Improvement and Verification of
Fast Reactor Safety Analysis Techniques

Progress Report

Dee H. Barker and Dean V. Wiberg

Department of Chemical Engineering
Brigham Young University
Provo, Utah

DISCLAIMER

This book was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

July 1, 1979 - September 30, 1979

MASTER

Prepared for the Department of Energy
Under Contract AT(11-1)2572-000

rb
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

LEGAL NOTICE

"This report was prepared as an account of Government-sponsored work. Neither the United States, nor the Energy Research and Development Administration or any person acting on behalf of the Commission;

A. Makes any warranty or representation, expressed or implied, with respect to the accuracy, completeness or usefulness of the information contained in this report, or that the use of any information, apparatus, method, or process disclosed in this report may not infringe privately owned rights; or

B. Assumes any liabilities with respect to the use of, or for damages resulting from the use of, any information, apparatus, method, or process disclosed in this report.

As used in the above, 'person acting on behalf of the Commission' includes any employee or contractor of the Administration or employee of such contractor, to the extent of such contractor prepares, disseminates, or provides access to, any information pursuant to his employment or contract with the Administration, or his employment with such contractor."

Abstract

The physical properties of the initial and final liquid phase of the Dimethyl Sulfoxide-Acetyl Chloride reaction system with either Acetone or Benzene as solvent are reported together with the method of collection. These properties include heat capacity, thermal conductivity, viscosity, density, heat of vaporization and thermal coefficient of volumetric expansion. A method of interpolation between initial and final liquid properties is described.

Introduction

In the progress report covering contract work during the period of April 1, 1979 to June 30, 1979 (C00-2571-17) several heat transfer correlations were described for both the sideward and downward heat transfer from an internally heated liquid pool. The liquid dependent parameters upon which the heat transfer correlations are based are as follows: thermal conductivity, viscosity, flow regime height, thermal coefficient of volumetric expansion, temperature difference between bulk phase and wall, density, heat capacity, volumetric heat generation and superficial vapor velocity.

As a measure of the accuracy with which the previously described heat transfer correlations may be used, an internally heated liquid pool is generated inside a wax cylinder by chemically reacting solutions of Dimethyl Sulfoxide (DMSO) and Acetyl Chloride (AC). The melt cavity in the wax is observed and compared with that calculated using the proposed heat transfer correlations. In order to evaluate the heat transfer correlations the parameters described in the previous paragraph must be determined for the liquid. This progress report details the determination of a number of these parameters.

Experimental

Time Weighting

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 the introduction to this report 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 vs. time is shown graphically for the 4 molar, 8 molar, and 12 molar systems using acetone as the solvent in figures 1, 2 and 3 respectively.

Figure 1. Plot of weight loss in reaction vessel versus time for the reaction of equal volumes of 4M-DMSO and 4M-AC with Acetone used as a solvent.

Figure 2. Plot of weight loss in reaction vessel versus time for the reaction of equal volumes of 8M-DMSO and 8M-AC with Acetone used as a solvent.

Figure 3. Plot of weight loss in reaction vessel versus time for the reaction of equal volumes of 12M-DMSO and 12M-AC with Acetone used as a solvent.

Based on the data of figures 1, 2 and 3 the extent of reaction reported as percentage of final value is represented in figure 4. All physical properties are weighted from initial value to final value based on the curves depicted in figure 4.

Heat Capacity

The initial heat capacity was calculated as that for the AC solution at 25°C using equation 1.

$$Cp_m = \omega_{AC} Cp_{AC} + \omega_S Cp_S \quad (1)$$

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 5 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 2 using acetone, water and toluene as substances of known mass and heat capacity.

$$(CpM)_{Vess} = Q / \left(\frac{dT}{dt} \right)_{Act} - (CpM)_1 \quad (2)$$

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

Figure 4. Weighting Curves from Initial to Final Properties for DMSO-AC Reaction System.

Figure 5. Calorimeter for determination of heat capacity.

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

Equation 2 may be rearranged to calculate the heat capacity of an unknown liquid as represented by equation 3.

$$Cp_1 = \left[\frac{Q}{\left(\frac{dT}{dt}\right)_{\text{Act}}} - 11.01 \right] \cdot \frac{1}{M_1} \left(\frac{\text{cal}}{\text{g}^\circ\text{K}} \right) \quad (3)$$

Where 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 1.

