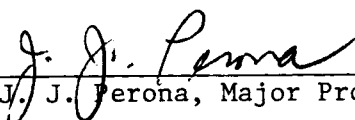
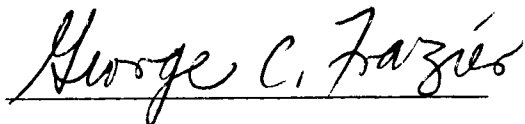


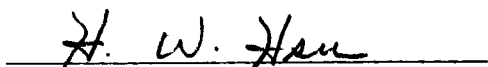
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I am submitting herewith a dissertation written by Walter David Bruce entitled "An Experimental Investigation of Direct Contact Three Phase Boiling Heat Transfer." I have examined the final copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Chemical Engineering.


J. J. Perona, Major Professor

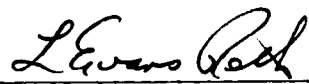
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and recommend its acceptance:







Accepted for the Council:


Vice Chancellor
Graduate Studies and Research

AN EXPERIMENTAL INVESTIGATION OF
DIRECT CONTACT THREE PHASE
BOILING HEAT TRANSFER

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Walter David Bruce

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ABSTRACT

Direct contact heat transfer between immiscible liquid phases is attractive for several reasons. It has potential applications in water desalination and geothermal energy utilization, and it is more efficient than conventional means of heat transfer utilizing metallic transfer surfaces, which are subject to corrosion and scale formation.

The system which was studied in the present work consisted of one liquid undergoing vaporization by contact with a hotter immiscible liquid. The liquids and vapor were contacted in a counterflow spray column with only differential increases in vapor quality. Experiments yielded vertical temperature profiles, flow rates of the phases, liquid holdups, pressure drops, and a characterization of flow patterns. A micro-computer was utilized for measuring temperatures in the column at the rate of 1500 to 1600 times per second at several depths.

Analysis of the experimental data indicate that the maximum temperature difference between the phases is 0.5°F , and that a temperature crossover occurs at the lower end of the column. The heat transfer fluid undergoes flash vaporization at its inlet at the top of the column, and much of its sensible heat is transferred to the dispersed phase near the top of the column. Temperature profiles along the length of the boiler are nearly flat, and very little heat transfer occurs in the lower part of the boiler.

A chemical method was developed for measuring effective interfacial area in a direct contact boiler. The theoretical basis of the method is discussed, and physico-chemical data necessary for application

of the technique are reported. Water solubility of methyl salicylate was measured as a function of temperature, and the second order reaction rate coefficient for saponification of methyl salicylate by sodium hydroxide was determined from sodium hydroxide concentration versus time data and a computer model of a well-mixed semibatch reactor. The activation energy for the reaction was found to be 9.58 kilocalories per gram mole.

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PART I: SYMBOLS AND ABBREVIATIONS

<u>Symbol or Abbreviation</u>	<u>Meaning or Description</u>	<u>Typical Units</u>
C_P	Specific Heat Capacity at Constant Pressure	BTU/lb _m °F
E	Electrical potential	millivolts
H_A	Aqueous Phase Holdup (Gas- Free Basis)	Dimensionless
H_A^*	Aqueous Phase Holdup	Dimensionless
LMTD	Logarithmic Mean Temperature Difference	F°
M	Molecular Weight	Grams per gram-mole
$\dot{m}$	Mass Flow Rate	lb _m /hr
M.S.	Methyl Salicylate	-
N_{Ja}	Jakob Number	Dimensionless
N_{Nu}	Nusselt Number	Dimensionless
N_{Pe}	Peclet Number	Dimensionless
N_{Pr}	Prandtl Number	Dimensionless
N_{St}	Stanton Number	Dimensionless
n	Number of Moles	Gram-moles
P	System Pressure	mm Hg
P_i	Equilibrium Vapor Pressure for Pure Component i	mm Hg
$\bar{P}_i$	Actual Partial Vapor Pressure of Component i	mm Hg
P_t	Total Vapor Pressure	mm Hg
Q	Volumetric Flow Rate	SCFM
$\dot{q}$	Rate of Heat Transfer	BTU/hr

PART I: SYMBOLS AND ABBREVIATIONS (continued)

<u>Symbol or Abbreviation</u>	<u>Meaning or Description</u>	<u>Typical Units</u>
SCFM	Standard Cubic Feet Per Minute	ft^3/min
T	Temperature	$^{\circ}\text{F}$
V	Volume	milliliters or ft^3
α	Void Fraction	Dimensionless
η	Efficiency	Dimensionless
ρ	Density	lb_m/ft^3 or Grams/ml
σ	Surface Tension	Dyne/cm
λ	Latent Heat of Vaporization	BTU/lb_m

Subscripts

A	Component A	-
B	Component B	-
c	Continuous Phase	-
d	Dispersed Phase	-
I	Inert Gas	-
l	Liquid	-
v	Vapor	-

PART II: SYMBOLS AND ABBREVIATIONS

<u>Symbol or Abbreviation</u>	<u>Meaning or Description</u>	<u>Typical Units</u>
a	Liquid-liquid interfacial area per unit volume of dispersion	cm^2/cm^3
A_i	Interfacial area in stirred cell.	cm^2
A°	Bulk concentration of species A in phase B	$\text{gm-moles}/\text{cm}^3$
B°	Bulk concentration of species B in phase B	$\text{gm-moles}/\text{cm}^3$
$\overline{B}^\circ$	Average bulk concentration of B in phase B	$\text{gm-moles}/\text{cm}^3$
C^*	Solubility of species A in phase B	$\text{gm-moles}/\text{cm}^3$
C_A	Concentration of species A	$\text{gm-moles}/\text{cm}^3$
C_{Ao}	Initial bulk concentration of species A in aqueous phase	$\text{gm-moles}/\text{cm}^3$
C_B	Concentration of species B	$\text{gm-moles}/\text{cm}^3$
$C_B(t)$	Concentration of species B as a function of time	$\text{gm-moles}/\text{cm}^3$
C_{Bo}	Initial bulk concentration of species B in aqueous phase	$\text{gm-mole}/\text{cm}^3$
CSMP	Continuous System Modeling Program	-
D	Inside Diameter of column	cm
D_a	Diameter of agitator	cm
D_{AB}	Diffusivity of species A in phase B	cm^2/sec
D_{BB}	Diffusivity of species B in phase B	cm^2/sec

PART II: SYMBOLS AND ABBREVIATIONS (continued)

<u>Symbol or Abbreviation</u>	<u>Meaning or Description</u>	<u>Typical Units</u>
E	Enhancement factor	Dimensionless
E_i	Enhancement factor corresponding to an instantaneous reaction	Dimensionless
E_a	Arrhenius activation energy	Calories/gm-mole
gm	Abbreviation for "gram," a unit of mass	-
k_L	Mass transfer coefficient	cm/sec
k_1	First order or pseudo-first order reaction rate coeffi- cient	sec ⁻¹
k_2	Second order reaction rate coefficient	cm ³ /(gm-mole sec)
L	Length of column filled with dispersion	cm
M	$M = D_{AB} k_2 B^0 / k_L^2$	Dimensionless
meq	Abbreviation for milliequivalent	
N_{Re_w}	Reynolds number for light phase, $\frac{D_a^2 n_p}{\mu}$	Dimensionless
N_{Re_m}	Reynolds number for heavy phase, $\frac{D_a^2 n_p}{\mu}$	Dimensionless
N_{Sc_w}	Schmidt number for light phase, $N_{Sc_w} = \frac{\mu}{\rho D_{AB}}$	Dimensionless
N_{Sh}	Sherwood number $N_{Sh} = \frac{k_L D_a}{D_{AB}}$	Dimensionless

PART II: SYMBOLS AND ABBREVIATIONS (continued)

<u>Symbol or Abbreviation</u>	<u>Meaning or Description</u>	<u>Typical Units</u>
n	Agitator speed	revolutions/sec
Q_d	Volumetric flowrate of dispersed phase	cm^3/sec
R	Universal Gas Law Constant	calories/gm- mole K
R	Rate of extraction per unit area over contact time t	$\text{gm-moles}/\text{cm}^2 \text{sec}$
$\bar{R}$	Average rate of extraction per unit area over contact time t	$\text{gm-moles}/\text{cm}^2 \text{sec}$
$\bar{R}_a$	Rate of extraction per unit volume of dispersion over contact time t	$\text{gm-moles}/\text{cm}^3 \text{sec}$
RPM	Abbreviation for Revolutions Per Minute	-
s	Laplace domain variable or fractional rate of surface renewal	sec^{-1}
r_A	Rate of chemical reaction based on species A	$\text{gm-moles}/\text{cm}^3 \text{sec}$
t	Time	sec
T	Absolute temperature	K
V	Volume of aqueous phase in stirred cell	cm^3
x	Distance away from interface into aqueous phase	cm
Z	Stoichiometric coefficient for species B	-
δ	Film thickness	cm

PART II: SYMBOLS AND ABBREVIATIONS (continued)

<u>Symbol or Abbreviation</u>	<u>Meaning or Description</u>	<u>Typical Units</u>
μ	Viscosity	gm/cm sec
ρ	Density	gm/cm ³
$\Rightarrow$	Implies	-

COMPUTER PROGRAM NOMENCLATURE

<u>Symbol Used In Program</u>	<u>Description or Synonymous Variable Described in List Above</u>
AI	A_i
CA	C_A
CB	C_B
CAO	C_{Ao}
CBO	C_{Bo}
CSTAR	C^*
DCADT	dC_A/dt
DCBDT	dC_B/dt
KL	k_L
TIME	t
TRANS	Mass Transport terms in model of stirred cell
Z	k_2

PART I

Characterization of the
Heat Transfer Processes
in a Direct Contact Boiler

I. INTRODUCTION

Recent interest in economical techniques for water desalination and quests for methods of geothermal energy utilization have stimulated research in direct contact heat transfer. Of special importance is a three-phase heat exchanger in which immiscible liquids are contacted and one of them simultaneously undergoes vaporization. In a three-phase heat exchanger, the sensible heat of one phase, usually the continuous phase, provides the latent heat for vaporization of the other phase.

Heat transfer in a three-phase heat exchanger is very efficient. Studies of evaporation of single pentane drops in water yielded overall heat transfer coefficients of $4097 \text{ BTU/hr ft}^2 \text{ }^\circ\text{F}$, based on the initial surface area of an evaporating drop.¹ In another study, evaporation of refrigerant-113 in water was investigated, and conservative values of $620 \text{ BTU/hr ft}^2 \text{ }^\circ\text{F}$ were reported, based on the total surface area of the injection manifold used for introduction of refrigerant-113.² Typical values of overall heat transfer coefficients for conventional heat exchangers utilizing metallic transfer surfaces range from 50 to 150 $\text{BTU/hr ft}^2 \text{ }^\circ\text{F}$.³

Direct contact exchangers have several other advantages. For example, corrosion or fouling of tubes is not a problem. Also, closer temperature approaches can be obtained between the fluids being contacted. Larger and more effective heat transfer area may be obtained. Equipment is of simple design, relatively inexpensive, and maintenance costs are low. Three-phase direct contact exchangers can be used for heat transfer

at various temperature levels, depending on the choice of the heat transfer fluids.

A few problems do exist with utilization of direct contact heat exchange. In the case of a dispersed phase passing through and simultaneously evaporating in a continuous phase, the continuous phase becomes saturated with the dispersed phase, and in some cases may require special design considerations.

Multiphase direct contact heat transfer is either being used or has been proposed for several industrial applications. One example is that of water desalination by direct contact freezing. In recent years, water desalination by this technique has been studied and experimental pilot plants have been built to generate useful design data.

Desalination by direct contact freezing is achieved in a four-phase heat exchanger in which a dispersed, immiscible, volatile fluid (such as liquid butane) evaporates in salt water. As the dispersed phase evaporates, part of the water is frozen. The dispersed phase vapor is removed from the top of the unit and is brought into contact with the ice that has been removed from the unit, thus melting the ice and simultaneously condensing the working fluid, which is recycled to the freezing unit.

With the current energy crisis, investigation of efficient techniques of heat transfer for energy conservation have become more important, and new alternate energy sources are under consideration. For example, utilization of geothermal brine in a direct contact heat exchanger in a secondary fluid power cycle has been proposed.

The scope of the present work includes characterization of the heat transfer processes occurring in a direct contact boiler, and development of a technique for measurement of liquid-liquid interfacial area in a direct contact heat exchanger. Characterization of the heat transfer processes includes reporting and manipulation of data describing temperature profiles in the boiler, flow rates of the phases, liquid holdup, and other pertinent information. Development of the interfacial area measurement technique includes a discussion of the theory of the proposed chemical technique, measurement of the required physico-chemical data, and a description of the data and equations needed to apply the technique to a direct contact boiler.

Additional research is required to supply the information needed to establish general design criteria for a direct contact boiler. For example, the effect of the physical properties of the heat transfer fluids used in the boiler must be determined by employing a variety of other heat transfer fluids. A mathematical model of the kinetics of flash vaporization in a direct contact boiler may be useful to establish the vessel volume necessary for equilibration of the phases. Finally, actual measurements of interfacial area in the boiler should be conducted to evaluate the proposed method.

Although much interest has developed recently concerning heat transfer with change of phase, additional research will serve to clarify the basic mechanisms of heat transfer between the dispersed and continuous phases. The present work contributes to the basic knowledge necessary for understanding these heat transfer mechanisms and to the parameters important for design of exchangers of this type.

II. BACKGROUND

A. Experimental

In a two-phase direct contact heat exchanger, a single phase of one fluid is brought into direct contact with a single phase of another fluid; however, a three-phase direct contact heat exchanger denotes a device in which a single phase of one fluid is directly contacted with a second phase of another fluid which simultaneously undergoes vaporization. Although many experimental and theoretical studies have been performed concerning two-phase direct contact heat exchangers, few studies dealing with three-phase direct contact heat exchangers are cited in the literature.²

Studies of single drops of an immiscible, dispersed liquid phase evaporating in a continuous liquid phase were conducted by Sideman and Taitel¹ and Sideman and Hirsch.⁴ Through cinecamera studies of butane or pentane drops evaporating in a stagnant water phase, Sideman and Taitel observed that as a droplet of dispersed phase evaporates, the vapor concentrates in the upper part of the drop, but the liquid portion collects at the bottom of the drop. They also found that the surface area of the bubble increases as it rises in the continuous phase, and the flow characteristics of the droplet approach those of a gas bubble as evaporation of the dispersed phase progresses.

Several other important results of the single drop studies discussed by Sideman⁵ are summarized below:

- (1) Some superheating of a drop is necessary to initiate ebullition.

Onset of nucleation depends on the drop size, external disturbances, and the degree of purity of the liquids being contacted.

Impurities in the liquids tend to promote nucleation.

- (2) Evaporation time of a drop is inversely proportional to the log-mean temperature driving force.
- (3) The optimal column height (defined as the height in which evaporation is complete but no superheating of the vapors occurs) is inversely proportional to the log-mean temperature driving force.
- (4) Based on the initial surface area of a drop, the overall heat transfer coefficient was found to be almost independent of the log-mean temperature driving force over the range studied (up to 27 F°).
- (5) Most of the heat transfer takes place at the liquid-liquid interface.
- (6) Based on the initial surface area of a drop, values of overall heat transfer coefficients for pentane drops evaporating in sea water ranged from 199 to 699 BTU/hr ft² °F, depending on initial drop diameter. The overall heat transfer coefficient values decrease linearly with increasing initial drop diameter.

A limited number of studies have been conducted concerning multidrop vaporization of a dispersed phase in continuous liquid media. Wilke, et al.,⁶ studied evaporation of water from sea water by direct cocurrent contact with hot Arochlor in a 3-inch pipe. The water vapor thus generated was condensed by direct contact with cold Arochlor in a packed column. They concluded that the volumetric heat transfer coefficient is a function of total mass velocity, and that neither the temperature driving force nor the flow ratio of dispersed to continuous phases significantly affects the volumetric heat transfer coefficient.

Harriott and Wiegandt⁷ proposed a closed evaporation and condensation refrigeration cycle for desalination of sea water. They also reported experimental data for condensation of methylene chloride in water (in counter-current flow) in a single-stage sieve plate column, and in a two stage packed bed. Limited data are also reported for evaporation of methylene chloride or pentane in continuous cocurrent upflow with water in a single stage 2-inch diameter column. The methylene chloride or pentane was mixed with water prior to its entry into the column. Based on an exit approach temperature of $0.9\text{ }^{\circ}\text{F}$ and 1 ft. length of pipe, volumetric heat transfer coefficients of 1.70×10^5 BTU/hr ft³ $^{\circ}\text{F}$ were obtained. Although this value is an order of magnitude larger than that reported for a countercurrent spray column, Sideman⁵ suggests that this is probably due to the close temperature approach ($0.9\text{ }^{\circ}\text{F}$) and better atomization of the dispersed phase.

Sideman, Hirsch, and Gat⁸ and Sideman and Gat⁹ have performed some very informative studies of three-phase heat exchangers. In Sideman and Gat's study, heat transfer characteristics were investigated for a 70mm diameter spray column in which a continuous water phase was contacted countercurrently with pentane droplets, which evaporated while rising in the continuous phase. Three distinct operating zones were observed for this spray column:

- (1) Free-rise zone
- (2) Turbulent zone
- (3) Foam zone

Sideman⁵ compares the free-rise zone at the bottom of the column to the "streamline" region in gas-liquid contacting systems at low flow rates

and low holdups. As the drops rise and evaporation occurs, the superficial gas velocity increases. Coalescence of drops begins and a turbulent zone is established. Above the turbulent zone a foam layer is developed. This layer was considered to have contributed little to the heat transfer. The most important results of Sideman's and Gat's study are summarized below:

- (1) The volumetric heat transfer coefficient was found to depend strongly on the log-mean temperature driving force, the water exit approach temperature and the pentane flow rate. The volumetric coefficient increases with decreasing values of the log-mean temperature difference and water exit approach temperature, and increasing values of pentane flow rate (up to the flooding point).
- (2) If volumetric heat transfer coefficient values are plotted as a function of the mass flow ratio of dispersed to continuous phases, the volumetric coefficient increases with increasing flow ratio up to a maximum value (flood point). Then the volumetric coefficient decreases with increasing flow ratio to an asymptotic value.
- (3) The effect of the continuous phase (water) flow rate on the volumetric heat transfer coefficient and on other variables studied was found to be small.
- (4) The optimal column height, defined as the column height in which evaporation is complete, but no superheating of vapors occurs, yields the maximum volumetric heat transfer coefficient. Optimum column height increases with increasing pentane flow

rate and decreases with decreasing water exit approach temperature.

- (5) It was found that single drop studies differed in several respects with this spray column study. In a spray column, the onset of nucleation is not simultaneous for all drops being vaporized, and coalescence of drops occurs in a spray column, thus affecting its heat transfer characteristics. Optimal column heights for this spray column study were found to differ from optimal column heights determined in single drop studies. Also, in this study, the volumetric heat transfer coefficient was found to be strongly dependent on the log-mean temperature driving force. In single drop studies, heat transfer coefficients based on initial surface area of an evaporating drop were found to be almost independent of the log-mean temperature driving force over the range studied.
- (6) Values of the volumetric heat transfer coefficient determined in this study ranged from 6230 to 12,510 BTU/hr ft³ °F for water exit approach temperatures of 3.1 F° or larger.
- (7) Sideman and Gat state that columns with larger diameters, better design, and closer water outlet temperature approaches would yield higher volumetric heat transfer coefficients. They also recommend a mixing device to increase turbulence to give a more uniform distribution of dispersed phase, and thus to increase the volumetric coefficient value.

Blair, Boehm and Jacobs² did an experimental study similar to that of Sideman and Gat. They studied heat transfer characteristics of a three-phase direct-contact spray column heat exchanger in which the

continuous water phase was contacted with refrigerant-113. Water entered at the top of the column and refrigerant-113 was injected at the bottom in an effort to achieve near counterflow operation. Values of volumetric heat transfer coefficients obtained for contacting water and refrigerant-113 ranged from 260 to 4260 BTU/hr ft³ °F with a water exit approach temperature of 23.4 F° or larger.

Blair, Boehm and Jacobs compared the results of their spray column study with the results obtained by Sideman and Gat; however, their comparison is not strictly valid. In Sideman's and Gat's study, true counterflow operation was achieved between pentane and water, but Blair, Boehm, and Jacobs injected refrigerant-113 into the aqueous stream. Since the injected refrigerant-113 liquid is denser than water, flow patterns of the evaporating refrigerant are obviously different than those of pentane drops evaporating while rising in the continuous water phase.

One study of great importance and relevance to the present work is a pilot plant study performed by DSS Engineers, Inc.¹⁰ The study was performed at a test facility located at Wrightsville Beach, North Carolina at the U.S. Department of Interior Office of Water Research Technology. The work was done under contract with the U.S. Department of Energy.

In this study by DSS Engineers, an aqueous synthetic brine solution (21% NaCl) was contacted countercurrently with the dispersed phase, isobutane. Isobutane was chosen as the working fluid because of all fluids studied, it yields the maximum gross work extractable from a pound of brine over a wide range of brine temperatures.

The test apparatus in the study included a direct contact spray column boiler and a separate direct contact preheater, each six inches in diameter by six feet tall. Brine entered at the top of each vessel and exited at the bottom. Isobutane entered at the bottom of the preheater through a distributor plate to produce 0.15 inch diameter drops. Isobutane leaving the preheater entered the boiler as a saturated liquid. Vapor leaving the boiler had between 0 and 25 F° of superheat.

The equipment described above operated with no major problems. Volumetric heat transfer coefficients for the boiler ranged up to 1.70×10^4 BTU/hr ft³ °F.

An important comment made by DSS Engineers¹⁰ is that there is presently no method of designing a spray tower heat exchanger with confidence. This is especially true of towers greater than sixteen inches in diameter, since the effect of backmixing on the heat transfer has not been defined.

Another pertinent pilot plant scale direct contact heat exchanger study is the one currently being conducted at East Mesa in southern California's Imperial Valley.¹¹ This 500-kW plant was funded by the United States Department of Energy and was designed and built by Barber-Nichols Engineering Company under the direction of the University of California's Lawrence Berkeley Laboratory. Data from this pilot plant will be used to design a commercial scale plant.

Rapier discusses the performance of the direct contact heat exchanger unit at East Mesa and makes some recommendations concerning performance evaluation and direct contact boiler design.¹² According to Rapier, the unit at East Mesa is a combined countercurrent preheater and boiler which utilizes geothermal brine to vaporize isobutane. During

preliminary tests, the unit has met or exceeded the performance of its predecessors, the volume and surface type boilers. Additional tests are planned for 1981.

Rapier made some interesting recommendations concerning boiler performance and design. He stated that the criterion for performance of the preheater-boiler combination is the classical steam distillation efficiency. This efficiency is defined as the partial pressure actually exerted by the working fluid to its saturation pressure at the vapor exit temperature. Another recommendation made by Rapier is that the best boiler configuration is obtained by conventional mixing nozzle and flash drum design. Heat transfer in the boiler occurs only as a result of adiabatic mixing and isothermal separation.

B. Theoretical

Sideman and Taitel¹ studied evaporation of pentane drops in a continuous, stagnant water phase. In addition to their experimental work, cited earlier, they also conducted a theoretical study. By assuming an evaporating, volatile liquid drop at constant boiling temperature to be a sphere of constant radius moving in a potential flow field and convection at the outside of the drop controlling, an analytical solution for the steady state heat transfer was obtained. Heat transfer coefficients were obtained as a function of the opening angle of the vapor phase.

Their expression for the average Nusselt number is

$$(N_{Nu})_c = \left(\frac{3 \cos \beta - \cos^3 \beta + 2}{\pi} \right)^{0.5} (N_{Pe})_c^{0.5} \quad (1)$$

Definition of the vapor phase opening angle is clarified in Figure 1. If the angle β is zero, the equation of Boussinesq and Higbie for potential flow past a sphere is obtained:

$$(N_{Nu})_c = 1.13 (N_{Pe})_c^{0.5} \quad (2)$$

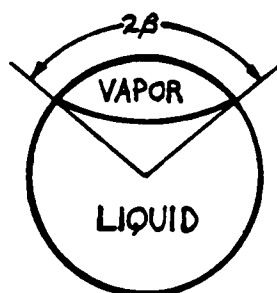


Figure 1. Definition of opening angle of vapor phase^a.

a. Based on Sideman, S. and Taitel, Y., "Direct Contact Heat Transfer With Change of Phase: Evaporation of Drops in an Immiscible Liquid Medium," International Journal of Heat and Mass Transfer, Vol. 7, 1964, pp. 1273-1289.

Sideman and Taitel also stated that the overall heat transfer coefficient related to the instantaneous total area of the two phase drop increases rapidly with evaporation up to 3-10% vapor content and then decreases until vaporization of the drop is completed. This indicates decreasing internal resistance in the initial stages of evaporation.

Sideman and Hirsch⁴ calculated the relative importance of internal and external resistance and stated that at the very beginning of evaporation of a drop, internal resistance to heat transfer is controlling and that this initial period of overcoming internal resistance requires about half the total evaporation time. Past this initial period, however, the external resistance to heat transfer is controlling over more than 70% of the evaporation process. Consequently, a smaller heat exchanger

volume is required if the dispersed phase is introduced as a saturated liquid or containing some vapor. Sideman and Gat⁹ confirmed this. They found that with only slight superheating of the pentane, vaporization occurred at the distribution plate, and the free-rise zone of the column was almost non-existent.

Jacobs, et al. have correlated overall heat transfer coefficient data for direct contact boilers of the surface type and spray column type¹³. Experimental data for their Freon-water system are correlated reasonably well by the equation:

$$N_{St} = \frac{\dot{q}}{(LMTD)(\dot{m} C_p)_{d.l.}} = 2.0 (N_{Ja} N_{Pr})_{d.v.}^{0.6} \left(\frac{\dot{m}_c}{\dot{m}_d} \right)^{0.15} \quad (3)$$

The success of the preceding correlation of Jacobs tends to illustrate which physical properties are likely to be of greatest overall importance. It is interesting to note that surface tension does not appear in the correlation, and this would indicate that in the macroscopic sense the effect of surface tension must be of minor importance.

Blander and Katz discuss the effect of surface tension on bubble nucleation at a liquid-liquid interface¹⁴. When a volatile liquid (liquid A) is superheated in the presence of another liquid (liquid B) the result depends on the relative magnitudes of the surface and interfacial tensions. Nucleation can occur in three possible ways (See Figure 2 for nomenclature and graphical illustration):

- (1) If $\sigma_B > \sigma_A + \sigma_{AB}$, homogeneous nucleation occurs within liquid "A" since more work is required to form a bubble at the interface in this case than to form a bubble in liquid "A."

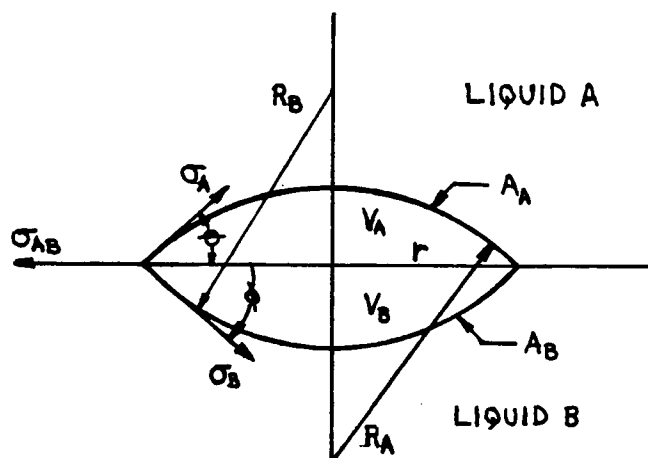


Figure 2. Gas Bubble at a Liquid-Liquid Interface^a.

Nomenclature for Figure 2.

- r: Radius of bubble at a planar interface
- A: Surface area of bubble
- R: Radius of curvature
- σ : Surface tension at liquid-gas interface
- V: Volume
- θ : Contact angle of liquid
- ϕ : Contact angle of liquid
- σ_{AB} : Interfacial free energy per unit area of the A-B interface

a. Taken from Blander, M. and Katz, J. L., "Bubble Nucleation in Liquids," AIChE Journal, Vol. 21, No. 5, 1975.

