

2

AD-A215 946

CHEMICAL
RESEARCH,
DEVELOPMENT &
ENGINEERING
CENTER

CRDEC-TR-095

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

Elwin C. Penski
Helen M. Walker

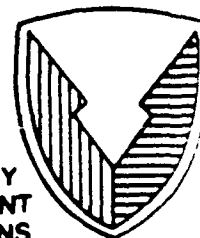
RESEARCH DIRECTORATE

DTIC
ELECTE
DEC 18 1989
S D CB D

July 1989

DISTRIBUTION STATEMENT A
Approved for public release
Distribution Unlimited

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.

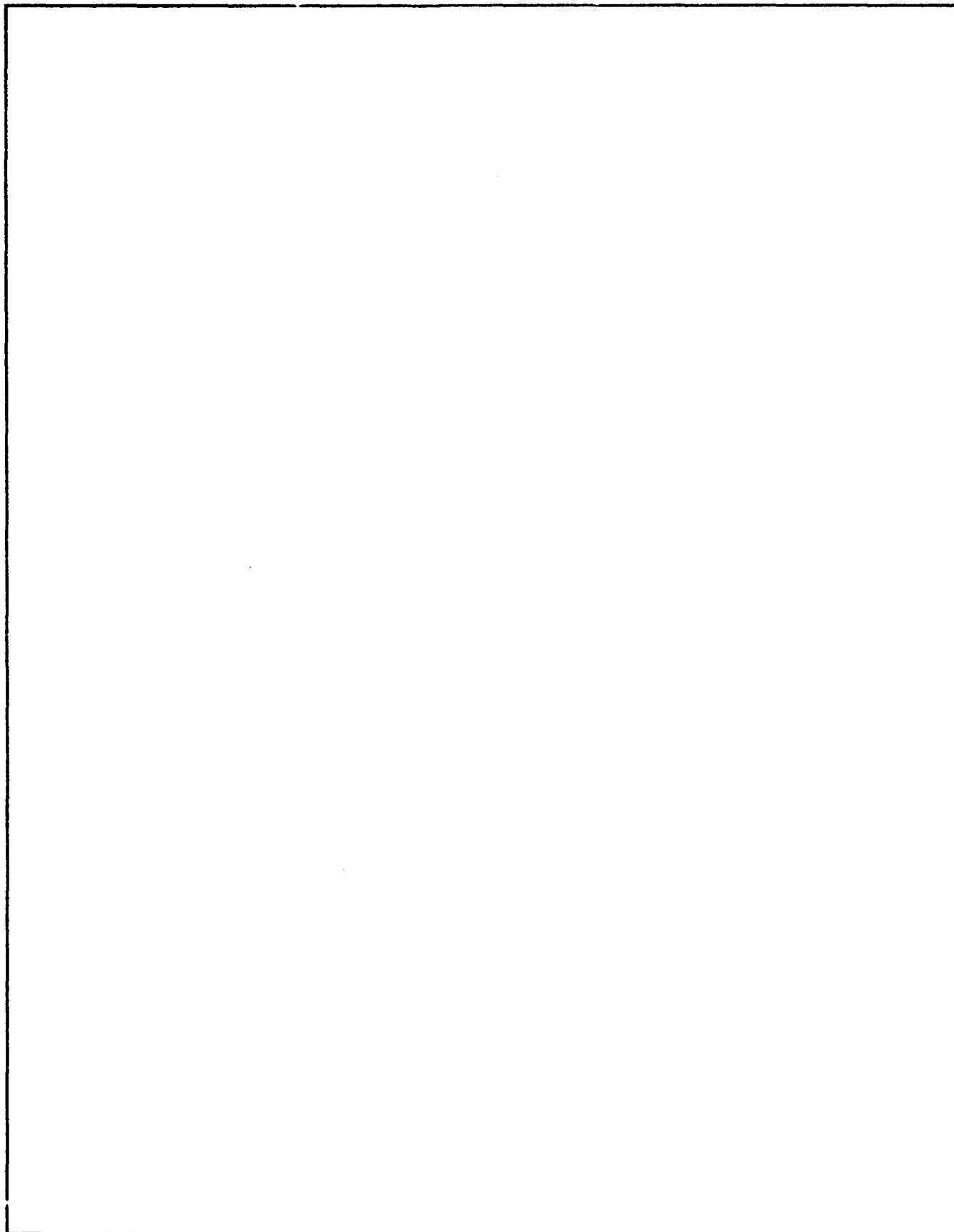
Distribution Statement

Approved for public release; distribution is unlimited.

