CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

AD-A215 946

CRDEC-TR-095

THE EVAPORATION OF SESSILE DROPLETS
I. THEORETICAL FACTORS
FOR A TWO-COMPONENT SYSTEM

Elwin C. Penski
Helen M. Walker

RESEARCH DIRECTORATE

DTIC
S ELECTE
DEC 18 1989
D
D

July 1989

U.S. ARMY
ARMAMENT
MUNITIONS
CHEMICAL COMMAND

Aberdeen Proving Ground, Maryland   21010-5423

89 12

Disclaimer

The findings in this report are not to be construed as an
official Department of the Army position unless so designated by
other authorizing documents.

Distribution Statement

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE

1a REPORT SECURITY CLASSIFICATION	1b. RESTRICTIVE MARKINGS
UNCLASSIFIED	

2a SECURITY CALSSIFICATION AUTHORITY	3. DISTRIBUTION/AVAILABILITY OF REPORT
	Approved for public release; distribution is unlimited.
2b. DECLASSIFICATION DOWNGRADING SCHEDULE	

4. PERFORMING ORGANIZATION REPORT NUMBER(S)	5. MONITORING ORGANIZATION REPORT NUMBER(S)
CRDEC TR 095	

6a. NAME OF PERFORMING ORGANIZATION	6b. OFFICE SYMBOL (if applicable)	7a. NAME OF MONITORING ORGANIZATION
CRDEC	SMCCR-RSC-P	

6c ADDRESS (City, State, and ZIP Code)	7b. ADDRESS (City, State, and ZIP Code)
Aberdeen Proving Ground, MD 21010-5423	

8a. NAME OF FUNDING/SPONSORING ORGANIZATION	8b. OFFICE SYMBOL (if applicable)	9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
CRDEC	SMCCR-RSC-P	

8c. ADDRESS (City, State, and ZIP Code)	10. SOURCE OF FUNDING NUMBERS			
	PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
Aberdeen Proving Ground, MD 21010-5423		1L162706	A553i	

11. TITLE (Include Security Classification)

The Evaporation of Sessile Droplets, I. Theoretical Factors for a Two-Component System

12. PERSONAL AUTHORS (S)
Penski, Elwin C., and Walker, Helen M.

13a. TYPE OF REPORT	13b. TIME COVERED	14. DATE OF REPORT (Year, Month, Day)	15. PAGE COUNT
Technical	FROM 79 Nov TO 88 May	1989 July	39

16. SUMPPLEMENTARY NOTATION

17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number)
FIELD	GROUP	SUB-GROUP	Hildebrand parameter Solutions Sessile droplet
07	04		Activity coefficients Water Evaporation
			Partial vapor pressures Surface chemistry

19. ABSTRACT (Continue on reverse if necessary and identify by block number)

The fundamental principles that need to be included in any analysis of the evaporation of a sessile droplet of a two-component solution are provided in this report. The equations needed to calculate the behavior of a sessile droplet of a two-component solution are integrated into a model. A computer program is provided, and a calculation with the model is compared with data for a sessile water droplet on an aluminum surface.

20 DISTRIBUTION/AVAILABILITY OF ABSTRACT	21. ABSTRACT SECURITY CLASSIFICATION
[x] UNCLASSIFIED UNLIMITED [ ] SAME AS RPT [ ] DTIC USERS	UNCLASSIFIED

22a NAME OF RESPONSIBLE INDIVIDUAL	22b. TELEPHONE (Include Area Code)	22c OFFICE SYMBOL
SANDRA J JOHNSON	(301) 671 2914	SMCCR SPS T

DD FORM 1473 84 MAR   83 APR edition may be used until exhausted.   SECURITY CLASSIFICATION OF THIS PAGE
All other editions are obsolete   UNCLASSIFIED
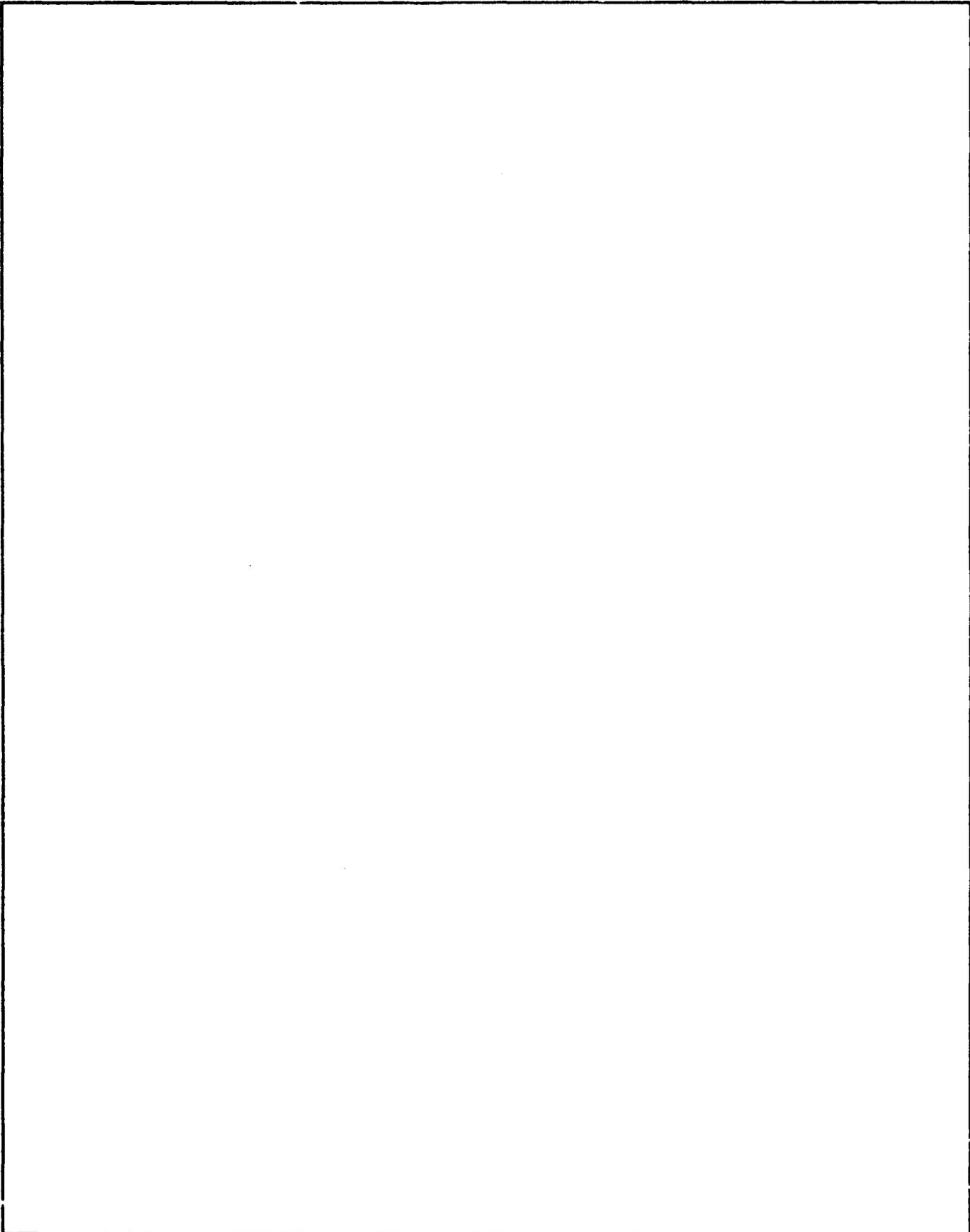
PREFACE

The work described in this report was authorized under Project No. 1L162706A553I, CB Defense and General Investigation. This work was started in November 1979 and completed in May 1988. The experimental data are recorded in laboratory notebook no. 9940.

The use of trade names or manufacturers' names in this report does not constitute an official endorsement of any commercial products. This report may not be cited for purposes of advertisement.

Reproduction of this document in whole or in part is prohibited except with permission of the Commander, U.S Army Chemical Research, Development and Engineering Center (CRDEC), ATTN: SMCCR-SPS-T, Aberdeen Proving Ground, Maryland 21010-5423. However, the Defense Technical Information Center and the National Technical Information Service are authorized to reproduce the document for U.S. Government purposes.

This report has been approved for release to the public.

