(\phi_T) - 1 \quad (41)$$

In the case of the wax cylinder containing an internally heated liquid pool, N_{bo} is considered to be 0. N_{ao} is calculated as

$$N_{ao} = \frac{dV_M}{dt} \frac{\rho_w}{AN_w} \quad (42)$$

where N_w = molecular weight of wall material.

The heat transferred to the wall is absorbed as latent heat as the wall is melted or is dissipated as sensible heat

$$Q_{W,T} = Q_M + Q_W \quad (43)$$

where

$$\begin{aligned} Q_{W,T} &= \text{Heat flux to the wall} \\ Q_M &= \text{Heat absorbed in melting wall} \\ Q_W &= \text{Heat dissipated in wall} \end{aligned}$$

Assuming Fourier's law to be valid

$$Q_W = -Ak \left. \frac{dT}{dr} \right|_{r=R} \quad (44)$$

For evaluation of the derivative, the temperature profile for a non-moving boundary is assumed. On this basis the equation of energy takes the form in cylindrical coordinates

$$\frac{\partial T}{\partial t} - \frac{\alpha}{r} \frac{\partial}{\partial r} \left(r \frac{\partial T}{\partial r} \right) = 0 \quad (45)$$

The following dimensionless parameters are defined as:

$$\tau = \frac{\alpha t}{R^2} \quad \text{dimensionless time}$$

where R = initial phase boundary

$$\theta = \frac{T - T_2}{T_m - T_2} \quad \text{dimensionless temperature}$$

where T_2 = temperature at outside boundary

$$\xi = \frac{r}{R} \quad \text{dimensionless radius}$$

In dedimensionalized form, Equation 45 becomes

$$\frac{\partial \theta}{\partial \tau} - \frac{1}{\xi} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial \theta}{\partial \xi} \right) = 0 \quad (46)$$

To solve Equation 46 assume θ to be a product of two functions.

$$\theta = TZ \quad (47)$$

where

$$\begin{aligned} T &= f(\xi) \\ Z &= f(\tau) \end{aligned}$$

By substituting Equation 47 into Equation 46, Equation 46 can be put in the form

$$\frac{1}{Z} \frac{dZ}{d\tau} = \frac{1}{\xi T} \frac{\partial}{\partial \xi} \left(\xi \frac{\partial T}{\partial \xi} \right) = 0, -\lambda^2, \delta^2 \quad (48)$$

where 0 represents the steady state solution and $-\lambda^2$ and δ^2 represent eigenvalues for the transient solution. The δ^2 solution produces an unrealistic solution and is therefore neglected. The T dependent portion of Equation 48 may be rearranged in the form

$$(\lambda \xi)^2 \frac{d^2 T}{d(\lambda \xi)^2} + \lambda \xi \frac{dT}{d(\lambda \xi)} + [(\lambda \xi)^2 - 0]T = 0 \quad (49)$$

Equation 49 is a Bessel's differential equation of order zero. The solution for T is

$$T = C_1 J_0(\lambda \xi) + C_2 Y_0(\lambda \xi)$$

where C_1 and C_2 are constants.

The Z dependent portion of Equation 48 is solved as

$$Z = C_3 e^{-\lambda^2 \tau}$$

where C_3 = a constant of integration. The steady state solution of Equation 48 is

$$\theta = C_4 \ln(C_5 \xi)$$

where C_4 and C_5 are constants. Combining the steady state and the transient solution

$$\theta = C_4 \ln(C_5 \xi) + \sum_{n=0}^{\infty} C_{6n} e^{-\lambda_n^2 \tau} [J_0(\lambda_n \xi) + C_{7n} Y_0(\lambda_n \xi)] \quad (50)$$

λ , C_4 , C_5 , C_{6n} , and C_{7n} are evaluated using the initial conditions and the boundary conditions of the particular problem.

The wax cylinders used in this study consisted of an initial inside diameter of 2.46 cm and an outside diameter of 4.8 cm. Based on these radii, ξ ranges from 1.0 at the inside diameter to 1.95 at the outside diameter.

For the purposes of evaluation, the outside boundary is considered to be a constant 25°C. At time equal zero, the inside wall temperature is assumed to be instantaneously raised to 55°C, the melting point of the wax, where it remains. Under these conditions θ is equal to 1.0 at the inside wall and 0.0 at the outside wall.

Evaluating Equation 50 at the conditions of θ and ξ described in the preceding paragraphs the first constants and first eigenvalue are found to be

$$\begin{aligned} \lambda_1 &= 3.288764 \\ C_4 &= -1.497388 \\ C_5 &= 0.512821 \\ C_6 &= 0.463514 \\ C_{71} &= 1.24996 \end{aligned}$$

Substituting these values into equation 50

$$\theta = -1.4974 \ln(0.5128\xi) + 0.4635 e^{-(3.2888)\tau} [J_0(3.2888\xi) + 1.2500 Y_0(3.2888\xi)] + \dots \quad (51)$$

By substituting Equations 3, 5 and 6 into Equation 43, and rearranging

$$\lambda_M \rho_w \frac{dv_w}{dt} = A \left[h \Delta T + k_2 \left(\frac{dT}{dr} \right)_{r=R} \right] \quad (52)$$

where

$$\Delta T = (T_l - T_w)$$

T_l = Bulk temperature of liquid

T_w = Temperature of wall at $r = R$

Solving Equation 52 for the melted volume

$$v_w = \frac{1}{\lambda_M \rho_w} \int_0^t A \left[h \Delta T + k_w \left(\frac{dT}{dr} \right)_{r=R} \right] dt \quad (53)$$

By comparing the melted volume of the wall determined experimentally with that obtained by evaluating Equation 53 the accuracy of the heat transfer coefficients may be determined within the limitations of experimental error.

CHAPTER IV

PHYSICAL PROPERTIES OF THE REACTION SYSTEM AND REACTION VESSEL

The methods used to obtain the physical properties and the values of the system properties used in subsequent calculation are contained in this chapter.

Time Dependency

The internally heated liquid pool is generated by injecting a DMSO solution into an equimolar solution of AC. As the reaction proceeds the properties of the liquid change as reactants are used up, reaction products are formed and portions of the mixture are vaporized. In order to evaluate the heat transfer correlations described in Chapter III, the liquid dependent parameters upon which the correlations are based must be known as a function of time or extent of reaction. Since the reaction cannot be quenched and the reaction mixture still evaluated at the conditions of the reaction, a method of interpolation between the properties of the initial mixture and final reaction mixture was developed. The initial properties were considered to be those of the AC solution prior to injection of the DMSO solution. The final properties were those of the reaction mixture after the reaction had gone to completion.

The easiest method of interpolation would be a straight line method between the initial and final properties. A more realistic representation was developed based on extent of reaction.

Mass loss was considered to be directly proportional to the extent of reaction. On this basis mass loss was measured as a function of time. This method was considered to be more accurate than the straight line method in spite of the error introduced by the changing heat of vaporization.

Mass loss versus time was determined by running the reaction in a 300 ml wide mouth Dewar flask which was located atop a Metler P11N top loading balance with scale divisions of 0.1 g. The injection tube was suspended above and into the flask in such a fashion as to allow the motion of the flask to be uninhibited by the injection tube. Runs conducted by injecting the AC solution without reaction showed injection effects to be negligible. Time zero was marked on a Gould Brush 220 strip chart recorder at the time of initial injection. Each 0.1 g weight change was marked on the moving strip chart as indicated on the balance. From the strip chart and the known injection time, weight loss versus time could then be determined. Mass loss versus time is shown graphically for the 4 molar, 8 molar, and 12 molar acetone and benzene solvent systems in Figures 3 through 8.