REPORT DOCUMENTATION PAGE				
1a. REPORT SECURITY CLASSIFICATION UNCLASSIFIED			1b. RESTRICTIVE MARKINGS	
2a. SECURITY CLASSIFICATION AUTHORITY			3. DISTRIBUTION/AVAILABILITY OF REPORT Approved for public release; distribution is unlimited.	
2b. DECLASSIFICATION DOWNGRADING SCHEDULE				
4. PERFORMING ORGANIZATION REPORT NUMBER(S) CRDEC TR 095			5. MONITORING ORGANIZATION REPORT NUMBER(S)	
6a. NAME OF PERFORMING ORGANIZATION CRDEC		6b. OFFICE SYMBOL (if applicable) SMCCR-RSC-P		7a. NAME OF MONITORING ORGANIZATION
6c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423			7b. ADDRESS (City, State, and ZIP Code)	
8a. NAME OF FUNDING SPONSORING ORGANIZATION CRDEC		8b. OFFICE SYMBOL (if applicable) SMCCR-RSC-P		9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER
8c. ADDRESS (City, State, and ZIP Code) Aberdeen Proving Ground, MD 21010-5423			10. SOURCE OF FUNDING NUMBERS	
			PROGRAM ELEMENT NO.	PROJECT NO. 1L162706
			TASK NO. A553i	WORK UNIT ACCESSION NO.
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 Technical		13b. TIME COVERED FROM 79 Nov TO 88 May		14. DATE OF REPORT (Year, Month, Day) 1989 July
15. PAGE COUNT 39				
16. SUPPLEMENTARY NOTATION				
17. COSATI CODES			18. SUBJECT TERMS (Continue on reverse if necessary and identify by block number) Hildebrand parameter Solutions Sessile droplet Activity coefficients Water Evaporation Partial vapor pressures Surface chemistry	
FIELD	GROUP	SUB-GROUP		
07	04			
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 ☒ UNCLASSIFIED UNLIMITED ☐ SAME AS RPT ☐ OTIC USERS			21. ABSTRACT SECURITY CLASSIFICATION UNCLASSIFIED	
22a. NAME OF RESPONSIBLE INDIVIDUAL CANDRA J JOHNSON			22b. TELEPHONE (Include Area Code) (301) 671 2914	22c. OFFICE SYMBOL SMCCR SPS T

UNCLASSIFIED

SECURITY CLASSIFICATION OF THIS PAGE



UNCLASSIFIED
SECURITY CLASSIFICATION OF THIS PAGE

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

The authors wish to thank Donald Bowie of the Physical Chemistry Branch, Chemical Division, Research Directorate, CRDEC, for making a computer available for this report's calculations.

Accession For	
NTIS CRA&I	☒
DTIC TAB	☐
Unannounced	☐
Justification	
By	
Distribution/	
Availability Codes	
Dist	Availability for Special
A-1	



Blank

CONTENTS

	Page
1. INTRODUCTION	7
2. FUNDAMENTAL EQUATIONS	7
2.1 Hildebrand Parameter	7
2.2 Activity Coefficients of Regular Two-Component Solutions	11
2.3 Picknett and Bexon Equations	11
2.4 Coutant and Penski Equation	12
2.5 Height of a Sessile Droplet	13
2.6 Concentration of Vapor	13
2.7 Partial Vapor Pressures	13
3. MATHEMATICAL MODEL	14
3.1 Starting Conditions and Properties	14
3.1.1 Atmospheric Conditions and Properties	14
3.1.2 Droplets	14
3.1.3 Properties of Two Components	14
3.2 Computational System Overview	14
3.2.1 Increment Time by a Small Number	15
3.2.2 Activity Coefficients	15
3.2.3 Drop Volume	15
3.2.4 Reynolds Number	15
3.2.5 Concentration of Vapor at Droplet Surface	15
3.2.6 Picknett and Bexon Equations	16
3.2.7 Height of Sessile Droplet	16
3.2.8 Mass of Droplet and Mass of Each Component	16
3.2.9 Volume Fraction	17
3.2.10 Contact Angle Decay	17
4. RESULTS	17
5. DISCUSSION	17
6. CONCLUSIONS	19
LITERATURE CITED	21
GLOSSARY	23

APPENDIXES

A - DEFINITIONS OF COMPUTER TERMS	25
B - COMPUTER PROGRAM	31
C - CALCULATION DETAILS	37

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 Penski¹ report a model for the evaporation of mixtures in a suspended droplet. Coutant and Penski² 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:

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

where

- ΔH_v = molar enthalpy of vaporization
- R = ideal gas law constant
- T = temperature (Kelvin)
- v = molar volume of liquid