Acknowledgment

Accesion For

NTIS CRA&I	V
UTIC TAB	[]
Unannounced	[]
Justification	

By
Distribution /

Availability Codes

| Dist | Avail and /or Special |

A-1

3

Blank

CONTENTS

APPENDIXES

THE EVAPORATION OF SESSILE DROPLETS
I. THEORETICAL FACTORS FOR A TWO-COMPONENT SYSTEM

1.   INTRODUCTION

There are many situations in which evaporating sessile droplets contain more than one component (e.g., agricultural spraying, forestry spraying, and chemical agent dissemination). As a result, a model for the evaporation of sessile droplets composed of two-component solutions is provided in this report. The purpose of this report is to provide a model and computer program that can be used for the evaporation of single-component sessile droplets in an unclassified and easy-to-follow form. A sample application to a single-component sessile droplet is provided. Also, the model and computer program provided are designed to be used to calculate the evaporation of sessile droplets composed of a two-component solution. This model was developed for solving numerous mission problems.

There are many reports that deal with related topics (e.g., the evaporation of unitary droplets into an atmosphere composed of mixtures of vapors and/or gases), but nothing has been found that deals directly with the topic discussed in this report. Walker and Penski[1] report a model for the evaporation of mixtures in a suspended droplet. Coutant and Penski[2] have published a report on the evaporation of neat sessile droplets as a function of wind velocity and contact angle. Figure 1 defines the contact angle and illustrates how the Coutant and Penski model regard it as a constant. Figure 2 illustrates a decreasing contact angle similar to that considered in this report. It is intended that this report's model will become a module in large computerized models. These larger models will consider additional situations including diffusion of the droplet fluid into the surface as illustrated in Figure 3.

2.   FUNDAMENTAL EQUATIONS

2.1   Hildebrand Parameter.

The Hildebrand Parameter,[3] δ, is commonly called the "solubility parameter" and less frequently the "total cohesion parameter." It is defined as follows:

$$\delta = [(\Delta H_v - RT)/v]^{1/2} \qquad (1)$$

where

ΔH_v =   molar enthalpy of vaporization

R   =   ideal gas law constant

T   =   temperature (Kelvin)