- (2) If $\sigma_A \geq \sigma_B + \sigma_{AB}$, homogeneous nucleation occurs within liquid "B." In this case, some mechanism is required to transport molecules of "A" into liquid "B." If the bubbles are near the interface, diffusion of "A" into "B" is a likely mechanism. If the bubble is entirely in "B" except for a small opening into phase "A," a bubble blowing mechanism can supply component "A" to the bubble.
- (3) If $\sigma_A < \sigma_B + \sigma_{AB}$ and $\sigma_B < \sigma_A + \sigma_{AB}$, heterogeneous nucleation at the interface between phases "A" and "B" can occur.

The better a given liquid wets the surface it contacts, the more probable is nucleation in the interior of the liquid and the less probable is heterogeneous nucleation at a liquid or solid interface¹⁴.

It has been found in studies for measurement of interfacial contact area in horizontal pipeline contactors¹⁵ and in agitated tanks¹⁶ at ambient temperature that an increase in interfacial tension results in an increase in dispersed phase droplet size with a subsequent reduction in interfacial area per unit volume. Therefore, one would expect surface tension to affect the rate of heat transfer in a direct contact boiler, since surface tension apparently affects the magnitude of the interfacial area per unit volume.

III. THEORY

A. Flash Distillation Kinetics

It was mentioned earlier that conventional mixing nozzle and flash-drum design have been suggested as the appropriate means for designing a direct contact boiler. It was also stated that the criterion for performance of a direct contact boiler is the classical steam distillation efficiency. In this section, the theory of flash distillation kinetics is discussed, and methods are developed for estimating the boiling point of a two-phase mixture and for calculating direct contact boiler efficiency. The effect of the presence of an inert gas on boiler efficiency is also addressed.

A search of the literature on flash distillation and flash distillation kinetics has revealed no information concerning the kinetics of flash distillation involving immiscible liquid phases. Only one paper, the study of Porteous and Muncaster,¹⁷ was found which deals with the kinetics of equilibration of a flashing liquid. That paper was directed largely toward design improvements in multistage flash distillation processes for water desalination.

Porteous and Muncaster¹⁷ developed a mathematical model applicable to flashing flow through open channels, nozzles, or short tubes. The model can be used to determine the rate at which a liquid in flashing flow achieves equilibrium with its own vapor, and shows that the equilibration process is governed by an exponential decay equation. A more complete description of the model of Porteous and Muncaster is given in Appendix A.

In a direct contact boiler, the flashing of the heat transfer fluid, methyl salicylate in the present case, is accompanied by boiling of the working fluid. Also, the flow of the fluids is countercurrent. Consequently, the model of Porteous and Muncaster¹⁷ is not directly applicable to the complex situation existing in a direct contact boiler; however, an approach that is analogous to theirs may prove to be useful in future direct contact boiler modeling efforts.

B. Boiling Point of a Two Phase Mixture

According to Smith,¹⁸ it is usually assumed that hydrocarbons and water are completely immiscible for flash distillation calculations. Consequently, each phase exerts its own vapor pressure, and the total vapor pressure is the sum of the individual vapor pressures:

$$P_t = P_A + P_B \quad (4)$$

The individual vapor pressures for liquids A and B are a function of temperature, and as the temperature is increased, P_t increases. When P_t equals the system pressure, P , the bubble point has been reached.

Calculation of the bubble point at equilibrium conditions for a system of immiscible liquids is a trial and error search to find a temperature such that

$$P = P_t = P_A + P_B \quad (5)$$

Equations giving the vapor pressure of a compound as a function of temperature, such as the Antoine equation, are useful for this calculation. Appendix B contains some vapor pressure data and other physical property data for methyl salicylate and water, and Appendix C contains sample calculations of this type.

C. Calculation of Direct Contact Boiler Efficiency

1. Case I: No Inert Gas Present. McCabe and Smith¹⁹ discuss the process of steam distillation in which live steam is used to vaporize a desired component from a mixture containing non-volatile impurities. The vaporization efficiency is defined, and is based on the desired materials being vaporized. In the case of the direct contact boiler in the present work, the situation is reversed. Steam is the desired product, and the heat transfer fluid is methyl salicylate. Therefore, the vaporization efficiency is based on water, rather than methyl salicylate. An expression for the vaporization efficiency is derived below.

The vaporization efficiency for water (component A) is defined by:

$$\eta_A = \frac{\bar{P}_A}{P_A} \quad (6)$$

Since the contacting of methyl salicylate (component B) and water is not perfect in the boiler, the actual partial pressure of water is less than the vapor pressure of water at the specified temperature. The vaporization efficiency accounts for this difference.

In the vapor going overhead to the condenser, the components are in the molecular ratio of their partial pressures

$$\frac{\dot{m}_A}{\dot{m}_B} = \frac{n_A M_A}{n_B M_B} = \frac{\bar{P}_A M_A}{\bar{P}_B M_B} = \frac{\bar{P}_A M_A}{(P - \bar{P}_A) M_B} \quad (7)$$

One may substitute for $\bar{P}_A$:

$$\bar{P}_A = \eta_A P_A \quad (8)$$

Rearranging and solving for η_A , the expression for vaporization efficiency based on component A is obtained:

$$\eta_A = \frac{P M_B}{\left[\left(\frac{\dot{m}_B}{\dot{m}_A} \right) M_A + M_B \right] P_A} \times 100\% \quad (9)$$

For a given period of operation of the direct contact boiler, an efficiency value may be calculated from equation (9) and experimental data. Measured values of the mass ratio of methyl salicylate to water in the overhead condensate and the barometric pressure are required. The vapor pressure of water at the temperature of the liquid in the boiler, and the molecular weights of the components are available in handbooks.

If one assumes that the water vaporization efficiency is 100% (i.e. perfect contacting of phases), equation (7) reduces to:

$$\frac{\dot{m}_A}{\dot{m}_B} = \frac{P_A M_A}{P_B M_B} \quad (10)$$

$$M_A = 18.016$$

A: water

$$M_B = 152.14$$

B: methyl salicylate

$$\frac{\dot{m}_A}{\dot{m}_B} = 0.118 \frac{P_A}{P_B} \quad (11)$$

Values of the theoretical mass ratio of water to methyl salicylate in the condensate were calculated from equation (11).

2. Case II: A Single Inert Gas Present. If an inert gas, such as nitrogen, is present, equation (5) must be modified because in this case

$$P = \bar{P}_A + \bar{P}_B + \bar{P}_I \quad (12)$$

where $\bar{P}_I$ is the partial pressure of the inert gas. The ratio of water to methyl salicylate in the overhead condensate is also affected:

$$\frac{\dot{m}_A}{\dot{m}_B} = \frac{\bar{P}_A M_A}{\bar{P}_B M_B} = \frac{\bar{P}_A M_A}{(P - \bar{P}_A - \bar{P}_I) M_B} \quad (13)$$

The original definition for η_A in equation (6) is still valid, and one may substitute for $\bar{P}_A$:

$$\bar{P}_A = \eta_A P_A$$

Therefore,

$$\frac{\dot{m}_A}{\dot{m}_B} = \frac{\eta_A P_A M_A}{(P - \eta_A P_A - \bar{P}_I) M_B} \quad (14)$$

One can solve for η_A to obtain

$$\eta_A = \frac{\left(\frac{\dot{m}_A}{\dot{m}_B}\right) M_B (P - \bar{P}_I)}{P_A \left(M_A + \left(\frac{\dot{m}_A}{\dot{m}_B}\right) M_B\right)} \times 100\% \quad (15)$$

This expression for η_A accounts for the presence of an inert gas. If no inert gas is present, the expression reduces to equation (9).

The effect of $\bar{P}_I$ on η_A can be demonstrated more clearly by taking the ratio of equation (15) to equation (9):

$$\frac{\eta_A \text{ inert gas}}{\eta_A} = \frac{\frac{\left(\frac{\dot{m}_A}{\dot{m}_B}\right) M_B (P - \bar{P}_I)}{P_A \left(M_A + \left(\frac{\dot{m}_A}{\dot{m}_B}\right) M_B\right)}}{\frac{\left(\frac{\dot{m}_A}{\dot{m}_B}\right) P M_B}{P_A \left(M_A + \left(\frac{\dot{m}_A}{\dot{m}_B}\right) M_B\right)}} \quad (16)$$

This expression shows that for a given value of $(\dot{m}_A/\dot{m}_B)$ and otherwise similar conditions, the effect of the inert gas is to reduce the vaporization efficiency in proportion to the partial pressure of inert gas.

To calculate water vaporization efficiency values from equation (15), the inert gas partial pressure, $\bar{P}_I$, must be known. An expression is derived below for $\bar{P}_I$ in terms of experimentally determined quantities. Ideal gas behavior has been assumed, and $\dot{m}_A$, $\dot{m}_B$ and $\dot{m}_I$ are steady with time.

$$y_I = \frac{\bar{P}_I}{P} = \frac{n_I}{n} = \frac{\frac{\dot{m}_I}{M_I}}{\frac{\dot{m}_A}{M_A} + \frac{\dot{m}_B}{M_B} + \frac{\dot{m}_I}{M_I}} \quad (17)$$

One may substitute for $\dot{m}_I$,

$$\dot{m}_I = \rho_I \dot{Q}_I$$

and rearrange equation (17) to solve for $\bar{P}_I$.

$$\bar{P}_I = P \frac{\frac{\rho_I \dot{Q}_I}{M_I}}{\frac{\dot{m}_A}{M_A} + \frac{\dot{m}_B}{M_B} + \frac{\rho_I \dot{Q}_I}{M_I}} \quad (18)$$

D. Calculation of Average Holdup and Void Fraction

The average volumetric aqueous phase holdup (on a gas-free basis) in the column is defined as follows:

$$H_A = \frac{V_A}{V_A + V_B} \times 100\% \quad (19)$$

Values of V_A (the volume of aqueous phase) and V_B (the volume of the oil phase) were measured at the end of experimental runs (as described in the "Experimental Equipment and Procedure" section) and H_A was calculated.

The more conventional definition of aqueous phase holdup includes the gas phase volume and is given by:

$$H_A^* = \frac{V_A}{V_{Total}} \times 100\%, \quad (20)$$

where

$$V_{Total} = V_A + V_B + V_G, \quad (21)$$

and V_G is the volume occupied by gas or vapor in the column. In the column used in this work, V_{Total} is the volume of the column up to the aqueous overflow, and is 9210 ml.

Given the quantities defined above, one can also define α , the average void fraction in the column.

$$\alpha = \frac{V_G}{V_{Total}} = \frac{V_{Total} - (V_A + V_B)}{V_{Total}} = 1 - \frac{(V_A + V_B)}{V_{Total}} \quad (22)$$

Values of H_A^* and α were calculated for several of the experimental runs.

IV. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. Description of Equipment

In previous studies of direct contact boiling heat transfer, researchers have only considered situations in which the working fluid was completely vaporized. The present work is unique in the respect that the equipment was designed to allow one to study differential increases in working fluid quality between the column inlet and outlet.

Figure 3 is a sketch of the equipment which was used in this study. In the center is the direct contact heat exchanger column. At the upper left is the methyl salicylate storage tank, and on the upper right is the distilled water storage tank. To the right of the column are the condenser and the condensate receiver. At the lower right is the aqueous phase collection vessel. Also at the lower right is the system for working fluid preheating and metering. At the bottom is the system for metering steam. The designations on Figure 3, such as T 36, R 1, and P 2, represent locations of temperature, flow rate, and pressure measurements, respectively. A summary of these designations and their description is given in Table 1.

Figure 4 focuses on the details of the spray column. The glass column's inside diameter is four inches, and its length is three feet. It was operated in a countercurrent fashion with hot methyl salicylate (the continuous phase) entering at the top and the dispersed phase, usually a mixture of steam and hot water, entering at the bottom. At the top of the column is a flanged brass connection piece which allows some space for vapor-liquid disengagement to minimize entrainment. At the bottom of the column, a stainless steel flanged connection piece

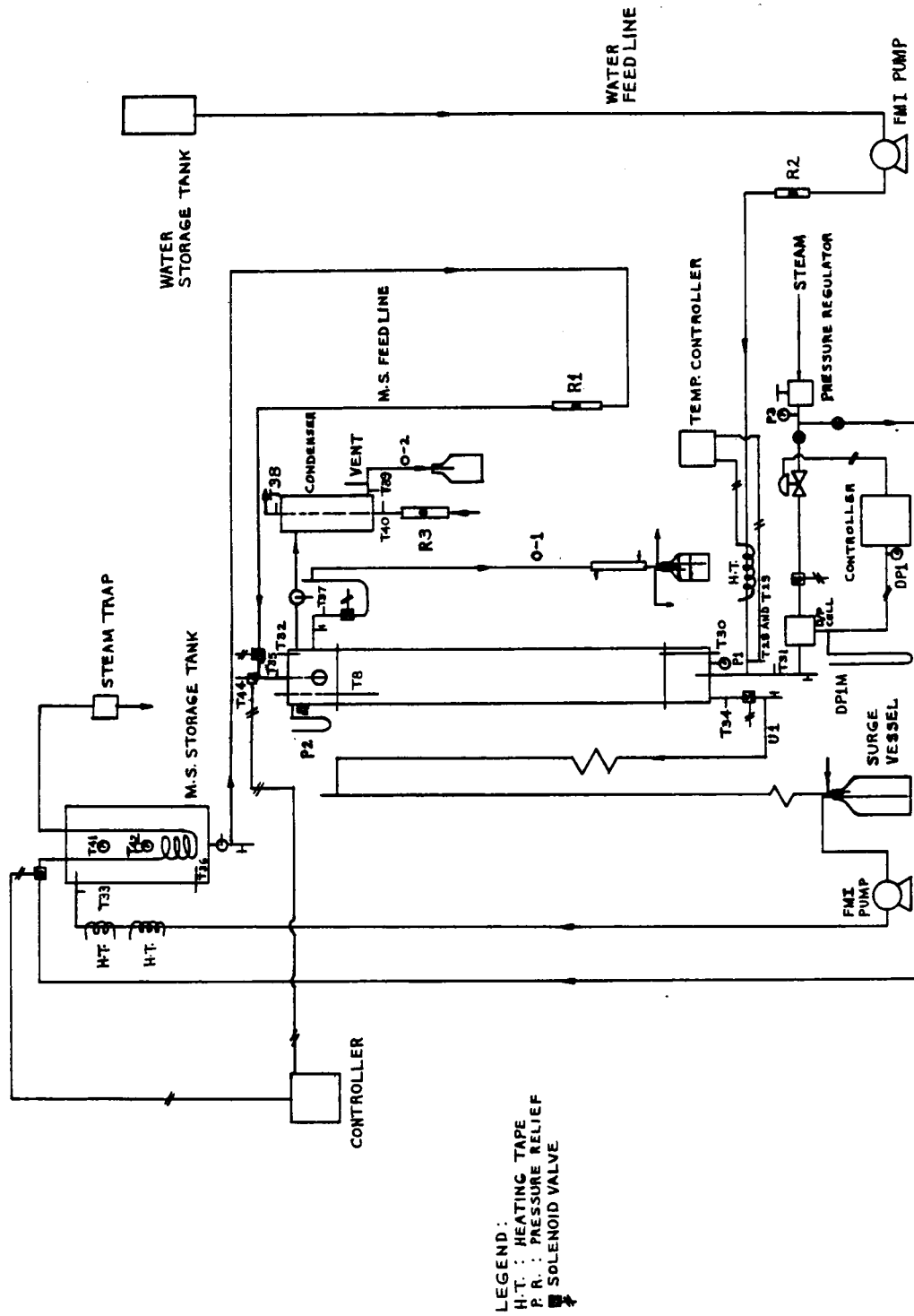


Figure 3. Experimental Apparatus for Study of Boiling Heat Transfer.

TABLE 1

Identification of Temperature, Flow Rate, and
Pressure Measurement Locations on Direct
Contact Boiler Apparatus

ABBREVIATION	DESCRIPTION
T8	Movable thermocouple in column
T28	Hot water to aspirator (controller feedback signal)
T29	Hot water to aspirator
T30	Continuous phase in boiler at bottom (just above demister mesh)
T31	Steam to aspirator
T32	Overhead vapor from column
T33	Methyl salicylate recycle stream to storage tank
T34	Methyl salicylate outlet stream at bottom of column
T35	Methyl salicylate inlet stream at top of column
T36	Methyl salicylate head tank
T37	Aqueous phase overflow from column
T38	Condenser cooling water out
T39	Condensate outlet stream at condenser
T40	Condenser cooling water inlet
T41	Upper dial thermometer on methyl salicylate head tank
T42	Lower dial thermometer on methyl salicylate head tank
T44	Thermometer on methyl salicylate inlet line to column
P1	Pressure gauge at bottom of column
P2	Manometer at top of column
P3	Steam pressure on low pressure side of pressure regulator
DP1	Pressure gauge on steam flow rate controller (differential pressure signal from d/p cell)

TABLE 1 (continued)

ABBREVIATION	DESCRIPTION
DP1M	Manometer on steam flow rate controller (differential pressure signal from d/p cell)
R1	Rotameter for methyl salicylate inlet flow rate
R2	Rotameter for hot water flow rate to aspirator
R3	Rotameter for condenser cooling water
O1	Aqueous phase overflow
O2	Condensate stream from condenser
U1	Methyl salicylate stream out at bottom of column

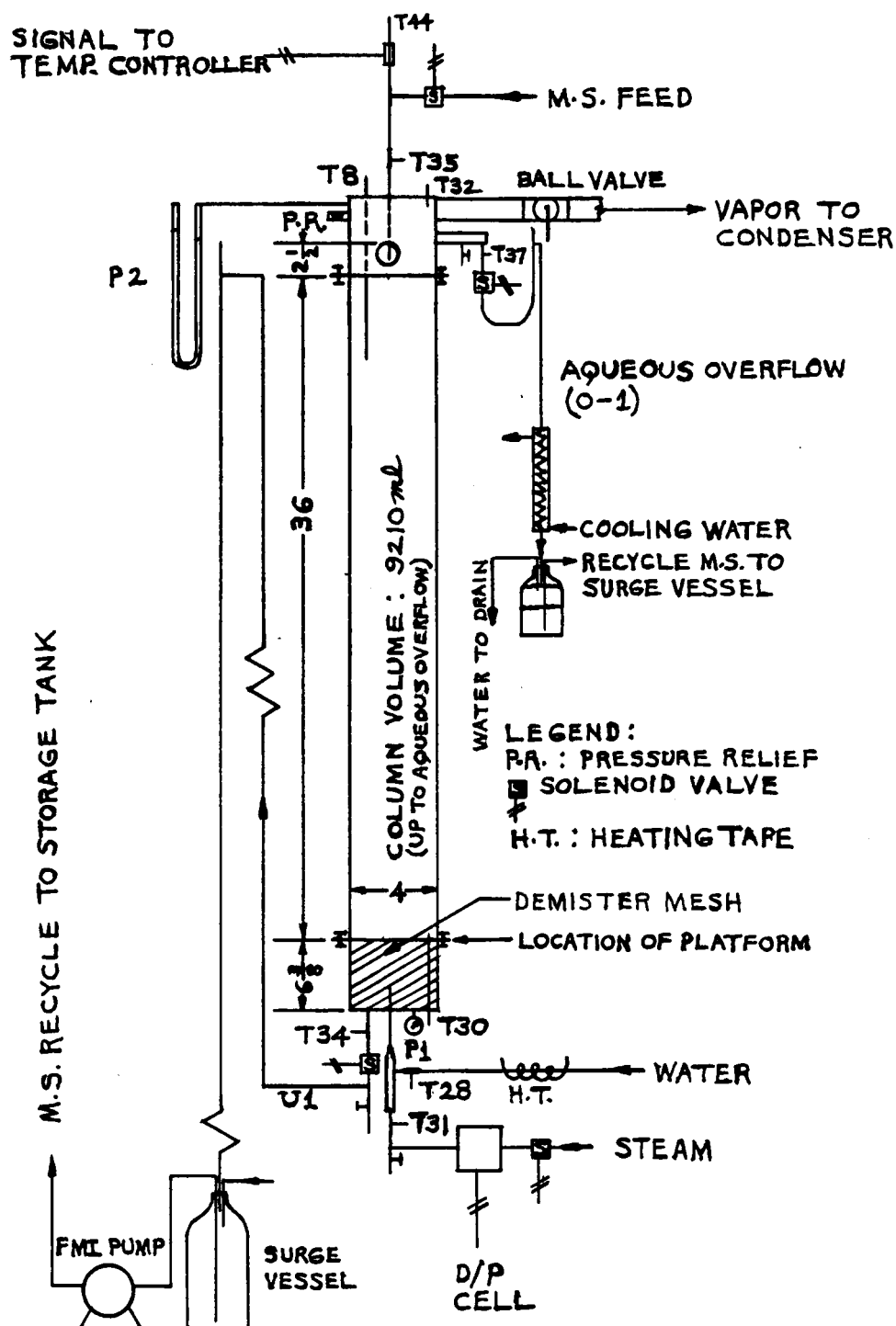


Figure 4. Direct Contact Heat Exchanger Column.

filled with demister mesh allows disengagement of methyl salicylate. The demister mesh disperses the steam-water feed stream randomly and uniformly over the column cross-section.

Flow rates to the apparatus were measured and controlled in various ways. Rotameters were used to measure the flow rates of methyl salicylate and condenser cooling water. Hot water flow rate to the column was metered with a piston pump (Model No. RP-G50-2CSY) manufactured by Fluid Metering, Inc. The steam flow rate was measured with a Foxboro d/p cell having a Type 15A transmitter equipped with an integral orifice manifold assembly which permits measurement of extremely low flow rates of liquids or gases. A pneumatic proportional controller and automatic valve were used in conjunction with the d/p cell for steam flow rate control.

The piston pump that was used for hot water flow rate control has a typical metering accuracy of 1%. It was found that flow pulsation generally occurred, but the time average flow rate was very steady and reproducible. It was also found that the calibration curve (flow rate versus pump setting) is linear over the pump's entire operating range.

Calibration of the d/p cell for steam flow rate measurement is discussed in Appendix D. The calibration curves for the d/p cell, the rotameters, and other flow rate measurement devices are given in Appendix E.

Good control of the temperatures of the feed streams to the column was achieved. Hot water feed temperature control was obtained with an API Instruments Company Model 732 controller to regulate the power input to a heating tape (ca 200 watt) wrapped around the hot water feed line. A thermocouple in the hot water line supplied the feedback signal to the controller. Methyl salicylate feed temperature control

was achieved in two ways. The steam supply pressure was adjusted at the pressure regulator, and a Brookstat proportional controller was used to regulate the steam flow rate to the coil in the methyl salicylate feed tank by opening and closing a solenoid valve in the steam line. The set point temperature was determined by adjusting a sensor clip on a thermometer in the methyl salicylate feed line. Operating experience revealed that the best control of the methyl salicylate feed temperature was achieved simply by adjusting the steam supply pressure.

Temperatures (except for T8) were measured with iron-constantan thermocouples made from 24 gauge wire. The junction was formed with a crimping tool. A Leeds and Northrup potentiometer (Catalog No. 8690) was used to measure the millivoltages.

In experimental runs through number 18, the thermocouple designated as "T8" was a commercially available iron-constantan thermocouple having a one-eighth inch outside diameter sheath. Thermocouple millivoltages were obtained manually by using a potentiometer. Temperatures inside the column were recorded over the entire column length by moving thermocouple T8 vertically.

For experimental runs 19, 20 and 21, thermocouple T8 was an Omega sub-miniature chromel-alumel thermocouple (Catalog No. SCASS-010E-18). The sheath outside diameter was 0.01 inch, but the actual thermocouple was made from 0.0015 inch diameter chromel and alumel wires welded to form a bead of 0.010 inch diameter.

During runs 19, 20 and 21 the signal from thermocouple T8 was fed to a Burr-Brown (Model 3456-B) isolated instrumentation amplifier and then to a Preston (8300XWB, Model A) amplifier. The Preston

amplifier output signal was then fed either to an oscilloscope or to an Applied Micro-Technology digital micro-computer. Data which were fed to the micro-computer were stored on an eight inch IBM Diskette. Temperature data were then retrieved from the disk and transferred to the printer. It should be noted that both amplifiers mentioned above were required to obtain a good signal to noise ratio. Temperatures were measured 1500-1600 times per second with the micro-computer. Temperature measurements were made at depths of 1.5, 6.5, and 10.5 inches below the liquid surface.

Information on thermocouples from vendor literature suggests that the accuracy of uncalibrated iron-constantan or chromel-alumel thermocouples is about ± 2 F°. Experimental measurements in the present work indicate that agreement between different thermocouples which were used for measuring essentially the same temperature were usually within 1.5 F° of each other. For example, in Run 15b, thermocouple T8 indicated 211.7 °F when it was positioned at the bottom of the column against the wire mesh. Thermocouple T30 indicated 212.7 °F at one-quarter inch above the mesh. Thermocouple T34 in the methyl salicylate outlet line indicated 211.5 °F. All of these values differ by no more than 1.2 F°. The precision of reading a given thermocouple is limited by the extent to which one can read the potentiometer, which is approximately to the nearest 0.2 F° in the temperature range under consideration. For the chromel-alumel thermocouple, the precision is limited by amplifier drift, which is no more than one microvolt per degree Celsius or an error of 0.08 F°.

The time constant for a step change in temperature was estimated for the iron-constantan and the chromel-alumel thermocouples. Worst case conditions of laminar flow of methyl salicylate in the column

with no localized agitation by gas bubbles was assumed. For the iron-constantan thermocouple, the time constant was 1.5 seconds, and the chromel-alumel thermocouple time constant was 0.13 seconds. The bead on the chromel-alumel thermocouple was 0.01 inch diameter, which partly accounts for a larger time constant than may have been expected for a thermocouple made from 0.0015 inch diameter wires.

The methyl salicylate used in this research was obtained from Aldrich Chemical Company. This product (Catalog No. M8, 050-4) is 98% pure and has a boiling point of 222°C.

B. Equipment Operation and Procedure

In a typical run for experimental data, the direct contact boiler startup was achieved in the following manner:

1. Condenser cooling water was turned on.
2. Steam was metered to the column through the differential pressure cell orifice for at least an hour to heat the column and the d/p cell body. For runs in which a low steam flow rate was used, a bypass line around the d/p cell was used for more rapid column warmup.
3. While the column was being heated, the methyl salicylate in the feed tank was also heated. Also, the hot water feed tank was filled with distilled water. The hot water temperature controller and feed pump were set at the appropriate values, and hot water feed to the column was begun.
4. When the methyl salicylate in the feed tank had reached the desired value, all steam condensate was drained from the column. With steam and hot water feeds already at the

appropriate values, the column was filled rapidly with methyl salicylate by using a bypass line around the methyl salicylate rotameter. As the level of methyl salicylate neared the aqueous phase overflow, feeding of methyl salicylate was stopped briefly and the standpipe was adjusted to maintain the desired level of dispersion in the column. The standpipe was usually adjusted such that the top of the foam zone was still in view in the sight glass, thus assuring some room was available for vapor-liquid disengagement at the top of the column. Methyl salicylate feed rate to the column was then set on the rotameter (R1).

5. When the level of spent methyl salicylate in the surge vessel was approaching half full, both upper (115 watt) and the lower (192 watt) heating tapes on the methyl salicylate recycle line were turned on, and the methyl salicylate recycle pump was started. The pump was adjusted so that a constant level was maintained in the recycle vessel. The upper heating tape was operated at full power, but the power input to the lower heating tape was varied by adjusting a variable transformer such that the methyl salicylate recycle stream entered the feed tank at its bubble point. Thermocouple T33 gives the temperature of the methyl salicylate recycle stream entering the overhead storage tank.
6. To prevent excessive water holdup in the column, which would cause a phase inversion, a mixture of water and methyl salicylate was removed at the aqueous phase overflow. The water was discarded, but the methyl salicylate was recycled to the

surge vessel receiving the outlet methyl salicylate stream from the column. At this point, the system startup had been completed.

The direct contact boiler was operated until heatup of the equipment had been achieved and stable operation had been attained. With steam flowing through the d/p cell at 0.45 SCFM, approximately two hours are required to achieve complete warmup. This result was obtained from experiments in which steam was fed to the empty column for a given time period, and the condensate was measured. The steam flow rate was calculated and compared to the value obtained from the d/p cell calibration curve.

When system warmup and stable operation had been achieved, a set of data including flow rates, temperatures and pressures was taken. The thermocouple designated as T8 is movable, and was used to obtain temperature data at various depths in the column. Liquid phase holdup was measured at the end of each run. To measure liquid holdup, a large ball valve, located in the vapor line going to the condenser, was closed and at the same time an electrical switch was thrown to close solenoid valves on the other lines. The depth of each phase in the column was noted; but in most cases holdup was measured by draining the contents of the column into glass jugs and then after a short cooling period, the volumes of the phases were measured with a graduated cylinder.