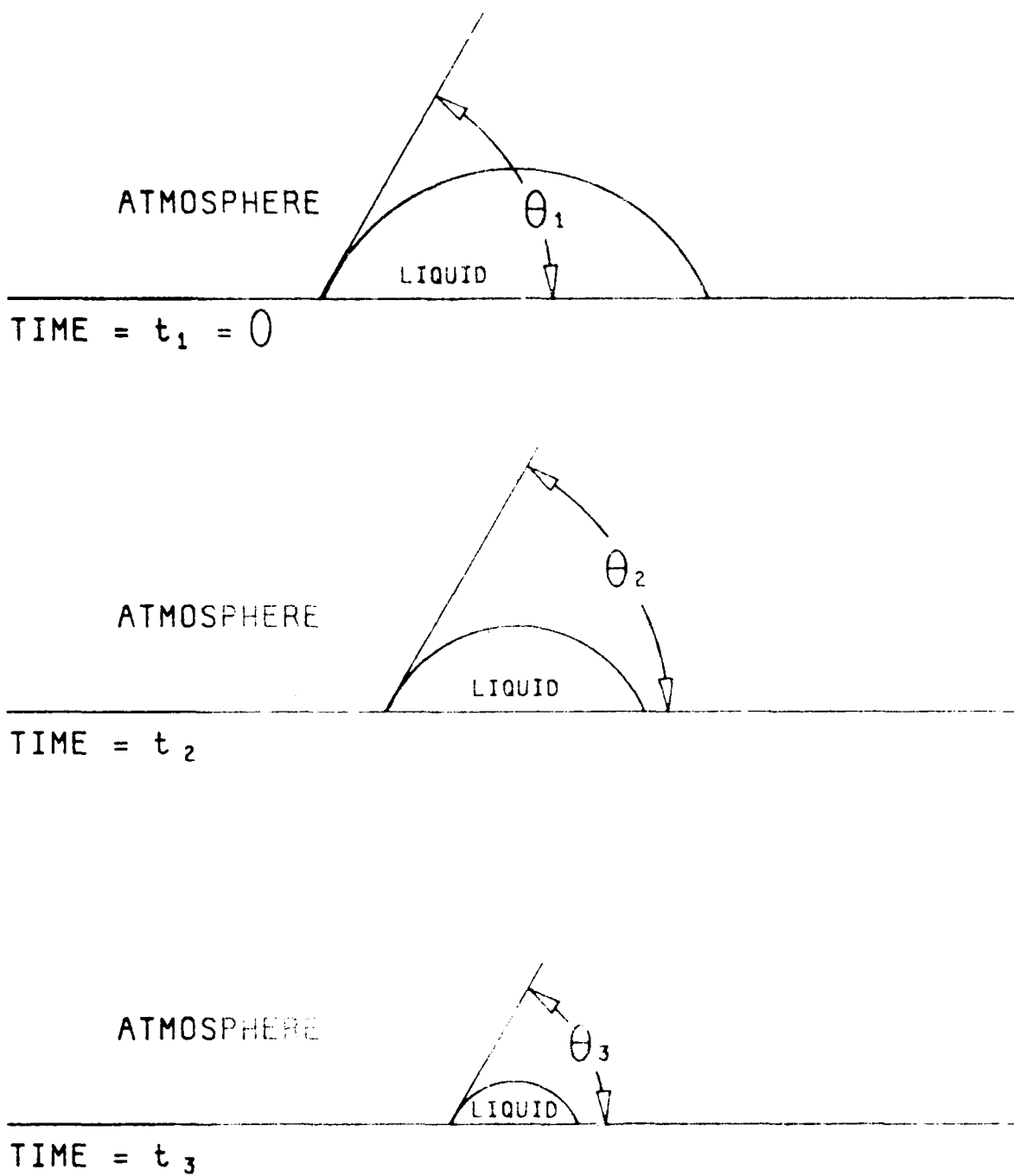


Figure 1. Sessile droplet evaporation with Constant Contact Angles: $\theta_1 = \theta_2 = \theta_3$, $t_1 < t_2 < t_3$.