v   =   molar volume of liquid
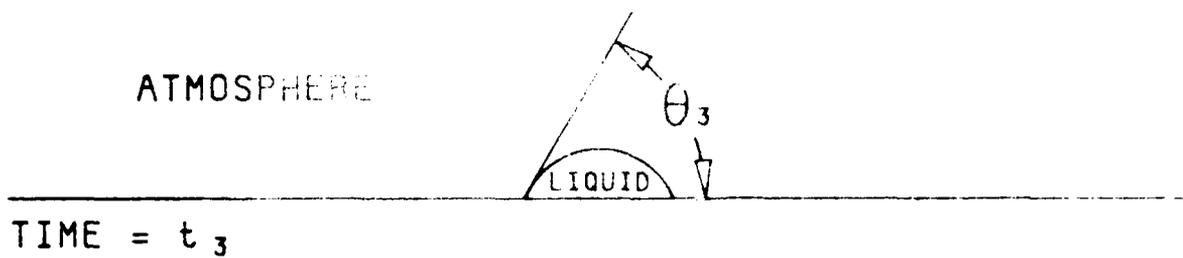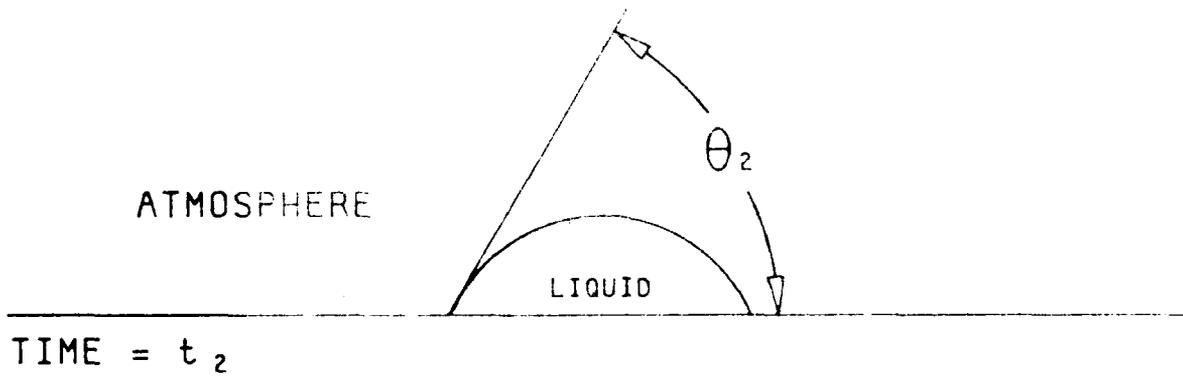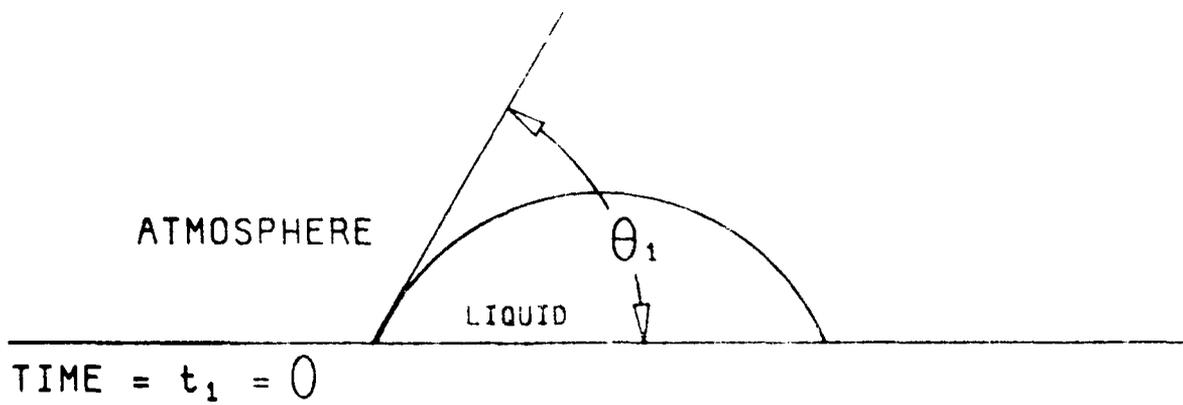
Figure 1. Sessile Droplet Evaporation with Constant Contact Angles: $\theta_1 = \theta_2 = \theta_3$, $t_1 < t_2 < t_3$.
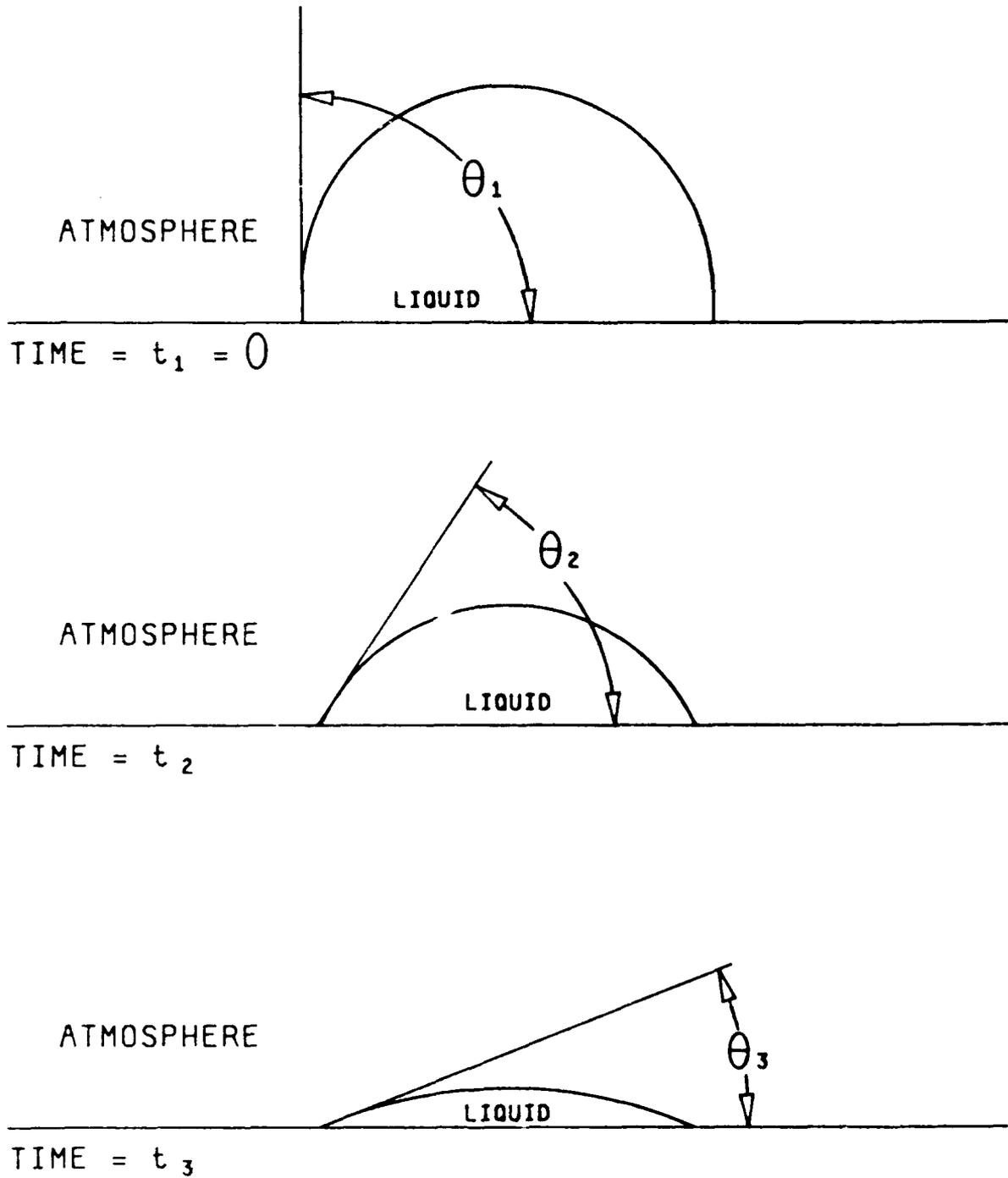
Figure 2.   Sessile Droplet Evaporation with Decreasing Contact
Angles: $\theta_1 > \theta_2 > \theta_3$, $t_1 < t_2 < t_3$.
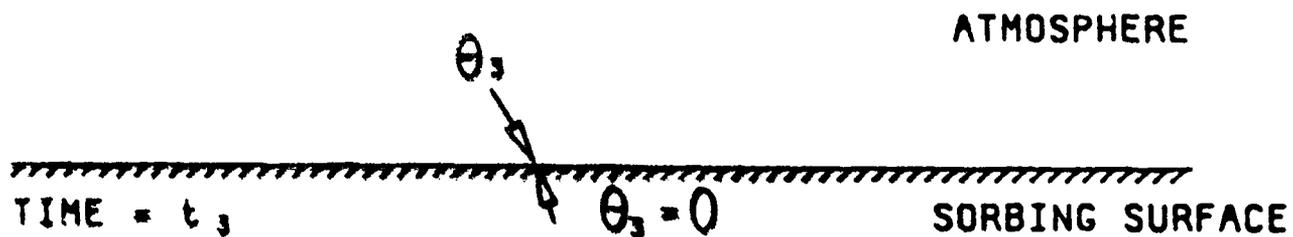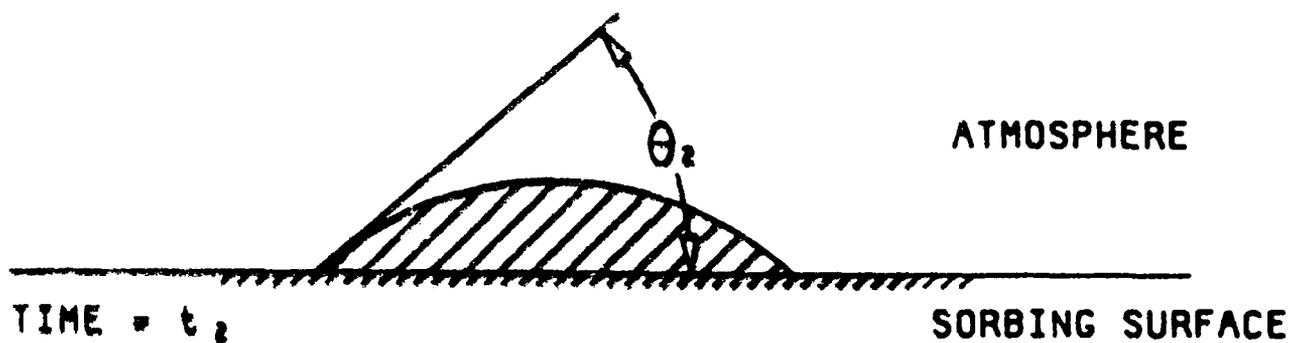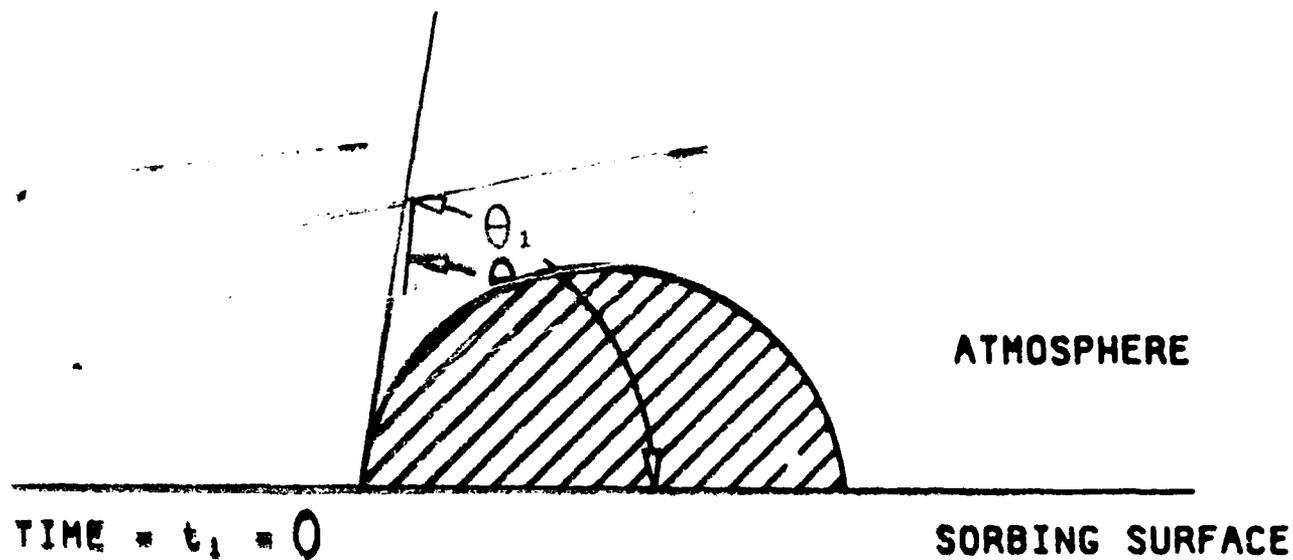
Figure 3. Sessile Droplet Evaporation with Surface Sorption:
$\theta_1 > \theta_2, \theta_3 = 0$; $t_1 < t_2 < t_3$.

2.2   Activity Coefficients of Regular Two-Component Solutions.

According to Hildebrand, Prausnitz, and Scott,[3] the equations for regular solutions can be written as follows:

$$RT \ln \gamma_1 = v_1 \phi_2^2 [(\delta_1 - \delta_2)^2 + 2 \Lambda_{12} \delta_1 \delta_2] \qquad (2)$$

$$RT \ln \gamma_2 = v_2 \phi_1^2 [(\delta_1 - \delta_2)^2 + 2 \Lambda_{12} \delta_1 \delta_2] \qquad (3)$$

where

γ_i = activity coefficient of component i

v_i = molar volume of component i

ϕ_i = volume fraction or volume of component i divided by total volume of mixture

δ_i = Hildebrand parameter of component i

Λ_{ij} = binary coefficient of components i and j

If equations 2 and 3 are solved for the activity coefficients, the following equations result:

$$\gamma_1 = e^{v_1 \phi_2^2 [(\delta_1 - \delta_2)^2 + 2 \Lambda_{12} \delta_1 \delta_2]/RT} \qquad (4)$$

$$\gamma_2 = e^{v_2 \phi_1^2 [(\delta_1 - \delta_2)^2 + 2 \Lambda_{12} \delta_1 \delta_2]/RT} \qquad (5)$$

2.3   Picknett and Bexon Equations.

The Picknett and Bexon equations[4] were developed for the evaporation of a sessile droplet in a static atmosphere. They are as follows:

$$\Gamma = 0.5 K E T \rho^{-1/3} \qquad (6)$$

where

$$K = 4 \pi D (C - C_\infty) \qquad (7)$$

11

D = diffusion coefficient of vapor in atmosphere

C = concentration of vapor in equilibrium with droplet fluid at surface of droplet

C_∞ = concentrations of vapor at a large distance from droplet, usually very near to zero in practical cases.