Based on the data of Figures 3 through 8, the extent of reaction is shown as a percentage for the acetone solvent system in Figure 9 and for the benzene solvent system in Figure 10. All time dependent properties were interpolated between initial and final values based on the curves shown in Figures 9 and 10. The numerical values for the percent extent of reaction versus time may be found in Appendix 1.

Figure 3. Plot of weight loss in reaction vessel versus time for the reaction of 30 mls of 4 M-DMSO injected into 30 mls of 4 M-AC at 72 mls/min using acetone as the solvent.

Figure 4. Plot of weight loss in reaction vessel versus time for the reaction of 30 mls of 8-M-DMSO injected into 30 mls of 3 M-AC at 72 mls/min using acetone as the solvent.

Figure 5. Plot of weight loss in reaction vessel versus time for the reaction of 10 mls of 12 H-DiSO injected into 10 mls of 12 H-AC at 24 mls/min using acetone as the solvent.

Figure 6. Plot of weight loss in reaction vessel versus time for the reaction of 20 mls of 4M-DMSO injected into 20 mls of 4M-AC at 48 mls/min with benzene as the solvent.

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Figure 8. Plot of weight loss in reaction vessel versus time for the reaction of 10 mls of 12M-DMSO injected into 10 mls of 12M-AC at 24 mls/min with benzene as the solvent.

Figure 9. Extent of Reaction vs. Time for Acetone Solvent Reaction System.

Figure 10. Extent of reaction versus time for the DMSO-AC reaction system with benzene as the solvent.

Heat Capacity

The initial heat capacity was calculated as that for the AC solution at 25°C using Equation 54.

$$Cp_m = \omega_{AC} Cp_{AC} + \omega_S Cp_S \quad (54)$$

where

- Cp_m = Mixture heat capacity $\frac{\text{cal}}{\text{g}^\circ\text{C}}$
- Cp_{AC} = Acetyl chloride heat capacity
- Cp_S = Solvent heat capacity
- ω_{AC} = Acetyl chloride mass fraction
- ω_S = Solvent mass fraction

The pure component heat capacities for benzene and acetone were taken from Perry and Chilton (1973). The pure component heat capacity for acetyl chloride was calculated using the method of Missenard as described by Reid, Prausnitz and Sherwood (1977).

The experimental setup shown in Figure 11 was used to determine experimentally the heat capacity of the final reaction mixture. Approximately 200 ml of liquid was weighed and placed into the Dewar flask. A current of measured voltage and amperage was applied across the heater. The solution was stirred and the temperature rise was observed as a function of time. At the conclusion of a run the current was discontinued from the heater and the temperature fall was observed as a function of time. This provided for a correction for the amount of heat being lost from the system during operation.

The system was calibrated on the basis of Equation 55 using acetone, water and toluene as substances of known mass and heat capacity.

Figure 11. Calorimeter for determination of heat capacity.

$$(Cp_M)_{Vess} = \dot{Q} / \left(\frac{dT}{dt} \right)_{Act} - (Cp_M)_1$$

where $\left(\frac{dT}{dt} \right)_{Act} = \left(\frac{dT}{dt} \right)_{obs} + \left(\frac{dT}{dt} \right)_{Corr}$.

$(Cp_M)_{vess}$ was determined to be 11.01 cal/°C for the vessel and components used.

Equation 55 may be rearranged to calculate the heat capacity of an unknown liquid as represented by equation 56

$$Cp_1 = \left[\frac{\dot{Q}}{\left(\frac{dT}{dt} \right)_{Act}} - 11.01 \right] \frac{1}{M_1} \left(\frac{cal}{g^{\circ}K} \right) \quad (56)$$

where $\dot{Q}$ is in cal/sec, temperature is in degrees K, time is in seconds and mass is in grams.

Using the described experimental setup, values for the heat capacity of water, toluene and acetone could be consistently determined within 8% of literature values.

The calculated initial heat capacities and experimentally determined final heat capacities are reported in Table 3.

Thermal Conductivity

The pure component thermal conductivity was taken from the literature where available and calculated at the temperature of interest where not available using the method of Robbins and Kingerea as outlined by Reid, Prausnitz and Sherwood (1977). Sufficient information was not available to calculate the thermal conductivity of chloromethyl-methyl sulfide (CMMS) using the method of Robbins and Kingerea. Therefore, the method of Sato, also outlined by Reid, Prausnitz and Sherwood (1977), was used to estimate the thermal

TABLE 3

Initial and Final Heat Capacities for the DMSO-AC Reaction
with Either Acetone or Benzene as the Solvent

<u>Initial Concentration</u>	<u>Solvent</u>	<u>Initial Heat Capacity (cal/g°C)</u>	<u>Final Heat Capacity (cal/g°C)</u>
4M	Acetone	0.47	0.46
8M	Acetone	0.41	0.55
12M	Acetone	0.37	0.53
4M	Benzene	0.39	0.49
8M	Benzene	0.37	0.68
12M	Benzene	0.36	0.73

conductivity of CMMS at the boiling point. The pure component thermal conductivities are shown in Table 4.

The mixture thermal conductivities were calculated using a particle number weighted average as shown in Equation 57

$$k_M = \sum_{i=1}^n x_i k_i \quad (57)$$

where

k_M = Mixture thermal conductivity
 n = Number of components in the mixture
 x_i = Mole fraction of i th species

The initial mixture was assumed to be the AC solution. The final mixture composition was determined on the basis of Nuclear Magnetic Resonance (NMR) work performed by Paul Wheeler (1978) on the DMSO-AC system using benzene as the solvent. The final mixture composition was based on the assumption that the solvent initially present remained throughout the reaction and that any solvent which was vaporized and lost was introduced into the system via the DMSO solution. It should be noted that as much as one third of the final mixture was not identified by Wheeler. A typical NMR analysis, as performed by Wheeler (1978) is reproduced in Table 5 for an initial concentration of 9 molar using benzene as the solvent.

The calculated initial and final thermal conductivity values for the DMSO-AC system are reported in Table 6 for both the acetone solvent and benzene solvent case.

Viscosity and Density

The viscosity and density were determined for the initial AC solution, the final reaction mixture without wax and the final

TABLE 4

Pure Component Thermal Conductivity

<u>Component</u>	<u>k (cal/cm s°K)</u>	<u>T (°C)</u>	<u>Source</u>	<u>Method of Calculation</u>
Acetyl Chloride	3.51×10^{-4}	30	Calculated	Robbins & Kingerea
	3.64×10^{-4}	57	"	" "
	3.73×10^{-4}	70	"	" "
	3.77×10^{-4}	80	"	" "
Benzene	3.80×10^{-4}	30	McAdams (1954)	
	3.04×10^{-4}	57	Calculated	Robbins & Kingerea
	3.19×10^{-4}	70	"	" "
	3.14×10^{-4}	80	"	" "
Toluene	3.55×10^{-4}	30	McAdams (1954)	
Acetone	4.21×10^{-4}		McAdams (1954)	
	3.27×10^{-4}		Calculated	Robbins & Kingerea
	3.23×10^{-4}		"	" "
	3.19×10^{-4}		"	" "
Chloromethyl- methylsulfide	2.68×10^{-4}	Boiling Point	Calculated	Sato

TABLE 5

NMR Results for the Final Reaction Mixture
of an Initial 9 Molar DMSO-AC System
Using Benzene as the Solvent (Wheeler, 1978)

Vapor:	<u>Peak</u>	<u>δ</u>	<u>Area</u>	<u>H</u>	<u>Norm A</u>	<u>Mol. %</u>	<u>Comp.</u>
	1	10.5	2	2	1	4	HCOH
	2	6.9	58	6	9.7	38	C ₆ H ₆
	3	4.1	4	2	2	(8)	CH ₂ Cl
	4	1.9	30	3	10	39	CH ₃ COC1
	5	1.7	6	3	2	8	CH ₃ S
	6	1.5	8	3	2.7	11	?
Liquid:	<u>Peak</u>	<u>δ</u>	<u>Area</u>	<u>H</u>	<u>Norm A</u>	<u>Mol. %</u>	<u>Comp.</u>
	1	7.0	56	6	9.3	41	C ₆ H ₆
	2	4.2	12	2	6	(26)	CH ₂ Cl
	3	1.8	18	3	6	26	CH ₃ S
	4	1.6	23	3	7.7	33	?