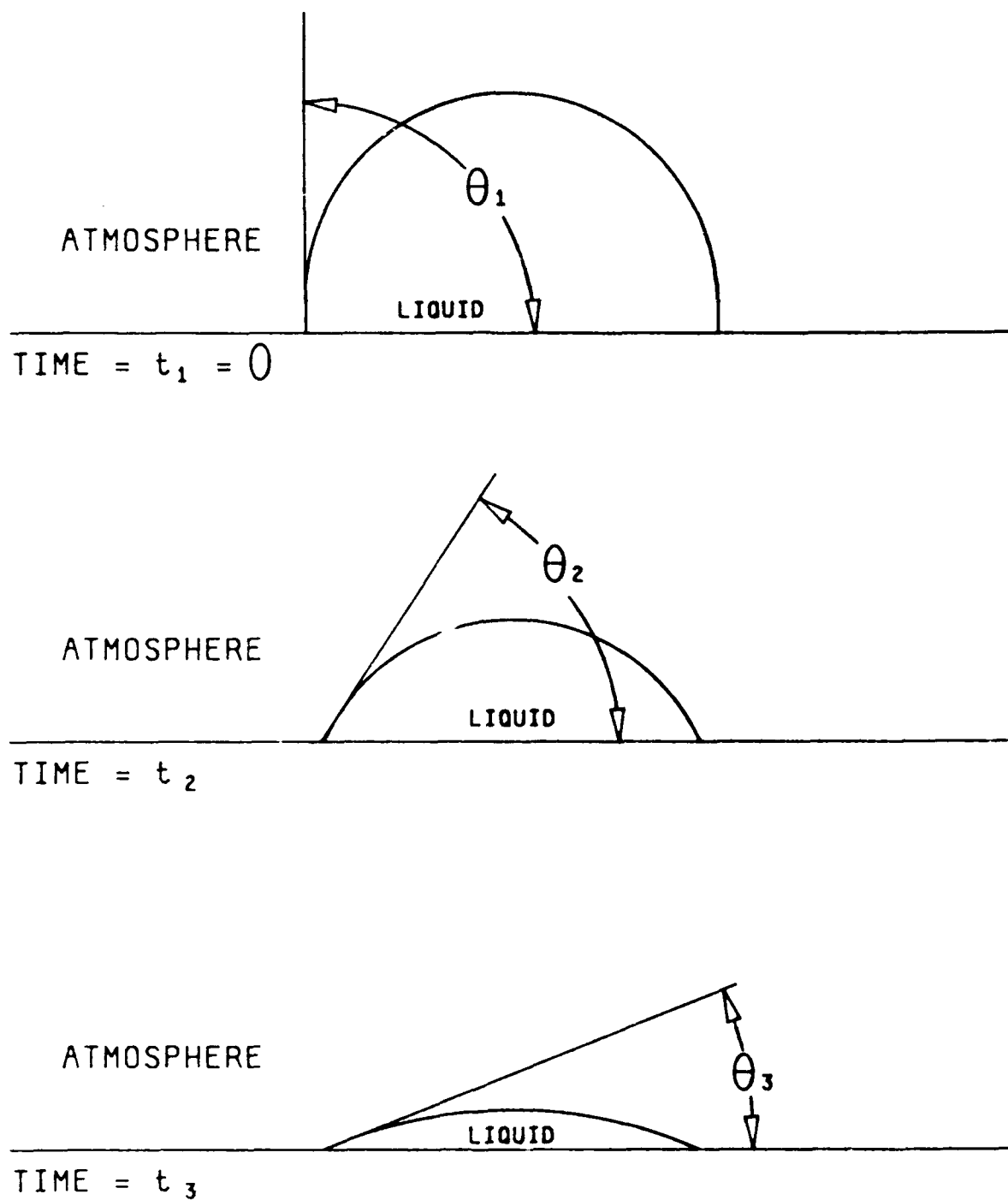


Figure 2. Sessile Droplet Evaporation with Decreasing Contact Angles: $\theta_1 > \theta_2 > \theta_3$, $t_1 < t_2 < t_3$.