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). Insufficient information was available to apply the method of Robbins and Kingerea to chloromethyl-methyl sulfide (CMMS), a major component in the final reaction mixture. Therefore, the method of Sato, also outlined by Reid, Prausnitz and Sherwood (1977) was used to estimate the thermal conductivity of CMMS at the boiling point. The pure component thermal conductivities used in subsequent calculations are shown in tabular form in Table 2.

The mixture thermal conductivities were calculated using a particle number weighted average as shown in equation 4.

Table 1

Heat Capacity for DMSO-AC System with
Acetone as the Solvent

<u>Initial Concentration</u>	<u>Initial Cp (cal/g^oK)</u>	<u>Temp (^oC)</u>	<u>Run</u>	<u>Final Cp (cal/g^oK)</u>	<u>Temp (^oC)</u>	<u>Mean Cp cal/g^oK</u>
4 M	0.47	25	1	0.44	30.8-51.7	0.46
4 M	0.47	25	2	0.48	24.5-40.2	
8 M	0.41	25	3	0.56	29.1-39.0	0.55
8 M	0.41	25	4	0.54	28.7-39.2	
12 M	0.37	25	5	0.61	25.5-38.9	0.53
12 M	0.37	25	6	0.47	28.9-49.6	
12 M	0.37	25	7	0.50	23.7-41.2	

Table 2

Pure Component Thermal Conductivity

<u>Component</u>	<u>k (cal/cm s⁰K)</u>	<u>T (°C)</u>	<u>Source</u>	<u>Method</u>
Acetyl Chloride	3.51 x 10 ⁻⁴	30	Calculated	Robbins & Kingerea
	3.64 x 10 ⁻⁴	57	"	"
	3.73 x 10 ⁻⁴	70	"	"
	3.77 x 10 ⁻⁴	80	"	"
Benzene	3.80 x 10 ⁻⁴	30	McAdams (1954)	
	3.04 x 10 ⁻⁴	57	Calculated	Robbins & Kingerea
	3.19 x 10 ⁻⁴	70	"	"
	3.14 x 10 ⁻⁴	80	"	"
Toluene	3.55 x 10 ⁻⁴	30	McAdams (1954)	
Acetone	4.21 x 10 ⁻⁴		McAdams (1954)	
	3.27 x 10 ⁻⁴		Calculated	Robbins & Kingerea
	3.23 x 10 ⁻⁴		"	"
	3.19 x 10 ⁻⁴		"	"
Chloromethhyl- methylsulfide	2.68 x 10 ⁻⁴	Boiling Point	Calculated	Sato

$$k = \sum_{i=1}^n x_i k_i \quad (4)$$

where 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 3 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 4 for both the acetone solvent and benzene solvent case.

Viscosity

The viscosity of the initial and final reaction mixture was determined using a Ubbelohde viscometer submerged in a temperature controlled water bath. Results for this determination are reported in Table 5 for the DMSO-AC system using acetone as the solvent.

Density

Densities for the initial and final reaction mixture were determined at several different temperatures. This was accomplished by heating the mixture to the temperature desired, removing a 10 ml

Table 3
NMR Results

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 4

Mixture Thermal Conductivity for DMSO-AC System

<u>Solvent</u>	<u>Initial Concentration</u>	<u>Initial k cal/(cm s⁰K)</u>	<u>Final k cal/(cm s⁰K)</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}

Table 5

Viscosity of DMSO-AC System Using
Acetone as the Solvent

<u>Initial Concentration</u>	<u>Initial Viscosity (Cp)</u>	<u>Final Viscosity (Cp)</u>
4 M	0.304±0.013	0.23±0.01
8 M	0.310±0.01	1.155±0.013
12 M	0.315±0.003	4.02±0.05

aliquot at that temperature by means of a pipet and then weighing the removed aliquot. The density was calculated as the mass of the aliquot divided by the volume of the aliquot. The experimentally determined densities for the DMSO-AC system using acetone as a solvent are shown in Table 6.