TABLE 6
Mixture Thermal Conductivity for DMSO-AC System

<u>Solvent</u>	<u>Initial Concentration</u>	<u>Initial k cal/(cm s°K)</u>	<u>Final k cal/(cm s°K)</u>
Acetone	4 M	4.01×10^{-4}	3.20×10^{-4}
Acetone	8 M	3.81×10^{-4}	3.08×10^{-4}
Acetone	12 M	3.61×10^{-4}	2.86×10^{-4}
Benzene	4 M	3.71×10^{-4}	2.99×10^{-4}
Benzene	8 M	3.62×10^{-4}	3.03×10^{-4}
Benzene	12 M	3.54×10^{-4}	2.83×10^{-4}

reaction mixture with wax. The final reaction mixture without wax was obtained by running the reaction in a glass cylinder. The final reaction mixture with wax was obtained by running the reaction in a wax cylindrical cavity of the same dimensions as those for the wax cylinders used to evaluate the melted volume described in Chapter V.

It was observed from experiments described in Chapter V that as the wax melted and boiling ceased, that two phases developed in the 8M and 12M cases for both the acetone and benzene systems. This phenomenon was not observed in the 4M case in either the acetone or benzene system. This post boiling phase phenomenon can be seen for the 8M case in Figure 13 and for the 12M case in Figure 14. The absence of this phenomenon can be seen for the 4M case in Figure 12.

An OB Ubbelohde viscometer was used to obtain the kinematic viscosity. The viscometer was submerged in a temperature controlled water bath to obtain viscosity data at the required temperatures.

The densities were obtained by removing a 5 to 10 ml aliquot at the temperature of interest by means of a Mohr pipette. The aliquot was placed in a preweighed 20 ml scintillation vial. Each vial was then reweighed and the mass of the aliquot determined as the mass of the aliquot and vial minus the predetermined mass of the vial. The density was then determined as the mass of the aliquot divided by the volume of the aliquot. The densities obtained are reported in Table 7.

The viscosity was obtained as the product of the kinematic viscosity and the density. The dynamic viscosity is reported for both the acetone and benzene systems in Table 8.

Acetone as Solvent

Benzene as Solvent

Figure 12. A half cylinder of SUN-3420 wax fused to a glass plate after melting had ceased following the injection of 5 ml of a 4M DMSO solution into a 4M AC solution contained within the cavity. (Note that no phase boundary exists)

Acetone as Solvent

Benzene as Solvent

Figure 13. A half cylinder of SUN-3420 wax fused to a glass plate after melting had ceased following the injection of 5 ml of a 8M DMSO solution into a 8M AC solution contained within the cavity. (Note the phase boundary)

Acetone as Solvent

Benzene as Solvent

Figure 14. A half cylinder of SUN-3420 wax fused to a glass plate after melting had ceased following the injection of 5 ml of a 12M DMSO solution into a 12M AC solution contained within the cavity. (Note the phase boundary)

TABLE 7

Densities of the DMSO-AC Reaction System with Either
Acetone or Benzene as the Solvent

Initial Concentration	Solvent	Initial Reaction Mixture		Final Reaction Mixture without Wax		Final Reaction Mixture with Wax	
		T (°C)	$\rho(\text{g/cm}^3)$	T (°C)	$\rho(\text{g/cm}^3)$	T (°C)	$\rho(\text{g/cm}^3)$
4M	Acetone	20	0.89	20	0.89	58	0.81
		50	0.86 $\pm$ 0.035	50	0.88		
8M	Acetone	20	1.00	20	1.074	58	0.62 (Upper Phase)
		50	0.92 $\pm$ 0.028	60	1.00	58	0.98 (Lower Phase)
12M	Acetone	20	1.07	20	1.12	58	0.74 (Upper Phase)
		50	1.00 $\pm$ 0.001	60	1.08	58	1.12 (Lower Phase)
4M	Benzene	22	1.06	21	0.93	58	0.89
		50	0.92	50	0.89		
8M	Benzene	22	1.15	21	1.01	58	0.88 (Upper Phase)
		50	0.95	50	0.92	58	1.04 (Lower Phase)
12M	Benzene	22	1.19	21	1.08	58	1.01 (Upper Phase)
		50	1.03	50	1.06	58	1.11 (Lower Phase)

TABLE 8
Viscosities of DMSO-AC Reaction System with Either
Acetone or Benzene as the Solvent

Initial Concentration	Solvent	Initial Reaction Mixture		Final Reaction Mixture without Wax		Final Reaction Mixture with Wax	
		T (°C)	μ (centipoises)	T (°C)	μ (centipoises)	T (°C)	μ (centipoises)
4M	Acetone	50	0.304	60	0.23	58	0.384
8M	Acetone	50	0.310	60	1.16	58	1.779 (Upper Phase)
						58	1.144 (Lower Phase)
12M	Acetone	50	0.315	60	4.02	58	2.044 (Upper Phase)
						58	2.829 (Lower Phase)
4M	Benzene	50	0.379	50	0.445	58	0.616
8M	Benzene	50	0.338	50	0.487	58	0.969 (Upper Phase)
						58	1.792 (Lower Phase)
12M	Benzene	50	0.321	50	1.65	58	2.279 (Upper Phase)
						58	2.999 (Lower Phase)

Heat of Vaporization

The heat of vaporization, H_v , for the initial mixture was calculated on the basis of the composition of the vapor at the initial temperature. The vapor composition was calculated from the known liquid composition using Raolt's Law. Pure component heat of vaporizations at the normal boiling point and Antoine constants for the calculation of pure component vapor pressures were taken from Reid, Prausnitz and Sherwood (1977).

The heat of vaporization for the final reaction mixture was determined experimentally for the acetone system using the setup illustrated in Figure 15. The amount of heat supplied by the heater was calculated by supplying a constant current to the heater of known voltage and amperage. The liquid level in the feed tube was maintained at a constant level. By determining the amount of liquid added to maintain a constant level, the amount of liquid vaporized could be determined. The heat of vaporization was then calculated as the amount of heat added per unit time minus the sensible heat used to heat the added liquid and divided by the mass of the vapor lost per unit time. Using this method the heat of vaporization could be measured within 4% of the literature values for acetone, water and ethanol indicated in Table 9. The heat of vaporization for the initial and final reaction mixture for the DMSO-AC system with acetone as the solvent is shown in Table 9.

The heat of vaporization for the benzene system was determined by placing approximately 200 mls of the final reaction mixture in a 300 ml wide mouth Dewar flask. The flask and mixture were placed

Figure 15. Open Calorimeter for Determination of Heat of Vaporization.