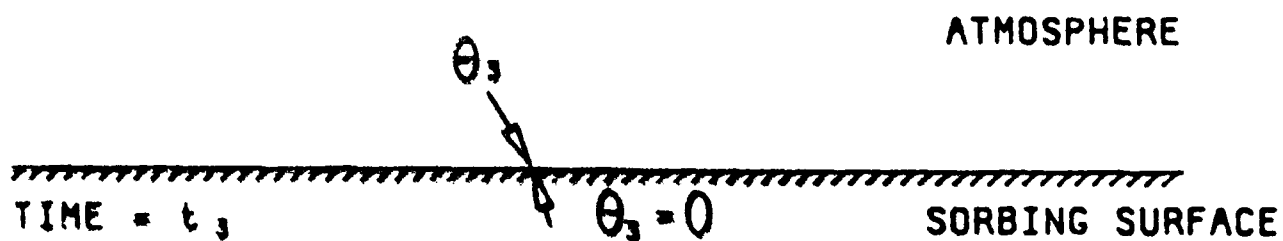
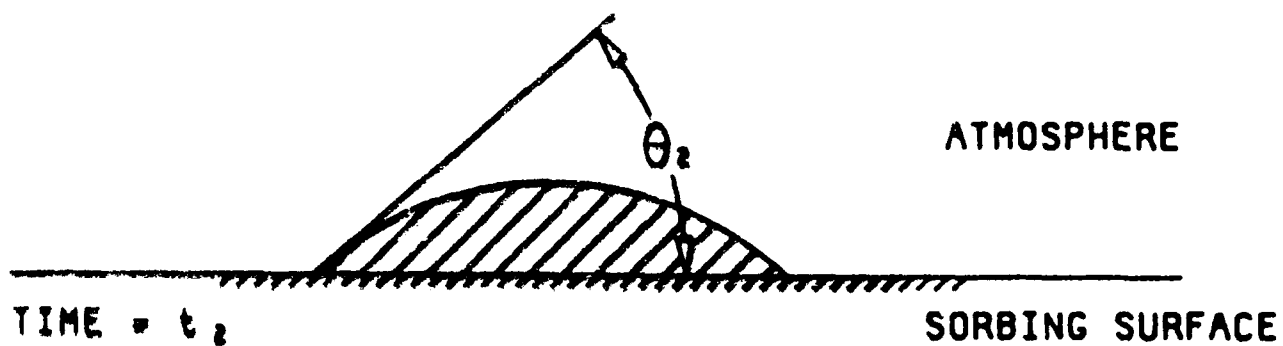
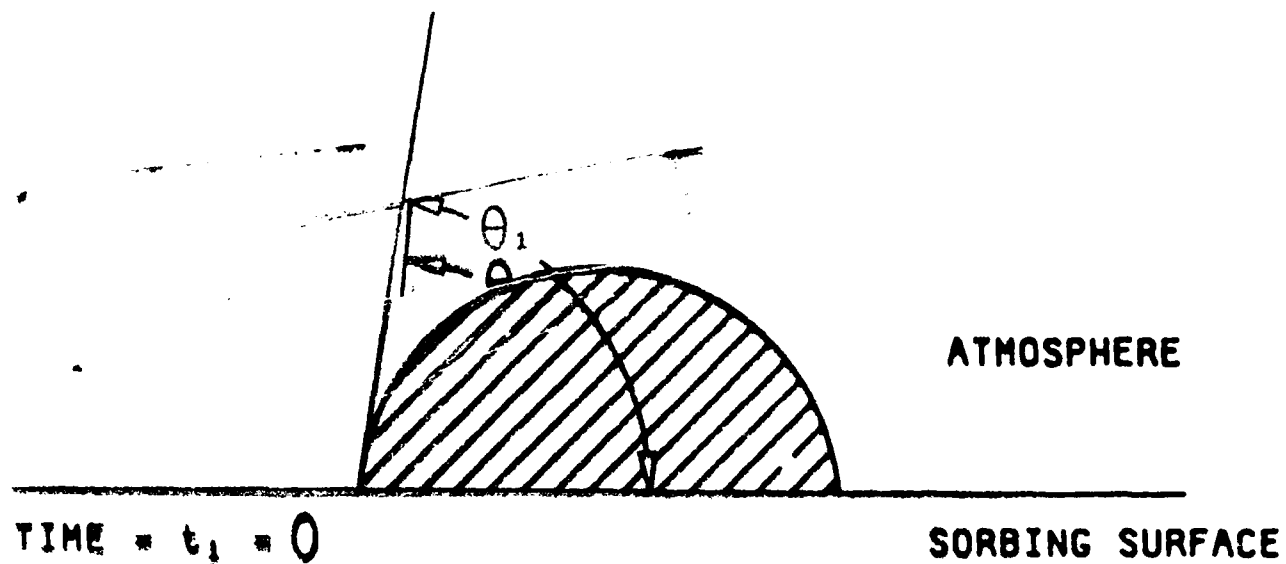


Figure 3. Sessile Droplet Evaporation with Surface Sorption:
 $\theta_1 > \theta_2, \theta_3 = 0; t_1 < t_2 < t_3$.

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:

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

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

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:

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

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

2.3 Picknett and Bexon Equations.

The Picknett and Bexon equations⁴ were developed for the evaporation of a sessile droplet in a static atmosphere. They are as follows:

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

where

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

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

$\omega = \pi - \theta$ = contact angle,^{2,4} Brit. definition (3)

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

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

The term T is defined as follows:

For $0 < \theta < 0.175$ radian,

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

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

$$T = 8.957 \cdot 10^{-7} + 0.6333 \theta + 0.1160 \theta^2 - 0.08878 \theta^3 + 0.01033 \theta^4 \quad (11)$$

2.4 Coutant and Penski Equation.

The Coutant and Penski² 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 .