It was mentioned at the beginning of this section that the equipment was designed to allow one to study differential increases in working fluid quality. Experimental runs were conducted at several values of

working fluid inlet quality, which was achieved by blending separate streams of saturated water and saturated steam. The flow rate or temperature of methyl salicylate was adjusted such that the quality of the working fluid leaving the column was only increased by about 10-20% above its entry condition.

The steam and water streams were mixed in an aspirator (Fisher Air-ejector). Hot water at approximately saturated liquid conditions was fed through the side arm of the aspirator, and saturated steam was fed at the wide end of the nozzle. As the steam passed through the converging nozzle, the water and steam were intimately mixed to yield the desired quality of the dispersed phase at the column inlet. The steam temperature and the water temperature were both measured just prior to their entry to the aspirator.

The steam flow rate to the column was always kept less than 17.6 grams per minute to ensure that the column was operated below flooding conditions. The figure of 17.6 grams per minute is based on the discussion of Sideman and Gat⁹ which indicates that the superficial vapor velocity should be kept below 6 cm/sec to avoid flooding in the column. In the experiments of Sideman and Gat, flooding was defined as occurring when the individual bubbles lose their identity.

In a few runs, nitrogen was used in place of or in combination with steam to study the effects of an inert gas on boiler efficiency, and to determine the importance of enhanced phase contacting on heat transfer (such as droplet deformation that increases droplet contact area). In these runs, nitrogen was fed to the column through the same aspirator as the steam and water. The nitrogen flow rate was measured with a rotameter.

V. ANALYSIS OF EXPERIMENTAL DATA

A. Boiler Performance Calculations

Much of the data analysis consisted of calculating vaporization efficiencies, theoretical condensate ratios, and two phase boiling point values for comparison with experimental data obtained for each run and for assessing boiler performance. The method of performing each of these calculations has already been mentioned briefly in the "Theory" section. These calculations are fairly straightforward and need no further clarification here.

One method of assessing boiler performance is to calculate an overall heat transfer coefficient, but this was only possible for Run No. 9. In the other runs, a temperature crossover occurred at the bottom of the column. The temperature of the continuous phase leaving the column was less than the temperature of the dispersed phase entering at the bottom of the column.

In Run No. 9, an overall heat transfer coefficient was calculated based on the volume of the column up to the aqueous overflow:

$$\dot{q} = U V \Delta T_{ln} \quad (23)$$

$$\text{or} \quad U = \frac{\dot{q}}{V \Delta T_{ln}} \quad (24)$$

The heat actually transferred, $\dot{q}$, was obtained from the overhead condensate flow rates of methyl salicylate and water and their respective latent heats of vaporization:

$$\dot{q} = (\dot{m}\lambda)_{\substack{\text{M.S.} \\ \text{Condensate}}} + (\dot{m}\lambda)_{\substack{\text{Water} \\ \text{Condensate}}} \quad (25)$$

The logarithmic mean temperature difference was obtained in the usual manner from the temperature difference between the continuous phase and dispersed phase at the top of the column, ΔT_1 , and the difference between the temperatures of those phases at the bottom of the column, ΔT_2 .

$$\Delta T_{\ln} = \frac{\Delta T_1 - \Delta T_2}{\ln \left(\frac{\Delta T_1}{\Delta T_2} \right)} \quad (26)$$

For Run No. 9, the numbers are given below:

$$\dot{q} = (2.69 \frac{\text{BTU}}{\text{hr}})_{\text{M.S.}} + (89.85 \frac{\text{BTU}}{\text{hr}})_{\text{Water}} = 92.5 \frac{\text{BTU}}{\text{hr}}$$

$$V = 0.325 \text{ ft}^3 \text{ (i.e., 9210 ml)}$$

$$\Delta T_{\ln} = \frac{(243.0 - 212.3) - (228.0 - 214.7)}{\ln \frac{30.7}{13.3}} = 20.8 \text{ F}^\circ$$

$$U = 13.7 \frac{\text{BTU}}{\text{hr ft}^3 \text{ }^\circ\text{F}}$$

B. Energy Balance Calculations

Calculations were performed to estimate the rate of water vaporization in the column and to account for the dissipation of the sensible heat of the methyl salicylate feed stream. The rate of water vaporization was obtained from two experimentally measured quantities, as indicated in the following equation:

$$\begin{array}{rcl} \dot{m}_{\text{Water}} & = & \dot{m}_{\text{Water}} - \dot{m}_{\text{Steam}} \\ \text{Vaporized} & & \text{Obtained As} \quad \text{Fed To} \\ & & \text{Overhead} \quad \text{Column} \\ & & \text{Condensate} \end{array} \quad (27)$$

An energy balance was employed to account for the sensible heat of the methyl salicylate.

$$\dot{q}_{\text{M.S. Sensible}} = \dot{q}_{\text{Required To Vaporize Water}} + \dot{q}_{\text{Required To Vaporize Methyl Salicylate}} + \dot{q}_{\text{Lost To Surroundings}} \quad (28)$$

$$\dot{q}_{\text{Required To Vaporize Water}} = \dot{m}_{\text{Water Vaporized}} \lambda_{\text{Water}} \quad (29)$$

$$\dot{q}_{\text{Required To Vaporize Methyl Salicylate}} = \dot{m}_{\text{Methyl Salicylate Obtained As Overhead Condensate}} \lambda_{\text{M.S.}} \quad (30)$$

$$\dot{q}_{\text{M.S. Sensible}} = \dot{m}_{\text{M.S. Feed}} C_{P_{\text{M.S.}}} \left(T_{\text{M.S. Feed}} - T_{\text{Continuous Phase in Column}} \right) \quad (31)$$

It has been assumed in the equations given above that operation was at steady state, and that the heat released by the steam and water inlet streams as a result of the decreasing hydrostatic pressure on the aqueous phase moving up the column is negligible.

To determine an approximate value for the heat loss term in equation (28), an experiment was run in which only hot methyl salicylate was contained in and fed to the column. By measuring the flow rate of methyl salicylate and its temperature difference between the column inlet and outlet, a value of 416 BTU/hr was obtained. The flow rate was 200 ml/min and the temperature difference was 28.1 F°.

Table 2 summarizes the calculations of water vaporization rate and the terms in the energy balance equation for several experimental runs. These results are discussed in the "Discussion of Results" section.

TABLE 2
Summary of Energy Balance Calculations ^{a,b,c}

Run No.	T ₃₅ °F	T ₈ °F	ΔT °F	$\dot{m}_{H_2O}$ to Column gm/min	$\dot{q}_{H_2O}$ Sensible BTU/hr	$\dot{m}_{H_2O}$ in OVHD Condensate gm/min	(1) $\dot{q}$ Required to Vaporize M.S. BTU/hr	(5) $\dot{m}$ Water in Overhead Condensate gm/min	(4) $\dot{m}$ Steam to Column gm/min	(5-4) $\dot{m}$ Water Vaporized gm/min	(2) $\dot{q}$ Required to Vaporize Water BTU/hr	(3) $\dot{q}$ Lost BTU/hr	(1)+(2)+(3) $\dot{q}$ BTU/hr	Error Percent
12	250.0	211.5	38.5	358	918.0	1.27	26.4	10.00	7.03	2.97	381.1	416	823.5	10.3
13	254.7	210.7	44.0	315	922.1	2.44	50.5	15.00	11.50	3.50	449.1	416	915.6	0.7
14	254.0	216.3	37.7	245	614.2	2.59	53.7	18.10	14.70	3.40	436.2	416	905.9	47.5
15b	236.3	211.8	24.5	248	404.6	0.87	18.1	8.09	7.82	0.27	34.6	416	468.7	15.8
17b	251.7	203.7	48.0	228	728.7	0.58	12.0	3.41	0	3.41	437.5	416	865.5	18.8
17c	254.0	188.0	66.0	216	948.2	0.70	14.4	5.29	0	5.29	678.7	416	1109.1	17.0
18	259.2	208.0	51.2	268	913.8	0.72	14.9	5.03	0	5.03	645.4	416	1076.3	17.8
19b	254.3	212.2	42.1	223	623.5	0.81	16.8	8.81	6.48	2.33	299.0	416	731.8	17.4
20	255.3	213.4	41.9	223	620.6	1.13	23.4	7.17	6.49	0.68	87.2	416	526.6	15.1
21a	251.0	213.2	37.8	223	559.8	1.03	21.2	7.26	6.46	0.80	102.6	416	539.8	3.6
21b	251.3	213.3	38.0	223	562.8	1.08	22.5	7.96	6.48	1.48	189.9	416	628.4	11.7
21c	257.3	212.7	44.6	223	660.6	1.07	22.2	8.00	6.45	1.55	198.9	416	637.1	3.6

^aTemperature in the column "T8" was measured at approximately 30 inches up from the platform for these calculations.

^bAn average value was used for the mass flow rate of methyl salicylate to the column if flow rate variation occurred during the run.

^cThe value of 970.0 BTU/lb was used for the latent heat of vaporization of water.

C. Rapid Temperature Measurement Data Acquisition

It was mentioned earlier in the section on "Experimental Equipment and Procedure" that temperatures were measured 1500 to 1600 times per second with the micro-computer. Measurements were made at several depths in the column. Figure 5 is the computer program which was used for the rapid temperature data acquisition. In the first part of the program, the baseline voltage is read for one second (1607 readings) and an average baseline voltage is computed. The time of day corresponding to the reading is also obtained. Control is then returned to the teletype. The operator must then introduce suppression on the Burr-Brown amplifier and zero the suppression readout (indicated by the display on a digital voltmeter). The gain on the Preston amplifier is adjusted (adjusted to 10 in this case) and the keys "G" and "Return" are punched on the teletype keyboard to acquire the voltages relative to the baseline for a one second sampling period. The computer program adds the average baseline voltage to each of the readings obtained relative to the baseline. These millivoltage values are converted to temperatures and stored on a disk.

Figure 6 is a short computer program which was used for recalling the temperature data from the computer disk to the teletype screen or to a printer. This program only recalls temperature data. The number of temperature readings obtained, the average baseline voltage, and the time of day that the samples were taken must be read from the teletype screen at the time the data are acquired.

The following equation was employed in the program for converting thermocouple millivoltage readings to temperatures in degrees Fahrenheit:

```

A>TYPE B:FADSTD.FOR
      PROGRAM FADSTD
      EXTERNAL ADINIT,ADC,TIME
      DIMENSION IRDC(1620),E(1620),TDECF(1620)
C      READ BASE LINE VOLTS
      WRITE(1,6)
6      FORMAT(1X,'REMOVE SUPPRESSION & TYPE 'G')
      READ(1,8)ISW
8      FORMAT(1X,16)
      NUM=1620
      M=1
12     DO 60 N=1,NUM
          IRDC(N)=2047
          TDECF(N)=0.
          E(N)=0.
60     CONTINUE
          A=25.35321
          B=0.3969518
          D=0.04117051
          CALL ADINIT
          ICHAN=0
          IHRS=0
          MINS=0
          ISECS=0
2      CALL TIME(IHRS,MINS,ISECS)
          IF (ISECS.LT.2.OR.ISECS.GT.8)GO TO 2
5      CALL TIME (IHRS,MINS,ISECS)
          ITENS=ISECS/10+10
          IUNIT=ISECS-ITENS
          IF (IUNIT.NE.0)GO TO 5
          I=1
10     CALL ADC(ICHAN,IRDC(I))
          CALL OUT(196,48)
          ISCS=INP(196)
          ISCS=.NOT.ISCS
          ISCS=ISCS.AND.15
          I=I+1
          IF (ISCS.NE.1)GO TO 10
          I=I-1
          WRITE(1,40)IHRS,MINS,ISECS,I
40     FORMAT(1X,'TIME=',I3,' ',I3,' ',I3,' ISAMP=',I7)
          K=I
          DO 30 I=1,K
              E(I)=FLOAT(IRDC(I))*5.000/2047.
30     CONTINUE
          IF (M.EQ.1)GO TO 35
C      ADD BASE LINE VOLTS TO DELTA T VOLTS
          DO 3 J=1,K
              E(J)=E(J)/10.
              E(J)=EAV+E(J)
              TDECF(J)=32.+1.8*(25.35321*E(J)-0.3969518*(E(J)**2)
          +0.04117051*(E(J)**3))
          CONTINUE
9      IF (M.EQ.2)GO TO 18
35     ETOT=0.
          DO 17 L=1,K
              ETOT=ETOT+E(L)
17     CONTINUE
          EAV=ETOT/(FLOAT(K))
          WRITE(1,21)EAV
21     FORMAT(1X,'AVERAGE BASELINE VOLTAGE=',F10.6,' MV.')
          WRITE(1,9)
9      FORMAT(1X,'ADD SUPPRESSION & TYPE 'G')
          READ(1,8)ISW
          M=M+1
          IF (M.GT.2)GO TO 88
          GO TO 12
18     WRITE (1,20)TDECF
20     FORMAT(1X,10F7.2)
          CALL OPEN(7,'DATA1  DAT',2)
          WRITE(7)TDECF
          ENDFILE 7
          STOP EXIT
88     END
      END

```

Figure 5. Computer Program for Rapid Temperature Acquisition.

```
A>TYPE B:DKTST.FOR
      PROGRAM DKTST
      DIMENSION TDEGF(1620)
      CALL OPEN(7,'DATA1  DAT',2)
      READ(7)TDEGF
      ENDFILE 7
      WRITE(1,20)TDEGF
20    FORMAT(1X,10F7.2)
      STOP EXIT
      END
```

Figure 6. Computer Program for Retrieving Temperature Data from Disk.

$$T = 32 + 1.8(25.35321 E - 0.3969518 E^2 + 0.04117051 E^3) \quad (32)$$

This equation was employed by Moresco and Marshall, who performed similar fast temperature measurements in a liquid-liquid direct contact heat exchanger (under conditions in which liquid was not vaporized).^{20,21} The equation was found to be within 0.01 F° of the chromel-alumel thermocouple table in the range of 211-213 °F.

D. Holdup and Void Fraction Calculations

The equations defining holdup and void fraction, which were given in the "Theory" section, were applied for all experimental runs in which aqueous phase holdup volume measurements were made. Table 3 summarizes the results of those calculations.

TABLE 3
Holdup, Void Fraction, and Run Duration Information for Experimental Runs^a

Run No.	Time of Run Start	Time of Shutdown	Run Duration, hr.	Aqueous Phase Holdup Volume, ml (At End of Run)	M.S. Holdup Volume, ml (At End of Run)	Avg. Aqueous Phase Holdup, H*, Vol. %	Avg. Aqueous Phase Holdup, H, Vol. %	Avg. Void Fraction, α	Inlet Steam Quality, Wt. %
4	10:18 A.M.	11:25 A.M.	1.12	---	---	---	---	---	51.9
5	4:42 P.M.	5:58 P.M.	1.27	---	---	---	---	---	46.7
8	2:51 P.M.	8:25 P.M.	5.57	---	---	---	---	---	0
9	8:10 P.M.	1:16 A.M.	5.10	---	---	---	---	---	0
10	12:38 P.M.	4:35 P.M.	3.95	---	---	---	---	---	44.8
11	2:00 P.M.	4:13 P.M.	2.22	1219	6769	13.2	15.3	0.133	32.9
12	10:40 A.M.	2:45 P.M.	4.08	1470	6800	16.0	17.8	0.102	33.3
13	12:27 P.M.	4:35 P.M.	4.13	315	7400	3.4	4.1	0.162	56.6
14	9:32 A.M.	11:59 A.M.	2.45	45	7148	0.49	0.63	0.219	77.3
15	7:25 A.M.	12:25 P.M.	5.00	2421	6001	26.3	28.7	0.086	46.5
16	12:45 P.M.	4:12 P.M.	3.45	1415	6792	15.4	17.2	0.109	---
17 ^b	6:50 P.M.	11:50 P.M.	5.00	1390	7020	15.1	16.5	0.087	0
18 ^b	2:10 P.M.	4:41 P.M.	2.52	1264	7519	13.7	14.4	0.0464	0
19	9:45 A.M.	11:45 A.M.	2.00	1433	6845	15.6	17.3	0.101	34.1
20	10:30 A.M.	4:05 P.M.	5.58	2137	6046	23.2	26.1	0.112	34.2
21	8:50 A.M.	4:26 P.M.	7.60	2362	5943	25.6	28.4	0.098	34.0

^aThe start of a run is defined as the time at which the addition of methyl salicylate to the column was begun.

^bIn these two runs, steam was not fed to the column, but nitrogen and hot water were fed into the aspirator at the bottom of the column.

VI. DISCUSSION OF RESULTS

A. Description of Experimental Runs

Table 4 is a condensed summary of the flow rates, pressures, liquid holdup and other useful information for experimental runs (through Run No. 15) with the direct contact boiler. Additional information concerning these runs and other runs is contained in Appendix F.

Prior to experimental Run No. 4, no useful data were obtained because of mechanical problems. In Run No. 4 some data were obtained, such as the ratio of water to methyl salicylate in the condensate. A great deal of difficulty was encountered in controlling the hot water feed temperature in this run, and very little additional data were obtained in this run.

In Run No. 5, satisfactory operation was achieved for a period of 76 minutes, and then the feed tank containing methyl salicylate ran dry. A pump had not yet been obtained for recycling methyl salicylate to the storage tank. During the run, a steady dribble of condensate (6.30 ml/min) was obtained. Column inlet and outlet temperatures and flowrates were measured, and observations were made concerning dispersed phase bubble size. Near the bottom of the column there were some large gas bubbles and several small liquid bubbles about one-sixteenth inch in diameter. The population of larger bubbles became greater as the top of the column was approached.

Two distinct regions were observed in the column. Most of the column contained a turbulent zone in which methyl salicylate was the continuous phase. At the top of the column, the dispersed phase formed a foam zone which was about one-quarter to one-half inch thick in

TABLE 4
Direct Contact Boiling Heat Transfer Data Summary for Experimental Runs
(Through Run No. 15)^a

Time of Data	Run No.	M.S. Inlet Flow Rate, ml/min.	M.S. Inlet Temp., °F	M.S. Outlet Temp., °F	Temp. Steam To Aspirator, °F	Temp. Hot Water To Aspirator, °F	Steam Flow Rate To Aspirator, SCFH	Inlet Steam Quality Wt. %	Hot Water Flow Rate To Aspirator, ml/min.	Overhead Vapor Temp., °F	Total Overhead Condensate Rate, ml/min.	Pressure At Bottom Of Column, Ft. Water	Pressure At Top Of Column, In. Water	Aqueous Phase Holdup At End of Run Vol. %
11:05 A.M.	4	130	224	214	-	210	0.359	51.9	7.3	211	6.87	4.0	0	-
5:25 P.M.	5	185	228	214	218	213	0.359	46.7	9.0	211	6.30	4.0	0	-
7:45 P.M.	8	265	219	204	-	212	0	0	17.4	204	0.43	4.6	0.1	-
12:43 P.M.	9	340	243	228	-	215	0	0	18.1	205	0.81	4.4	0	-
1:52 P.M.	10a	265	215	211	217	216	0.526	44.8	14.2	210	16.6	3.9	0.25	-
3:44 P.M.	10b	217	221	212	217	216	0.527	44.8	14.2	211	10.9	3.8	0.10	-
4:05 P.M.	11	287	257	212	216	217	0.317	32.9	14.2	215	12.1	4.0	0.30	15.3
12:08 P.M.	12	322	250	211	216	216	0.321	33.3	14.1	215	11.1	4.0	0.45	17.8
3:42 P.M.	13	283	255	212	216	216	0.526	56.6	8.82	214	17.1	3.6	0.15	4.3
11:19 A.M.	14	220	254	216	217	216	0.670	77.3	4.3	220	20.3	3.6	1.70	0.6
10:45 A.M.	15a	203	227	212	217	215	0.357	46.5	9.0	211	5.50	4.0	0.9	-
11:53 A.M.	15b	223	236	212	217	214	0.357	46.5	9.0	212	8.83	4.0	0.9	28.7

^aMore than one set of data was taken per run, a small letter suffix was added to differentiate between the data sets (e.g. 15a, 15b, etc.).

Temperatures were rounded to the nearest degree. An average value was recorded in the table for runs in which the methyl salicylate inlet flowrate was somewhat unstable.

Run No. 5. In the turbulent zone the continuous phase, methyl salicylate, had the characteristic blood-red color caused by the presence of ferric ion. Dispersed phase liquid and vapor rising through the continuous phase caused substantial mixing of the phases, which was easily observed because of the red color of the methyl salicylate.

From the temperature data obtained in Run No. 5, it was observed that the methyl salicylate outlet temperature was below the dispersed phase inlet temperature. Based on this observation, a wire demister mesh was installed at the bottom of the column to provide better initial distribution of the dispersed phase.

Run No. 8 was the next run of importance. It was the first run in which a controller was used to control the temperature of the hot water feed to the column, and it was the first run in which metering pumps were used to control the hot water flow rate and to recycle methyl salicylate to the overhead storage tank. Run No. 8 was also important because no steam was fed to the column with the hot water stream. Data for Run No. 8 included the first column temperature profile, and observations revealed that almost no overhead condensate was obtained without steam being fed to the column.

In Run No. 9, no steam was supplied to the column, but the methyl salicylate inlet temperature was increased in an effort to obtain more overhead condensate. This time, the temperature profile in the column was essentially flat at 229°F; but, as in Run No. 8, very little overhead condensate was obtained. Also, as in Run No. 8, a layer of water about one to one and one-half inches thick was maintained on top of the continuous phase to allow continuous water removal at the aqueous phase overflow. Very little boiling was occurring in the continuous phase, which

was clear and red. The entire continuous methyl salicylate phase was a free-rise zone. Almost all of the boiling was confined to the aqueous layer. Most of that boiling was occurring near or on the methyl salicylate inlet tube, which passed through the aqueous layer and released hot methyl salicylate at the base of the aqueous layer.

Run No. 9 was unique in one important respect. Shortly after the temperature profile data were taken, an eruption occurred. Methyl salicylate and water gushed overhead and out at the condenser. Poor contacting of the phases had allowed the water in the column to become superheated. A piece of dirt or a gas bubble entering the column apparently caused rapid heterogeneous nucleation to occur.

Based on the discussions given in the articles of Blander and Katz¹⁴ and Avedisian,²² it is clear that heterogeneous nucleation and not homogeneous nucleation was responsible for the eruption in Run No. 9. Homogeneous nucleation occurs at the liquid's limit of superheat, which is usually at about 88-90% of the critical point temperature of the substance at atmospheric pressure. Heterogeneous nucleation occurs at lower temperatures than homogeneous nucleation but may still be violent. The presence of gas bubbles or dirt in a liquid provides sites for heterogeneous nucleation to occur; and since the water in the column was not at a temperature anywhere near its critical point temperature of 705.7 °F, heterogeneous nucleation of the superheated water in the column was undoubtedly responsible for the eruption.

In Run No. 10, steam was again mixed with hot water in the dispersed phase feed. No eruption occurred, as in Run No. 9, but after the system had operated for about 3.5 hours, the methyl salicylate's red color became less and less intense until it became obvious that a

phase inversion had occurred. A comparison of water flow rates into and out of the column verified that water had been accumulating in the column. Run No. 10 was the only one in which a phase inversion occurred.

Runs 11 through 15 were made to gather additional data at various values of inlet steam quality. Several useful observations were made in these runs. For example, in Run No. 14 at 77% inlet steam quality, the foam zone extended from near the top of the sight glass downward about 6 to 9 inches. The depth of the foam zone varied with the boiling activity in the column. In Run No. 11 at 32.9% inlet steam quality, the depth of the foam zone was only about two inches. It is apparent that the depth of the foam zone increases with the flow rate of vapor fed to or generated in the column.

Another useful observation which was made in Runs 11 through 15 is that with the demister mesh installed at the bottom of the column, the average water droplet size near the bottom of the column is smaller. Just above the mesh, a haze of small droplets was present and consisted of droplets about one thirty-second of an inch in diameter or smaller.

In Runs 16, 17 and 18, nitrogen gas was fed at the bottom of the column with the other constituents of the dispersed phase feed stream. Results of these runs are discussed below in relation to boiler performance evaluation and phase contacting.

Runs 19, 20, and 21 were made primarily for the purpose of making rapid temperature measurements in the column. These runs are discussed later in this section in relation to column temperature profiles.

B. Evaluation of Direct Contact Boiler Performance

To evaluate direct contact boiler performance in experimental runs through Run No. 15, water vaporization efficiency, theoretical two-phase boiling point, and theoretical phase ratio in the condensate were calculated. Vaporization efficiency was calculated from equation (9), and the numbers which were obtained are summarized in Table 5. The efficiency values are 90% or above for all the runs, except Run No. 9. This low water vaporization efficiency in Run No. 9 indicates poor contacting between the phases. Recall that Run No. 9 was one in which very little overhead condensate was obtained and the run in which the eruption occurred.

Based on the total pressure at the top of the boiler column, values were estimated for the boiling point of the immiscible liquid pair. These calculated values are shown in Table 5, as well as the actual bulk phase temperatures measured in the column near the top of the continuous phase. The predicted values agree with the actual measured values, except for Run No. 9. In general, the measured values are slightly higher than the calculated values.

Assuming perfect contacting between the phases (see p. 19), a value of the condensate phase ratio was estimated from equation (11) for each of the runs. In general, agreement is fairly good between theoretical and experimental values, except for Run No. 4 and Run No. 5. These two runs were made before the demister mesh was installed at the bottom of the column to bring about better dispersion of the inlet water stream. Consequently, lack of contacting between the phases was responsible for the poor agreement of theoretical and experimental phase ratio values in Run No. 4 and Run No. 5.

TABLE 5
Summary of Vaporization Efficiency, Condensate Phase Ratio, and Two-Phase
Boiling Point Calculations and Experimental Data (Through Run No. 15)^a

Time of Data	Run No.	EXPERIMENTAL DATA					CALCULATED VALUES			
		Condensate Volumetric Phase Ratio, Water/H.S.	Condensate Mass Ratio, Water/H.S.	Temp. Measured in Column, °F	Position of Temp. Measurement Upward From Platform at Bottom of Column, In.	Barometric Pressure, mm. Hg.	Pressure at Top of Column, mm. Hg.	Total System Pressure mm. Hg.	Two-Phase Boiling Point in Column @ System Total Pressure, °F	Water Vaporization Efficiency, %
11:05 A.M.	4	42.74	36.28	214.0	0	750.4	0	750.4	210.92	95.2
5:25 P.M.	5	20.00	16.98	213.8	0	747.9	0	747.9	210.76	94.9
7:45 P.M.	8	-	-	212.3	32	743.3	0.2	743.5	210.47	-
12:43 A.M.	9	6.36	5.40	229.7	31.5	744.6	0	744.6	210.54	68.3
1:52 P.M.	10a	7.30	6.20	210.3	8	735.8	0.5	736.3	209.99	99.1
3:44 P.M.	10b	7.22	6.13	210.3	8	735.8	0.2	736.0	209.967	99.0
4:05 P.M.	11	8.31	7.05	212.3	0	736.2	0.6	736.8	210.02	95.5
12:08 P.M.	12	9.26	7.86	211.3	26.9	739.6	0.8	740.4	210.26	98.0
3:42 P.M.	13	7.27	6.17	210.7	30	748.2	0.3	748.5	210.80	99.9
11:19 A.M.	14	8.23	6.99	216.3	30	752.3	3.2	755.5	211.26	90.4
10:45 A.M.	15a	11.15	9.51	212.0	30	742.5	1.7	744.2	210.51	97.4
11:53 A.M.	15b	7.45	6.33	211.8	30	742.2	1.7	743.9	210.49	97.2

^aWhen more than one set of data was taken per run, a small letter suffix was added to differentiate between the data sets (e.g. 15a, 15b, etc.). In runs 15a and 15b the condensate was collected over long time periods to obtain the values in this table. The total overhead condensate rates shown in Table 4, p. 40 for runs 15a and 15b were averaged over shorter time periods.

C. The Importance of Interphase Contact

Runs 16, 17, and 18 were made to try to establish the importance of phase contacting on the boiler's performance. In Run No. 16, nitrogen was added to the steam and water stream at the bottom of the column. Run No. 16 was performed at about the same conditions as Run No. 15, except for the nitrogen added to the dispersed phase feed stream. The water vaporization efficiency for Run No. 16 was close to 100% but it was only 97% for Run No. 15. The presence of a larger total volumetric gas flow rate in Run No. 16 was probably responsible for better contacting of the phases and thus a higher vaporization efficiency.