TABLE 9

Heat of Vaporization for DMSO-AC Reaction System
with Either Acetone or Benzene as Solvent
and for Pure Compounds

<u>Initial Concentration</u>	<u>Solvent</u>	<u>Initial Mixture H_v (cal/g)</u>	<u>Final Mixture H_v (cal/g)</u>
4M	Acetone	106.5	124.2
8M	Acetone	97.1	151.1
12M	Acetone	90.3	153.5
4M	Benzene	90.0	79.5
8M	Benzene	88.4	174.5
12M	Benzene	87.6	276.5

<u>Compound</u>	<u>H_v (cal/g)</u>	<u>Source</u>
Benzene	94.1	Reid, Prausnitz, Sherwood (1977)
Acetone	119.8	Ibid
Acetyl Chloride	87.3	Ibid
Water	539.4	Ibid
Ethanol	201.0	Ibid

atop a Metler P11N top loading balance. A resistive heater was suspended into the mixture in such a fashion as to afford motion of the Dewar uninhibited by the heater. A current with sufficient voltage was applied to the heater to provide a heat input of between 10 to 12 calories per second. The current, voltage and weight loss were recorded as a function of time. The heat of vaporization was determined as the heat input per unit time divided by the weight lost per unit time. The heat of vaporization for benzene and acetone using this method were determined within 10% of literature values indicated in Table 9. The values for the heat of vaporization for the benzene and acetone systems are reported in Table 9.

Thermal Coefficient of Volumetric Expansion

The thermal coefficient of volumetric expansion, β , is defined by Bird, Stewart and Lightfoot (1960) as

$$\beta = - \frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (58)$$

β is approximated using the density data previously described as

$$\beta = - \frac{1}{\bar{\rho}} \frac{\Delta \rho}{\Delta T} \quad (59)$$

where $\bar{\rho}$ = Average density. The initial and final values of β for the DMSO-AC system are reported in Table 10.

Bulk Temperature and ΔT

Bulk temperatures were measured by locating a thermistor approximately 1.5 cm above the floor of a wax cylinder in a concentric fashion. 10 ml's of an AC solution were introduced into the cylinder.

TABLE 10

Thermal Coefficient of Volumetric Expansion for
DMSO-AC Reaction System with either Acetone or
Benzene as the Solvent

<u>Initial Concentration</u>	<u>Solvent</u>	<u>Initial Reaction Mixture $\beta(^{\circ}\text{K})$</u>	<u>Final Reaction Mixture $\beta(^{\circ}\text{K})$</u>
4M	Acetone	1.14×10^{-3}	0.38×10^{-3}
8M	Acetone	2.78×10^{-3}	1.78×10^{-3}
12M	Acetone	2.25×10^{-3}	0.91×10^{-3}
4M	Benzene	5.07×10^{-3}	1.60×10^{-3}
8M	Benzene	7.99×10^{-3}	3.17×10^{-3}
12M	Benzene	4.16×10^{-3}	0.78×10^{-3}

10 mls of an equimolar DMSO solution were then injected at a rate of 24 ml/min. The millivolt output of the thermistor circuit was recorded on a Heath EU-20B recorder. The mV readings were then converted into temperature readings by means of a previously determined calibration curve. Numerical values of temperature at various times are presented in Appendix 2.

ΔT was determined as the difference between the bulk temperature and the melting temperature of the wall (55°C). ΔT versus time is reported graphically for the acetone and benzene systems in Figures 16 and 17 respectively.

Pool Height Versus Time

Wheeler (1978) found that the diameter of the cylinder in which the DMSO-AC reaction was conducted had a significant effect on the void fraction and thus the total pool height. Therefore, pool heights were measured in a glass cylinder of the same inside radial dimensions as those of the wax cylinders using in experiments described in Chapter V. The experiment was conducted by injecting 10 mls of a DMSO solution into 10 mls of an equimolar AC solution in the glass cylinder at an injection rate of 24 ml/min. A small amount of ground bakelite was added to provide nucleation sites. A timer with scale divisions of 0.1 sec was placed near the cylinder. The timer and reaction were photographed by means of a super 8 movie camera. From the developed film, the pool height could be determined as a function of time.

The DMSO-AC reaction is very vigorous. As a result the pool height fluctuates rapidly. These rapid fluctuations are centered

Figure 16. Temperature difference between the bulk liquid and the melting wax wall versus time for the DMSO-AC reaction system with acetone as the solvent.

Figure 17. Temperature difference between the bulk liquid and melting wax wall versus time for the DMSO-AC reaction system with benzene as the solvent.

around a mean pool height. The mean pool height was approximated by observing more stable heights which could be measured and linearly interpolating values between these more stable heights.

As mentioned in the discussion of viscosities and densities, the 8M and 12M reactions divide into two phases. From the observed geometry of the melt, it appears that heat generation occurs predominantly in the lower phase. On the basis of this phenomenon, the 8M and 12M pool height is taken as that of the lower phase after the void collapses and boiling ceases. Prior to the void collapse the pool motion is considered to be sufficiently vigorous to provide heat generation over the entire pool. Pool height versus time is shown graphically for the acetone and benzene system in Figures 18 and 19 respectively.

Superficial Vapor Velocity

The superficial vapor velocity was calculated as

$$U_v = \frac{\dot{Q} V_v}{A H_v} \quad (60)$$

where

- U_v = Superficial vapor velocity (cm/sec)
- $\dot{Q}$ = Heat generation rate (cal/sec)
- V_v = Vapor specific volume (cm³/g)
- A = Cross-sectional area
- H_v = Heat of vaporization

$\dot{Q}$ was determined as the product of weight lost per unit time and heat of vaporization.

Figure 18. Heat generating pool height versus time for the DMSO-AC reaction system with acetone as the solvent.

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V_v was calculated as a mass weighted average.

$$V_v = \phi_{AC} V_{v,AC} + \phi_S V_{v,S} \quad (61)$$

where

$$\begin{aligned} \phi_{AC} &= \text{Weight fraction of AC in vapor} \\ \phi_S &= \text{Weight fraction of solvent in vapor} \\ V_{v,AC} &= \text{Vapor specific volume of AC} \\ V_{v,S} &= \text{Vapor specific volume of solvent} \end{aligned}$$

Based on NMR work performed by Wheeler (1978), the composition of the vapor was considered to be AC and solvent in the proportion of their initial vapor composition. The initial vapor composition was calculated from the initial liquid composition using Raolt's law. Using the ideal gas law the vapor specific volume may be calculated as

$$V_v = \frac{RT}{PN} \quad (62)$$

where

$$\begin{aligned} R &= \text{Gas constant (82.05 atm cm}^3/\text{g mole}^\circ\text{K)} \\ T &= \text{Temperature (}^\circ\text{K)} \\ P &= \text{Pressure (atm)} \\ N &= \text{Molecular weight} \end{aligned}$$

The cross-sectional area was calculated as 4.753 cm^3 based on the initial diameter of the cavity used to measure wax volume change as described in Chapter V.

The temperature used was that determined experimentally as the bulk temperature.

The heat of vaporization used was that determined experimentally and time weighted as described previously in this chapter.

Volumetric Heat Generation

Volumetric heat generation was calculated as

$$q = \frac{\dot{Q}}{AL} \quad (63)$$

where

$\dot{Q}$ = Heat generation (cal/sec)
 A = Cross-sectional area (cm²)
 L = Pool height (cm)

$\dot{Q}$ was determined as the product of weight lost per unit time and the heat of vaporization. The cross-sectional area was that of the initial cavity in the wax cylinders described in Chapter V. The pool heights are those described in the section of this chapter entitled "Pool Heights" and shown graphically in Figures 18 and 19.