$$-dm/dt = \Gamma m^{1/2} [1 + c Re^{0.12} (a/h)^{1.2}] \quad (12)$$

where

$-dm/dt$ = rate of droplet evaporation

m = droplet mass

t = time

c = constant of Coutant and Penski equation

$$Re = \text{Reynolds number} = 2 h \Psi / \nu \quad (13)$$

a = height of droplet

h = height of tunnel

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

ν = kinematic viscosity of the atmosphere

2.5 Height of Sessile Droplet.

The droplet height² is given by the following equations:

$$\lambda = 1 + 0.75 [2 \sin \theta / (1 - \cos \theta)]^2 \quad (14)$$

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

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

$$P^\circ V = nRT \quad (16)$$

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:

$$C = nM/V = MP^\circ / (RT) \quad (17)$$

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

$$p_i = P_i^\circ \gamma_i \phi_i \quad (18)$$

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.

ν = 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 Penski¹

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

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:

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

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

3.2.3 Drop Volume.

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

where

Ω = volume of droplet

ρ_i = density of component i

3.2.4 Reynolds Number.

$$Re = 2 h \Psi/\nu \quad (23)$$

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:

$$p_i = P_i^o \gamma_i \phi_i \quad (24)$$

$$p_i = P_i^o \gamma_i \phi_i \quad (25)$$

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

$$C_1 = M_1 p_1 / (RT) \quad (26)$$

$$C_2 = M_2 p_2 / (RT) \quad (27)$$

C_i = 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.

$$\Gamma_1 = 0.5 K_1 E T_p^{-1/3} \quad (28)$$

$$\Gamma_2 = 0.5 K_2 E T_p^{-1/3} \quad (29)$$

where

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

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

$$\omega = \pi - \theta \quad (32)$$

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

For $0 < \theta < 0.175$ radian,

$$T = 0.6366 \theta + 0.09591 \theta^2 - 0.06144 \theta^3 \quad (34)$$

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

$$T = 8.957 \cdot 10^{-5} + 0.6333 \theta + 0.1160 \theta^2 - 0.08878 \theta^3 + 0.01033 \theta^4 \quad (35)$$

3.2.7 Height of Sessile Droplet.

The droplet height² is given by the following equations:

$$\lambda = 1 + 0.75 [2 \sin \theta / (1 - \cos \theta)]^2 \quad (36)$$

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

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:

$$m_i = m_{iJ} - \Gamma_i m^{1/3} [1 + c Re^{0.63} (a/h)^{0.9}] \tau \quad (38)$$

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

$$m = m_1 + m_2$$

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

3.2.9 Volume Fraction.

$$\phi_1 = m_1 / (\rho_1 \Omega) \quad (41)$$

$$\phi_2 = m_2 / (\rho_2 \Omega) \quad (42)$$

3.2.10 Contact Angle Decay.

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

$$\theta = \theta_0 (A_0 - A_1 m/m_0) \quad (43)$$

where θ_0 is the initial contact angle, and A_0 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 authors⁶ 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 equation⁷ may be used to vary p_i^o and $\Delta H_{v,i}$ (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.