Steam was omitted from the dispersed phase feed stream in Runs 17 and 18. In Run No. 17, only hot water was contacted with methyl salicylate in the column at the first part of the run and very little condensate was obtained overhead. The methyl salicylate phase was very clear and red. Shortly after a set of data was recorded at these conditions, a low flow rate of nitrogen ($623 \text{ cm}^3/\text{min}$) was started. Immediately an eruption occurred, and methyl salicylate and water gushed out overhead through the condenser. The water dispersed in the column was undoubtedly superheated, and the presence of the nitrogen bubbles triggered the sudden vaporization of water. Nitrogen displaced some of the liquid in the column and forced it overhead.

Three different nitrogen flow rates were used in Runs 17 and 18, and water vaporization efficiency was calculated for each set of conditions. Equations (15) and (18) and the required experimental data were utilized to make the calculations, which are summarized in Table 6.

TABLE 6
Summary of Experimental Data and Vaporization Efficiency Calculations for
Experimental Runs 16, 17 and 18^a

Time of Run	Run No.	EXPERIMENTAL DATA							CALCULATED VALUES				
		Nitrogen Flow Rate To Aspirator, cm ³ /min @60°F, 14.7 PSIA	Nitrogen Flow Rate To Aspirator, SCFH	Condensate Volumetric Phase Ratio, Water/N.S.	Total DWD Cond. Rate, ml/min	Cond. Ratio, Water/N.S.	Temp. Measured In Column °F	Position of Temp. Measurement Upward From Platform at Bottom of Column, in.	Barometric Pressure mm. Hg.	Pressure At Top of Column, mm. Hg.	Total System Pressure, mm. Hg.	Partial Pressure of Nitrogen, mm. Hg.	Vaporization Efficiency, %
2:41 P.M.	16a	827	0.0292	10.70	10.44	9.08	206.7	12	744.8	0.2	745.0	45.75	101.8
3:31 P.M.	16b	827	0.0292	8.59	8.85	7.29	206.3	32	744.8	0.2	745.0	54.25	101.1
3:55 P.M.	16c	827	0.0292	6.92	8.41	5.88	206.3	32	744.7	0.2	744.9	57.99	100.1
8:40 P.M.	17a	0	0	-	-0	-	228.3	36	740.7	0.5	741.2	0	-
9:45 P.M.	17b	705	0.0249	6.93	3.91	5.89	203.7	30	740.1	0.5	740.6	99.47	98.6
11:16 P.M.	17c	4446	0.157	9.00	5.88	7.64	188.0	30	741.7	0.5	742.2	287.8	97.0
4:00 P.M.	18	207	0.00731	8.30	5.63	7.05	208.0	30	746.5	0.1	746.6	22.43	102.3

^aWhen more than one set of data was taken per run, a small letter suffix was added to differentiate between the data sets (e.g. 16a, 16b, etc.).

As equation (15) indicates, an increasing nitrogen flow rate does cause a decrease in vaporization efficiency.

From experimental observations made in Runs 9 and 17a and theoretical and experimental condensate phase ratios obtained for Runs 4 and 5, contacting of phases is important for three reasons. From the standpoint of safety, an increased amount of contacting prevents eruptions, such as occurred in Runs 9 and 17a. A dispersed phase distributor at the bottom of the column results in condensate phase ratios much closer to the theoretical values. Finally, very poor heat transfer is obtained when contacting between the phases is poor. The poor heat transfer coefficient value that was calculated for Run No. 9 in the "Data Analysis" section, and the almost zero value for overhead condensate rate in Runs 9 and 17a establish this fact.

D. Discussion of the Column Temperature Profiles

In all of the experimental runs in which temperature profiles were measured, the profiles were very flat, except in Run No. 8. By examining the phase rule, which applies to a system at equilibrium, one predicts that with three phases present (water vapor, liquid water, and methyl salicylate) and two components, the system should have only one degree of freedom, as indicated by the following equations:

$$f = c - p + 2$$

For the present system, $c = 2$ and $p = 3$, so that

$$f = 2 - 3 + 2 = 1 \quad .$$

Since the system pressure is fixed, the system is invariant under equilibrium conditions, and the temperature is fixed. On the other

hand, when nitrogen is added to the system, another component has been added, and there are two degrees of freedom:

$$f = 3 - 3 + 2 = 2 \quad .$$

Since the pressure of the system is fixed, there is one degree of freedom remaining, and the temperature of the system can vary. It has been observed that even when nitrogen is present in the column, the temperature profile for the column is still flat. Consequently, one tends to believe that there may be some other cause for the flat temperature profile, such as backmixing (or mixing in the axial direction) of the phases.

In a study of air-agitated liquid-liquid extraction columns by Fernandes and Sharma, it was stated that there is complete backmixing in the continuous phase.²³ An examination of the literature upon which Fernandes and Sharma had based this statement revealed that in those studies only one liquid and one gas phase had been contacted. Fernandes and Sharma have evidently extrapolated that two-phase contacting situation to their own case of air-agitated, immiscible liquid phases.

The idea of backmixing cannot be totally ruled out. Observation of the mixing that occurs between the continuous and dispersed phases in the boiler column suggests that backmixing does occur; however, further work is necessary to remove any doubt that backmixing is responsible for the flat temperature profile in the column. A few runs with some packing in the column to suppress backmixing may yield temperature profiles which are not flat, especially if some nitrogen is fed to the column with the steam and hot water.

The temperature level of the flat bulk temperature profile depends on several factors. In Table 5, the results of two-phase boiling

point calculations indicate that the system pressure affects the temperature level in the column. The degree of contacting of the phases affects the water vaporization efficiency, and the degree of contacting apparently affects the temperature level. In the runs in which nitrogen, or a mixture of steam and nitrogen, was fed with hot water into the column, the added vapor pressure of nitrogen resulted in a lower bulk phase temperature level. The greater the nitrogen flow rate, the greater was its influence on the temperature level in the column.

To obtain additional insight concerning the temperatures of the phases in the column at various depths near the top of the column, rapid temperature measurements were made. In Runs 19 and 20 the thermocouple T8 signal was displayed on an oscilloscope screen. It was observed that the temperatures relative to the bulk average temperature in the column varied at most by about 0.6°F and that the greatest deviations occurred near the liquid surface. At a depth of 1.5 inches below the surface, sudden and distinct deviations occurred every few seconds. This will be discussed later.

Run No. 20 was conducted at the same conditions as Run No. 19, but in this run, pictures were taken of the oscilloscope display with thermocouple T8 positioned at depths of 1.5, 6.5, and 10.5 inches below the liquid surface. Figure 7 corresponds to the 1.5 inch depth. The temperature was initially at a fairly constant baseline level until the abrupt disturbance, and after the disturbance the temperature returned to the baseline. The peak disturbance in this case was a maximum of 12 microvolts (about 0.5°F) above the baseline value of 213.27°F and occurred over a time interval of about 400 milliseconds. Pulses of this type occurred every few seconds.

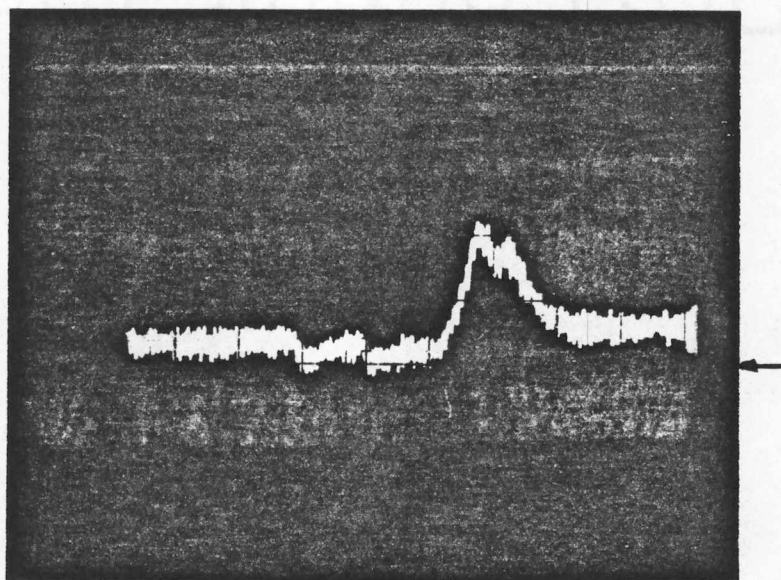


Figure 7. Photograph of the Oscilloscope Display of the Signal from the Rapid Response Thermocouple in the Direct Contact Boiler (Thermocouple position: 1.5 Inches Below Surface of Liquid; Baseline: 4.128 millivolts (213.27 °F))^a.

a. The level of the baseline is indicated by the arrow in the picture. On the grid in the picture: (Vertical Scale: 5 microvolts/cm; Horizontal Scale: 200 milliseconds/cm).

Figure 8 corresponds to the oscilloscope signal with the thermocouple at the 6.5 inch depth, and Figure 9 corresponds to the 10.5 inch depth. At these depths the magnitude of the deviation from the baseline was not as great as at the 1.5 inch depth, and not as sharp and distinct.

The abrupt disturbance relative to baseline illustrated in Figure 7 is believed to have been caused by methyl salicylate vapor bubbles. This seems logical because the thermocouple was located about one-quarter inch above and 1.5 inches to the left of the methyl salicylate inlet tube. Also, if the methyl salicylate feed entering the column at about 255 °F undergoes flash vaporization to form some vapor and releases heat to achieve a liquid phase temperature at 212 to 213 °F it is reasonable that the vapor is slightly superheated.

It was at first thought that the disturbance shown in Figure 7 may have been caused by steam bubbles rising rapidly from the aspirator at the bottom of the column. Steam has poor thermal properties and would not be expected to achieve rapid equilibrium with the surrounding medium. Since steam bubbles are much less dense than the surrounding liquid and the viscosity of the medium is low, the steam bubbles rise rapidly. It is believed that the deviations above the baseline in Figures 8 and 9 were caused by steam bubbles because thermocouple T8 was much lower in the column in relation to the methyl salicylate inlet spout.

In Run No. 21, a micro-computer was used to record temperatures 1500 to 1600 times per second. Over a period of 13 minutes, temperature measurements were made in the liquid near the top of the column at depths of 1.5, 6.5, and 10.5 inches below the liquid surface. Figures

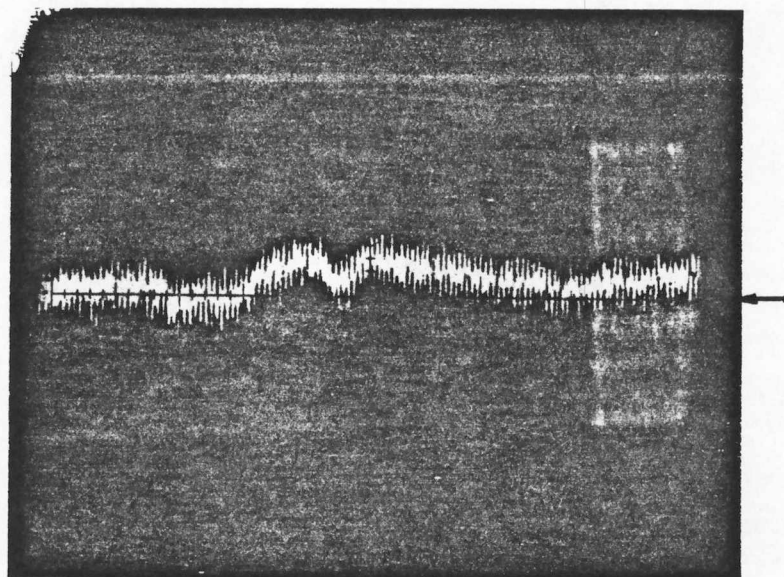


Figure 8. Photograph of the Oscilloscope Display of the Signal from the Rapid Response Thermocouple in the Direct Contact Boiler (Thermocouple Position: 6.5 Inches Below Surface of Liquid; Baseline: 4.132 millivolts (213.40 °F))^a.

a. The level of the baseline is indicated by the arrow in the picture. On the grid in the picture: (Vertical Scale: 5 microvolts/cm; Horizontal Scale: 200 milliseconds/cm).

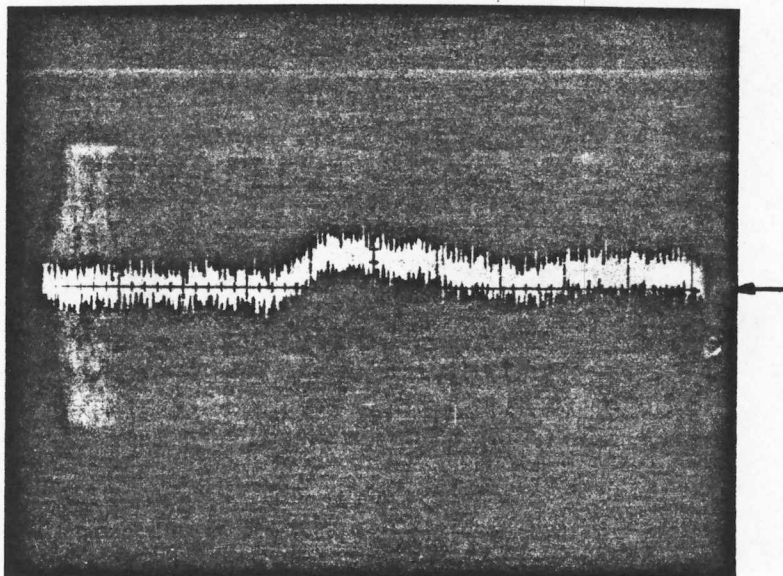


Figure 9. Photograph of the Oscilloscope Display of the Signal from the Rapid Response Thermocouple in the Direct Contact Boiler (Thermocouple Position: 10.5 Inches Below Surface of Liquid; Baseline: 4.134 millivolts (213.47 °F))^a.

a. The level of the baseline is indicated by the arrow in the picture. On the grid in the picture: (Vertical Scale: 5 microvolts/cm; Horizontal Scale: 200 milliseconds/cm).

10 and 11 are samples of the data corresponding to the 1.5 inch depth in the column. The data shown in Figure 10 are in the vicinity of the maximum temperature of 213.01 °F recorded for the 1.5 inch depth, and the data in Figure 11 are in the vicinity of the minimum temperature. In both figures, the repeated departure and return to the baseline may have been caused by noise or possibly rapid and repeated contact with small bubbles. As the boiling occurs in the column, the thermocouple "sees" first one phase and then another, such that rapid perturbations occur about a bulk average temperature value called the "baseline."

The complete sets of temperature data taken at the three different depths are given in Figures 25, 26 and 27 in Appendix G. A survey of those data revealed that the bulk average temperature in the column was almost constant at the three different depths, confirming the findings of previous experimental runs. The difference between maximum and minimum temperatures at each depth shows that the oil and aqueous temperatures differed by no more than about 0.5 F° at any of the three depths at which the probe was located.

E. Comparison of the Present Work with the Study of Sideman and Gat

Because of the similarity of the present study with that of Sideman and Gat, which has already been mentioned in the "Background" section, a more detailed comparison of the two studies was made.⁹ Table 7 summarizes the conditions of the present study and those in their study.

Sideman and Gat only studied the case in which the dispersed phase entered the column as a subcooled liquid and was totally vaporized. They identified three regions in the column:

- a. A free-rise zone

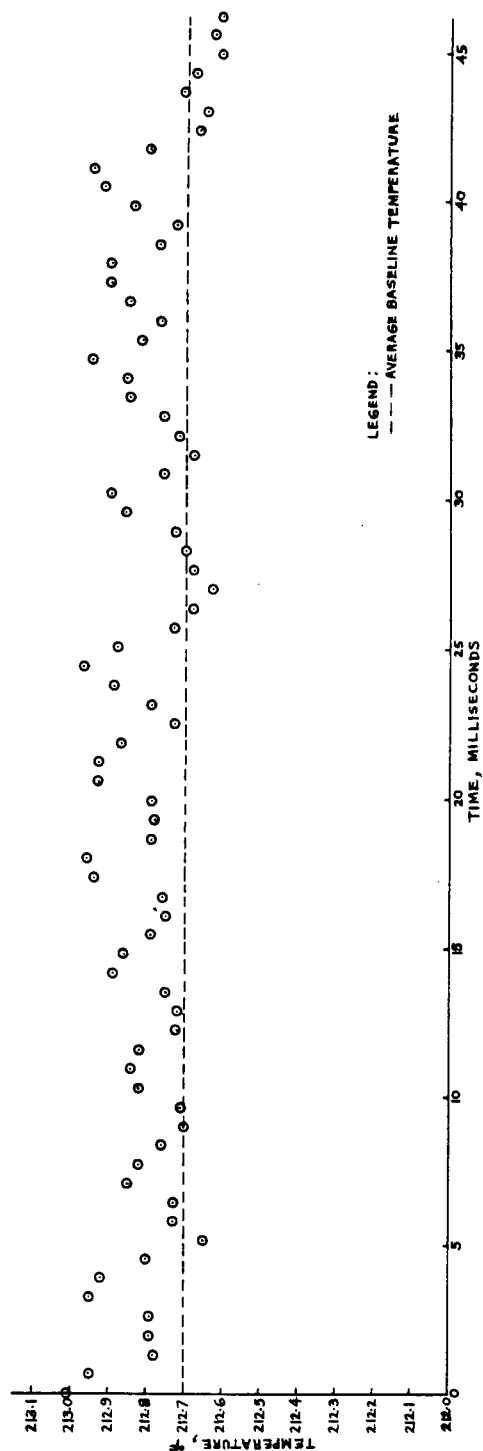


Figure 10. Rapid Temperature Measurement Data (1.5 Inches Below Liquid Surface Near Top of Column, Sample of Data Near Maximum Measured Temperature of 213.01 °F).

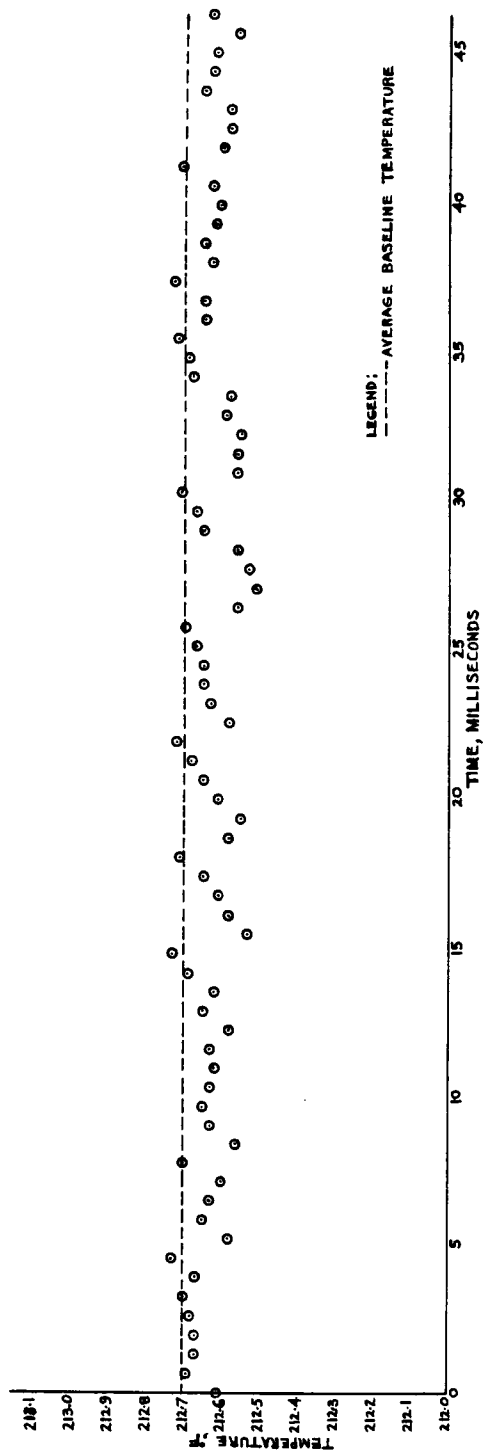


Figure 11. Rapid Temperature Measurement Data (1.5 Inches Below Liquid Surface Near Top of Column, Sample of Data Near Minimum Measured Temperature of 212.51 °F).

TABLE 7

Comparison of Experimental Conditions in the Present Study with
Those in the Study of Sideman and Gat^a

Item	Sideman's and Gat's Study	This Study
Dispersed Phase	n-pentane	water
Continuous Phase	water	methyl salicylate
Specific Gravity of Dispersed Phase (20°C/40°C)	0.63	0.998
Latent Heat of Vaporization of Dispersed Phase @ 760 mm Hg, BTU/lb	154	970.4
Normal Boiling Point of Dispersed Phase, °F	97.0	212.0
Boiling Point of Two-Phase Mixture @ 760 mm Hg	94.82	211.55
Spray Column Inside Diameter, Inches	2.76	4.0
Range of Mass Flow Ratios Continuous/Dispersed	5.56-30.3	10.0-55.1 M.S./Water (Liquid) 9.5-20.9 M.S./(Water + Steam)
Range of Flow Rates of Continuous Phase, gm/min	590-1300	145-378
Range of Flow Rates of Dispersed Phase, gm/min	42-107	4.3-18.1 Water (Liquid) 15.2-20.3 (Water + Steam)
Condition of Dispersed Phase Entering Column	Liquid Subcooled by 2.7-3.2 F°	Inlet Steam Quality Ranged from 0-77.3 wt.%

TABLE 7 (continued)

Item	Sideman's and Gat's Study	This Study
Range of ΔT at Top of Column, F°	8.1-31.5	4.7-61.7
Range of ΔT at Bottom of Column, F°	3.06 (All Runs)	13.0 F° (Run No. 9) 4.0 F° (Run No. 8) Temp. of M.S. was greater than temp. of entering dispersed phase for all other runs (i.e., crossover)
Range of Dispersed Phase Holdup, Volume % (i.e., H_A^*)	15-22	0.49-26.3
Volumetric Heat Transfer Coefficient, BTU/(hr ft ³ of F)	6.2×10^3 - 12.5×10^3	13.7 (Run No. 9)

^aSideman, S., and Gat, Y. "Direct Contact Heat Transfer with Change of Phase: Spray Column Studies of a Three-Phase Heat Exchanger," American Institute of Chemical Engineers Journal, Vol. 12, No. 2, March 1966, pp. 296-303.

b. A turbulent zone

c. A foam zone

If the feed is introduced partially vaporized, the free-rise zone is eliminated.

Only Run No. 9 of the present work can be directly compared to the study of Sideman and Gat. In Run No. 9, almost the entire column was a free-rise zone and very little boiling occurred, except in an aqueous layer at the top of the column. Very little overhead condensate was obtained, and the heat transfer coefficient which was calculated for Run No. 9 was only $13.7 \text{ BTU/hr ft}^3 \text{ }^\circ\text{F}$. The dispersed phase feed in Run No. 9 was essentially a saturated liquid.

In the other runs of the present study, steam was mixed with saturated water as the dispersed phase feed. Runs were made at several values of inlet steam quality, and only small amounts of water were vaporized. Heat transfer coefficients could not be calculated because a temperature crossover occurred at the bottom of the column. In all runs with steam and water as the dispersed phase feed a turbulent zone filled most of the column, and a foam zone ranging from 0.5 to 9 inches was present at the top of the column.

The most unusual observation in the present work that was not observed by Sideman and Gat is the temperature crossover at the bottom of the column. The fact that readings from thermocouples T8, T30, and T34 were all just about the same and below the inlet temperature of the dispersed phase, reveals that the crossover observation was not caused by a bad thermocouple. In fact, an experiment was conducted in which saturated steam at essentially atmospheric pressure (758.7 mm Hg at the time of the test) was made to flow past thermocouples T31 and T34. These

thermocouples are the inlet steam and outlet methyl salicylate thermocouples, respectively. Temperature readings were taken with a potentiometer until the readings became constant with time and remained constant. It was found by comparing the readings of the thermocouples with the boiling point temperature of water at the measured value of pressure in the column that T31 (at 212.0 °F) agreed well with the steam table value of 211.9 °F and that T34 (at 210.9 °F) was 1.0 F° low. When this correction was applied to the data obtained in the experimental runs, the crossover still occurred.

The temperature crossover indicates that heat transfer between the fluids due to a temperature difference is not occurring over the entire column. Energy balance information in Table 2, p. 39 shows good accountability for the sensible heat of methyl salicylate and indicates that heat is being transferred by some mechanism.

The data obtained thus far indicate that methyl salicylate undergoes a flash vaporization when it enters the column. This idea is supported by the fact that one can use vapor pressure data to calculate the two phase boiling point temperature to within a few degrees. Condensate phase ratios can also be estimated fairly accurately (see Table 5, p. 51).

As indicated earlier, Sideman and Gat did not observe a temperature crossover. Since water was a common component in both studies, the observed temperature crossover in the present study could possibly be explained in terms of the physical properties of methyl salicylate.

In the "Background" section, the point was made that when one liquid is superheated in contact with another liquid, the phase in which nucleation occurs is governed by the relative magnitudes of the surface and interfacial tensions. Evaluation of the criteria of Blander and Katz¹⁴ was performed for pentane-water and methyl salicylate-water systems. The calculations are in Appendix H. It was found that nucleation occurs in the pentane phase (dispersed phase) in the pentane-water system, but nucleation occurs in the methyl salicylate phase (continuous phase) in the methyl salicylate-water system. The phase in which nucleation occurs is another important difference between the present work and the work of Sideman and Gat, and probably explains the greatly different heat transfer behavior in Run No. 9 of the present work and the runs made by Sideman and Gat.

F. Direct Contact Boiler Design Considerations

Given that a temperature crossover occurs and that heat transfer in the column results from flash vaporization of the heat transfer fluid entering the column, how does one design a direct contact boiler? A conventional flash drum is designed with a diameter sufficiently large to limit the vapor velocity to an acceptable value, and has a volume sufficient for equilibration of the phases, plus additional volume for surge capacity. For a direct contact boiler, the requirements of limiting the vapor velocity to minimize liquid entrainment and providing sufficient volume for equilibration of the phases are still necessary. In addition, a distribution plate or a wire mesh is needed for distribution of the dispersed phase entering the column. A means of promoting additional contacting of the immiscible phases is

also required. If the column is operated at elevated pressure, a slight reduction in pressure at the boiler entrance could be utilized to provide the vapor necessary for agitation.

The idea of designing a direct contact boiler in a manner similar to a flash drum is not totally new. Rautenbach and Hoeck²⁴ proposed a modified multistage flash evaporation process for desalination. In their process, a heat exchange fluid, such as a mineral oil, is heated and then undergoes direct contact with hot brine in a series of flash chambers. The heat exchange fluid furnishes a major part of the latent heat of vaporization of the water, but the large latent heat for vaporization of water requires a large flow ratio of oil to brine.

VII. CONCLUSIONS

1. Heat transfer in a direct contact boiler is believed to occur as a result of flash vaporization of the heat transfer fluid entering at the top of the column. Three observations support this hypothesis:
 - a. The boiling point of the two phase mixture in the column can be estimated to within a few degrees from vapor pressure data.
 - b. Phase ratios of overhead condensate can also be estimated very closely.
 - c. A temperature crossover occurs at the dispersed phase inlet end of the boiler, such that the temperature of the continuous phase effluent is less than the temperature of the dispersed phase feed.
2. The temperature difference at the dispersed phase inlet end of the boiler (or approach temperature difference) is small; however, a crossover does occur, and there appears to be no way to calculate a heat transfer coefficient.
3. Computer-assisted temperature measurements at three different depths near the top of the liquid phase in the column revealed that the temperature profile in the column at the upper end is essentially flat, and the maximum temperature difference between the phases is about 0.5 F°.
4. In all the experimental runs in which a gas was mixed with the hot water feed stream to the column, the temperature profile in the column was very flat. Also, two types of heat transfer zones were present in the column:
 - a. A turbulent zone filled most of the column.