ρ = droplet density

π = 3.1416

ω = $\pi - \theta$ = contact angle,[2,4] Brit. definition (8)

θ = contact angle of droplet with surface (Figure 1)

E = $[\pi/3(1 - \cos \theta)^2(2 + \cos \theta)]^{-1/3}$ (9)

The term T is defined as follows:

For $0 < \theta < 0.175$ radian,

$$T = 0.6366\,\theta + 0.09591\,\theta^2 - 0.06144\,\theta^3 \tag{10}$$

For $0.175 < \theta < \pi$ radian,

$$T = 8.957\;10^{-4} + 0.6333\,\theta + 0.1160\,\theta^2 - 0.08878\,\theta^3 + 0.01033\,\theta^4 \tag{11}$$

2.4   Coutant and Penski Equation.

The Coutant and Penski[2] equation relates the evaporation of a sessile droplet to its mass, Γ, degree of ventilation (as measured by its Reynolds number), and droplet height. A number of additional factors are included in Γ.

$$-dm/dt = \Gamma m^{1/3}[1 + cRe^{1/2} (a/h)^{1/2}] \tag{12}$$

where

$-dm/dt$ = rate of droplet evaporation

m = droplet mass

t = time

c = constant of Coutant and Penski equation

Re = Reynolds number = $2 h \Psi/\upsilon$ (13)

a = height of droplet

h = height of tunnel

Ψ = wind velocity or relative velocity of the droplet to that of the atmosphere

υ = kinematic viscosity of the atmosphere

2.5   Height of Sessile Droplet.

The droplet height[2] is given by the following equations:

$$\lambda = 1 + 0.75 \left[2 \sin \theta / (1 - \cos \theta) \right]^2 \tag{14}$$

$$a = \left[6 \, m / (\pi \rho \lambda) \right]^{1/3} \tag{15}$$

The variable λ is introduced only to simplify the equation for droplet height.

2.6   Concentration of Vapor.

The concentration of vapor from the evaporating droplet can be determined fairly accurately near ambient temperatures for the ideal gas law:[5]

$$P^\circ V = nRT \tag{16}$$

where

P° = vapor pressure of fluid

V = volume of vapor at P°

n = number of moles of vapor in V

At the low partial vapor pressures under consideration, corrections for nonideality usually prove unnecessary. Equation 16 can easily be transformed to provide concentration as follows:

$$C = nM/V = MP^\circ / (RT) \tag{17}$$

where M = molecular weight of vapor.

2.7   Partial Vapor Pressures.

The partial vapor pressure of component i of a mixture is given by the following equation:[5]

$$P_i = P_i^\circ \gamma_i \phi_i \tag{18}$$

where

P_i = partial pressure of component i

P_i° = vapor pressure of component i

γ_i = activity coefficient of component i

ϕ_i = volume fraction or volume of component i divided by total volume of mixture

Volume fractions are more widely used for nonelectrolytes than mole fractions because volume fractions deal more adequately with molecular size effects.

3. MATHEMATICAL MODEL

3.1 Starting Conditions and Properties.

3.1.1 Atmospheric Conditions and Properties.

v = kinematic viscosity of the atmosphere

Ψ = wind velocity or relative velocity of the droplet to that of the atmosphere

T = temperature in degrees Kelvin. In this case, evaporation is assumed to be slow. Therefore, atmospheric and droplet temperature are equal.

$C_{\infty i}$ = concentration of vapor at a large distance from the droplet for each component, usually equal to zero in practical cases.

h = height of tunnel

3.1.2 Droplets.

m_0 = initial droplet mass

ϕ_1 = volume fraction of component 1

ϕ_2 = volume fraction of component 2

θ = contact angle of droplet with surface

3.1.3 Properties of Two Components.

D_i = diffusion coefficient of component i vapor in atmosphere

M_i = molecular weight of component i

P_i^o = vapor pressure of component i

δ_i = Hildebrand parameter of component i

Λ_{ij} = binary coefficient of components i and j

ρ_i = density of component i

3.2 Computational System Overview.

Calculate all the dependent variables by stepping from Sections 3.2.1 through 3.2.9 in the order given.

3.2.1 Increment Time by a Small Number.

The calculation follows the procedure previously described by Penski[1]

$$t = t_j + \tau \qquad (19)$$

where

t_j = time after previous increment

τ = small increment in time

3.2.2 Activity Coefficients.

Calculate the activity coefficients (equations 4 and 5) as follows:

$$\gamma_1 = e^{v_1 \phi_2^2 [(\delta_1 - \delta_2)^2 + 2 \Lambda_{12} \delta_1 \delta_2]/RT} \qquad (20)$$

$$\gamma_2 = e^{v_2 \phi_1^2 [(\delta_1 - \delta_2)^2 + 2 \Lambda_{12} \delta_1 \delta_2]/RT} \qquad (21)$$

3.2.3 Drop Volume.

$$\Omega = m_1/\rho_1 + m_2/\rho_2 \qquad (22)$$

where

Ω = volume of droplet

ρ_i = density of component i

3.2.4 Reynolds Number.

$$Re = 2 h \Psi/\upsilon \qquad (23)$$

3.2.5 Concentration of Vapor at Droplet Surface.

The partial vapor pressure of component i of a mixture is given by the following equation:

$$P_1 = P_1^o \gamma_1 \phi_1 \qquad (24)$$

$$P_2 = P_2^o \gamma_2 \phi_2 \qquad (25)$$

and the concentration of vapor of the two components is as follows:

15

$$C_1 = M_1 \, p_1/(RT) \tag{26}$$

$$C_2 = M_2 \, p_2/(RT) \tag{27}$$

C_1 = concentration of vapor of component i in equilibrium with the fluid at surface of droplet.

M_i = molecular weight of vapor of component i

3.2.6 Picknett and Bexon Equations.

$$\Gamma_1 = 0.5 \, K_1 E \, \Upsilon \rho^{-1/3} \tag{28}$$

$$\Gamma_2 = 0.5 \, K_2 E \, \Upsilon \rho^{-1/3} \tag{29}$$

where

$$K_1 = 4 \, \pi D_1 (C_1 - C_{\infty 1}) \tag{30}$$

$$K_2 = 4 \, \pi D_2 (C_2 - C_{\infty 2}) \tag{31}$$

$$\omega = \pi - \theta \tag{32}$$

$$E = [\pi/3(1 - \cos \theta)^2 (2 + \cos \theta)]^{-1/3} \tag{33}$$

For $0 < \theta < 0.175$ radian,

$$\Upsilon = 0.6366 \, \theta + 0.09591 \, \theta^2 - 0.06144 \, \theta^3 \tag{34}$$

For $0.175 < \theta < \tau$ radian,

$$\Upsilon = 8.957 \; 10^{-5} + 0.6333 \, \theta + 0.1160 \, \theta^2 - 0.08878 \, \theta^3 + 0.01033 \, \theta^4 \tag{35}$$

3.2.7 Height of Sessile Droplet.

The droplet height[2] is given by the following equations:

$$\lambda = 1 + 0.75 \, [2 \sin \theta/(1 - \cos \theta)]^2 \tag{36}$$

$$a = [6 \, m/(\pi \rho \lambda)]^{1/3} \tag{37}$$

3.2.8 Mass of Droplet and Mass of Each Component.

The Coutant and Penski equation relates the evaporation of a sessile droplet to its mass, Γ_i, and degree of ventilation as measured by its Reynolds number:

$$m_1 = m_{1j} - \Gamma_1 \, m^{1/3}[1 + c \, Re^{0.63} \, (a/h)^{0.9}] \, \tau \tag{38}$$

$$m_2 = m_{2j} - \Gamma_2 m^{1/3}[1 + c\,Re^{0.63}(a/h)^{0.9}]\,\tau \qquad (39)$$

$$m = m_1 + m_2$$

where m_{ij} = mass of component i for last iteration.