Wax Solubility

The solubility of SUN-3420 wax in the final reaction mixture with acetone as the solvent was determined. Approximately 40 ml of the final reaction mixture was placed in a 100 ml graduated cylinder. The volume of the solution was noted. A sample of wax of known weight was introduced. The weight of the cylinder, solution and wax, was noted. The system was heated until the wax was melted. A phase boundary existed between the reaction mixture and the molten wax. The volume of the molten wax phase was noted. This experimental setup is illustrated in Figure 20. The system was again weighed to determine the amount of the solution vaporized. Any weight difference was considered to be vapor lost. Any wax not found to be in the liquid wax phase was assumed to be in solution in the reaction mixture. The solubility was then calculated as volume of liquid

Figure 20. Experimental Setup for Determination of Wax Solubility.

wax per volume of reaction mixture. The solubility was then calculated as volume of liquid wax per volume of reaction mixture. These results are reported in Table 11. It was found that the wax was less soluble in the 12M case than in either the 4M or 8M case.

Physical Properties of the Wax

The density of the wax and the coefficient of expansion for the transition from the solid to the liquid state were determined experimentally. The volume of a sample of SUN-3420 wax was determined by submerging a preweighed sample of the wax in a graduated cylinder partially filled with water. The volume of the water displaced was taken as the volume of the sample. The sample was then dried and returned to a graduated cylinder. The wax was melted and the volume of the melted wax noted. The solid to liquid expansion factor was calculated as the volume occupied by the liquid divided by the volume occupied by the solid. The density of the solid was calculated as the mass of the sample divided by the volume of the sample. The density of the liquid was determined as the mass of the sample divided by the liquid volume of the sample. The expansion factor and densities are reported in Table 12.

The heat capacity, thermal conductivity and average molecular weight of the Sun-3420 wax were obtained from the SUN Petroleum Company. The latent heat of fusion was obtained from Warth (1956) based on the average carbon chain length of a paraffinic wax. These properties are reported in Table 12.

TABLE 11

Solubility of SUN-3420 Wax in the Final Reaction
Mixture with Acetone as the Solvent

Initial Molar Concentration of Reaction Mixture	Temperature (°C)	Solubility of Wax in Final Reaction Mixture (Volume Wax/Volume Mixture)
4M	22	0
	60	1
8M	22	0
	60	1
12M	22	0
	60	0.5

TABLE 12
Properties of SUN-3420 Wax

Density of solid wax (25°C)	0.89 g/cm ³
Density of liquid wax (50-60°C)	0.75 g/cm ³
Expansion factor from liquid to solid phase	1.18
Heat capacity	0.6 cal/g°C
Thermal conductivity	$5.3 \times 10^{-4} \frac{\text{cal}}{\text{sec cm}^\circ\text{C}}$
Latent heat of fusion	58 cal/g
Average molecular weight	387
Average carbon chain length	28 carbons

CHAPTER V

RESULTS

Two experimental methods were employed to obtain a melt volume to compare with that calculated using the methods of Chapter III.

Downward Heat Transfer

A cavity from downward heat transfer was obtained by using the experimental setup illustrated in Figure 21. A glass cylinder was embedded perpendicular to the surface in a flat slab of SUN-3420 wax. The glass cylinder was used so that the melt cavity could be formed without any mass transfer effects which may occur as a result of the melting sidewall. The glass cylinder used had an inside diameter of 3.62 cm.

Several runs were made by injecting 10 ml of a 12M DMSO solution into 10 ml of a 12M AC solution in the vessel. A small amount of ground bakelite was added to form nucleation sites. Acetone was used as the solvent in the DMSO and AC solutions. The melt cavity generated was not of sufficient magnitude to allow for accurate measurement.

Sideward Heat Transfer

The experimental setup illustrated in Figure 22 was used to obtain a melt cavity for sideward heat transfer. A cylinder constructed

Figure 21. Experimental Setup for Determination of Downward Heat Transfer.

Figure 22. Glass bottom reaction vessel.

of SUN-3420 wax was fused perpendicularly to a flat glass plate. The flat glass plate was used to avoid any mass transfer effects which may occur as a result of the melting cylinder floor.

The cylinder consisted of an inside diameter of 2.46 cm, an outside diameter of approximately 4.8 cm and a height of between 19 cm to 25 cm, depending upon the concentration of the reactants used. The cylinder was obtained by casting the wax in a polypropylene tube similar to that shown in Figure 2. After the tube was cooled to room temperature, a 2.46 cm (31/32 inch) hole was drilled axially through the cylinder with the polypropylene mold still attached. The mold was removed, and at least one end of the cylinder was squared by cutting off a portion of the cylinder using a mitre box and back saw. The glass plate was heated using a Bunson burner to a temperature slightly above the melting point of the wax. The squared end of the cylinder was then placed on the hot glass. A small portion of the wax melted and resolidified forming an effective seal and attachment.

A number of runs were made at each reactant concentration by injecting 10 ml of a DMSO solution into 10 ml of an equimolar AC solution, using either acetone or benzene as the solvent. Approximately 1 gram of ground bakelite was added to provide nucleation sites.

Two procedures were followed to determine the volume of wax melted during different regimes. The first procedure consisted of removing the reaction mixture from several runs immediately after the void collapsed and boiling ceased. This allowed for the determination of the melt volume which occurred during the boiling regime. The second procedure consisted of removing the reaction mixture from

several runs after the mixture temperature had dropped below the melting temperature of the wax (55°C). This allowed for the determination of the total volume of wax melt which occurred during reaction. The melt volume which occurred in the non-boiling regime was then determined as the difference between the total melt and the boiling regime melt.

Each cylinder was bisected axially using a mitre box and back saw. To ensure that the cylinder was bisected symmetrically a V-Slot holder was used. This apparatus is illustrated in Figure 23.

The diameter of each half cylinder was measured at various heights. The diameter for each cylinder was taken as the average of the diameters measured for the two half cylinders. From the measured diameters the final volume of each cylinder was calculated by numerically integrating over the height of the cylinder. The melted volume was then obtained by subtracting the known initial volume from the calculated final volume. The volumes obtained are reported in Table 13. The axial cavity profile for the measured diameters were plotted to provide a graphic illustration of the melt geometry. These cavity profiles are found in Figures 24 through 32 for the acetone solvent system and Figures 33 through 42 for the benzene solvent system.

Time Dependency of the Melt Volume and Surface Area

The geometry of the cylinder cavity must be known as a function of time to obtain the surface area for use in Equation 53 and the time derivative of the volume for use in Equation 42.

Figure 23. Device for Axial Bisection of Wax Cylinder.

TABLE 13
Melted Volumes

<u>Initial Concentration</u>	<u>Solvent</u>	<u>Reaction Mixture Removed After Void Collapse</u>	<u>Reaction Mixture Removed After Temp. Drop Below 55°C</u>
4M	Acetone	5.3	5.3
8M	Acetone	6.9	11.6
12M	Acetone	19.4	21.2
4M	Benzene	4.5	4.9
8M	Benzene	6.7	12.2
12M	Benzene	10.2	18.3

Figure 24. Radial melt pattern for the reaction of 10 ml of 12M acetyl chloride with 10 ml of 12M dimethyl sulfoxide in a wax cylinder. Reaction products were allowed to cool below 55°C before being removed from the cylinder. Two different runs are shown. Acetone was the solvent.

Figure 25. Radial melt pattern for the reaction of 10 ml of 8M acetyl chloride with 10 ml of 8M dimethyl sulfoxide in a wax cylinder. Reaction products were allowed to cool below 55°C before being removed from the cylinder. Three different runs are shown. Acetone was the solvent.

Figure 26. Radial melt pattern for the reaction of 10 ml of 4M acetyl chloride with 10 ml of 4M dimethyl sulfoxide in a wax cylinder. Reaction products were allowed to cool below 55°C before being removed from the cylinder. Three different runs are shown. Acetone was the solvent.

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Figure 28. Radial melt pattern for the reaction of 10 ml of 8M acetyl chloride with 10 ml of 8M dimethyl sulfoxide in a wax cylinder. Reaction products were removed from the wax cylinder immediately after the void collapsed. Three different runs are shown. Acetone was the solvent.