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 Raoult'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, Parusnitz and Sherwood (1977).

The heat of vaporization for the final reaction mixture was determined experimentally using the setup illustrated in Figure 6. 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 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. The heat of vaporization for the initial and final reaction mixture for the DMSO-AC system with acetone as the solvent are shown in Table 7.

Figure 6. Open Calorimeter for Determination of Heat of Vaporization.

Table 6

Density of DMSO-AC System
Using Acetone as the Solvent

<u>Initial Concentration</u>	<u>Initial Mixture Density (g/ml)</u>		<u>Final Mixture Density (g/ml)</u>	
	<u>T = 20°C</u>	<u>T = 50°C</u>	<u>T = 20°C</u>	<u>T = 50°C</u>
4 M	0.893±0.003	0.86±0.03	0.892±0.002	0.88±0.005
8 M	1.00±0.005	0.92±0.02	1.074±0.001	1.00±0.01
12 M	1.070±0.001	1.00±0.01	1.12± --	1.08±0.001

Table 7

Heat of Vaporization for the DMSO-AC
System Using Actone as the Solvent

<u>Initial Concentration</u>	<u>Initial Hv at 30°C (cal/g)</u>	<u>Final Hv (cal/g)</u>
4 M	106.5	124.2
8 M	97.1	151.1
12 M	90.3	153.5

Thermal Coefficient of Volumetric Expansion

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

$$\beta = -\frac{1}{\rho} \left(\frac{\partial \rho}{\partial T} \right)_p \quad (5)$$

β is approximated using the density data previously described as

$$\beta \approx -\frac{1}{\rho} \frac{\Delta \rho}{\Delta T} \quad (6)$$

where the density used is that taken at approximately 50°C as more closely representing the conditions occurring during the melt phase in the wax cylinder. The initial and final values of β for the DMSO-AC system using acetone as the solvent are reported in Table 8.

Continuing Work

Work is presently being conducted which will allow the reaction and melt to be observed through a glass plate as it occurs. This will allow a time dependency to be attached to the changing radius. Work is also continuing in the area of determining phase height and flow regime as a function of time.

Work has begun on repeating many of the previously described experiments for the DMSO-AC system using benzene as a solvent rather than acetone.

Table 8

Thermal Coefficient of Volumetric Expansion for
for DMSO-AC System Using Acetone as the Solvent

<u>Initial Concentration</u>	<u>Initial β ($^{\circ}\text{K}^{-1}$)</u>	<u>Final β ($^{\circ}\text{K}^{-1}$)</u>
4 M	1.3×10^{-3}	0.5×10^{-3}
8 M	2.9×10^{-3}	2.5×10^{-3}
12 M	2.3×10^{-3}	1.2×10^{-3}

Nomenclature

AC	Acetyl Chloride
CMMS	Chloromethyl-methylsulfide
Cp	Heat Capacity Cal/(g ⁰ K)
DMSO	Dimethyl Sulfoxide
k	Thermal Conductivity Cal/(S cm ⁰ K)
M	Mass
NMR	Nuclear Magnetic Resonance
Q	Heat Input Cal/sec
t	Time
T	Temperature
x	Mole Fraction
ρ	Density
ω	Mass Fraction

Subscripts

AC	Acetyl Chloride
Act	Actual
Corr	Correction
i	Species i
l	Liquid
M	Mixture
Obs	Observed
P	Pressure
S	Solvent
Vess	Vessel

List of References

Barker, D.H., Wiberg, D.V., Progress Report, April 1, 1979 - June 30, 1979, C00-2571-17, Dept. of Energy Contract, AT(11-1)2572-000.

Perry, R.H., Chilton, C.H., 1973, Chemical Engineers' Handbook, 5 ed., McGraw-Hill, New York.

Reid, R.C., Prausnitz, J.M., Sherwood, T.K., 1977, The Properties of Gases and Liquids, 3 ed., McGraw-Hill, New York.

McAdams, W.H., Heat Transmission, 3 ed., pp. 455-56, McGraw-Hill, New York, 1954.

Bird, R.B., Stewart, W.E., Lightfoot, E.N., Transport Phenomena, John Wiley & Sons, New York, 1960.