3.2.9 Volume Fraction.

$$\phi_1 = m_1/(\rho_1\,\Omega) \qquad (41)$$

$$\phi_2 = m_2/(\rho_2\,\Omega) \qquad (42)$$

3.2.10 Contact Angle Decay.

Provision for contact angle decay is provided in the model. The following equation is used.

$$\theta = \theta_o(A_o - A_1 m/m_o) \qquad (43)$$

where θ_o is the initial contact angle, and A_o and A_1 are constants.

At this point, calculation returns to Section 3.2.1 and starts over providing all the variables as a function of time through multiple repetitions.

4. RESULTS

The definitions of the terms used in the program and their units are provided in Appendix A. Appendix B provides the computer program developed in this effort. Figure 4 compares data collected by experimental methodology by the authors[6] with calculations performed with the model and computer program described in this report. The data used was for a sessile water droplet on an aluminum surface in a small wind tunnel with a low air flow. Details of the calculations are provided in Appendix C.

5. DISCUSSION

To keep this report unclassified and relatively simple, only water data is included. By taking the concentrations of the second component as zero, the model may be applied to neat liquids.

If equations are introduced to vary the properties of the components, the model may be used for conditions other than isothermal. For example, the Antoine equation[7] may be used to vary p_1^o and ΔH_{v1} (vapor pressures and enthalpy of vaporization for each component).

This model implicitly assumes complete mixing inside the droplet which is, in fact, the actual case for most low viscosity liquid droplets in a moving air stream. High viscosity mixtures may not mix well, resulting in concentration gradients existing inside the droplet. The volatile liquid would be expected to have a higher concentration near the center of the droplet rather than near the edges. Comparing this model with data for thickened droplets will determine when the sessile droplet starts to develop concentration gradients.
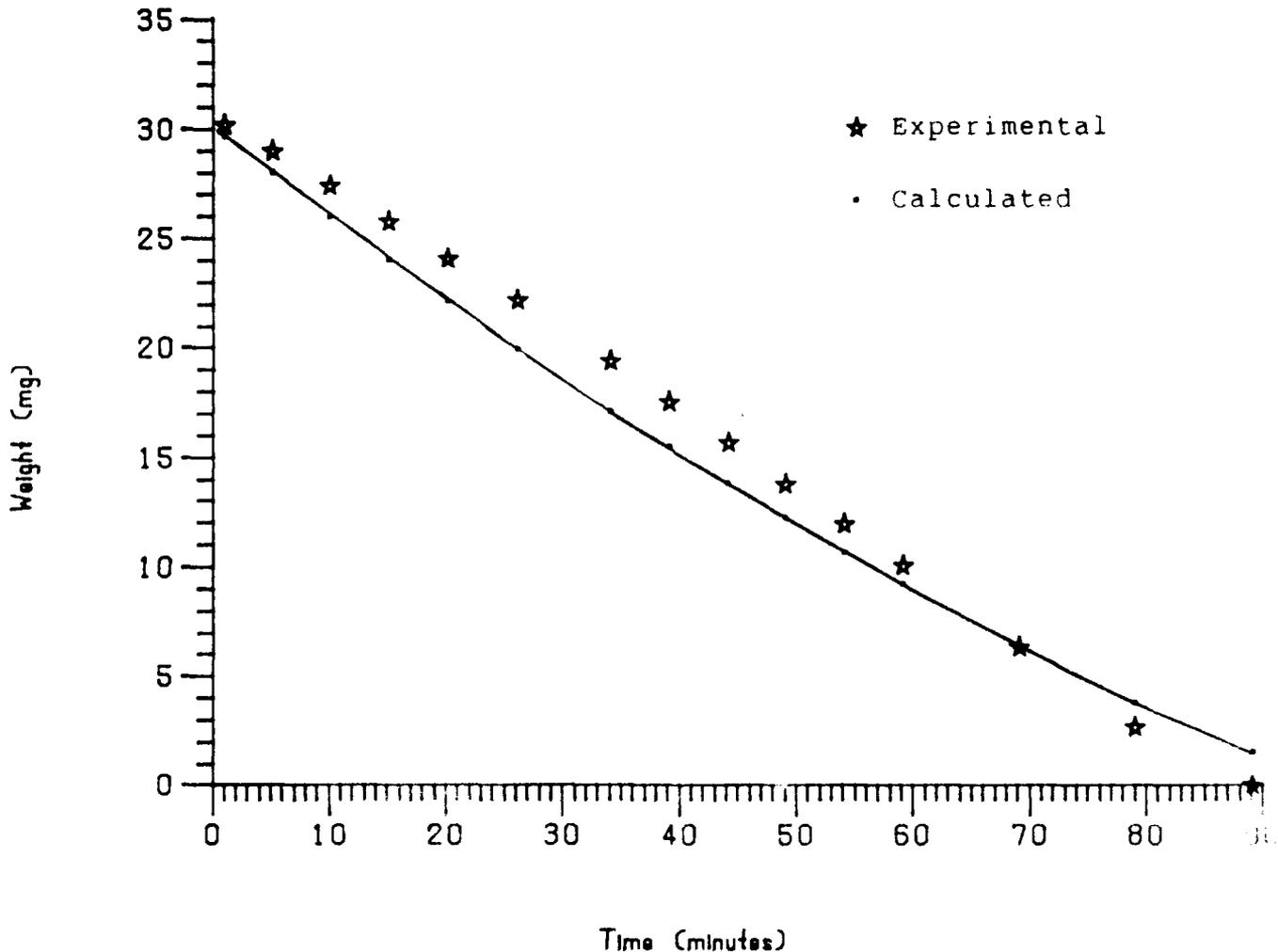
Figure 4.   Evaporation of a Sessile Droplet of Distilled Water at 18 °C, 0% Relative Humidity, 0.63 cm/s Air Velocity from an Aluminum Surface Compared to Calculations.

18

6.   CONCLUSIONS

        This report provides a model and computer program that
can be used to calculate evaporation of single-component sessile
droplets.

        A model and computer program are provided that can be
used to calculate the evaporation of sessile droplets composed
of two-component solutions.

        Data for the evaporation of a sessile water droplet on
an aluminum surface in a small wind tunnel with a low air flow
compares favorably with calculations using the model and
computer program.

Blank

LITERATURE CITED

1. Penski, E.C., The Evaporation of Macroscopic Droplets, I. Theoretical Factors for a Two-Component System, CRDEC-TR-88124, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, June 1988, UNCLASSIFIED Report.

2. Coutant, R.W., and Penski, E.C., "Experimental Evaluation of Mass Transfer of Sessile Drops," Industrial and Engineering Chemistry Fundamentals Vol. 21, p 250 (1982).

3. Hildebrand, J.H., Prausnitz, J.M., and Scott, R.L., Regular and Related Solutions, The Solubility of Gases, Liquids, and Solids, Van Nostrand Reinhold Company, NY, 1970.

4. Picknett, R.G., and Bexon, R., "The Evaporation of Sessile or Pendent Droplets in Still Air," J. Colloid and Interface Science Vol. 61, No. 2, p 336 (1977).

5. Gerasimov, Y.A., Physical Chemistry, p 56, MIR Publishers, Moscow, USSR, 1978.

6. Walker, H.M., and Penski, E.C., Experimental Techniques for Measuring the Evaporation of Suspended and Sessile Droplets, CRDEC-TR-88072, U.S. Army Chemical Research, Development and Engineering Center, Aberdeen Proving Ground, MD, May 1988, UNCLASSIFIED Report.

7. Penski, E.C., and Latour, L.J., Conversational Computation Method for Fitting the Antoine Equation to Vapor Pressure - Temperature Data, EATR 4491, Edgewood Arsenal, Aberdeen Proving Ground, MD, February 1971, UNCLASSIFIED Report.