- b. A foam zone was present at the top of the column, and the thickness of this zone depends on the total quantity of vapor fed to the column and generated in the column.
5. In runs in which no gas was fed to the column with the hot water stream, the water vaporization efficiency was very low and very little vapor condensate was obtained. Also, the danger of a vapor explosion exists in this type of situation due to poor contacting of the phases and consequent superheating of the water in the column.
6. Several supportive results that were obtained in this study are summarized below:
 - a. Contacting between continuous and dispersed phases is important to achieve high water vaporization efficiency.
 - b. An equation was developed which shows that the presence of an inert gas results in a decrease in water vaporization efficiency because of the contribution of the partial pressure of the inert gas. This effect was verified experimentally.
 - c. A method was summarized for estimating the boiling point of a two-phase mixture. It was shown that predicted values of the two-phase boiling point are quite close to the bulk phase temperatures measured in the column. Also, it was shown that calculated values of the two-phase boiling points of pentane and Freon-113 are very close to heterogeneous azeotrope boiling point values given in the literature.
 - d. Experimental data including temperature profiles, flow rates, pressure drops, and liquid holdups were obtained for several values of inlet steam quality.

7. Design of a direct contact boiler is similar to flash drum design, and the following guidelines are recommended:
 - a. As in conventional flash drum design, the vapor velocity must be low enough to minimize entrainment of liquid.
 - b. The boiler volume must be large enough to allow sufficient time for equilibration of the phases being contacted.
 - c. A means of phase contacting, such as vapor bubble agitation, is necessary to obtain a high vaporization efficiency for the dispersed phase. Phase contacting is also important for safe operation.
 - d. A distributor is needed for uniform dispersion of the entering dispersed phase, so that the overhead condensate phase ratio will be about the same as the predicted theoretical value.
8. By evaluating the criteria of Blander and Katz it was shown that when water is superheated by contact with methyl salicylate, nucleation occurs in the methyl salicylate phase (continuous phase in this study). This fact probably explains the difference between the heat transfer results of this work and the results obtained by Sideman and Gat for the pentane-water system.

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PART I. LIST OF REFERENCES

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APPENDICES

APPENDIX A

THE FLASH DISTILLATION MODEL OF PORTEOUS AND MUNCASTER¹⁷

The following is a description of the mathematical model of Porteous and Muncaster for calculating the rate at which a liquid in flashing flow achieves equilibrium with its own vapor.

Consider the case of a saturated liquid at temperature T_o entering a duct in which the pressure is P , and the corresponding temperature of the saturated vapor is T_s . Figure 12 illustrates an element of fluid in the duct. The local fluid temperature in the element is T .

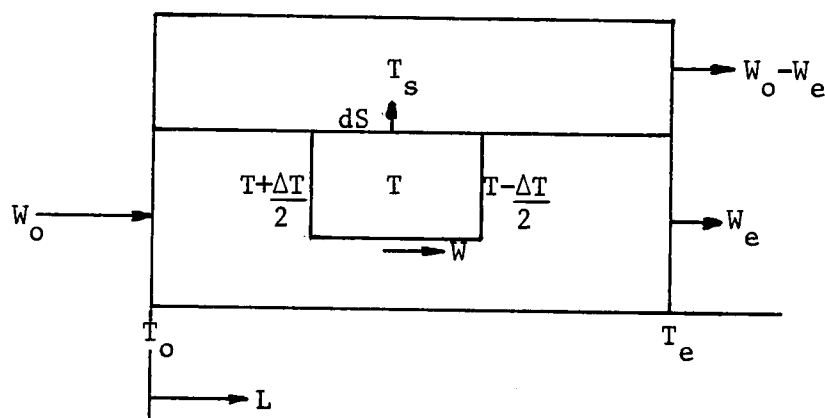


Figure 12. A Liquid in Flashing Flow in a Duct^a.

NOMENCLATURE FOR Figure 12

S	Interfacial Area Per Pound of Fluid
W	Mass Flow Rate of Fluid
T	Temperature
L	Duct Length

Subscripts

s	Saturation
o	Initial
e	Exit

a. Taken from Porteous, A. and Muncaster, R., "A Model for Equilibration Rates in Flashing Flow Through Open Channels, Nozzles, and Short Tubes," British Chemical Engineering, Vol. 16, No. 1, 1971, p. 59.

Heat is transferred by convection to surface area S , and energy is removed from the liquid in the evaporation process. Equation (33) is an energy balance describing the process.

$$C_p \frac{dT}{dt} = -hS(T - T_s) \quad (33)$$

h : An overall heat transfer coefficient including the effects of convection in the fluid and evaporation at the gas-liquid interface

C_p : Fluid specific heat capacity

t : Time

Define the fraction of equilibration by:

$$\beta = \frac{T_o - T}{T_o - T_s} \quad (34)$$

Also, substitute,

$$dt = \frac{dL}{u} \quad (35)$$

where u is the bulk fluid velocity. One can then make the indicated substitutions and rearrange to obtain:

$$\frac{d\beta}{1-\beta} = \frac{hS}{C_p u} dL = d\sigma \quad (36)$$

Define the evaporation parameter, σ , as follows:

$$\sigma = \frac{hS}{C_p u} L \quad (37)$$

One can integrate equation (36), assuming S is constant, to obtain:

$$\ln(1-\beta) = -\sigma + c \quad (38)$$

The constant of integration, c , is evaluated from the condition

$$T = T_0 \text{ at } t = 0 . \quad (39)$$

This condition is equivalent to the condition

$$\beta = 0 \text{ when } \sigma = 0 . \quad (40)$$

Consequently, $c = 0$, and the following result is obtained:

$$\beta = 1 - e^{-\sigma} . \quad (41)$$

Therefore, the rate at which a flashing liquid attains equilibrium with its own vapor is an exponential decay governed by the evaporation parameter σ .

Porteous and Muncaster¹⁷ continued the development of equation (41) to obtain:

$$\beta = 1 - e^{-nL} . \quad (42)$$

In this expression, n is the evaporation index, a lumped parameter describing the flashing process and is a constant for a given set of conditions. A plot of $\ln (1-\beta)$ versus L is a straight line of slope $-n$.

APPENDIX B

PHYSICAL PROPERTIES OF METHYL SALICYLATE AND WATER

Tables 8 and 9 contain values of some of the physical properties of methyl salicylate and water. Some of the values are from the literature, and others were either measured in the laboratory or calculated from well established correlations or equations.

TABLE 8

Physical Properties of Methyl Salicylate

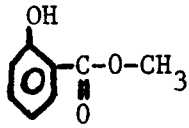
Item Description	Information	Reference
Compound	Methyl Salicylate, $C_8H_8O_3$	-
Synonyms	Oil of Wintergreen, 2-Hydroxybenzoic Acid Methyl Ester	a
Structure		a
Molecular Weight	152.14	a
Method of Purification	Rectification	b
Toxicity	Average Lethal Dose Oral, Human 30 ml adult 10 ml children	a
To Fight Fire	Use CO_2 or dry chemical fire extinguisher.	c
Freezing Point	$-8.6^\circ C$	a
Boiling Point	$223.3^\circ C$ @760mmHg $101^\circ C$ @12mmHg	c
Refractive Index	$n_D^{18.1^\circ C} = 1.538$	d
Flash Point	$214^\circ F$ closed cup $225^\circ F$ open cup	d e
Autoignition Temperature	$850^\circ F$	c

TABLE 8 (continued)

Item Description	Information	Reference
Vapor Specific Gravity	5.24 relative to air	c
Liquid Specific Gravity	$D_{4^{\circ}\text{C}}^{18.5^{\circ}\text{C}} = 1.1851$	d
	$D_{4^{\circ}\text{C}}^{25^{\circ}\text{C}} = 1.1787$	d
Density of Liquid	1.122 gm/ml @ 178°F	f
	1.120 gm/ml @ 182°F	f
	1.113 gm/ml @ 196°F	f
Surface Tension	44.2 dynes/cm @ -19.8°C	g
	31.9 dynes/cm @ 94°C	g
(liquid in contact with nitrogen gas)	31.2 dynes/cm @ 100°C	h
	19.8 dynes/cm @ 212.2°C	g
Critical Temperature	704.5 K	h
Latent Heat of Vaporization	156.6 BTU/lb _m Temp. Range: 130 to 280°F	h
Solubility in Water	0.1% by weight Temp. Range: 15-30°C	i
Viscosity of Liquid	0.945 centipoise @ 100°C	h
Vapor Pressure	12.4mmHg @ 212°F	j
	20.8mmHg @ 232°F	j
Specific Heat Capacity of Liquid	0.503 BTU/lb _m °F @ 100°C	h
Thermal Conductivity of Liquid	0.0817 $\frac{\text{BTU}}{\text{hr.ft}^{\circ}\text{F}}$ @ 100°C	h

a. Windholz, M., Ed., The Merck Index, 9th Ed., Merck and Co., Inc., Rahway, N.J., 1976.

TABLE 8 (continued)

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f. These numbers were obtained by approximate measurements in the laboratory.

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h. These data were estimated by methods outlined by: Reid, R. C., Prausnitz, John M., and Sherwood, T. K., The Properties of Gases and Liquids, 3rd Ed., McGraw-Hill, New York, N.Y., 1977.

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TABLE 9
Physical Properties of Water

Item Description	Information	Reference
Compound	Water	-
Molecular weight	18.016	a
Critical Temperature	647.4 K	a
Surface Tension (liquid in contact with air)	61.80 dynes/cm @ 212°F	a
Density of Liquid	59.82 lb _m /ft ³ @ 212°F	b
Latent Heat of Vaporization	970.3 BTU/lb _m @ 212°F	c
Viscosity of Liquid	0.2818 centipoise @ 212°F	d
Thermal Conductivity of Liquid	0.406 BTU/hr ft°F @ 200°F	e
Coefficient of Thermal Expansion of Liquid	0.39 X 10 ⁻³ °F ⁻¹ @ 200°F	e

a. Dean, John A., Ed., Lange's Handbook of Chemistry, 12th Ed., McGraw-Hill, New York, N.Y., 1978.

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APPENDIX C

CALCULATION OF THE BOILING POINT OF A TWO

PHASE LIQUID-LIQUID MIXTURE

A few sample calculations are given to illustrate the prediction of the boiling point of a two phase liquid-liquid mixture under equilibrium conditions. Some values from the literature have been included for comparison.

Estimate the two-phase boiling point for each of the following pairs of immiscible liquids at a total pressure of 760 mm Hg:

- (a) Water-Freon 113
- (b) Water-Pentane
- (c) Water-Methyl Salicylate

Compare the calculated value for each two-phase boiling point with data from the literature.

The total pressure is equal to the sum of the vapor pressure of the components:

$$P = P_A + P_B \quad . \quad (43)$$

P_A : Vapor pressure of water

P_B : Vapor pressure of organic compound

The vapor pressure of a component as a function of temperature may be estimated from Antoine's Equation:

$$\ln P_i = A - \frac{B}{T+C} \quad (44)$$

P_i : Vapor pressure of component i , mm Hg

T : Temp., Kelvins

The constants A , B and C , applicable in the pressure range of 10 to 1500 mm Hg, have been tabulated by Reid, Prausnitz, and Sherwood.²⁵

Determination of the two phase boiling point under equilibrium conditions is simply a trial and error search for a temperature that will give P_A and P_B values which add up to the total pressure. A simple algorithm for the calculation is outlined below:

- (1) Specify the total pressure, P .
- (2) Guess a value for the two phase boiling point temperature.

- (3) Calculate the vapor pressure of each component from Antoine's equation, or a similar equation.
- (4) Calculate the sum of the vapor pressures for the components, P_t .
- (5) Compare P with P_t .
- (6) If P and P_t are equal, within the specified limits of error, the value of the two phase boiling point has been obtained.
- (7) If P and P_t are not equal, a new trial value for the two phase boiling point must be guessed, and steps (2) through (5) must be repeated.

For the system, water-Freon- 113, the values of the constants in Antoine's equation for Freon - 113 are:

$$A = 15.8424$$

$$B = 2532.61$$

$$C = -45.67$$

The constants for water are:

$$A = 18.3036$$

$$B = 3816.44$$

$$C = -46.13$$

Using the algorithm described above, the two phase boiling point for water-Freon 113 under equilibrium conditions was calculated as 112.47°F. The value given by Horsley for the boiling point of the azeotrope of water - 1,1,2 - trichlorotrifluoroethane is 44.5°C (112.1°F).²⁶ If the value given by Horsley is assumed to be correct, the estimated value of 112.47°F is only in error by 0.33%.

Similar calculations were performed for water-pentane and water-methyl salicylate, and the results are given in Table 10. Since the Antoine constants for methyl salicylate are not given by Reid, Prausnitz, and Sherwood, the vapor pressure data were obtained from Perry's Handbook,²⁷ and a straight line was fit through the data plotted on $\log P_B$ versus $\frac{1}{T}$ coordinates. A similar plot was made for the vapor pressure of water. The equations given below were then used in the algorithm described above to calculate the boiling point of the two-phase mixture:

$$\ln P_B = 20.361 - \frac{11,989.627}{T} \quad (\text{range } 130 \text{ to } 280^\circ\text{F}) \quad (45)$$

$$\ln P_A = 20.0961 - \frac{9046.1058}{T} \quad (\text{range } 194 \text{ to } 215^\circ\text{F}) \quad (46)$$

B: methyl salicylate; A: water

In equations (45) and (46), the units of temperature are degrees Rankine, and the units of vapor pressure are millimeters of mercury.

TABLE 10

Comparison of Calculated Values and Literature Values
for the Two-Phase Boiling Point of Systems
of Immiscible Liquids

System of Immiscible Liquids	Calculated Value of Two-Phase Boiling Point, °F	Boiling Point of Two Phase Azeotrope from Horsley's data ^a , °F	Percent Error
water-Freon 113	112.47	112.10	0.33
water-pentane	94.07	94.82	0.79
water-methyl salicylate	211.55	No Data	-

a. Horsley, Lee H., Azeotropic Data-III, Advances in Chemistry Series 116, Robert T. Gould, Ed., American Chemical Society, Washington, D.C., 1973.

APPENDIX D

CALIBRATION OF THE D/P CELL FOR STEAM FLOW RATE

MEASUREMENT AND CONTROL

The following is a description of the apparatus, procedure, and calculation for calibration of the d/p cell which was used for steam flow rate measurement and control in this work.

9

1. Description of Apparatus and Procedure

Figure 13 illustrates the experimental setup which was used for calibration of the d/p cell for measuring steam flow rate to the column. Compressed air was fed through the automatic valve, to the d/p cell, and then to a wet test meter for flow rate measurement. The pneumatic controller was used to control the air flow rate to the d/p cell. At a given air flow rate, the corresponding reading on the manometer (DP1M) was taken so that a plot could be made of the manometer reading as a function of flow rate. Given the air flow rate, the equivalent steam flow rate was calculated from an equation obtained from the Foxboro instruction literature.²⁸ A sample calculation is given later in this appendix, and the calibration curves are in Appendix E.

According to the Foxboro literature, the pneumatic signal back to the controller is proportional to the square of the flow rate.²⁸ This was verified by plotting the square of the steam flow rate as a function of the manometer (DP1M) reading. As predicted, the data fell on a straight line. This figure is included in Appendix E.

The calibration curves which were used for steam flow rate in experimental runs through Run No. 16 are Figures 14 and 15 in Appendix E. After Run No. 16, the d/p cell was recalibrated because it was suspected that after several runs, the erosive action of the steam may have enlarged the d/p cell orifice slightly. The new calibration curves are Figures 16 and 17 in Appendix E.

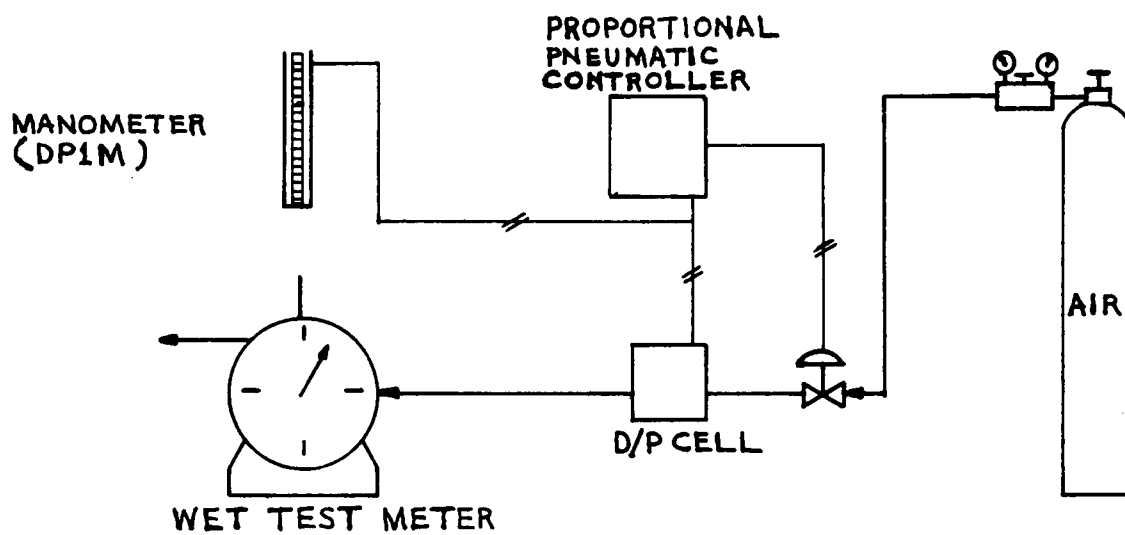


Figure 13. Apparatus for Calibration of D/P Cell.

2. Sample Calculation of Equivalent Steam Flow Rate

$$Q = \frac{Q_e}{(0.17) \sqrt{\frac{TG}{P}}} \quad (47)$$

Q: Steam flow rate, SCFM (60°F, 14.7 PSIA)

Q_e : Air flow rate, SCFM

T: Absolute temperature of steam, °R

P: Absolute pressure of steam, PSIA

G: Steam density compared to air at the same conditions

For an air flow rate of 0.652 cubic feet per minute at 70°F and a pressure of 745.7 mm Hg, calculate the equivalent steam flow rate at 60°F and 14.7 PSIA. The manometer (DPIM) reading at this air flow was 762.0 mm Hg.

Step 1: Correct the air flow rate to the standard conditions of 60°F and 14.7 PSIA:

$$745.7 \text{ mm Hg} \times \frac{14.7 \text{ PSIA}}{760 \text{ mm Hg}} = 14.4 \text{ PSIA}$$

$$\frac{P_1 V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad \text{or} \quad V_2 = \frac{P_1}{P_2} \frac{T_2}{T_1} V_1 \quad (48)$$

$$V_1 = 0.652 \text{ ft}^3$$

$$T_1 = 460 + 70 = 530^\circ\text{R}$$

$$T_2 = 460 + 60 = 520^\circ\text{R}$$

$$P_1 = 14.4 \text{ PSIA}$$

$$P_2 = 14.7 \text{ PSIA}$$

$$V_2 = \frac{(14.4)(520)(0.652)}{(14.7)(530)} = 0.627 \text{ ft}^3$$

The air flow rate at 60°F and 14.7 PSIA is 0.627 ft³/min.

Step 2: Calculate a value for G at 60°F and 14.7 PSIA:

Density of air = 0.0765 lb_m/ft³ at 60°F and 14.7 PSIA
(from a handbook)

Density of saturated steam = 0.0373 lb_m/ft³ at 212°F and 14.7 PSIA
(from steam tables)

Correct the density of steam to 60°F and 14.7 PSIA:

$$v_2 = \frac{520^\circ\text{R}}{672^\circ\text{R}} (26.80 \text{ ft}^3) = 20.74 \text{ ft}^3 \text{ (for 1 lb}_m \text{ of steam)}$$

The calculated density of steam at 60°F and 14.7 PSIA is 0.0482 lb_m/ft³.

$$G = \frac{0.0482}{0.0765} = 0.630$$

Step 3: Calculate the equivalent steam flow rate at 60°F and 14.7 PSIA:

$$\begin{aligned} T &= 520^\circ\text{F} & Q_e &= 0.627 \text{ ft}^3/\text{min} \\ P &= 14.7 \text{ PSIA} & G &= 0.630 \end{aligned}$$

$$Q = \frac{0.627}{(0.17) \sqrt{\frac{(520)(0.630)}{14.7}}} = 0.781 \text{ SCFM}$$

The equivalent steam flow rate is 0.781 SCFM at 60°F and 14.7 PSIA.

This value of steam flow rate corresponds to a manometer reading (DPlM) of 762.0 mm Hg. This is one of the data points shown on the calibration curve, Figure 14, Appendix E.

APPENDIX E

CALIBRATION CURVES

Figures 14 through 24 are the calibration curves for the flow meters used in this work.

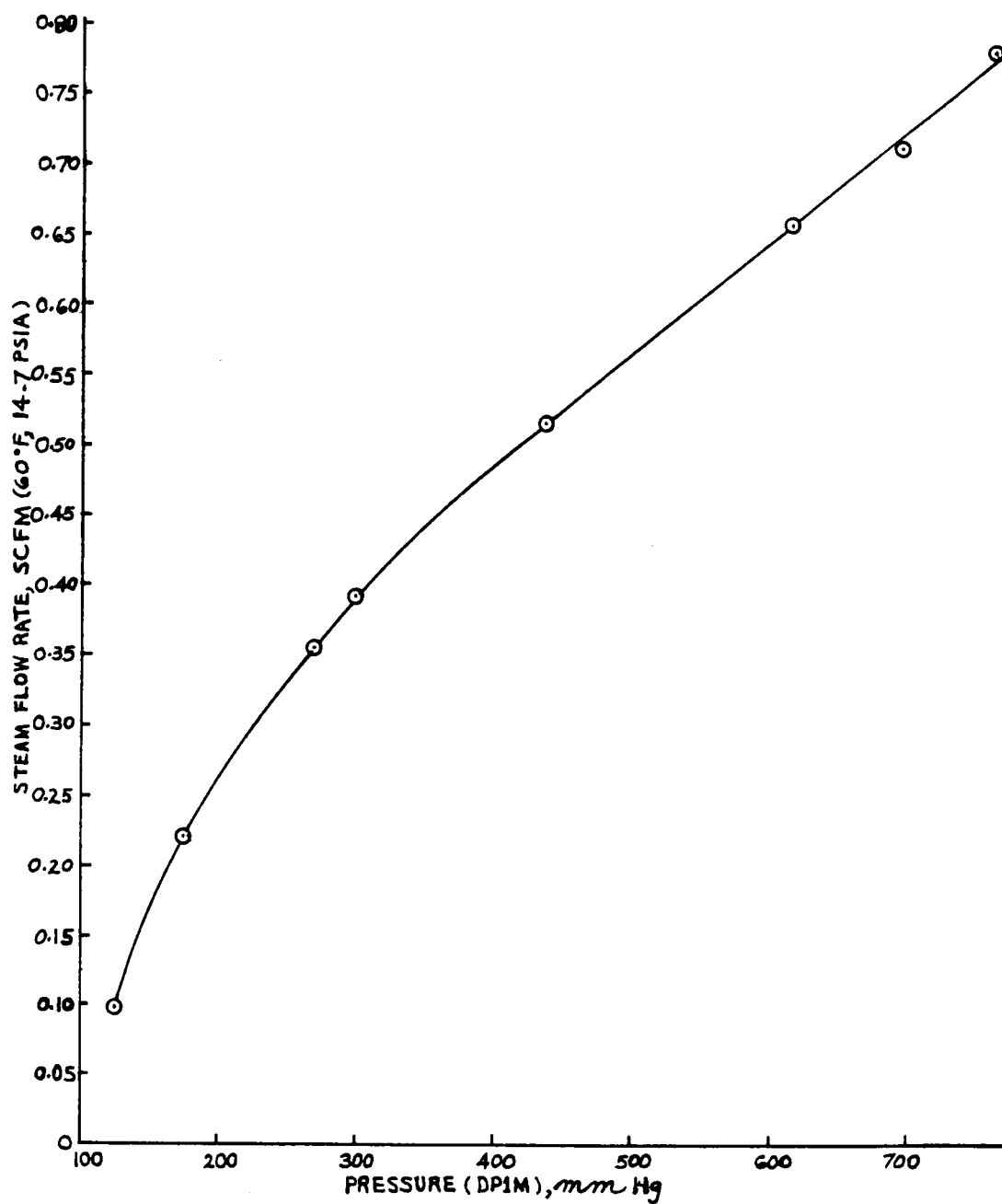


Figure 14. Steam Flow Rate as a Function of D/P Cell Transmitter Output Manometer Reading (Curve for Runs Through No. 16).

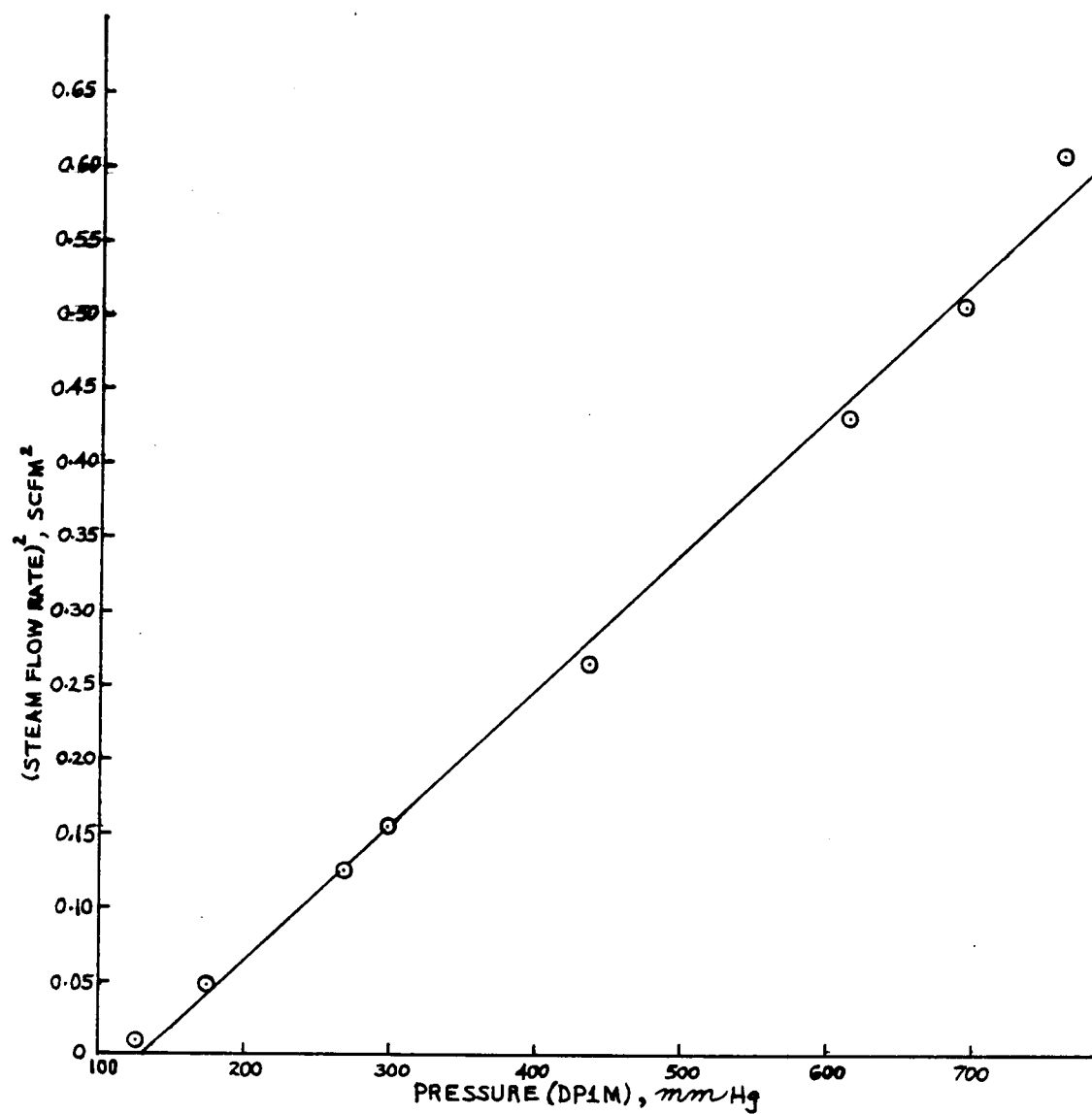


Figure 15. Linearized Plot of Steam Flow Rate as a Function of D/P Cell Transmitter Output Manometer Reading (Curve for Runs Through No. 16).