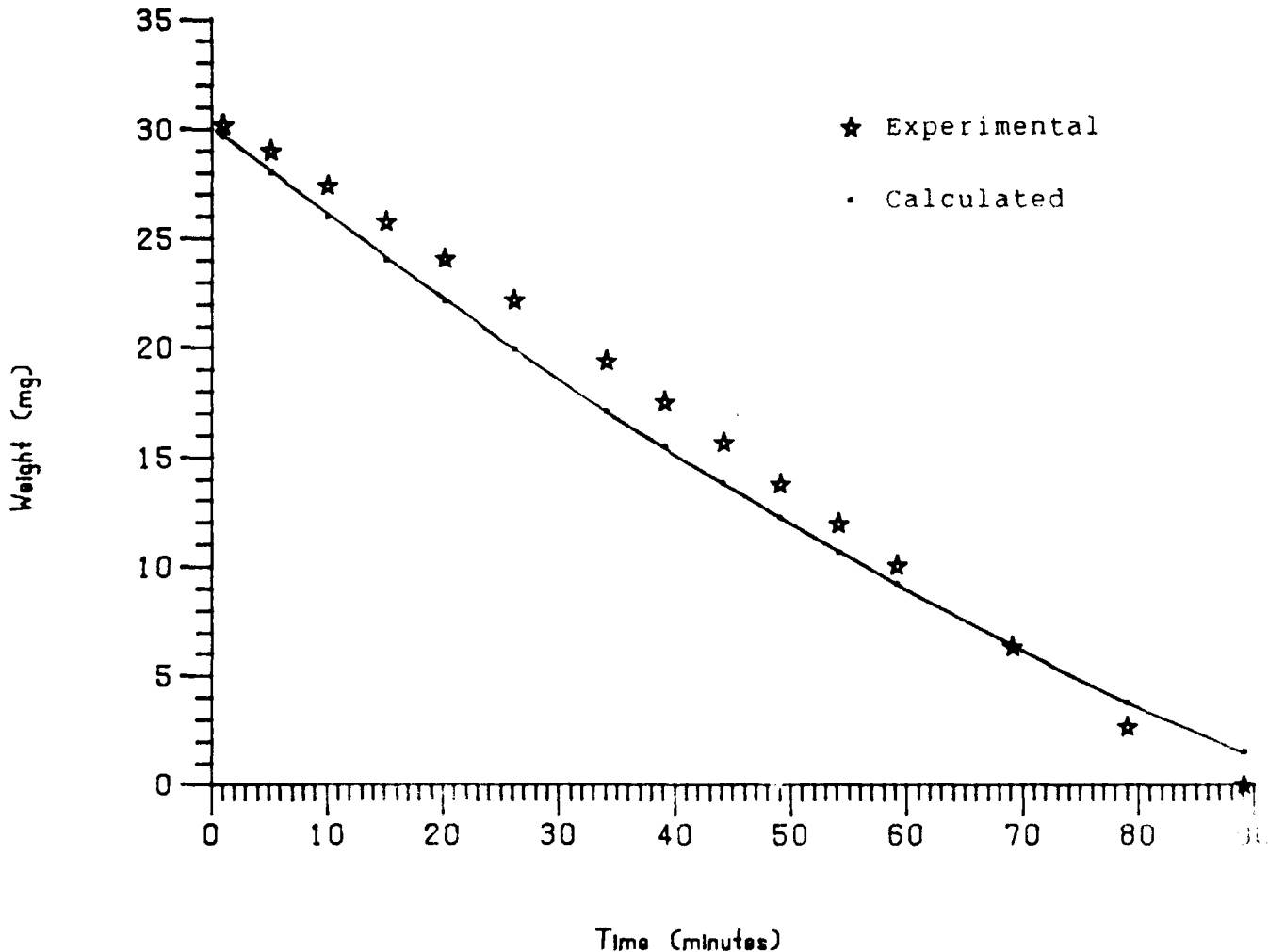


Figure 4. Evaporation of a Sessile Droplet of Distilled Water at 18 °C, 0% Relative Humidity, 0.63 cm/s Air Velocity from an Aluminum Surface Compared to Calculations.

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_0 = initial droplet mass
- m_i = mass of component i in droplet
- $m_{i,j}$ = 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 = $2 h \Psi / \nu$
- T = temperature in Kelvin
- t = time
- t_j = time after last increment

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_0 = initial contact angle of droplet with surface

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

λ = defined by equation 14

ν = kinematic viscosity of the atmosphere

n = 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

T = 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, $\mu\text{g}/\text{cm}^3$
C5	Concentration of component 2 in atmosphere leaving tunnel, $\mu\text{g}/\text{cm}^3$
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, $(\text{cal}/\text{cm}^3)^{1/2}$
S9	Hildebrand parameter of component 2, $(\text{cal}/\text{cm}^3)^{1/2}$
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, $\text{mg}/\text{cm}^3/\text{g}$

Blank

APPENDIX B
COMPUTER PROGRAM

Blank

```

LIST
      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=TT*SET(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 I300
      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
      370 PRINT "TEMPERATURE IN CELSIUS = ";T1;"
      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

```

SUMMARY OF DATA AND CALCULATIONS FOR RUN NUMBER ";I7
VELOCITY IN CM/S = ";V1

```

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*(2^1.5/(K2+124))
590 PRINT "ABSOLUTE VISCOSITY OF ATMOSPHERE (CGS) = ";N
600 D5=1.29300E-03*(P/(760*.1*3.46700E-03*AT2))
610 PRINT "DENSITY OF ATMOSPHERE (G/CC) = ";D5
620 V=N/D5
630 PRINT "PURITIES (WGT %) COMPONENT 1 = ";P4; " COMPONENT 2 = ";P5
640 PRINT "VAPOR PRESSURES (TORR) OF COMPONENT 1 = ";P7; " COMPONENT 2 = ";P9
650 PRINT "HILDEBRAND PARAMETER (CAL^1.5 CM^-3/2) OF COMPONENT 1 = ";S8; " COMPONENT 2 = ";S9
660 PRINT "BINARY COEFFICIENT = ";L
670 PRINT "CONTACT ANGLE (DEG.) = ";T/180/3.1416
680 PRINT \ PRINT
690 PRINT "T/MIN M/MC W/MC W1/MC PP 1 PP 2 C1 C2 X1 X2 G1 G2 A"
700 GOSUB 1200
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*AL*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-.0878*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*MB/(K1*R)
960 C1=P1*M4/(K1*R)
970 REM FICKNETT & PEXSON EQUATIONS
980 K5=4*3.1416*DR^2
990 K6=4*3.1416*DR^2