Blank

GLOSSARY

a = Height of droplet

C_i = Concentration of vapor of component i in equilibrium with the fluid at surface of droplet

$C_{\infty i}$ = Concentration of vapor at a large distance from droplet for each component, usually equal to zero in practical cases

c = constant of Coutant and Penski equation

ΔH_v = molar enthalpy of vaporization

D = diffusion coefficient of vapor in atmosphere

E = defined by equation 9

h = height of tunnel

K = defined by equation 7

M_i = molecular weight of component i

m = droplet mass

m_o = initial droplet mass

m_i = mass of component i in droplet

m_{ij} = mass of component i for last iteration

n = number of moles of vapor

P_i^o = vapor pressure of component i

p_i = partial pressure of component i

R = ideal gas law constant

Re = Reynolds number = $2 h \Psi / \upsilon$

T = temperature in Kelvin

t = time

t_j = time after last increment

23

v_i = molar volume of component i

V = volume of vapor

GREEK TERMS

δ_i = Hildebrand parameter of component i

ϕ_i = volume fraction or volume of component i divided by total volume of mixture

Γ = defined by equation 6

γ_i = activity coefficient of component i

θ = contact angle of droplet with surface

θ_o = initial contact angle of droplet with surface

Λ_{ij} = binary coefficient of components i and j

λ = defined by equation 14

υ = kinematic viscosity of the atmosphere

π = 3.1416

Ψ = wind velocity or relative velocity of the droplet to that of the atmosphere

ρ_i = density of component i

τ = small increment in time

Ω = volume of droplet

Υ = defined by equations 10 and 11

APPENDIX A

DEFINITIONS OF COMPUTER TERMS

Blank

A1   Height of droplet, cm

C1   Concentration of component 1 in vapor, g/cm^3

C2   Concentration of component 2 in vapor, g/cm^3

C4   Concentration of component 1 in atmosphere leaving
          tunnel, $\mu g/cm^3$

C5   Concentration of component 2 in atmosphere leaving
          tunnel, $\mu g/cm^3$

C6   Constant of Coutant and Penski equation

D1   Density of component 1, g/cm^3

D2   Density of component 2, g/cm^3

D5   Density of atmosphere, g/cm^3

D8   Diffusion coefficient of component 1 in atmosphere,
          $cm^2 s^{-1}$

D9   Diffusion coefficient of component 2 in atmosphere,
          $cm^2 s^{-1}$

E8 T, see equations 10 and 11

E9 E, see equation 9

F1 Γ_1, see equation 28

F2 Γ_2, see equation 29

F3   Right most two factors in equation 12

F4 Γ_1/K_1

G3   Activity coefficient of component 1, unitless

G4   Activity coefficient of component 2, unitless

H1   Height of tunnel, cm

I2   Number of points per data set

I3   Point counter

I7   Data set number

K   273.16

K1	Temperature of droplet, Kelvin
K2	Atmospheric temperature, Kelvin
K5	K_1, equation 30, g/(cm s)
K6	K_2, equation 31, g/(cm s)
L	Binary coefficient, unitless
M	Droplet mass, experimental, mg as input converted to g
M1	Mass of component 1, calculated, g
M2	Mass of component 2, calculated, g
M4	Molecular weight of component 1, g
M5	Initial droplet mass, g
M7	Droplet mass for previous iteration, g
M8	Molecular weight of component 2, g
N	Viscosity of atmosphere, poise
O	Initial volume of droplet minus volume of impurities, cm^3
O4	Initial volume of component 1, cm^3
O5	Initial volume of component 5, cm^3
P	Total of component partial vapor pressures, Torr
P1	Partial vapor pressure of component 1, Torr
P2	Partial vapor pressure of component 2, Torr
P3	Pressure of atmosphere, Torr
P4	Purity of component 1 in weight fraction, unitless
P5	Purity of component 2 in weight fraction, unitless
P7	Vapor pressure of component 1, Torr
P9	Vapor pressure of component 2, Torr
R	Ideal gas law constant, cm^3 Torr/(Kelvin mole)
R2	Ideal gas law constant, cal/(Kelvin mole)

R3	Reynolds number, unitless
S8	Hildebrand parameter of component 1, $(cal/cm^3)^{1/2}$
S9	Hildebrand parameter of component 2, $(cal/cm^3)^{1/2}$
T	Measured time, input as min, converted and used as s
T1	Droplet temperature, C
T2	Atmospheric temperature, C
T6	Contact angle, initially in deg then converted to rad
T7	Initial contact angle, deg
T8	Calculated time, s
T9	Increment in time, s
V	Kinematic viscosity of atmosphere, cm^2/s
V1	Atmospheric velocity, cm/s
V9	Droplet volume, cm^3
V4	Volume of component 1, cm^3
V5	Volume of component 2, cm^3
W1	Increment of mass of component 1, g
W2	Increment of mass of component 2, g
W3	Droplet mass, g
X1	Volume fraction of component 1, g
X2	Volume fraction of component 2, g
X4	Weight of component 1 divided by initial mass of droplet, unitless
X5	Weight of component 2 divided by initial mass of droplet, unitless
Z	Concentration of vapor component in atmosphere leaving tunnel per gram of component leaving droplet, $mg/cm^3/g$