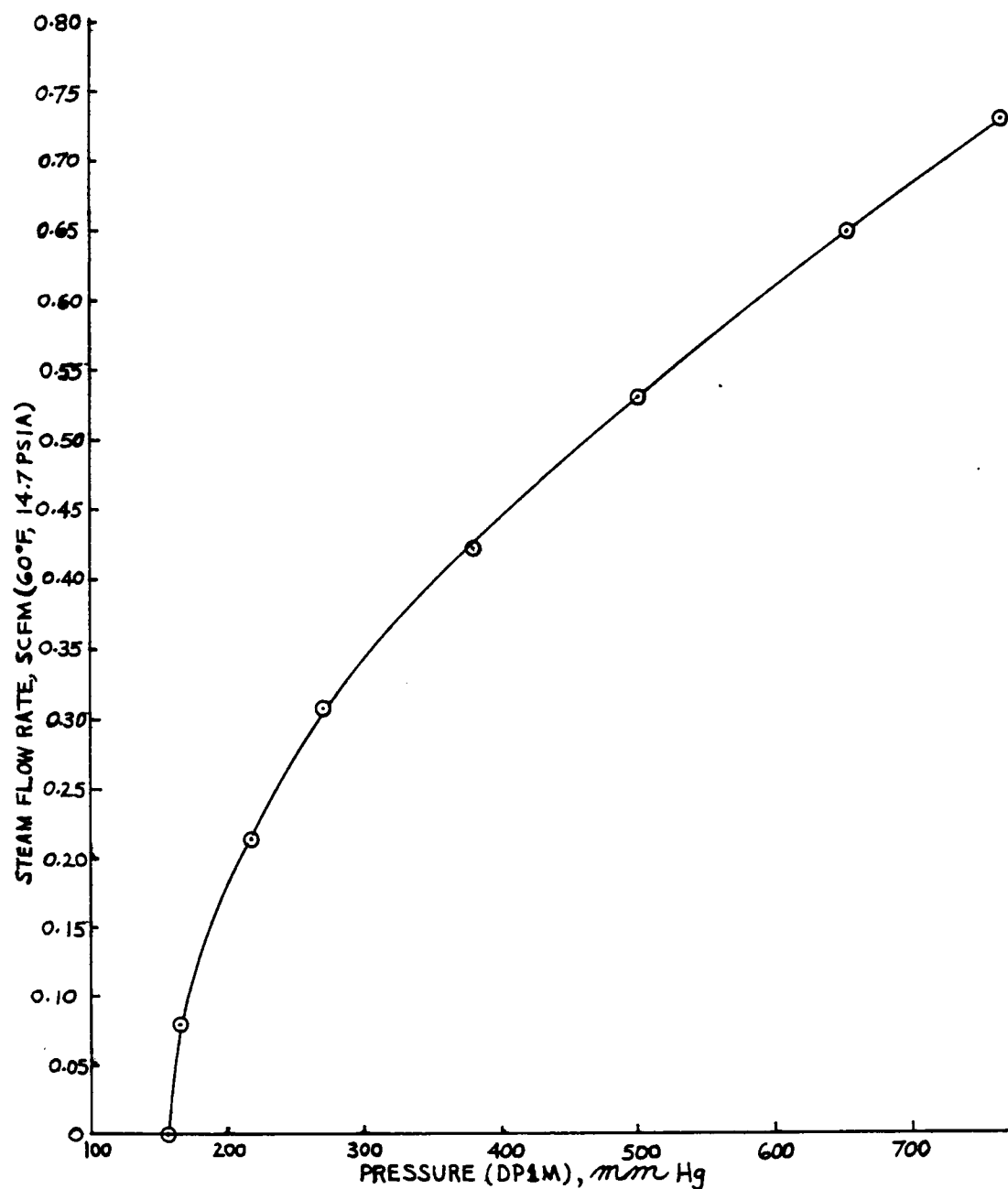


Figure 16. Steam Flow Rate as a Function of D/P Cell Transmitter Output Manometer Reading (Curve for Runs After No. 16).

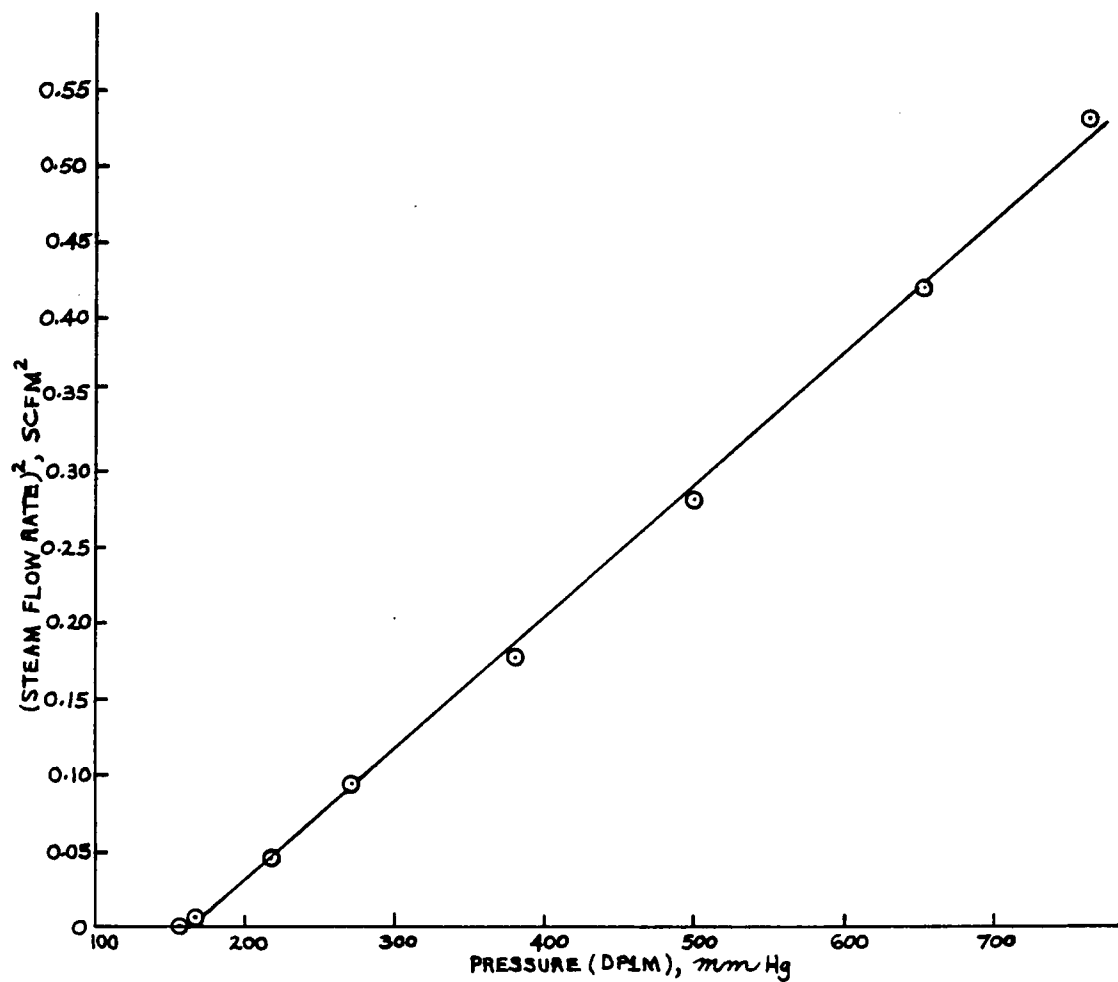


Figure 17. Linearized Plot of Steam Flow Rate as a Function of D/P Cell Transmitter Output Manometer Reading (Curve for Runs After No. 16).

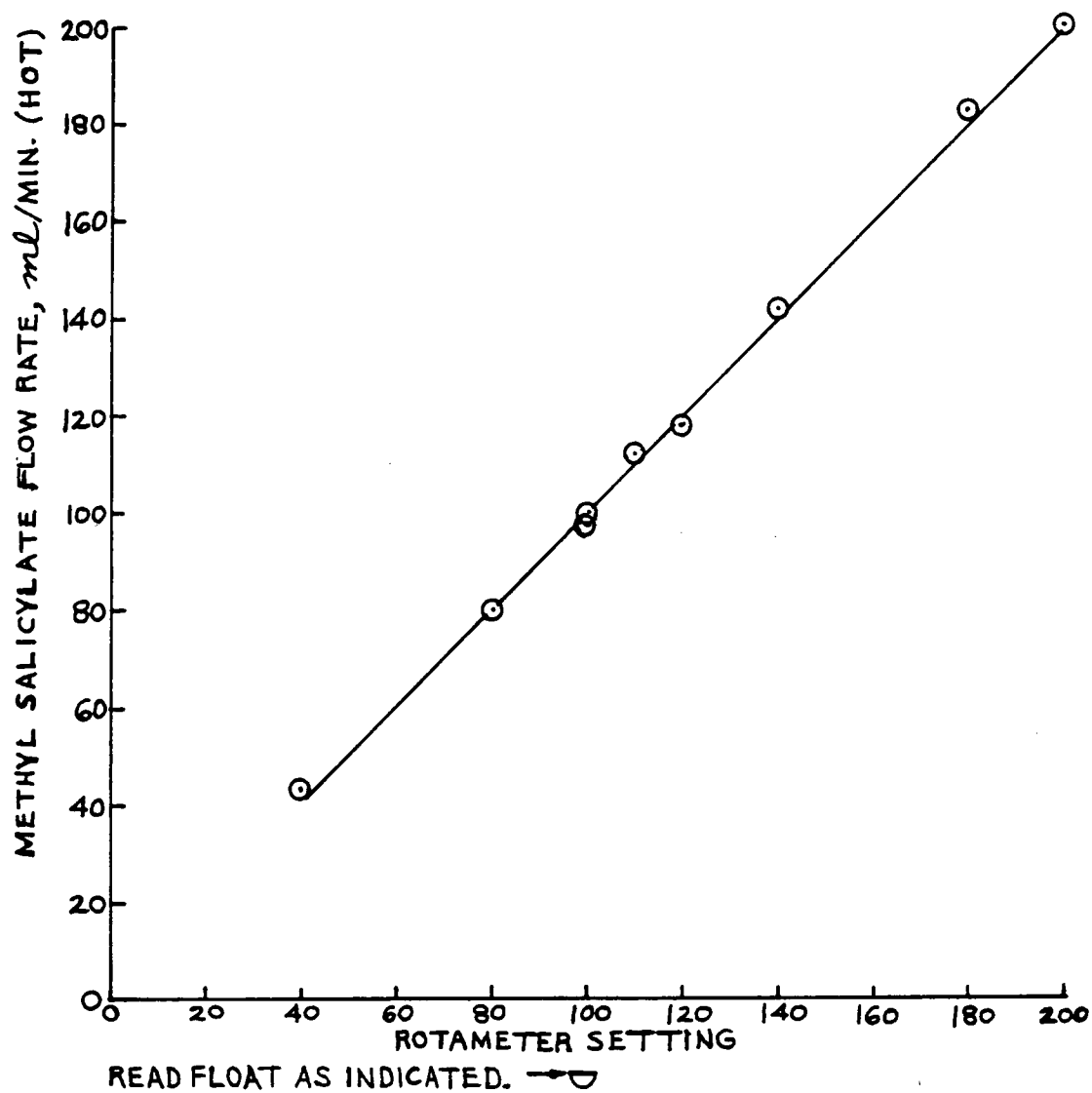


Figure 18. Calibration Curve for Low Flow Rates for Methyl Salicylate Feed Rotameter.

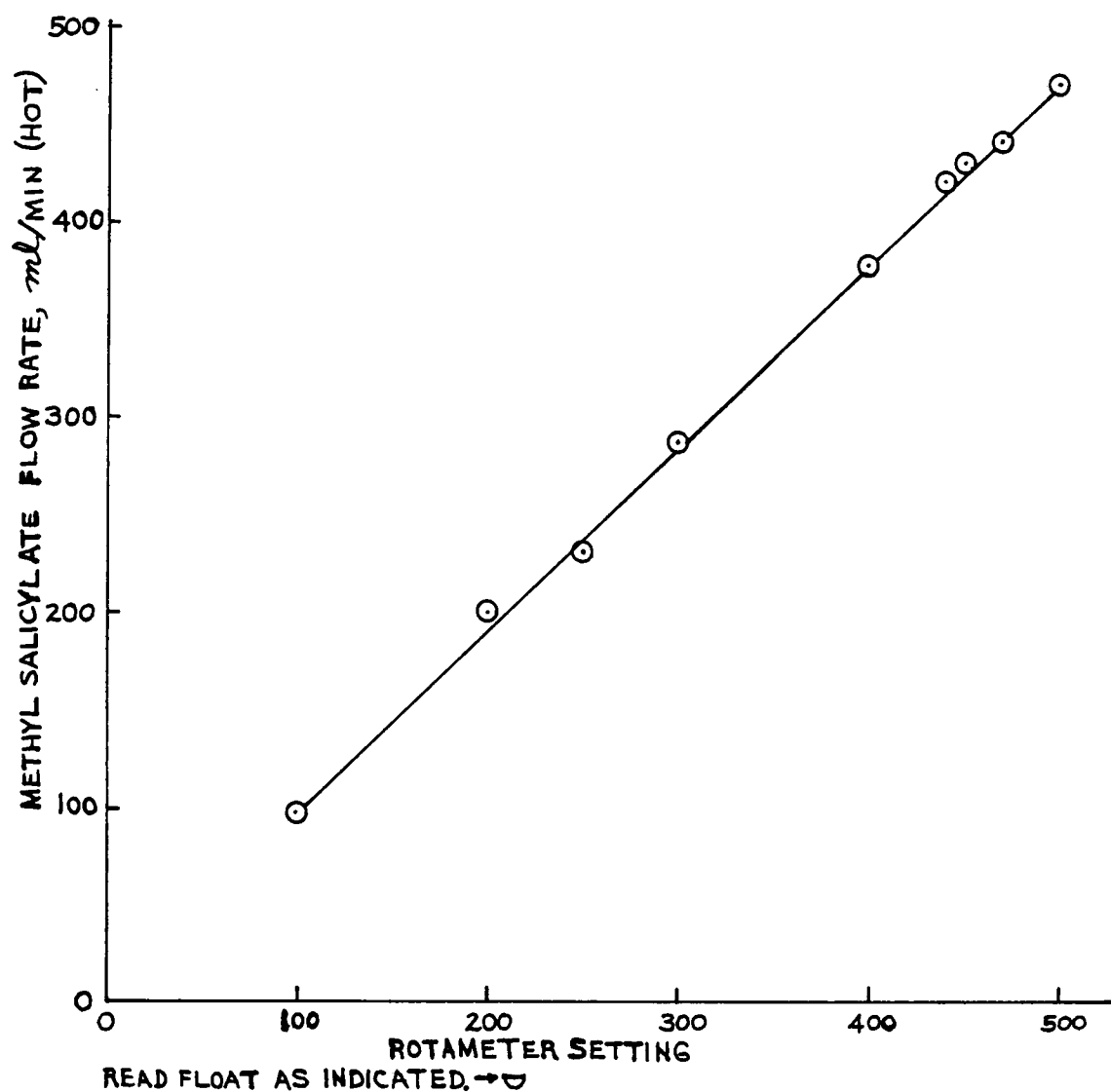


Figure 19. Calibration Curve (Volumetric Basis) for Methyl Salicylate Feed Rotameter.

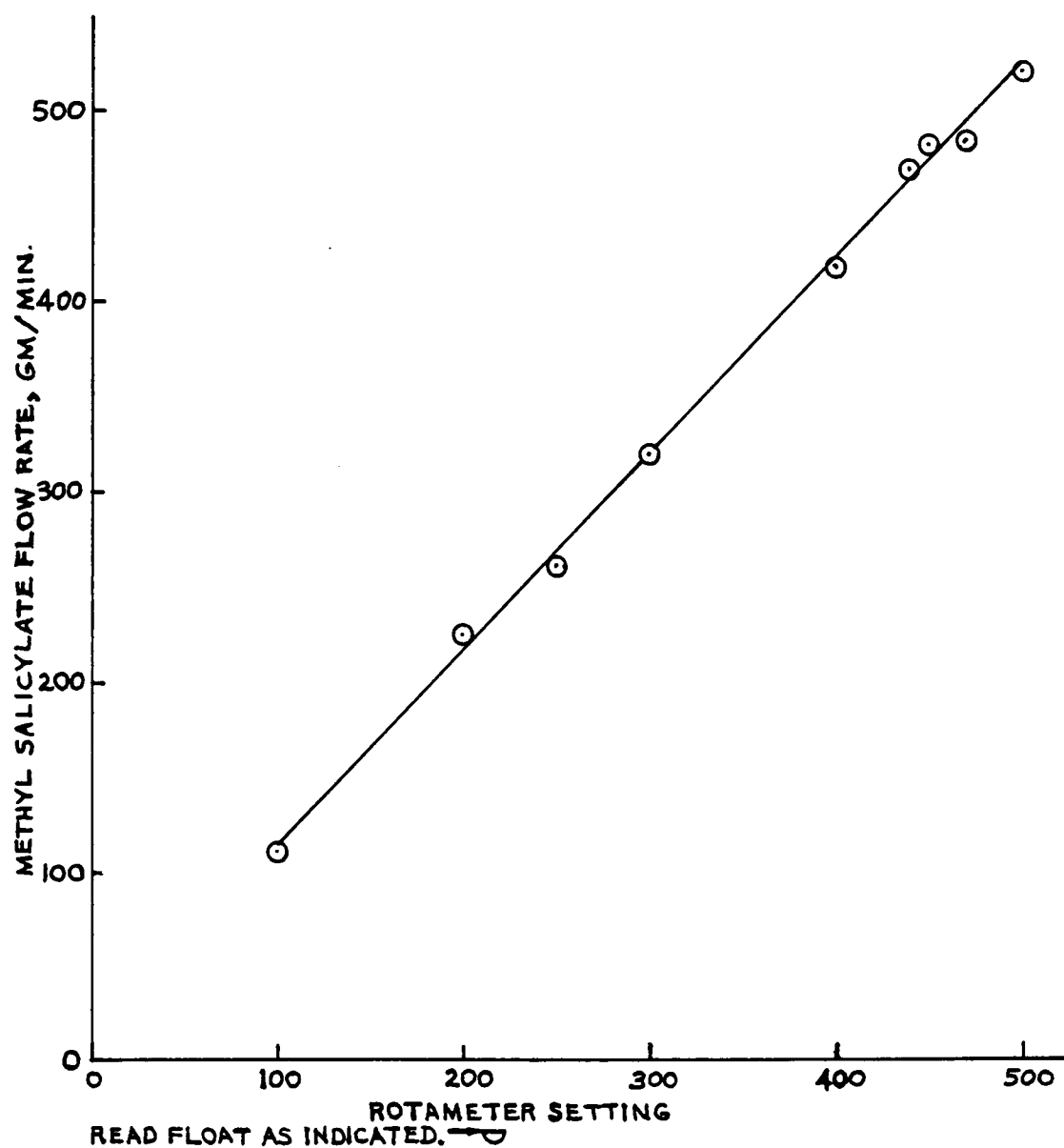


Figure 20. Calibration Curve (Mass Basis) for Methyl Salicylate Feed Rotameter.

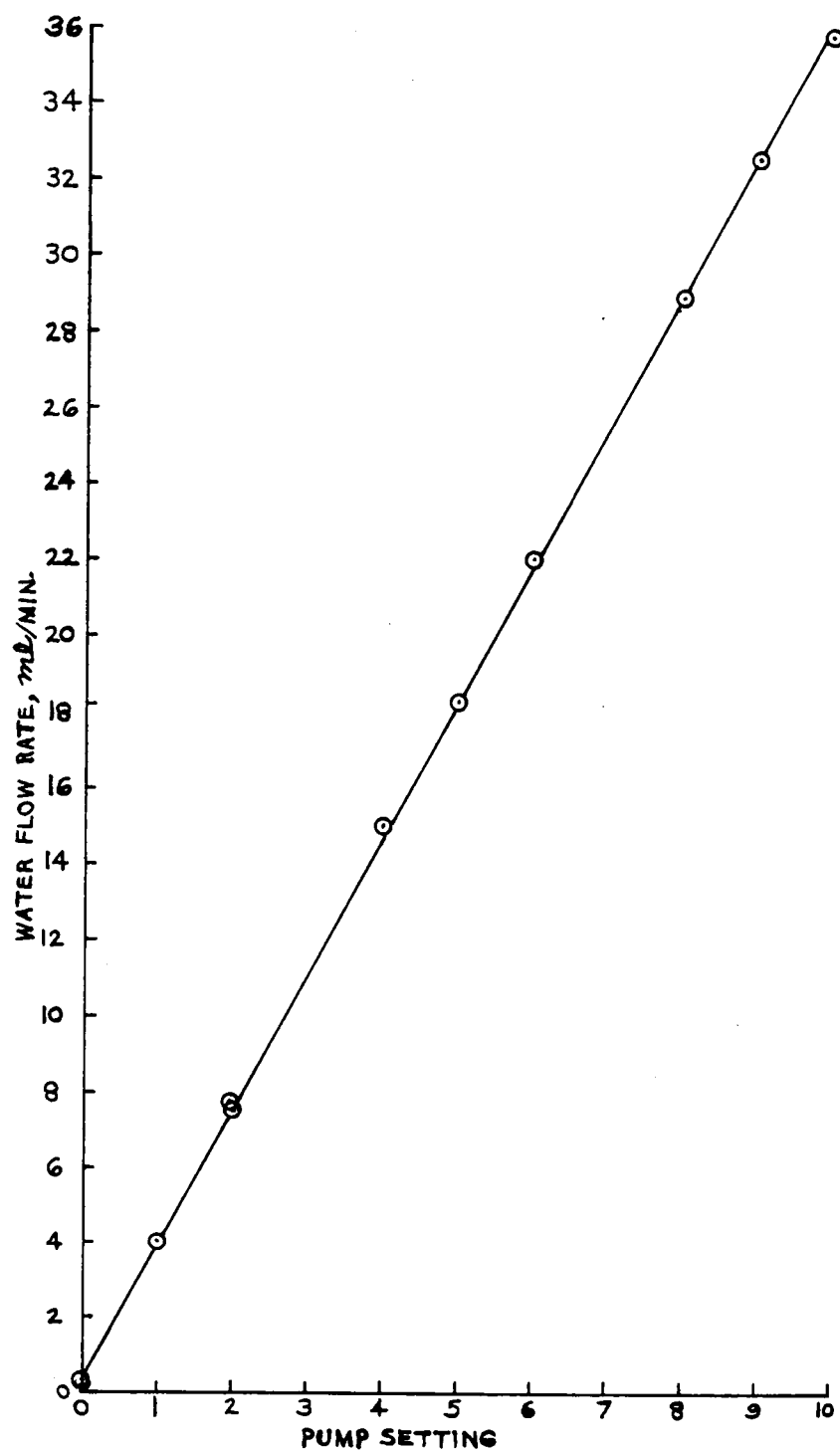


Figure 21. Hot Water Feed Pump Calibration Curve.

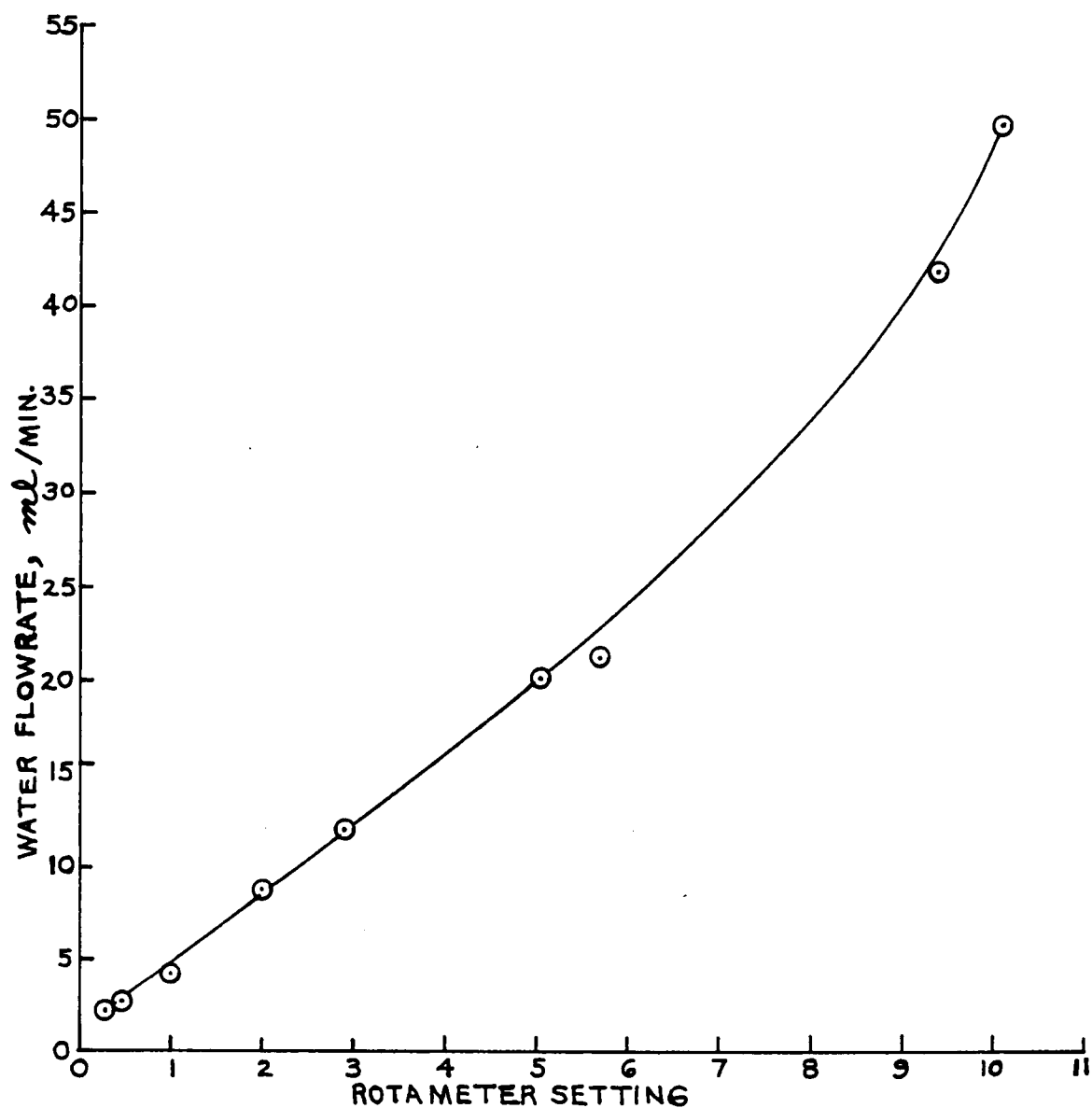


Figure 22. Calibration Curve for Hot Water Feed Rotameter.

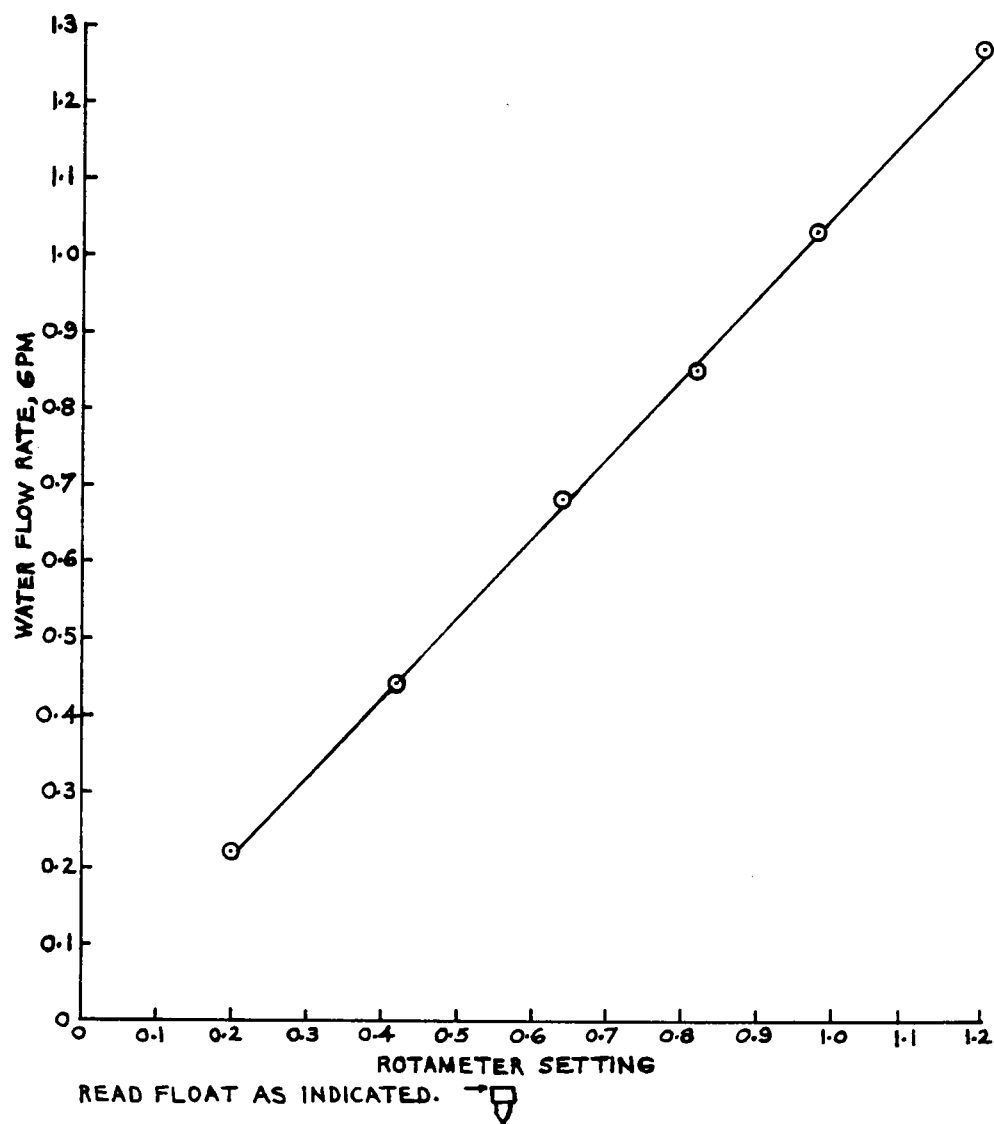


Figure 23. Calibration Curve for Condenser Cooling Water Rotameter.