Figure 29. Comparison of mean diameters from Figures 24 and 27.
12 M Solution with acetone as the solvent.

Figure 30. Comparison of mean diameters from Figures 25 and 28.
8 M Solution with acetone as the solvent.

Figure 31. Comparison of mean diameters from Figures 24, 25, and 26. The reaction mixture was allowed to cool in the wax cylinder below 55°C. Acetone was the solvent.

Figure 32. Comparison of mean diameters from Figures 26, 27, and 28. The reaction mixture was removed immediately after the void had collapsed. Acetone was the solvent.

Figure 33. Radial melt pattern for the reaction of 10 ml of 12M acetyl chloride with 10 ml of 12M dimethyl sulfoxide in a wax cylinder. Reaction products were allowed to cool below 55°C before being removed from the cylinder. Two different runs are shown. Benzene was the solvent.

Figure 34. Radial melt pattern for the reaction of 10 ml of 8M acetyl chloride with 10 ml of 8M dimethyl sulfoxide in a wax cylinder. Reaction products were allowed to cool below 55°C before being removed from the cylinder. Two different runs are shown. Benzene was the solvent.

Figure 35. Radial melt pattern for the reaction of 10 ml of 4M acetyl chloride with 10 ml of 4M dimethyl sulfoxide in a wax cylinder. Reaction products were allowed to cool below 55°C before being removed from the cylinder. Two different runs are shown. Benzene was the solvent.

Figure 36. Radial melt pattern for the reaction of 10 ml of 12M acetyl chloride with 10 ml of 12M dimethyl sulfoxide in a wax cylinder. Reaction products were removed from the wax cylinder immediately after the void collapsed. Two different runs are shown. Benzene was the solvent.

Figure 37. Radial melt pattern for the reaction of 10 ml of 8M acetyl chloride with 10 ml of 8M dimethyl sulfoxide in a wax cylinder. Reaction products were removed from the wax cylinder immediately after the void collapsed. Two different runs are shown. Benzene was the solvent.

Figure 38. Radial melt pattern for the reaction of 10 ml of 4M acetyl chloride with 10 ml of 8M dimethyl sulfoxide in a wax cylinder. Reaction products were removed from the wax cylinder immediately after the void collapsed. Two different runs are shown. Benzene was the solvent.

Figure 39 Comparison of mean diameters from Figures 33 and 36.
12M Solution with benzene as the solvent.

Figure 40. Comparison of mean diameters from Figures 34 and 37. 8M Solution with benzene as the solvent.

Figure 41. Comparison of mean diameters from Figures 33, 34, and 35. The reaction mixture was allowed to cool in the wax cylinder below 55°C. Benzene was the solvent.

Figure 42. Comparison of mean diameters from Figures 36, 37, and 38. The reaction mixture was removed immediately after the void had collapsed. Benzene was the solvent.

To observe the melt cavity as the reaction progressed, a half cylinder was fused to a glass plate. 5 ml of an AC solution was placed in the cavity together with a small portion of ground bakelite to provide nucleation sites. 5 ml of an equimolar DMSO solution was then injected into the AC solution at 12 ml/min. 35 mm photographs were taken every 5 seconds from the time injection began through the first 100 seconds. After the first 100 seconds, photographs were taken every 10 seconds. The reaction and half cylinder were photographed for approximately 250 seconds total. Samples of the photographs taken may be seen in Figures 12, 13 and 14.

The photographs were used to obtain volumes as a function of time. The diameter of the cylinder was measured from the photographs at various heights. The measured diameters were used to obtain a volume by numerically integrating over the total height of the cylinder. This process was repeated a number of times. The initial volume was determined as that measured from the photograph at 0 seconds.

The melted volume was determined as the total volume at a particular time minus the initial volume. The melted volumes were converted to a percent melted volume by dividing each melted volume by the final melted volume and multiplying by 100. The percent melted volumes at various times were then used to fit a curve of the form

$$\%_{VM} = a + b \ln t \quad (64)$$

where

$\%V_M$ = Percent melted volume
 a, b = Constants
 t = Time (seconds)

The equation was fit such that $\%V_M$ would equal 0 at the time the liquid temperature would rise to the melting temperature of the wax (55°C). After fitting the curve it was normalized to equal 100 at the time the liquid dropped to the melting point of the wax. The 4M runs required a two section curve to obtain a reasonable fit. The 8M and 12M runs were fit satisfactorily with one curve. The constants a , b and the normalization factors are reported in Table 14.

Using Equation 64, the volume may be calculated at any time within the range of applicability as

$$V_M = \frac{(a + b \ln t) V_f \xi}{100} \quad (65)$$

where

V_f = Final melted volume
 ξ = Normalization factor

From Equation 65 the time derivation of the melted volume may be evaluated explicitly as

$$\frac{dV_M}{dt} = \frac{b}{t} \frac{V_f \xi}{100} \quad (66)$$

The ratio of the radial surface area of a cylinder to the volume of the cylinder is a function of the radius.

$$A = \frac{2V}{r} \quad (67)$$

For small changes in r the area may be approximated as

$$A \cong CV \quad (68)$$

where $C = \frac{2}{r}$.

TABLE 14

Constant and Normalization Factors for Curve Fit
of Percent Melted Volume as a Function of Time

<u>Initial Concentration</u>	<u>Solvent</u>	<u>Range (sec)</u>	<u>a</u>	<u>b</u>	<u>Correlation</u>	<u>Normalization Factor (ξ)</u>
4M	Acetone	13.9-20	-490.25	186.17	1.0	0.988
		20-55	- 23.365	31.082	0.911	0.988
8M	Acetone	6.7-140	- 69.338	34.158	0.983	1.005
12M	Acetone	5.7-220	- 50.307	34.092	0.970	0.749
4M	Benzene	13.7-20	-504.11	192.71	1.0	1.0
		20-75	16-160	19.339	0.987	1.0
8M	Benzene	7.6-190	- 78.993	37.589	0.986	0.846
12M	Benzene	6.1-220	- 53.488	29.814	0.999	

By making the assumption of Equation 68 the equations and constants used to evaluate the volume as a function of time may be used to evaluate the increase in surface area as a function of time

$$A = A_o + \frac{(a + b \ln t)}{100} (A_f - A_o)\xi \quad (69)$$

where

$$\begin{aligned} A_o &= \text{Initial surface area (t = 0)} \\ A_f &= \text{Final surface area} \end{aligned}$$

The same values of a, b and ξ found in Table 14 are used. The ratio of $\frac{A}{V}$ changed by only 9% for the 12 molar benzene case indicating that the assumption of Equation 68 is reasonable for the relatively small changes in radius encountered in this experiment.

The surface area for heat transfer is also a function of the liquid pool height. The surface area for heat transfer was calculated by dividing the cylinder into axial sections. The height of each section is defined as

$$h_i = h_{1i} - h_{oi} \quad (70)$$

where

$$\begin{aligned} h_i &= \text{Height of section } i \\ h_{1i} &= \text{Upper height of section } i \text{ as measured from the base} \\ h_{oi} &= \text{Lower height of section } i \text{ as measured from the base} \end{aligned}$$

The surface area of any section is then determined on the basis of Equation 69 providing the total pool height, h_{1i} . If h lies between h_{1i} and h_{oi} then the surface area is calculated as

$$A_i = (A_{iT}) \frac{h - h_{oi}}{h_i} \quad (71)$$

where

$$\begin{aligned} A_i &= \text{Section surface area (from Equation 69)} \\ A_{iT} &= \text{Total section surface area from Equation 69.} \end{aligned}$$

The total surface area for heat transfer at a given time is taken as the sum of the individual sections in which h_{oi} is less than h .