Blank

APPENDIX B

COMPUTER PROGRAM

Blank

```
SESS        10-JUN-88  11:09:19

10 REM        PROGRAM SHORT NAME:SESS
20 REM        LONG NAME: EVAPORATION OF A TWO COMPONENT MIXTURE SESSILE DROPLET
30 REM        LANGUAGE: BASIC-11/RT-11 V02-03, ALL OPTIONS
40 REM        COMPUTER: DIGITAL EQUIPMENT CORP, PDP-11/45, ROOM 205, BLDG E3300, APG
50 REM        PROGRAMMER: ELWIN C. PENSKI, SMCCR-RSC-P, PHONE: 301-671-3953
60 REM        SET UP: SET TT:WIDTH=132
70 A=TTYSET(255%,133%)
80 REM ********** INPUT DATA *********************
90 DATA 15,1,97,5.08
100 DATA 18.016,18.016, 23.4,23.4,0
110 DATA 15.477,15.477,.9986,.9986
120 DATA 18,.63,.03044,1,.0000
130 DATA 1,30.16,5,28.96,10,27.36, 15,25.71, 20,24.01,
140 DATA 26,22.12, 34,19.34, 39,17.5,44,15.63, 49,13.77
150 DATA 54,11.9, 59,10.03, 69,6.3,79,2.68, 89,.02
160 DATA 999,0,0,0
170 REM ********** SET CONSTANTS *************
180 C6=.3
190 P3=760 \ K=273.16
200 R=82.055*760
210 R2=1.987
220 REM ********** START NEW RUN *************
230 READ I2,I7,T6,H1
250 IF I2=999 THEN 1300
260 T9=30
270 T6=T6*3.1416/180
280 T7=T6
290 READ M4,M8,S8,S9,L
300 READ P7,P9,D1,D2
310 I3=0 \ M1=0 \ M2=0
320 READ T1,V1,M5,P4,P5
330 T2=T1
340 GOSUB 1260
350 PRINT  \ PRINT "
360 GOSUB 1260                          SUMMARY OF DATA AND CALCULATIONS FOR RUN NUMBER ";I7
370 PRINT "TEMPERATURE IN CELSIUS = ";T1;"     VELOCITY IN CM/S = ";V1
380 PRINT "INITIAL DROPLET MASS IN GRAMS = ";M5
390 M7=M5
400 M1=P4*M5
410 M2=P5*M5
420 W3=M1+M2
430 V4=M1/D1
440 V5=M2/D2
450 V9=V4+V5
460 O4=V4 \ O5=V5
470 O=O4+O5
480 X1=V4/O \ X2=V5/O
490 T8=0
```

```
500 K1=K+T1 \ K2=T2+K
510 D8=.08*(140/M4)^.5*(K2/300)^1.5
520 D9=.08*(140/M8)^.5*(K2/300)^1.5
530 IF M4<>18.016 THEN 550
540 D8=.248 \ D9=0
550 PRINT "DIFFUSION COEFFICIENT (CM^2 / S) OF COMPONENT 1 = ";D8
560 PRINT "DIFFUSION COEFFICIENT (CM^2 / S) OF COMPONENT 2 = ";D9
570 N=1.50300E-05
580 N=N*K2^1.5/(K2+124)
590 PRINT "ABSOLUTE VISCOSITY OF ATMOSPHERE (CGS) = ";N
600 D5=1.29300E-03*P0/(760*.1+3.46700E-03*T2))
610 PRINT "DENSITY OF ATMOSPHERE (G/CC) = ";D5
620 V=N/D5
630 PRINT "PURITIES (WT %) COMPONENT 1 = ";P4;"        COMPONENT 2 = ";P5
640 PRINT "VAPOR PRESSURES (TORR) OF COMPONENT 1 = ";P7;"  COMPONENT 2 = ";P9
650 PRINT "HILDEBRAND PARAMETER (CAL^.5 CM^-3/2) OF COMPONENT 1 = ";S8;"    COMPONENT 2 = ";S9
660 PRINT "BINARY COEFFICIENT = ";L
670 PRINT "CONTACT ANGLE (DEG.) = ";T7*180/3.1416
680 PRINT \ PRINT
690 PRINT "T/MIN  M/MG     W/MG     WI/MG     PP 1     PP 2     C1     C2     X4     X5     X1     X2     G1     G2     A"
700 GOSUB 1260
710 REM ************** TOP OF OUTER LOOP ****************************
720 READ T,M
730 T=T*60 \ M=M/1000
740 I3=I3+1
750 REM ********** TOP OF ITERATION LOOP **************
760 T8=T8+T9
770 REM     CALCULATION OF ACTIVITY COEFFICIENTS
780 S1=((S9-S8)^2+2*L*S8*S9)/(R2*K1)
790 G3=EXP((M4/D1)*X2^2*S1)
800 G4=EXP((M8/D2)*X1^2*S1)
810 REM ********** TRANSFER TO CONTACT ANGLE DECAY MODULE ****************
820 GOSUB 1480
830 REM     CALCULATION OF E
840 E9=((1-COS(T6))^2*(2+COS(T6))*3.1416/3)^(-1/3)
850 IF T6>.175 THEN 880
860 E8=T6*.6366+.09591*T6^2-.06144*T6^3
870 GO TO 900
880 E8=8.95700E-05+.6333*T6+.116*T6^2-.0H878*T6^3+.01033*T6^4
890 REM     CALCULATION OF NEW REYNOLDS NUMBER
900 R3=2*V1*H1/V
910 A1=(W3/(3.1416*W3/(V9*6)*(1+.75*(2*SIN(T6)/(1-COS(T6)))^2))^(1/3))
920 REM     CALCULATE SATURATION VAPOR CONCENTRATIONS
930 P1=X1*G3*P7
940 P2=X2*G4*P9
950 C2=P2*M8/(K1*R)
960 C1=P1*M4/(K1*R)
970 REM FICKNETT & DIXON EQUATIONS
980 K5=4*3.1416*D8*.1
990 K6=4*3.1416*D9*.1
```

```
1000 F4=E9*E8*.5*(V9/W3)^(1/3)
1010 F1=K5*F4 \ F2=K6*F4
1020 REM    CALCULATE WEIGHT LOSS
1030 F3=W3^(1/3)*(1+C6*R3^(.63)*(A1/H1)^(.9))
1040 W1=F1*F3 \ W2=F2*F3
1050 Z=(1.00000E+06/T9)/((2*2.54)^2*V1)
1060 C4=2*W1 \ C5=Z*W2
1070 M1=M1-W1*T9 \ M2=M2-W2*T9
1080 V4=M1/D1 \ V5=M2/D2
1090 X4=M1/M5 \ X5=M2/M5
1100 V9=V4+V5
1110 X1=V4/V9 \ X2=V5/V9
1120 W3=M1+M2
1130 IF W3<1.00000E-07 THEN 1160
1140 IF T>T8 THEN 760
1150 REM *****************BOTTOM OF ITERATION LOOP **********
1160 PRINT USING "####.# ##.## ",T/60,M*1000;
1170 PRINT USING "  ##.## ",W3*1000,M1*1000;
1180 PRINT USING "###.### ##.###",P1,P2;
1190 PRINT USING " #.##^^^^ #.##^^^^",C4,C5;
1200 PRINT USING "##.### ##.###",X4,X5;
1210 PRINT USING " ##.### ##.###",X1,X2;
1220 PRINT USING " ##.### ##.### #.####",G3,G4,A1
1230 IF I2=I3 THEN 230
1240 GO TO 720
1250 REM ******* BOTTOM OF OUTER LOOP ****************
1260 REM    LINE GENERATOR ROUTINE
1270 FOR I=1 TO 57
1280 PRINT "-";
1290 NEXT I \ PRINT \ RETURN
1300 PRINT \ PRINT "********** EXPLANATION OF COLUMN HEADINGS **************"
1310 PRINT "T/MIN   = TIME IN MINUTES"
1320 PRINT "M/MG    = EXPERIMENTAL MASS OF DROPLET IN MILLIGRAMS"
1330 PRINT "W/MG    = CALCULATED MASS OF DROPLET IN MILLIGRAMS"
1340 PRINT "W1/MG   = CALCULATED MASS OF COMPONENT 1 REMAINING IN MILLIGRAMS"
1350 PRINT "PP 1    = CALCULATED PARTIAL PRESSURE OF COMPONENT 1 IN TORR"
1360 PRINT "PP 2    = CALCULATED PARTIAL PRESSURE OF COMPONENT 2 IN TORR"
1370 PRINT "C1      = CALCULATED CONCENTRATION OF COMPONENT 1 IN GAS LEAVING TUNNEL IN MICROGRAMS/CC"
1380 PRINT "C2      = CALCULATED CONCENTRATION OF COMPONENT 2 IN GAS LEAVING TUNNEL IN MICROGRAMS/CC"
1390 PRINT "X4      = WEIGHT OF COMPONENT 1 DIVIDED BY INITIAL MASS OF DROPLET"
1400 PRINT "X5      = WEIGHT OF COMPONENT 2 DIVIDED BY INITIAL MASS OF DROPLET"
1410 PRINT "X1      = VOLUME FRACTION OF COMPONENT 1"
1420 PRINT "X2      = VOLUME FRACTION OF COMPONENT 2"
1430 PRINT "G1      = ACTIVITY COEFFICIENT OF COMPONENT 1"
1440 PRINT "G2      = ACTIVITY COEFFICIENT OF COMPONENT 2"
1450 PRINT "A       = DROPLET HEIGHT (CM)"
1460
1470 REM ********** CONTACT ANGLE DECAY MODULE ********************
1480 ...
1490 RETURN
1500 END
```

Blank

APPENDIX C

CALCULATION DETAILS

37

Blank

SUMMARY OF DATA AND CALCULATIONS FOR RUN NUMBER

VELOCITY IN M/S

TEMPERATURE
INITIAL DROPLET MASS IN GRAMS
DIFFUSION COEFFICIENT OF COMPONENT 1
DIFFUSION COEFFICIENT OF COMPONENT 2
DENSITY OF ATMOSPHERE (CGS)
VAPOR PRESSURES OF COMPONENT 1
HILDEBRAND PARAMETER
BINARY COEFFICIENT
CONTACT ANGLE

I MIN	M MG	M MG	2F 1	2F 2	C1	C2	X4	X5	X1	X2	C1	C2	A
			15.477	0.000	1.4+E-02	0.4 3E+00	.985	0.000	1.000	0.000	1.000	1.000	0.2563
			15.477	0.000	1.41E-02	0.5E+00	0.928	0.000	1.000	0.000	1.000	1.000	0.2414
			15.477	0.000	1.5 E-02	0.7E+00	3.861	0.000	1.000	0.040	1.000	1.000	0.2 68
			15.477	0.000	1.3 E-02	0.9 E+00	0.797	0.000	1.000	0.000	1.000	1.000	0.190
			15.477	0.000	1.29E-02	0.9 E+00	0.735	0.000	1.000	0.000	1.000	1.000	0.1
			15.477	0.000	1. E-02	1.00E+00	.671	0.000	1.000	0.000	1.000	1.000	0.1
			15.477	0.000	1.1 E-02	1.00E+00	0.515	0.000	1.000	0.000	1.000	1.000	0.1
			15.477	0.000	1.1 E-02	1.00E+00	0.462	0.000	1.000	0.000	1.000	1.000	0.1
			15.477	0.000	1.0 E-02	0.00E+00	0.410	0.000	1.000	0.000	1.000	1.000	0.0
			15.477	0.000	1.04E-02	1.00E+00	0.159	0.000	1.000	0.000	1.000	1.000	0.0
			15.477	0.000	9.29E-03	0.00E+00	0.311	0.000	1.000	0.000	1.000	1.000	0.0
			15.477	0.000	7.27E-03	1.00E+00	0.218	0.000	1.000	0.000	1.000	1.000	0.0
			15.477	0.000	6.38E-03	0.2E-6	0.1 3	0.000	1.000	0.000	1.000	1.000	0.0493
			15.477	0.000	7.01E-03	0.3E-03	.054	0.000	1.000	0.000	1.000	1.000	0.02