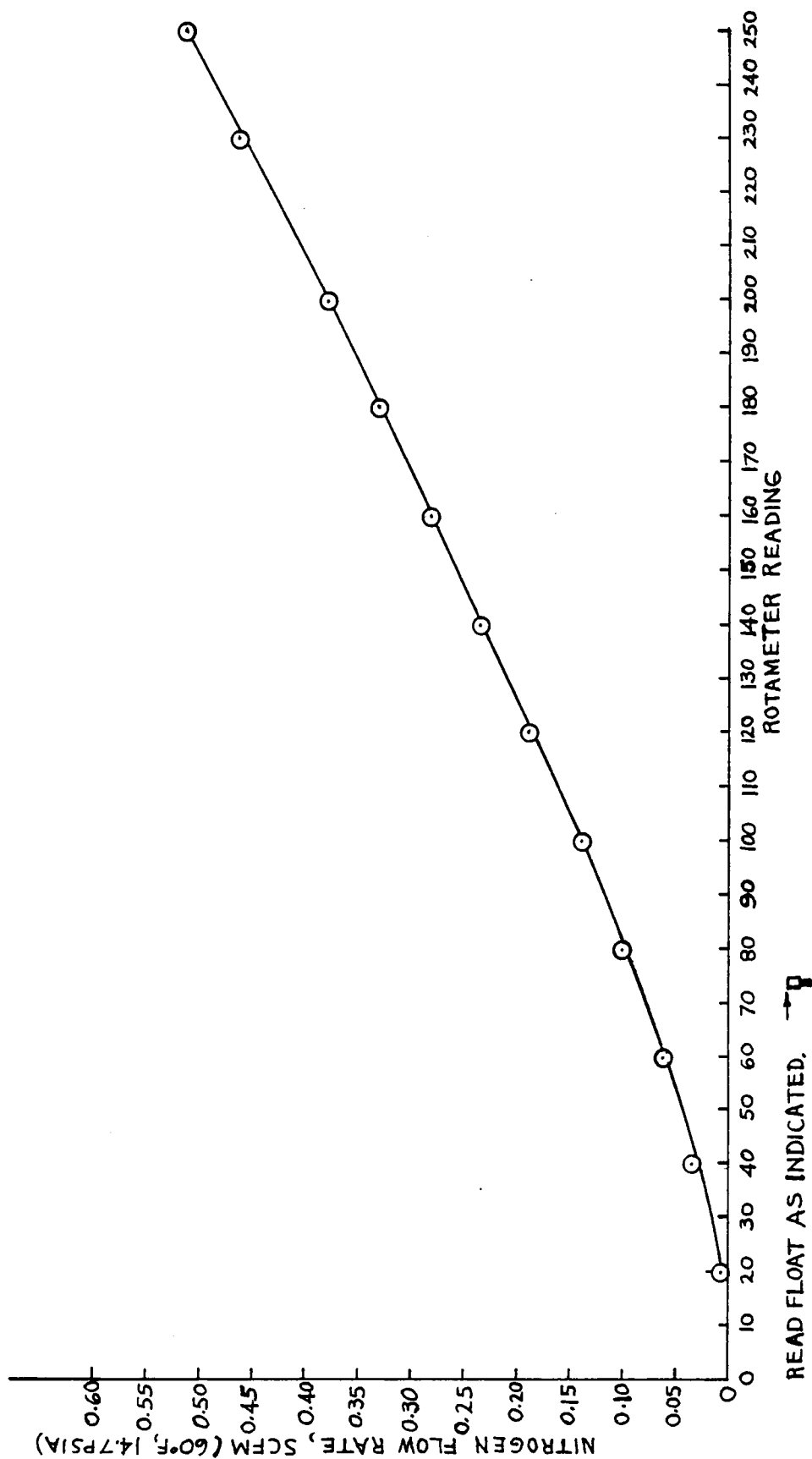


Figure 24. Nitrogen Feed Rotameter Calibration Curve.

APPENDIX F

EXPERIMENTAL DATA

Tables 11 through 39 contain the experimental data obtained in experiments with the direct contact boiler.

TABLE 11

Direct Contact Boiling Heat Transfer Experimental Data (Run No.^e 4, Date 2/14/81)

TEMPERATURE DATA ^a					FLOW RATE DATA										PRESSURE DATA									
Run No.	Time	T8	Dist. inches	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.								
4/11:05AM	-	-	-	210	214	-	211	-	214	224	245	-	48	68	44	66								
/																								
/																								
Run No.	Time	R1	R2	R3	O1:Total/M.S. (ml/min.)	O2:Total/H ₂ O (ml/min.)	Time ^d Period Min.	U1 ml/min.	DP1M mm Hg	PSIG	Ft. Water	In. Water	P1	P2	P3	Barom. Press. mm Hg								
4/11:05AM	-	130	7.3	0.83	0/0	6.90/6.71	67	-	-	6	4.0	0	30	0	30	750.4								
/					/	/																		
/					/	/																		

INLET STEAM QUALITY: 51.9% by wt.

AQUEOUS PHASE HOLDUP AT END OF RUN: -% by vol.

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate O2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

TABLE 12

Direct Contact Boiling Heat Transfer Experimental Data (Run No.^e 5, Date 2/6/81)

TEMPERATURE DATA ^a																
Run No.	Time	T8	Dist. ^b Inches	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.
5/5:25P.M.	-	-	-	213	214	218	211.3	-	213.8	226-229	243.7	-	68	72.3	47.7	72
/																
/																

FLOW RATE DATA																
Run No.	Time	R1 ml/min.	R2 ml/min.	R3 GPM	Q1:Total/M.S. (ml/min.)	Q2:Total/H ₂ O (ml/min.)	Time ^d Period Min.	U1 ml/min.	DPLM mm Hg	PSIG	Ft. Water	In. Water	P1	P2	P3	Barom. Press. mm Hg
5/5:25P.M.	170-200	170-200	9.0	0.35	0/0	6.30/6.0	5	221	-	6	4.0	0	45	0	45	747.9
/					/	/										
/					/	/										

PRESSURE DATA																
Run No.	Time	R1 ml/min.	R2 ml/min.	R3 GPM	Q1:Total/M.S. (ml/min.)	Q2:Total/H ₂ O (ml/min.)	Time ^d Period Min.	U1 ml/min.	DPLM mm Hg	PSIG	Ft. Water	In. Water	P1	P2	P3	Barom. Press. mm Hg
5/5:25P.M.	170-200	170-200	9.0	0.35	0/0	6.30/6.0	5	221	-	6	4.0	0	45	0	45	747.9
/					/	/										
/					/	/										

INLET STEAM QUALITY: 46.7% by wt. AQUEOUS PHASE HOLDUP AT END OF RUN: % by vol.

INLET STEAM QUALITY: 46.7% by wt.

AQUEOUS PHASE HOLDUP AT END OF RUN: -Z by vol.

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate Q2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

TABLE 13

Direct Contact Boiling Heat Transfer Experimental Data (Run No. 8^{e f}, Date 2/28/81)

TEMPERATURE DATA ^a																	FLOW RATE DATA										PRESSURE DATA						
Run No.	Time	T8	Dist.: Inches ^b	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.	Run No.	Time	R1	R2	R3	Q1: Total/M.S. (ml/min.)	Q2: Total/H ₂ O (ml/min.)	Time ^d Period Min.	U1 ml/min.	DP1M mm Hg	PSIG	P1 Ft. Water	P2 In. Water	P3 PSIG	Barom. Press. mm Hg		
8/7:45P.M.		212.3	32	212	206.3	-	204	-	203.7	219.3	219	203	52	67	52	75		-															
/																		/				14.0/4.5	0.43/-	20	264	0		4.6	0.1	35	743.3		
/																		/				/	/										

INLET STEAM QUALITY: 0% by wt.

AQUEOUS PHASE HOLDUP AT END OF RUN: -% by vol.

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate O2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

f. Run No. 8 was the first run in which the heating tape temp. control was used on hot water feed to the column. Run No. 8 was also the first run in which the FMI pumps were used, and the first run with demister mesh in the bottom of the column. No steam was fed to the column in Run No. 8.

TABLE 14

Temperature Profile Data (Run No. 8,
Date 2/28/81, Time 8:10 P.M.)

T8, °F	Distance Upward From Platform, Inches
208.3	8
209.3	15 3/8
211.0	22
213.0	27
213.0	32

TABLE 16

Temperature Profile Data (Run No. 9^a,
Date 3/3/81, Time 12:55 A.M.)

T8, °F	Distance Upward From Platform, Inches
228.0	0
229.0	8
229.0	16
229.7	24
229.7	31.5
229.3	35

a. The bottom of the M.S. inlet was about one-quarter inch above the bottom of the sight glass. The bottom of the M.S. inlet line was at the base of the aqueous layer that was floating on the M.S. phase.

TABLE 17

Direct Contact Boiling Heat Transfer Experimental Data (Run No. e 10^f, Date 3/5/81)

TEMPERATURE DATA ^a																
Run No.	Time	T8	Dist. Inches ^b	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.
10a/1:52PM		210.3	8	215.7	212.7	216.7	210.3	-	211.3	215.0	225.7	206.3	71.7	86	56	76
10b/3:44PM		210.3	8	215.7	213.0	217.0	210.7	-	211.7	220.7	235.0	210.3	73	88.3	54	72
/																

FLOW RATE DATA																
Run No.	Time	R1	R2	R3	01: Total/H.S. (ml/min.)	02: Total/H ₂ O (ml/min.)	Time ^d Period Min.	U1 ml/min.	DP1M mm Hg	DP1 PSIG	P1 Ft. Water	P2 In. Water	P3 PSIG	Barom. Press. mm Hg		
10a/1:52PM	-	265	14.2	0.17	20.8/18.3	16.6/14.6	1	248	453.0	9.2	3.88	0.25	28	732.6		
10b/3:44PM		217	14.2	0.16	7.50/5.00	10.93/9.60	3	240	454.0	9.2	3.75	0.10	28	735.8		
/					/	/										

INLET STEAM QUALITY: 44.8% by wt.

AQUEOUS PHASE HOLDUP AT END OF RUN: -% by vol.

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate 02 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

f. Run No. 10 is the one in which a phase inversion occurred after four hours of operation.

TABLE 18

Direct Contact Boiling Heat Transfer Experimental Data (Run No.^e 11, Date 3/17/81)

TEMPERATURE DATA ^a																
Run No.	Time ^c	T8	Dist. ^b inches	T29	T30	T31-	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.
11a/3:10PM	-	-	-	214	211	215	212.3	-	209.7	250.3	258	207.3	-	-	-	75
11b/4:05PM	-	-	-	216.7	213.3	216.3	215	-	212.3	256.7	261.3	210.3	68.7	93	56	75
/																

FLOW RATE DATA										PRESSURE DATA				
Run No.	Time	R1	R2	R3	O1:Total/M.S. (ml/min.)/ml/min.	O2:Total/H ₂ O (ml/min.)/ml/min.	Time Period Min.	U1	DP1M mm Hg	DP1 PSIG	P1 Ft. Water	P2 In. Water	P3 PSIG	Barom. mm Hg
-	-	ml/min. 274-287	ml/min. 14.2	GPM -	-/-	-/-	-	-	239.0	5.3	3.90	0.3	52.5	736.2
11a/3:10PM		287	14.2	0.15	5.91/5.31	12.1/10.8	47	-	239.0	5.3	3.95	0.3	57	736.2
11b/4:05PM					/	/								
/														

INLET STEAM QUALITY: 32.9% by wt.

AQUEOUS PHASE HOLDUP AT END OF RUN: 15.3% by vol.

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate O2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

TABLE 19

Direct Contact Boiling Heat Transfer Experimental Data (Run No.^e 12, Date 3/20/81)

TEMPERATURE DATA ^a		Dist. ^b																Room Temp.	
Run No.	Time	T8	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40					
12a/12:08PM	See Profile	216	213	216.3	215	-	211	250	256	212	73.7	93	55	73					
12b/2:08AM	See Profile	-	-	-	-	-	-	-	245-250	-	-	-	-	-					
/																			

FLOW RATE DATA										PRESSURE DATA									
Run No.	Time	R1 ^f	R2	R3	O1:Total/M.S.	O2:Total/H ₂ O	Time ^d	U1	DPLM	DP1	P1	P2	P3	Barom. Press.					
		ml/min.	ml/min.	GPM	(ml/min.)/ml/min.	(ml/min.)/ml/min.	Min.	ml/min.	mm Hg	PSIG	Ft. Water	In. Water	PSIG	mm Hg					
12a/12:08PM		322	14.1	0.15	18.8/18.4	11.1/10.0	37	-	242	5.3	3.97	0.45	58	739.6					
12b/2:08PM		208-265	14.1	0.175	-/-	-/-	-	217	242	5.7	4.0	0.30	58.2	-					
/					/	/													

INLET STEAM QUALITY: 33.3% by wt.

AQUEOUS PHASE HOLDUP AT END OF RUN: 17.8% by vol.

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate O2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

f. Bubbles passing through rotameter made it difficult to read flowrate at times.

TABLE 20

Temperature Profile Data (Run No. 12,
Date 3/20/81, Time 12:08 P.M.)

T8, °F	Distance Upward From Platform, Inches
211.3	8
211.3	14
211.3	20.9
211.3	26.9
211.5	32
211.7	36
212.3	36.8 ^a
211.7	38.4 ^b

a. Near the bottom of the M.S. inlet tube
(located even with bottom of sight glass)

b. Near the top of the foam zone

TABLE 21

Temperature Profile Data (Run No. 12,
Date 3/20/81, Time 2:08 P.M.)

T8, °F	Distance Upward From Platform, Inches
212.2	0
212.7	8
211.7	15
212.0	20.8
211.7	26
211.5	32
210.7	37

TABLE 23

Temperature Profile Data (Run No. 13,
Date 4/2/81, Time 3:42 P.M.)

T8, °F	Distance Upward From Platform, Inches
213.0	0
212.3	6
212.3	12
212.0	18
211.0	24
210.7	30
211.0	36
211.7	38

TABLE 24

Direct Contact Boiling Heat Transfer Experimental Data (Run No.^e 14, Date 4/10/81)

TEMPERATURE DATA ^a																	PRESSURE DATA									
Run No.	Time	T8	Dist. ^b Inches	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.										
14/11:19AM		See Profile		216.0	217.7	216.7	220.0	207	215.7	254	-	217.7	94.3	110.7	64.7	79.5										
/																										
/																										

FLOW RATE DATA										PRESSURE DATA																
Run No.	Time	R1 ml/min.	R2 ml/min.	R3 GPM	O1: Total/M.S. (ml/min.)/ml/min.	O2: Total/H ₂ O (ml/min.)/ml/min.	Time ^d Period Min.	U1 ml/min.	DP1M mm Hg	PSIG	Ft. Water	In. Water	P1 PSIG	P2 PSIG	P3 PSIG	Barom. mm Hg										
14/11:19AM		213-227	4.3	0.155	2.51/2.48	20.3/18.1	31.8	214	632.0	12.8	3.60	1.70	58	58	752.3											
/					/	/																				
/					/	/																				

INLET STEAM QUALITY: 77.3% by wt.

AQUEOUS PHASE HOLDUP AT END OF RUN: 0.6% by vol.

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate O2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

TABLE 25

Temperature Profile Data (Run No. 14,
Date 4/10/81, Time 11:19 A.M.)

T8, °F	Distance Upward From Platform, Inches
216.5	0
216.8	6
217.0	12
216.7	18
216.3	24
216.3	30
217.3	36
218.3	39 ^a

a. At the top of foam zone, which was six to nine inches thick in this run.

TABLE 26

Direct Contact Boiling Heat Transfer Experimental Data (Run No. 15, Date 5/1/81)^e

TEMPERATURE DATA ^a																
Run No.	Time ^c	T8	Dist. Inches ^b	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.
15a/10:45AM	See Profile			215.0	213.0	217	211.3	233.7	211.7	228	237.7	211.3	76.7	91.7	67.3	79
15b/11:53AM	See Profile			213.7	212.7	217	212.0	211.5	211.5	236.3	244.7	210.7	79.3	94.7	68.0	80
/																

FLOW RATE DATA														PRESSURE DATA					
Run No.	Time	R1	R2	R3	Q1:Total/M.S. (ml/min.)/ml/min.	Q2:Total/H ₂ O (ml/min.)/ml/min.	T _{Time} ^d Period Min.	U1	DP1M mm Hg	DP1	P1	P2	P3	Barom. mm Hg					
15a/10:45AM	161-245	9.0	0.191		1.6/1.6	7.36/6.76	198	175	269.0	6.0	4.0	0.9	45	742.5					
15b/11:53AM	201-245	9.0	0.170		29.0/28.5	8.83/8.09	23	175	269.0	6.0	4.0	0.9	45	742.2					
/					/	/													

INLET STEAM QUALITY: 46.5% by wt.

AQUEOUS PHASE HOLDUP AT END OF RUN: 28.7% by vol.

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate O2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

TABLE 27

Temperature Profile Data (Run No. 15,
Date 5/1/81, Time 10:45 A.M.)

T8, °F	Distance Upward From Platform, Inches
211.7	0
211.7	6
211.7	12
211.7	18
212.0	24
212.0	30
211.0	36 ^a
211.0	38

a. The bottom of the M.S. inlet line was
at 36.8 inches upward from the platform.

TABLE 28

Temperature Profile Data (Run No. 15,
Date 5/1/81, Time 11:53 A.M.)

T8, °F	Distance Upward From Platform, Inches
211.8	0
211.8	6
211.8	12
211.8	18
211.8	24
211.8	30
211.8	36
211.7	38
211.7	39

TABLE 29

Direct Contact Boiling Heat Transfer Experimental Data (Run No. 16^e, Date 5/9/81)

TEMPERATURE DATA ^a																
Run No.	Time ^c	T8	Dist. Inches ^b	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.
16a	2:41PM	206.7	12	213	207.3	212.3	207	238.7	206.7	233.3	-	207.7	70	91	65.3	77
16b	3:31PM	See Profile	-	-	-	-	-	-	-	243.5	-	-	-	-	-	-
16c	3:55PM	See Profile	213.3	206.7	212.7	212.7	206.7	240.3	209	228.3	237.7	207	69.7	89.7	66.0	78

FLOW RATE DATA						PRESSURE DATA								
Run No.	Time	R1 g	R2	R3	O1: Total/M.S.	O2: Total/H ₂ O	Time Period	U1	DPIM	DPI	P1	P2	P3	Barom. Press.
		ml/min.	ml/min.	GPM	(ml/min.)	(ml/min.)	Min.	ml/min.	mm Hg	PSIG	Ft. Water	In. Water	PSIG	mm Hg
	-	-237	9.2	0.473	-/-	10.44/9.55	56	206.7	267.0	6.3	4.0	0.1	58	744.8
16a/2:41PM		100-290	9.2	-	-/-	8.85/7.93	92	-	267.0	6.3	-	-	58	
16b/3:31PM		125-134	9.2	0.460	-/-	8.41/7.35	49	-	267.0	6.3	4.0	0.1	58	744.7

17.2% by vol.

- COMMENTS:
- All temperatures are degrees Fahrenheit.
 - Distance upward from platform.
 - "Time" means the time that the data set was begun.
 - Time period over which flow rate 02 was measured
 - When more than one data set was taken per run, a small letter suffix was appended to Run No.
 - The nitrogen flowrate was 0.0292 SCFM (60°F, 14.7 PSIA); steam was also fed to the column.
 - Flow rate was difficult to determine due to the presence of bubbles in rotameter.

TABLE 30

Temperature Profile Data (Run No. 16,
Date 5/9/81, Time 3:31 P.M.)

T8, °F	Distance Upward From Platform, Inches
206.3	0
206.3	8
206.3	12
206.7	14
207.0	20
206.3	26
206.3	32

TABLE 31

Temperature Profile Data (Run No. 16^a,
Date 5/9/81, Time 3:55 P.M.)

T8, °F	Distance Upward From Platform, Inches
206.3	0
206.3	8
206.3	14
206.3	20
206.3	26
206.3	32
206.3	38

a. The bottom of the M.S. inlet line was
even with the bottom of the sight glass.

TABLE 33

Temperature Profile Data (Run No. 17^a,
Date 5/18/81, Time 10:07 P.M.)

T8, °F	Distance Upward From Platform, Inches
203.0	0
203.7	6
203.7	12
203.7	18
203.7	24
203.7	30
203.7	36
203.7	38

a. The bottom of the M.S. inlet line was even with the bottom of the sight glass.

Table 34

Temperature Profile Data (Run No. 17,
Date 5/18/81, Time 11:28 P.M.)

T8, °F	Distance Upward From Platform, Inches
188.3	0
188.3	6
188.3	12
188.0	18
188.0	24
188.0	30
188.0	36

TABLE 35

Direct Contact Boiling Heat Transfer Experimental Data (Run No.^e 18^f, Date 5/22/81)[illegible]

FLOW RATE DATA							PRESSURE DATA							
Run No.	/ Time	R1 ml/min.	R2 ml/min.	R3 GPM	O1:Total/M.S. (ml/min.)	O2:Total/H ₂ O (ml/min.)	Time Period Min.	U1 ml/min.	DPIIM mm Hg	DPI PSIG	P1 Ft. Water	P2 In. Water	P3 PSIG	Barom. press. mm Hg
18/4:00PM		237-245	18.0	0.21	16.0/16.0	5.63/5.03	71	260	0	0	4.20	0.05	58	746.5
/					/	/								
/					/	/								
/					/	/								

INLET STEAM QUALITY: -

14.4% by vol.

- COMMENTS:
- a. All temperatures are degrees Fahrenheit.
 - b. Distance upward from platform.
 - c. "Time" means the time that the data set was begun.
 - d. Time period over which flow rate 02 was measured
 - e. When more than one data set was taken per run, a small letter suffix was appended to Run No.
 - f. No steam was fed to the column in this run; nitrogen flowrate was 0.00731 SCFM (60°F, 14.7 PSIA).

TABLE 36

Temperature Profile Data (Run No. 18,
Date 5/22/81, Time 4:00 P.M.)

T8, °F	Distance Upward From Platform, Inches
207.3	0
208.7	6
208.3	12
208.0	18
208.0	24
208.0	30
208.0	36
208.0	38 ^a

a. At the top of the liquid in the
column.

TABLE 37

Direct Contact Boiling Heat Transfer Experimental Data (Run No.^e 19, Date 9/22/81)

TEMPERATURE DATA ^a																
Run No.	Time	T8 ^f	Dist. b Inches	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.
19a/10:11AM	212.2	36	215.3	212.5	216.0	214.0	214.7	209.0	209.7	253.3	272.0	211.7	80.0	102.0	74.3	77.0
19b/11:15AM	212.2		214.7	211.7	215.3	212.3	209.0			254.3	272.0	209.3	78.0	99.0	73.7	79.0
/																

FLOW RATE DATA										PRESSURE DATA				
Run No.	Time	R1	R2	R3	O1: Total/M.S. (ml/min.)/(ml/min.)	O2: Total/H ₂ O (ml/min.)/(ml/min.)	Time ^d Period Min.	U1	DP1M mm Hg	DP1 PSIG	P1 Ft. Water	P2 In. Water	P3 PSIG	Barom. mm Hg
-		ml/min.	ml/min.	GPM			Min.	ml/min.	mm Hg	PSIG				
19a/10:11AM		180	12.5	0.182	0/-	-/-	-	-	265	5.8	4.10	0.30	52.5	745.6
19b/11:15AM		200	12.5	0.177	0/-	9.50/8.81	16	193	266	5.8	4.15	0.25	54.0	746.3
/					/	/								

INLET STEAM QUALITY:

AQUEOUS PHASE HOLDUP AT END OF RUN:

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate O2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

f. Observations of signal on oscilloscope screen indicated a maximum deviation of about 0.6 °F from the baseline temperature of 212.2 °F. The duration of the deviation from the baseline temperature was typically 100 to 300 milliseconds.

TABLE 39

Direct Contact Boiling Heat Transfer Experimental Data (Run No.^e 21, Date 10/2/81)

TEMPERATURE DATA^a

Run No.	Time ^c	T8 ^f	Dist. ^b inches	T29	T30	T31	T32	T33	T34	T35	T36	T37	T38	T39	T40	Room Temp.
21a/9:44AM		213.24	37	216.0	213.0	216.8	214.0	217.7	210.7	251.0	275.7	212.7	88.0	96.7	74.7	74.0
21b/1:45PM		212.29	37	214.7	212.3	215.9	212.7	193.0	209.7	251.3	271.7	210.7	88.0	98.7	73.0	72.0
21c/4:00PM		212.70	37	214.3	211.7	215.7	211.7	211.7	211.3	257.3	276.3	210.5	90.3	99.5	72.7	72.5

FLOW RATE DATA

Run No.	Time	R1	R2	R3	Q1:Total/H.S. (ml/min.)/ml/min.	Q2:Total/H ₂ O (ml/min.)/ml/min.	Time ^d Period Min.	U1 ml/min.	DPIH mm Hg	DP1 mm Hg	PSIG	Ft. Water	In. Water	P1	P2	P3	Barom. mm Hg
21a/9:44AM	-	200	12.5	0.12	6.50/6.00	8.13/7.26	15.0	208	264	264	5.8	4.13	0	55.0	0	55.0	743.8
21b/1:45PM		200	12.5	0.12	70.67/60.00	8.88/7.96	187.8	155	265	265	5.8	4.10	0.1	53.5	0.1	53.5	744.1
21c/4:00PM		200	12.5	0.11	70.0 /53.0	8.91/8.00	11.0	135	264	264	5.8	4.05	0	53.5	0	53.5	744.1

PRESSURE DATA

INLET STEAM QUALITY:

AQUEOUS PHASE HOLDUP AT END OF RUN:

COMMENTS: a. All temperatures are degrees Fahrenheit.

b. Distance upward from platform.

c. "Time" means the time that the data set was begun.

d. Time period over which flow rate O2 was measured

e. When more than one data set was taken per run, a small letter suffix was appended to Run No.

f. Computer was used for acquisition of temperature data.

APPENDIX G

TEMPERATURE DATA OBTAINED IN RAPID TEMPERATURE MEASUREMENT EXPERIMENTS

Figures 25, 26 and 27 contain the temperature data that were obtained in the computer-assisted rapid temperature measurement experiments.