CHAPTER VI

CONCLUSIONS

The melted volumes calculated using Equation 53 were compared with those obtained experimentally using the methods of Chapter V. In each case all parameters in Equation 53 were the same at a given time with the exception of the heat transfer coefficient, h . The comparison of the calculated melt with the experimental melt then provided a measure of the accuracy of the correlation from which h was calculated. The heat transfer coefficient, h , was compared for both correction for mass transfer using Equation 39 and without correction for mass transfer.

For reference purposes the correlations used to calculate the heat transfer coefficients are denoted as:

- C_0 This correlation is used to calculate the Nusselt Number for heat transfer from a vertical plate to a fluid by natural convection. This correlation is calculated using Equation 7.
- C_{0c} Correlation C_0 corrected for mass transfer using Equation 39.
- C_1 This correlation is used to calculate the heat transfer from an internally heated liquid pool to a vertical sidewall. Correlation C_1 is Correlation C_0 corrected for volumetric heat generation in the fluid using Equation 9.
- C_{1c} Correlation C_1 corrected for mass transfer using Equation 39.
- C_2 This correlation is used to calculate a Nusselt number based on the laminar flow model described in Chapter III. The bulk density of the fluid was used in this calculation. The superficial vapor

velocity was used for the boiling regime and $0.78 V_{TC}$ was used for the non-boiling regime using Equation 21. This correlation is calculated using Equation 19.

C_{2c} Correlation C_2 corrected for mass transfer using Equation 39.

C_3 This correlation is used to calculate a Nusselt number based on the turbulent flow model as described in Chapter III. The bulk density of the fluid is used in this calculation. The superficial vapor velocity was used for the boiling regime and $0.78 V_{TC}$ was used for the non-boiling regime using Equation 21. This correlation was calculated using Equation 20.

C_{3c} Correlation C_3 corrected for mass transfer using Equation 39.

C_4 This correlation is the same as that described for correlation C_2 with the exception that the density used was the average of the bulk density and the density of the molten wall. This correlation was calculated using Equation 19.

C_{4c} Correlation C_4 corrected for mass transfer using Equation 39.

The calculated melt volume was compared with the experimental melt volume by dividing the calculated volume by the experimental volume and multiplying by 100. This represents the percent of the experimental volume calculated using the proposed heat transfer correlations. This comparison is reported in Table 15.

The melt occurring during boiling was essentially the same as the total melt for the 4M case using acetone as the solvent. Therefore, no comparison was made for the non-boiling regime for this case since it would involve division by zero. Correlations C_0 , C_{0c} , C_1 and C_{1c} apply only to the non-boiling regime. Therefore, no values are reported for the boiling regime and total melt for these correlations.

TABLE 15

Percent of the Experimental Melt Calculated
Using the Proposed Heat Transfer Correlations

Initial Concent.	Solvent	C_o	C_{oc}	C_1	C_{1c}	C_2	C_{2c}	C_3	C_{3c}	C_4	C_{4c}
4M	Acetone										
Boiling		--	--	--	--	4.1	3.8	5.4	5.1	3.9	3.7
Non-Boiling		--	--	--	--	--	--	--	--	--	--
Total Melt		--	--	--	--	4.1	3.8	5.4	5.1	3.9	3.7
8M	Acetone										
Boiling		--	--	--	--	141	130	169	157	136	126
Non-Boiling		67.0	60.2	69.1	62.1	85.6	77.0	114	103	78.5	71.9
Total Melt		--	--	--	--	118	109	147	135	113	104
12M	Acetone										
Boiling		--	--	--	--	95.6	88.4	143	127	87.2	76.9
Non-Boiling		46.5	43.4	48.7	45.5	62.3	58.4	116	110	55.1	51.6
Total Melt		--	--	--	--	92.8	85.8	141	126	84.5	70.8
4M	Benzene										
Boiling		--	--	--	--	12.6	11.7	17.6	16.5	13.0	12.1
Non-Boiling		243	233	249	237	256	243	337	321	272	259
Total Melt		--	--	--	--	9.3	8.8	12.5	7.8	9.8	6.3
8M	Benzene										
Boiling		--	--	--	--	66.6	61.0	97.2	89.4	61.7	56.5
Non-Boiling		56.2	53.5	57.7	53.5	67.1	62.4	125.6	98.6	61.6	57.2
Total Melt		--	--	--	--	66.8	61.6	110	93.5	61.6	56.8

TABLE 15 (cont.)

<u>Initial</u> <u>Concent.</u>	<u>Solvent</u>	<u>C₀</u>	<u>C_{0c}</u>	<u>C₁</u>	<u>C_{1c}</u>	<u>C₂</u>	<u>C_{2c}</u>	<u>C₃</u>	<u>C_{3c}</u>	<u>C₄</u>	<u>C_{4c}</u>
12M	Benzene	--	--	--	--	202	179	322	286	184	184
Boiling		--	--	--	--	23.2	21.7	43.2	40.8	20.0	20.0
Non-Boiling		18.1	16.7	20.0	18.8	23.2	21.7	43.2	40.8	20.0	20.0
Total Melt		--	--	--	--	123	109	198	177	111	98.6

The data of Table 15 were evaluated using the methods of Dean and Dixon (1951) for small numbers of observations. Deviant data was eliminated by using the rejection quotient for 90% confidence. The confidence limits reported were obtained using the 95% confidence factor. The results of this statistical evaluation are reported in Table 16.

From the data of Table 16, correlation C_2 provided the most accurate calculation of the observed melt. Correlation C_2 is calculated using Equation 19 and the bulk fluid density. This correlation is based on the laminar flow model near the wall. The superficial vapor velocity is used in the boiling regime and $0.78 V_{TC}$ as calculated using Equation 21 is used in the non-boiling regime.

Correlation C_3 based on Equation 20 and the turbulent flow model near the wall produced results approximately 50% higher than those of correlations C_2 and C_4 and the laminar flow model near the wall.

Crust Formation

As the reaction mixture cooled, a crust was observed to form over the top of the liquid. In the case where acetone was used as the solvent in the dimethyl sulfoxide (DMSO) and acetyl chloride (AC) solutions, the crust appeared to form while a void still existed. The crust formed was more dense at the top and became less dense toward the bottom of the crust. In the acetone case this crust was observed to be as deep as several centimeters. In the case where benzene was used as the solvent in the DMSO and AC solutions, the crust appeared to have a more uniform density and the total crust depth was less.

TABLE 16

Mean Percent of Experimental Melt Calculated Using
the Proposed Heat Transfer Correlations

Correlation	Boiling Regime			Non-Boiling Regime			Total Melt		
	Mean	Standard Deviation	95% Confidence Limit	Mean	Standard Deviation	95% Confidence Limit	Mean	Standard Deviation	95% Confidence Limit
C_0	--	--	--	47.0	21.0	35.3	--	--	--
C_{0c}	--	--	--	43.5	19.1	31.3	--	--	--
C_1	--	--	--	48.9	21.0	35.3	--	--	--
C_{1c}	--	--	--	45.0	18.7	31.2	--	--	--
C_2	103	72.5	97.0	59.5	26.2	44.9	100	26.0	40.4
C_{2c}	94.2	64.1	85.2	54.9	23.5	42.0	91.4	22.7	34.1
C_3	149	112	155	99.7	38.0	59.4	149	36.5	63.4
C_{3c}	135.2	99.3	137	88.0	31.8	49.6	133	34.4	60.2
C_4	95.4	66.3	87.5	53.8	24.6	42.1	92.5	24.4	38.7
C_{4c}	91.2	66.3	87.9	50.2	21.9	37.4	82.6	22.5	34.0

Proposed Future Research

All experiments in this study were conducted in an open system at atmospheric pressure. Many core disruptive accident (CDA) scenarios describe a crust of fuel and steel forming in the reactor void spaces during the CDA. Should this occur, a closed system would be formed. To observe the effects which may occur as a consequence of the system closure, many of the experiments in this study will be repeated in a closed environment where pressure will change as a function of time. The crust formation in the DMSO-AC system conducted in a cavity in SUN-3420 wax will be quantified to better understand the crust formation which may occur in a CDA in an actual reactor.