********** COLUMN HEADINGS **********

EXPLANATION

MASS OF DROPLET IN MILLIGRAMS
MASS OF COMPONENT 1 REMAINING IN MILLIGRAMS
PARTIAL PRESSURE OF COMPONENT 1 IN TORR
PARTIAL PRESSURE OF COMPONENT 2 IN TORR
CONCENTRATION OF COMPONENT 1 IN GAS LEAVING TUNNEL IN M L GRAMS
CONCENTRATION OF COMPONENT 2 IN GAS LEAVING TUNNEL IN M L GRAMS
MASS OF COMPONENT 1 DIVIDED BY INITIAL MASS OF DROPLET
MASS OF COMPONENT 2 DIVIDED BY INITIAL MASS OF DROPLET
FRACTION OF COMPONENT 1
FRACTION OF COMPONENT 2
NT OF COMPONENT 1
NT OF COMPONENT 2

SUPPLEMENTARY

INFORMATION

ERRATA

DEPARTMENT OF THE ARMY
Chemical Research, Development and Engineering Center
Aberdeen Proving Ground, Maryland 21010-5423

ERRATUM SHEET

21 December 1989

Report No.   CRDEC-TR-095

Title   The Evaporation of Sessile Droplets
                    I. Theoretical Factors For a Two-Component System

Authors   Elwin C. Penski
                    Helen M. Walker

Date   July 1989

Report
Classification   UNCLASSIFIED

1. The subject report was mailed to your activity on or after 20 November 1989.

2. Remove pages 11, 12, 15, and 16 from your copy and insert the attached pages 11, 12, 15, and 16.
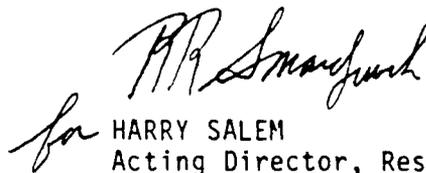
for HARRY SALEM
Acting Director, Research

2.2   Activity Coefficients of Regular Two-Component Solutions.

According to Hildebrand, Prausnitz, and Scott,[3] the equations for regular solutions can be written as follows:

$$RT \ln \gamma_1 = v_1 \, \phi_2^2 \, [(\delta_1 - \delta_2)^2 + 2 \, \Lambda_{12} \, \delta_1 \, \delta_2] \qquad (2)$$

$$RT \ln \gamma_2 = v_2 \, \phi_1^2 \, [(\delta_1 - \delta_2)^2 + 2 \, \Lambda_{12} \, \delta_1 \, \delta_2] \qquad (3)$$

where

γ_i = activity coefficient of component i

v_i = molar volume of component i

ϕ_i = volume fraction or volume of component i divided by total volume of mixture

δ_i = Hildebrand parameter of component i

Λ_{ij} = binary coefficient of components i and j

If equations 2 and 3 are solved for the activity coefficients, the following equations result:

$$\gamma_1 = e^{v_1 \, \phi_2^2 \, [(\delta_1 - \delta_2)^2 + 2 \, \Lambda_{12} \, \delta_1 \, \delta_2]/RT} \qquad (4)$$

$$\gamma_2 = e^{v_2 \, \phi_1^2 \, [(\delta_1 - \delta_2)^2 + 2 \, \Lambda_{12} \, \delta_1 \, \delta_2]/RT} \qquad (5)$$

2.3   Picknett and Bexon Equations.

The Picknett and Bexon equations[4] were developed for the evaporation of a sessile droplet in a static atmosphere. They are as follows:

$$\Gamma = 0.5 \, K \, E \, T \rho^{-1/3} \qquad (6)$$

where

$$K = 4 \, \pi \, D \, (C - C_\infty) \qquad (7)$$

D = diffusion coefficient of vapor in atmosphere

C = concentration of vapor in equilibrium with droplet fluid at surface of droplet

C_∞ = concentrations of vapor at a large distance from droplet, usually very near to zero in practical cases.

ρ = droplet density

π = 3.1416

ω = $\pi - \theta$ = contact angle,[2,4] British definition $\qquad$ (8)

θ = contact angle of droplet with surface (Figure 1)

E = $[\pi/3(1 - \cos\theta)^2(2 + \cos\theta)]^{-1/3}$ $\qquad$ (9)

The term T is defined as follows:

For $0 < \theta < 0.175$ radian,

$$T = 0.6366\,\theta + 0.09591\,\theta^2 - 0.06144\,\theta^3 \qquad (10)$$

For $0.175 < \theta < \pi$ radian,

$$T = 8.957\ 10^{-5} + 0.6333\,\theta + 0.1160\,\theta^2 - 0.08878\,\theta^3 + 0.01033\,\theta^4 \qquad (11)$$

2.4   Coutant and Penski Equation.

The Coutant and Penski[2] equation relates the evaporation of a sessile droplet to its mass, Γ, degree of ventilation (as measured by its Reynolds number), and droplet height. A number of additional factors are included in Γ.

$$-dm/dt = \Gamma m^{1/3}[1 + cRe^{0.63}(a/h)^{0.9}] \qquad (12)$$

where

$-dm/dt$ = rate of droplet evaporation

m = droplet mass

t = time

c = constant of Coutant and Penski equation

Re = Reynolds number = $2h\,\Psi/\upsilon$ $\qquad$ (13)

a = height of droplet

h = height of tunnel

Ψ = wind velocity or relative velocity of the droplet to that of the atmosphere

υ = kinematic viscosity of the atmosphere

12

3.2.1 Increment Time by a Small Number.

The calculation follows the procedure previously described by Penski[1]

$$t = t_J + \tau \tag{19}$$

where

t_J = time after previous increment

τ = small increment in time

3.2.2 Activity Coefficients.

Calculate the activity coefficients (equations 4 and 5) as follows:

$$\gamma_1 = e^{v_1 \phi_2^2 [(\delta_1 - \delta_2)^2 + 2 \Lambda_{12} \delta_1 \delta_2]/RT} \tag{20}$$

$$\gamma_2 = e^{v_2 \phi_1^2 [(\delta_1 - \delta_2)^2 + 2 \Lambda_{12} \delta_1 \delta_2]/RT} \tag{21}$$

3.2.3 Drop Volume.

$$\Omega = m_1/\rho_1 + m_2/\rho_2 \tag{22}$$

where

Ω = volume of droplet

ρ_i = density of component i

3.2.4 Reynolds Number.

$$Re = 2 h \, \Psi/\upsilon \tag{23}$$

3.2.5 Concentration of Vapor at Droplet Surface.

The partial vapor pressure of component i of a mixture is given by the following equation:

$$p_1 = P_1^o \gamma_1 \phi_1 \tag{24}$$

$$p_2 = P_2^o \gamma_2 \phi_2 \tag{25}$$

and the concentration of vapor of the two components is as follows:

$$C_1 = M_1 \, p_1/(RT) \tag{26}$$

$$C_2 = M_2 \, p_2/(RT) \tag{27}$$

C_1 = concentration of vapor of component i in
equilibrium with the fluid at surface of droplet.

M_1 = molecular weight of vapor of component i

3.2.6 Picknett and Bexon Equations.

$$\Gamma_1 = 0.5 \, K_1 E \, T \rho^{-1/3} \tag{28}$$

$$\Gamma_2 = 0.5 \, K_2 E \, T \rho^{-1/3} \tag{29}$$

where

$$K_1 = 4 \, \pi D_1(C_1 - C_{\infty 1}) \tag{30}$$

$$K_2 = 4 \, \pi D_2(C_2 - C_{\infty 2}) \tag{31}$$

$$\omega = \pi - \theta \tag{32}$$

$$E = [\pi/3(1 - \cos \theta)^2 \, (2 + \cos \theta)]^{-1/3} \tag{33}$$

For $0 < \theta < 0.175$ radian,

$$T = 0.6366 \, \theta + 0.09591 \, \theta^2 - 0.06144 \, \theta^3 \tag{34}$$

For $0.175 < \theta < \tau$ radian,

$$T = 8.957 \; 10^{-5} + 0.6333 \, \theta + 0.1160 \, \theta^2 - 0.08878 \, \theta^3 + 0.01033 \, \theta^4 \tag{35}$$

3.2.7 Height of Sessile Droplet.

The droplet height[2] is given by the following equations:

$$\lambda = 1 + 0.75 \, [2 \sin \theta/(1 - \cos \theta)]^2 \tag{36}$$

$$a = [6 \, m/(\pi \rho \lambda)]^{1/3} \tag{37}$$

3.2.8 Mass of Droplet and Mass of Each Component.

The Coutant and Penski equation relates the evaporation of a sessile droplet to its mass, Γ_i, and degree of ventilation as measured by its Reynolds number:

$$m_1 = m_{1j} - \Gamma_1 \, m^{1/3}[1 + c \, Re^{0.63} \, (a/h)^{0.9}] \, \tau \tag{38}$$