```

```

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=Z*W1 \ C5=Z*W2
1070 M1=M1-W1*T9 \ M2=M2-W2*T9
1080 V4=M1/D1 \ V5=M2/D2
-090 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 COMPONENT 1 REMAINING IN MILLIGRAMS"
1340 PRINT "M1/MG = CALCULATED PARTIAL PRESSURE OF COMPONENT 1 IN TORR"
1350 PRINT "PP 1 = CALCULATED PARTIAL PRESSURE OF COMPONENT 2 IN TORR"
1360 PRINT "PP 2 = CALCULATED CONCENTRATION OF COMPONENT 1 IN GAS LEAVING TUNNEL IN MICROGRAMS/CC"
1370 PRINT "C1 = CALCULATED CONCENTRATION OF COMPONENT 2 IN GAS LEAVING TUNNEL IN MICROGRAMS/CC"
1380 PRINT "C2 = WEIGHT OF COMPONENT 1 DIVIDED BY INITIAL MASS OF DROPLET"
1390 PRINT "X4 = WEIGHT OF COMPONENT 2 DIVIDED BY INITIAL MASS OF DROPLET"
1400 PRINT "X5 = WEIGHT FRACTION OF COMPONENT 1"
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 PRINT "CONTACT ANGLE DECAY MODULE"
1470 PRINT "*****"
1480 PRINT "*****"
1490 RETURN
1500 EN

```

Blank

APPENDIX C
CALCULATION DETAILS

Blank

39

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

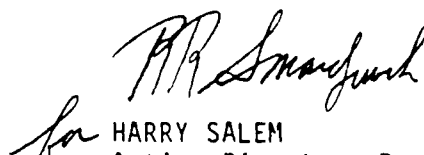
Title The Evaporation of Sessile Droplets
I. Theoretical Factors For a Two-Component System

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

AD-A215946

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:

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

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

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:

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

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

2.3 Picknett and Bexon Equations.

The Picknett and Bexon equations⁴ were developed for the evaporation of a sessile droplet in a static atmosphere. They are as follows:

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

where

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

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

n = 3.1416

$\omega = n - \theta$ = contact angle,^{2,4} British definition (8)

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

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

The term T is defined as follows:

For $0 < \theta < 0.175$ radian,

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

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

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

2.4 Coutant and Penski Equation.

The Coutant and Penski² 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 .

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

where

$-dm/dt$ = rate of droplet evaporation

m = droplet mass

t = time

c = constant of Coutant and Penski equation

$$Re = \text{Reynolds number} = 2 h \Psi / \nu \quad (13)$$

a = height of droplet

h = height of tunnel

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

ν = kinematic viscosity of the atmosphere

3.2.1 Increment Time by a Small Number.

The calculation follows the procedure previously described by Penski¹

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

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:

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

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

3.2.3 Drop Volume.

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

where

Ω = volume of droplet

ρ_i = density of component i

3.2.4 Reynolds Number.

$$Re = 2 h \Psi/\nu \quad (23)$$

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:

$$p_i = p_i^0 \gamma_i \phi_i \quad (24)$$

$$p_2 = p_2^0 \gamma_2 \phi_2 \quad (25)$$

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

$$C_1 = M_1 p_1 / (RT) \quad (26)$$

$$C_2 = M_2 p_2 / (RT) \quad (27)$$

C_i = 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.

$$\Gamma_1 = 0.5 K_1 E T_p^{-1/3} \quad (28)$$

$$\Gamma_2 = 0.5 K_2 E T_p^{-1/3} \quad (29)$$

where

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

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

$$\omega = \pi - \theta \quad (32)$$

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

For $0 < \theta < 0.175$ radian,

$$T = 0.6366 \theta + 0.09591 \theta^2 - 0.06144 \theta^3 \quad (34)$$

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

$$T = 8.957 \cdot 10^{-5} + 0.6333 \theta + 0.1160 \theta^2 - 0.08878 \theta^3 + 0.01033 \theta^4 \quad (35)$$

3.2.7 Height of Sessile Droplet.

The droplet height² is given by the following equations:

$$\lambda = 1 + 0.75 [2 \sin \theta / (1 - \cos \theta)]^2 \quad (36)$$

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

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:

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