Should a CDA occur in which total core melt occurred within 1000 seconds and the containment maintained its integrity for 24 hours, as required by the NRC for the Clinch River breeder reactor, (Nuc. News, July 1976), the physical properties of the system would be more constant after the initial 1000 seconds than those of the DMSO-AC system used in this study. To provide for more constant physical properties in the DMSO-AC reaction system future research will consist of repeating many of the experiments of this study in such a fashion that fresh reactant may be added and reaction mixture removed in a controlled fashion. This will sustain the heat generation over a more prolonged period of time and will maintain the physical properties of the system at a more constant value. To control the reaction would allow properties such as pool height and temperature difference to be maintained at a more constant value.

This would eliminate much of the scatter observed in the data of this study and would provide for a sustained temperature difference of sufficient magnitude to allow the accurate measurement of the downward heat transfer.

APPENDICES

APPENDIX 1

APPENDIX 1

Percent Extent of Reaction

Init. Conc. Solvent Time (Sec.)	4M Acetone	8M Acetone	12M Acetone	4M Benzene	8M Benzene	12M Benzene
0	0	0	0	0	0	0
2	63.5	4.3	5.3	16.9	5.0	3.5
4	73.4	8.7	11.3	30.6	9.4	7.0
6	74.4	12.8	19.4	34.6	13.6	11.7
8	76.5	16.7	29.4	36.1	19.6	16.9
10	86.6	22.1	35.1	37.7	25.6	22.2
12	85.7	27.0	42.9	43.4	32.9	27.5
14	87.3	33.1	51.3	48.4	41.0	32.8
16	94.6	40.1	59.4	53.0	49.0	38.1
18	100.0	47.2	61.7	59.3	56.2	43.3
20		52.7	63.0	65.8	62.8	47.7
22		57.9	64.6	71.9	67.5	50.1
24		61.9	65.3	75.1	71.3	51.1
25		63.9	65.5	76.9	72.2	51.2
30		68.4	66.9	83.5	74.2	53.5
35		71.8	68.2	89.0	74.9	53.4
40		74.5	69.6	91.1	75.4	57.1
45		76.3	70.9	92.4	76.2	59.0
50		77.8	72.3	94.5	77.1	61.5
55		78.7	73.1	96.7	77.7	63.5
60		79.5	74.9	100.0	78.5	65.3
65		80.4	76.3		79.2	66.1
70		81.2	77.6		79.6	68.8
75		81.8	78.8		80.6	70.5
80		82.3	80.3		81.2	72.5
85		82.8	81.7		82.0	74.5
90		83.3	83.0		82.7	75.6
95		83.8	83.4		83.1	77.1
100		84.2	83.8		83.6	78.4
120		85.7	85.4		85.9	82.7
140		87.1	87.5		87.8	85.7
160		89.0	88.7		89.7	89.2
180		91.0	90.3		91.7	91.5
200		92.8	91.9		93.5	93.3
220		94.5	93.5		93.8	96.1
240		96.1	95.1		95.1	97.5
260		97.5	96.8		96.1	98.7
280		98.8	98.4		98.1	99.2
300		100.0	100.0		100.0	100.0

APPENDIX 2

APPENDIX 2

Bulk Temperature vs. Time

Init. Conc. Solvent Time (Sec.)	4M Acetone	8M Acetone	12M Acetone	4M Benzene	8M Benzene	12M Benzene
4			47.8			
6		51.7	56.3			54.3
8		60.7	64.5		56.6	65.1
10		65.5	72.8		63.8	76.0
12		67.2	77.6		66.9	80.7
14	55.1	69.1	81.3	55.8	69.6	82.6
16	58.1	70.9	83.8	60.7	71.8	83.9
18	59.9	71.9	85.1	64.0	73.4	84.9
20	60.7	73.2	85.6	66.1	74.7	85.2
22	61.2	74.3	85.6	67.0	75.2	85.4
24	61.5	74.9	85.2	67.8	75.6	85.3
25	61.5	75.2	85.0	68.0	75.7	85.2
30	60.5	76.4	83.0	68.3	75.3	83.7
35	59.1	77.2	81.0	68.0	73.8	81.7
40	57.6	76.9	79.7	66.9	71.8	80.0
45	56.4	75.7	77.9	66.0	70.5	79.0
50	55.3	74.4	76.8	64.8	69.2	78.2
55	54.2	73.1	75.5	63.6	68.1	77.6
60	53.2	71.8	74.5	62.2	67.0	77.0
65		70.5	73.7	60.0	66.2	76.6
70		69.2	73.2	58.1	66.0	76.4
75		67.8	72.8	56.4	65.0	75.9
80		66.5	72.5	54.7	64.8	75.2
85		65.0	71.6	53.9	64.3	74.7
90		63.9	70.8		64.1	74.1
95		62.8	69.9		63.9	73.5
100		61.8	68.9		63.7	72.7
120		58.3	67.7		61.7	70.2
140		55.6	66.0		59.7	67.7
160		53.6	63.4		57.9	65.1
180			61.1		56.0	62.2
200			58.2		53.9	59.2
220			55.8			56.3
240			53.4			53.4

APPENDIX 3

APPENDIX 3

NOTATION

a	= Constant
A	= Area
b	= Constant
C	= Constant, heat transfer correlation
C _p	= Heat capacity
f	= Frequency of bubble formation
g	= Gravitational constant
Gr	= Grashof number
HCDA	= Hypothetical core disruptive accident
K	= Thermal conductivity
LMFBR	= Liquid metal fast breeder reactor
N	= Molar flux
Nu	= Nusselt number
Pr	= Prandtl Number
Q	= Heat generation or dissipation, Energy/Time, heat flux Energy/(Time) (Area)
r	= Radius
R	= Radius at interphase or phase boundary, component of mass transfer correction
Ra	= Rayleigh number
t	= Time
T	= Temperature
U	= Velocity
V	= Velocity, volume

W = Volumetric vapor generation rate

% = Percent

Greek

α = Thermal diffusivity

β = Coefficient of volumetric expansion

δ = Boundary layer thickness, Eigenvalue

ξ = Dimensionless radius, normalization factor

z = Component of dimensionless temperature function

η = Fraction of heat transferred downward

θ = Mean packet residence time at the wall, dimensionless temperature

λ = Latent heat of change, Eigenvalue

ν = Kinematic viscosity

ρ = Density

τ = Dimensionless time

T = Component of dimensionless temperature function

ϕ = Component of mass transfer corrections

Superscripts

$\sim$ = Per mole

$\wedge$ = Per unit mass, horizontally averaged maximum

' = Defined in terms of actual sublayer

Subscripts

a = Component a

AV = Average

b = Boiling, component b

c	= Corrected for mass transfer
cor	= corrected
E	= External
f	= Evaluated at film conditions, final
KG	= Kulacki-Goldstein
l	= Liquid
M	= Melt
MV	= Melted volume
loc	= Local
M	= Melt
p	= Bulk phase conditions
T	= Thermal, total
TC	= Thermal convection
V	= Vapor
W	= Wall, wax
X	= Localized value
Z	= Viscous terms
0	= Initial value, uncorrected value, at interface, lower thermal boundary
1	= Upper thermal boundary
∞	= At approach or bulk conditions

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