A>B:DKTST

```

212.86 212.95 212.86 212.77 212.72 212.86 213.01 212.95 212.78 212.79
212.79 212.95 212.92 212.80 212.65 212.73 212.73 212.85 212.82 212.76
212.70 212.71 212.82 212.84 212.82 212.72 212.72 212.75 212.89 212.86
212.79 212.75 212.76 212.94 212.96 212.79 212.78 212.79 212.93 212.93
212.87 212.73 212.79 212.89 212.97 212.88 212.73 212.68 212.63 212.68
212.70 212.73 212.86 212.90 212.76 212.68 212.72 212.76 212.85 212.86
212.95 212.82 212.77 212.85 212.90 212.90 212.77 212.73 212.84 212.92
212.95 212.80 212.67 212.65 212.71 212.68 212.61 212.63 212.61 212.67
212.76 212.65 212.67 212.68 212.70 212.73 212.85 212.86 212.82 212.71
212.77 212.90 212.94 212.89 212.73 212.76 212.82 212.88 212.82 212.73
212.71 212.78 212.93 212.82 212.68 212.70 212.63 212.67 212.65 212.65
212.73 212.68 212.72 212.77 212.90 212.93 212.88 212.72 212.76 212.97
212.90 212.76 212.70 212.73 212.82 212.89 212.78 212.68 212.69 212.67
212.73 212.68 212.72 212.76 212.84 212.90 212.85 212.76 212.75 212.86
212.89 212.88 212.82 212.75 212.86 212.94 212.90 212.75 212.63 212.71
212.73 212.75 212.88 212.71 212.65 212.63 212.59 212.63 212.72 212.65
212.63 212.67 212.69 212.70 212.71 212.77 212.86 212.93 212.79 212.76
212.79 212.92 212.88 212.76 212.72 212.71 212.82 212.84 212.82 212.66
212.71 212.63 212.61 212.59 212.56 212.61 212.65 212.68 212.70 212.63
212.71 212.73 212.84 212.90 212.79 212.76 212.78 212.86 212.95 212.85
212.71 212.65 212.70 212.72 212.78 212.84 212.71 212.56 212.60 212.58
212.63 212.63 212.65 212.69 212.73 212.56 212.69 212.69 212.68 212.73
212.68 212.73 212.71 212.85 212.87 212.73 212.63 212.61 212.70 212.60
212.54 212.55 212.58 212.62 212.58 212.59 212.56 212.59 212.60 212.68
212.65 212.73 212.72 212.62 212.66 212.68 212.65 212.65 212.71 212.63
212.67 212.70 212.63 212.68 212.62 212.65 212.61 212.61 212.56 212.59
212.56 212.59 212.61 212.63 212.71 212.56 212.59 212.63 212.68 212.73
212.65 212.62 212.65 212.65 212.63 212.71 212.62 212.69 212.59 212.59
212.71 212.63 212.61 212.60 212.61 212.56 212.56 212.63 212.67 212.70
212.59 212.58 212.56 212.61 212.70 212.63 212.62 212.65 212.65 212.73
212.71 212.78 212.87 212.79 212.63 212.62 212.63 212.63 212.67 212.73
212.59 212.63 212.65 212.61 212.68 212.65 212.71 212.65 212.68 212.71
212.65 212.62 212.59 212.69 212.73 212.67 212.65 212.65 212.65 212.70
212.65 212.65 212.63 212.63 212.65 212.59 212.56 212.61 212.63 212.63
212.70 212.61 212.59 212.68 212.65 212.70 212.68 212.65 212.70 212.75
212.84 212.94 212.82 212.73 212.75 212.79 212.84 212.78 212.65 212.67
212.68 212.70 212.59 212.61 212.61 212.61 212.65 212.70 212.56 212.62
212.65 212.65 212.71 212.70 212.76 212.85 212.89 212.76 212.63 212.67
212.68 212.71 212.71 212.72 212.82 212.71 212.65 212.68 212.70 212.63
212.58 212.56 212.63 212.69 212.62 212.73 212.62 212.68 212.72 212.65
212.65 212.69 212.63 212.73 212.72 212.85 212.90 212.78 212.71 212.67
212.65 212.65 212.60 212.62 212.61 212.65 212.66 212.63 212.68 212.75
212.65 212.65 212.70 212.68 212.65 212.68 212.65 212.73 212.72 212.82
212.86 212.79 212.68 212.73 212.68 212.68 212.67 212.61 212.68 212.63
212.63 212.71 212.61 212.59 212.62 212.59 212.68 212.75 212.70 212.73
212.82 212.86 212.76 212.71 212.75 212.84 212.89 212.79 212.65 212.63
212.68 212.68 212.71 212.59 212.65 212.59 212.61 212.59 212.67 212.70
212.61 212.56 212.68 212.73 212.68 212.65 212.62 212.72 212.73 212.86
212.94 212.86 212.75 212.73 212.84 212.96 212.82 212.72 212.73 212.77
212.90 212.85 212.73 212.73 212.68 212.70 212.84 212.88 212.75 212.67
212.70 212.73 212.79 212.99 212.89 212.78 212.70 212.76 212.93 212.95
212.79 212.73 212.82 212.82 212.86 212.80 212.68 212.70 212.70 212.76
212.82 212.80 212.61 212.65 212.70 212.70 212.73 212.88 212.92 212.85
212.71 212.80 212.89 212.94 212.86 212.73 212.72 212.80 212.90 212.85

```

Figure 25. Temperature Data Obtained in Rapid Temperature Measurement Experiments (T8 Position: 1.5 Inches Below Surface of Liquid)^a.

212.73 212.68 212.65 212.68 212.61 212.70 212.68 212.65 212.68 212.63
 212.68 212.67 212.66 212.73 212.71 212.85 212.89 212.93 212.73 212.73
 212.82 212.92 212.96 212.86 212.72 212.73 212.86 212.90 212.79 212.67
 212.70 212.65 212.65 212.65 212.65 212.68 212.68 212.67 212.71 212.72
 212.84 212.93 212.94 212.78 212.71 212.85 212.90 212.97 212.85 212.65
 212.68 212.73 212.68 212.73 212.78 212.86 212.84 212.72 212.62 212.61
 212.65 212.65 212.63 212.70 212.68 212.65 212.65 212.68 212.71 212.68
 212.65 212.73 212.73 212.86 212.85 212.75 212.63 212.65 212.67 212.69
 212.65 212.71 212.65 212.63 212.56 212.63 212.65 212.65 212.65 212.76
 212.65 212.65 212.69 212.73 212.65 212.67 212.65 212.70 212.68 212.65
 212.70 212.76 212.84 212.84 212.68 212.73 212.61 212.63 212.65 212.61
 212.60 212.63 212.69 212.68 212.73 212.61 212.63 212.71 212.65 212.61
 212.71 212.72 212.78 212.90 212.86 212.73 212.65 212.65 212.63 212.68
 212.65 212.65 212.68 212.70 212.63 212.61 212.56 212.55 212.56 212.65
 212.63 212.63 212.68 212.73 212.65 212.72 212.62 212.69 212.68 212.68
 212.65 212.61 212.71 212.63 212.68 212.61 212.61 212.59 212.63 212.63
 212.68 212.65 212.69 212.69 212.69 212.71 212.65 212.70 212.63 212.55
 212.69 212.70 212.70 212.79 212.95 212.85 212.72 212.69 212.70 212.78
 212.90 212.86 212.72 212.62 212.65 212.61 212.65 212.61 212.70 212.56
 212.61 212.65 212.63 212.67 212.69 212.76 212.68 212.63 212.66 212.71
 212.70 212.75 212.85 212.84 212.75 212.72 212.73 212.79 212.78 212.69
 212.71 212.68 212.65 212.65 212.65 212.68 212.68 212.79 212.62 212.56
 212.60 212.69 212.73 212.71 212.71 212.82 212.84 212.79 212.72 212.70
 212.86 212.90 212.80 212.69 212.65 212.65 212.71 212.67 212.65 212.59
 212.56 212.62 212.68 212.68 212.73 212.65 212.65 212.67 212.73 212.70
 212.76 212.88 212.84 212.76 212.71 212.70 212.79 212.90 212.79 212.67
 212.65 212.69 212.69 212.73 212.68 212.63 212.59 212.61 212.61 212.61
 212.65 212.77 212.65 212.67 212.66 212.70 212.72 212.78 212.90 212.90
 212.78 212.73 212.72 212.85 212.82 212.73 212.59 212.63 212.67 212.65
 212.71 212.62 212.60 212.63 212.61 212.59 212.68 212.72 212.65 212.61
 212.67 212.65 212.68 212.82 212.71 212.79 212.86 212.88 212.78 212.67
 212.63 212.65 212.65 212.65 212.68 212.73 212.59 212.62 212.63 212.58
 212.59 212.69 212.73 212.63 212.70 212.63 212.65 212.71 212.75 212.86
 212.90 212.77 212.77 212.73 212.86 212.90 212.77 212.65 212.69 212.67
 212.68 212.68 212.71 212.63 212.67 212.67 212.70 212.60 212.62 212.65
 212.67 212.68 212.73 212.68 212.68 212.68 212.69 212.76 212.80 212.86
 212.94 212.86 212.69 212.68 212.70 212.59 212.59 212.59 212.69 212.68
 212.69 212.71 212.63 212.63 212.67 212.65 212.68 212.72 212.65 212.69
 212.68 212.71 212.73 212.80 212.82 212.86 212.65 212.67 212.69 212.75
 212.61 212.67 212.63 212.68 212.73 212.65 212.60 212.65 212.66 212.70
 212.68 212.60 212.65 212.61 212.63 212.73 212.72 212.80 212.92 212.85
 212.77 212.73 212.76 212.90 212.88 212.70 212.69 212.62 212.63 212.63
 212.77 212.65 212.68 212.62 212.68 212.67 212.70 212.73 212.78 212.86
 212.80 212.75 212.68 212.72 212.76 212.86 212.93 212.76 212.70 212.69
 212.72 212.78 212.80 212.73 212.65 212.63 212.67 212.68 212.75 212.65
 212.70 212.70 212.82 212.88 212.73 212.67 212.69 212.79 212.73 212.73
 212.87 212.92 212.77 212.63 212.73 212.72 212.82 212.88 212.73 212.68
 212.65 212.71 212.65 212.63 212.65 212.68 212.71 212.61 212.59 212.65
 212.69 212.71 212.71 212.82 212.92 212.86 212.76 212.76 212.82 212.90
 212.88 212.73 212.72 212.72 212.86 212.85 212.77 212.65 212.62 212.69
 212.68 212.68 212.71 212.65 212.65 212.67 212.65 212.67 212.73 212.68
 212.65 212.72 212.73 212.88 212.93 212.88 212.71 212.72 212.84 212.86
 212.78 212.73 212.63 212.61 212.56 212.62 212.65 212.65 212.70 212.65
 212.67 212.65 212.59 212.63 212.71 212.68 212.71 212.73 212.86 212.89
 212.77 212.68 212.68 212.68 212.73 212.67 212.65 212.67 212.63 212.67
 212.70 212.68 212.61 212.63 212.61 212.63 212.65 212.70 212.63 212.65
 212.68 212.65 212.71 212.69 212.72 212.84 212.95 212.92 212.77 212.70
 212.82 212.86 212.85 212.71 212.60 212.61 212.65 212.68 212.65 212.69
 212.68 212.68 212.73 212.61 212.67 212.72 212.68 212.70 212.70 212.88
 212.92 212.86 212.71 212.73 212.82 212.88 212.85 212.70 212.71 212.78
 212.77 212.78 212.61 212.63 212.71 212.65 212.62 212.65 212.65 212.71
 212.67 212.63 212.62 212.65 212.65 212.78 212.65 212.71 212.79 212.90
 212.90 212.71 212.65 212.67 212.67 212.63 212.72 212.68 212.65 212.61

Figure 25. (continued)

212.56	212.68	212.67	212.68	212.73	212.65	212.63	212.70	212.65	212.65
212.65	212.68	212.63	212.65	212.71	212.73	212.75	212.84	212.79	212.70
212.61	212.60	212.70	212.68	212.68	212.63	212.61	212.61	212.60	212.58
212.59	212.65	212.69	212.70	212.65	212.70	212.76	212.82	212.88	212.76
212.68	212.73	212.76	212.86	212.89	212.80	212.69	212.71	212.63	212.65
212.69	212.63	212.67	212.59	212.67	212.69	212.71	212.67	212.65	212.69
212.70	212.65	212.68	212.71	212.75	212.90	212.92	212.79	212.71	212.65
212.68	212.69	212.63	212.62	212.63	212.63	212.68	212.71	212.59	212.62
212.54	212.59	212.68	212.65	212.69	212.70	212.70	212.73	212.88	212.90
212.82	212.65	212.67	212.70	212.70	212.80	212.90	212.82	212.70	212.63
212.67	212.61	212.63	212.63	212.65	212.65	212.69	212.70	212.59	212.63
212.71	212.63	212.63	212.65	212.68	212.75	212.75	212.88	212.92	212.85
212.80	212.71	212.77	212.95	212.84	212.70	212.65	212.65	212.59	212.65
212.68	212.70	212.62	212.65	212.68	212.62	212.70	212.65	212.68	212.70
212.76	212.90	212.88	212.80	212.67	212.70	212.68	212.73	212.80	212.82
212.76	212.65	212.67	212.62	212.72	212.59	212.59	212.62	212.61	212.68
212.65	212.75	212.68	212.59	212.69	212.76	212.63	212.65	212.71	212.71
212.89	212.96	212.82	212.70	212.73	212.85	212.82	212.73	212.63	212.73
212.67	212.61	212.61	212.63	212.62	212.65	212.68	212.69	212.70	212.69
212.71	212.68	212.72	212.86	212.99	212.89	212.80	212.73	212.82	212.89
212.89	212.77	212.70	212.73	212.82	212.82	212.72	212.58	212.61	212.65
212.67	212.67	212.73	212.68	212.65	212.68	212.70	212.70	212.82	212.88
212.88	212.76	212.68	212.71	212.72	212.85	212.89	212.85	212.69	212.69
212.65	212.63	212.73	212.61	212.59	212.65	212.70	212.68	212.65	212.65
212.67	212.65	212.70	212.71	212.90	212.89	212.82	212.71	212.73	212.82
212.90	212.88	212.72	212.69	212.69	212.65	212.63	212.70	212.65	212.63
212.61	212.65	212.59	212.63	212.65	212.71	212.63	212.63	212.65	212.75
212.73	212.79	212.92	212.84	212.73	212.69	212.67	212.70	212.71	212.85
212.82	212.68	212.67	212.73	212.59	212.60	212.56	212.61	212.65	212.71
212.58	212.59	212.65	212.65	212.68	212.76	212.65	212.62	212.63	212.63
212.71	212.60	212.59	212.62	212.67	212.62	212.56	212.68	212.63	212.65
212.63	212.62	212.65	212.71	212.55	212.61	212.69	212.67	212.67	212.68
212.70	212.67	212.73	212.58	212.65	212.63	212.60	212.70	212.56	212.63
212.65	212.63	212.62	212.63	212.58	212.65	212.62	212.69	212.73	212.53
212.58	212.61	212.65	212.71	212.58	212.55	212.61	212.65	212.68	212.72
212.58	212.63	212.65	212.65	212.67	212				

Figure 25. (continued)

- a. Average baseline temperature: 212.70 °F (4.111380 millivolts)
Maximum temperature recorded: 213.01 °F
Minimum temperature recorded: 212.51 °F
Temperature measurement rate: 1558 samples/sec.
Sampling time: 1 second
Time of sample: 03:43:10 P.M.

B:DKTST

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212.62 212.60 212.64 212.67 212.69 212.59 212.54 212.55 212.61 212.61
212.67 212.79 212.64 212.69 212.61 212.59 212.66 212.64 212.60 212.62
212.71 212.61 212.59 212.63 212.63 212.61 212.54 212.64 212.61 212.67
212.66 212.69 212.54 212.54 212.61 212.69 212.55 212.63 212.61 212.64
212.72 212.67 212.60 212.61 212.64 212.62 212.64 212.69 212.62 212.58
212.58 212.58 212.59 212.55 212.59 212.64 212.64 212.69 212.59 212.61
212.61 212.64 212.64 212.75 212.62 212.63 212.70 212.64 212.64 212.66
212.67 212.65 212.67 212.64 212.70 212.55 212.61 212.51 212.52 212.55
212.64 212.63 212.62 212.69 212.59 212.55 212.62 212.63 212.69 212.59
212.55 212.61 212.62 212.67 212.66 212.71 212.54 212.61 212.61 212.63
212.59 212.67 212.66 212.70 212.59 212.52 212.61 212.67 212.63 212.68
212.75 212.60 212.59 212.63 212.71 212.55 212.62 212.64 212.63 212.69
212.62 212.63 212.61 212.63 212.58 212.66 212.63 212.69 212.54 212.62
212.51 212.51 212.59 212.59 212.63 212.71 212.55 212.62 212.62 212.62
212.76 212.71 212.64 212.67 212.61 212.67 212.64 212.55 212.58 212.61
212.63 212.64 212.63 212.62 212.59 212.59 212.67 212.68 212.67 212.72
212.63 212.61 212.64 212.67 212.77 212.67 212.69 212.59 212.54 212.61
212.64 212.64 212.68 212.72 212.63 212.60 212.67 212.62 212.58 212.64
212.67 212.68 212.66 212.69 212.51 212.60 212.66 212.64 212.64 212.69
212.61 212.64 212.72 212.59 212.65 212.68 212.70 212.63 212.64 212.67
212.62 212.59 212.59 212.59 212.62 212.61 212.64 212.61 212.64 212.63
212.71 212.55 212.66 212.66 212.68 212.71 212.64 212.67 212.64 212.72
212.67 212.67 212.66 212.71 212.68 212.66 212.70 212.70 212.75 212.72
212.66 212.64 212.72 212.59 212.62 212.55 212.59 212.63 212.67 212.70
212.60 212.64 212.61 212.68 212.71 212.64 212.63 212.62 212.66 212.72
212.54 212.64 212.59 212.61 212.63 212.67 212.64 212.68 212.70 212.59
212.59 212.58 212.62 212.58 212.64 212.68 212.75 212.66 212.69 212.64
212.61 212.64 212.66 212.64 212.69 212.68 212.62 212.64 212.63 212.66
212.68 212.67 212.70 212.61 212.55 212.54 212.50 212.59 212.62 212.64
212.61 212.70 212.59 212.61 212.68 212.67 212.70 212.64 212.59 212.61
212.69 212.61 212.63 212.67 212.64 212.63 212.64 212.61 212.60 212.55
212.60 212.68 212.64 212.68 212.71 212.55 212.65 212.64 212.67 212.72
212.63 212.65 212.68 212.64 212.69 212.68 212.64 212.67 212.69 212.59
212.63 212.59 212.55 212.55 212.59 212.59 212.63 212.64 212.66 212.69
212.55 212.62 212.64 212.69 212.58 212.66 212.65 212.69 212.66 212.64
212.68 212.63 212.61 212.64 212.69 212.59 212.64 212.63 212.55 212.60
212.55 212.64 212.61 212.64 212.62 212.69 212.61 212.61 212.61 212.67

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Figure 26. Temperature Data Obtained in Rapid Temperature Measurement Experiments (T8 Position: 6.5 Inches Below Surface of Liquid)^a.

212.71 212.61 212.67 212.64 212.68 212.72 212.70 212.76 212.85 212.76
 212.67 212.67 212.69 212.61 212.60 212.63 212.62 212.66 212.63 212.64
 212.68 212.72 212.54 212.61 212.71 212.58 212.61 212.64 212.72 212.63
 212.64 212.64 212.68 212.67 212.70 212.64 212.64 212.64 212.63 212.58
 212.61 212.59 212.64 212.66 212.69 212.52 212.51 212.54 212.59 212.63
 212.67 212.69 212.61 212.66 212.66 212.67 212.70 212.70 212.70 212.79
 212.89 212.70 212.64 212.63 212.63 212.64 212.64 212.64 212.64 212.66
 212.71 212.61 212.63 212.63 212.64 212.68 212.79 212.61 212.71 212.63
 212.64 212.71 212.71 212.76 212.78 212.72 212.62 212.63 212.63 212.64
 212.61 212.63 212.64 212.64 212.69 212.64 212.63 212.55 212.63 212.68
 212.72 212.61 212.63 212.66 212.72 212.54 212.59 212.69 212.67 212.59
 212.64 212.64 212.60 212.61 212.64 212.61 212.61 212.68 212.64 212.67
 212.67 212.69 212.63 212.59 212.63 212.63 212.63 212.63 212.64 212.64
 212.71 212.68 212.63 212.63 212.67 212.64 212.64 212.72 212.61 212.60
 212.64 212.62 212.63 212.64 212.68 212.69 212.54 212.53 212.61 212.59
 212.64 212.68 212.72 212.63 212.67 212.71 212.66 212.69 212.71 212.81
 212.89 212.77 212.63 212.61 212.63 212.62 212.63 212.60 212.63 212.63
 212.63 212.69 212.59 212.53 212.55 212.61 212.59 212.64 212.69 212.63
 212.69 212.63 212.59 212.69 212.66 212.64 212.68 212.64 212.71 212.71
 212.77 212.81 212.69 212.64 212.55 212.56 212.59 212.60 212.61 212.64
 212.63 212.66 212.68 212.70 212.63 212.67 212.69 212.64 212.68 212.67
 212.64 212.68 212.70 212.61 212.67 212.62 212.62 212.70 212.54 212.49
 212.55 212.50 212.53 212.59 212.61 212.63 212.64 212.67 212.70 212.63
 212.63 212.68 212.76 212.67 212.64 212.64 212.77 212.69 212.70 212.83
 212.85 212.72 212.67 212.60 212.51 212.54 212.55 212.64 212.58 212.62
 212.64 212.64 212.66 212.68 212.75 212.64 212.61 212.66 212.70 212.64
 212.63 212.70 212.64 212.67 212.61 212.65 212.67 212.69 212.67 212.59
 212.63 212.59 212.62 212.63 212.64 212.58 212.69 212.53 212.55 212.61
 212.64 212.61 212.72 212.61 212.61 212.64 212.70 212.62 212.66 212.61
 212.60 212.66 212.64 212.66 212.64 212.65 212.64 212.64 212.68 212.69
 212.61 212.60 212.61 212.63 212.64 212.69 212.60 212.67 212.67 212.72
 212.63 212.61 212.64 212.64 212.70 212.59 212.61 212.66 212.66 212.67
 212.68 212.68 212.61 212.66 212.67 212.67 212.70 212.62 212.55 212.62
 212.67 212.72 212.60 212.62 212.66 212.67 212.75 212.64 212.69 212.67
 212.66 212.64 212.55 212.68 212.64 212.61 212.61 212.64 212.68 212.64
 212.69 212.63 212.63 212.55 212.62 212.66 212.64 212.72 212.58 212.69
 212.64 212.61 212.54 212.64 212.63 212.68 212.70 212.54 212.64 212.64
 212.64 212.64 212.62 212.63 212.61 212.63 212.64 212.64 212.70 212.63
 212.64 212.61 212.66 212.69 212.61 212.63 212.64 212.72 212.61 212.59
 212.67 212.66 212.62 212.69 212.63 212.59 212.60 212.63 212.64 212.58
 212.63 212.59 212.62 212.62 212.67 212.68 212.68 212.75 212.66 212.66
 212.76 212.61 212.72 212.62 212.63 212.61 212.64 212.66 212.67 212.68
 212.64 212.69 212.55 212.55 212.61 212.55 212.56 212.62 212.61 212.62
 212.69 212.50 212.55 212.58 212.64 212.69 212.61 212.67 212.66 212.67
 212.69 212.64 212.62 212.59 212.64 212.63 212.64 212.69 212.60 212.54
 212.52 212.61 212.59 212.55 212.63 212.64 212.64 212.67 212.71 212.63
 212.63 212.69 212.60 212.62 212.67 212.64 212.72 212.59 212.60 212.64
 212.61 212.63 212.66 212.67 212.72 212.54 212.58 212.61 212.55 212.59
 212.63 212.67 212.69 212.47 212.54 212.64 212.64 212.66 212.69 212.63
 212.58 212.62 212.64 212.68 212.72 212.64 212.64 212.61 212.63 212.66
 212.68 212.69 212.59 212.59 212.51 212.59 212.63 212.62 212.64 212.67
 212.70 212.55 212.64 212.72 212.59 212.59 212.61 212.64 212.67 212.68
 212.64 212.66 212.72 212.64 212.60 212.55 212.59 212.66 212.69 212.63
 212.55 212.54 212.59 212.60 212.61 212.63 212.69 212.60 212.70 212.60
 212.55 212.62 212.64 212.61 212.64 212.67 212.70 212.64 212.61 212.64
 212.59 212.59 212.59 212.64 212.62 212.64 212.64 212.66 212.67 212.69
 212.62 212.64 212.69 212.60 212.59 212.64 212.71 212.61 212.61 212.61
 212.67 212.62 212.66 212.68 212.72 212.59 212.54 212.55 212.59 212.61
 212.62 212.64 212.58 212.67 212.70 212.60 212.66 212.69 212.54 212.61
 212.64 212.67 212.70 212.64 212.61 212.64 212.64 212.64 212.71 212.71
 212.64 212.61 212.59 212.59 212.66 212.62 212.63 212.67 212.71 212.53
 212.56 212.61 212.59 212.63 212.67 212.75 212.66 212.67 212.69 212.61
 212.64 212.69 212.64 212.64 212.61 212.64 212.58 212.52 212.60 212.58

Figure 26. (continued)

212.61	212.61	212.61	212.67	212.64	212.70	212.55	212.58	212.64	212.64
212.69	212.64	212.63	212.67	212.67	212.66	212.70	212.55	212.59	212.63
212.69	212.67	212.63	212.59	212.55	212.55	212.55	212.61	212.59	212.59
212.67	212.69	212.52	212.54	212.64	212.66	212.67	212.71	212.64	212.64
212.67	212.69	212.63	212.68	212.61	212.61	212.64	212.63	212.67	212.67
212.70	212.59	212.55	212.51	212.61	212.61	212.61	212.68	212.67	212.72
212.61	212.64	212.68	212.67	212.68	212.67	212.76	212.69	212.62	212.64
212.61	212.61	212.60	212.66	212.61	212.63	212.64	212.69	212.58	212.55
212.63	212.59	212.61	212.63	212.63	212.71	212.61	212.59	212.60	212.64
212.69	212.61	212.59	212.68	212.68	212.72	212.63	212.59	212.59	212.59
212.63	212.61	212.63	212.65	212.64	212.69	212.54	212.55	212.55	212.63
212.66	212.65	212.68	212.76	212.63	212.66	212.70	212.61	212.66	212.71
212.69	212.72	212.84	212.81	212.65	212.67	212.67	212.64	212.72	212.53
212.53	212.58	212.59	212.63	212.60	212.61	212.69	212.63	212.69	212.59
212.61	212.65	212.61	212.63	212.69	212.62	212.59	212.61	212.64	212.67
212.63	212.64	212.64	212.64	212.64	212.67	212.66	212.64	212.69	212.61
212.61	212.64	212.67	212.75	212.64	212.69	212.59	212.59	212.63	212.68
212.68	212.66	212.69	212.68	212.64	212.64	212.60	212.63	212.59	212.64
212.69	212.59	212.58	212.47	212.54	212.53	212.60	212.61	212.67	212.72
212.64	212.68	212.72	212.55	212.67	212.63	212.69	212.63	212.59	212.60
212.61	212.59	212.58	212.58	212.54	212.59	212.64	212.67	212.70	212.51
212.54	212.59	212.63	212.64	212.67	212.76	212.67	212.66	212.67	212.71
212.62	212.64	212.61	212.64	212.67	212.72	212.62	212.61	212.60	212.63
212.55	212.58	212.63	212.64	212.69	212.52	212.54	212.59	212.63	212.67
212.70	212.64	212.63	212.64	212.69	212.61	212.66	212.64	212.63	212.64
212.72	212.63	212.61	212.55	212.59	212.63	212.61	212.64	212.61	212.64
212.64	212.69	212.61	212.59	212.63	212.69	212.64	212.69	212.65	212.67
212.67	212.64	212.61	212.63	212.70	212.67	212.69	212.76	212.81	212.76
212.63	212.61	212.67	212.64	212.69	212.55	212.59	212.55	212.63	212.63
212.69	212.64	212.59	212.64	212.70	212.59	212.63	212.64	212.64	212.68
212.64	212.63	212.67	212.75	212.62	212.61	212.61	212.69	212.58	212.55
212.54	212.52	212.55	212.64	212.54	212.58	212.72	212.62	212.60	212.67
212.68	212.67	212.71	212.64	212.64	212.64	212.68	212.64	212.66	212.64
212.70	212.55	212.55	212.55	212.63	212.61	212.55	212.61	212.66	212.67
212.72	212.59	212.67	212.72	212.64	212.64	212.63	212.64	212.72	212.64
212.66	212.66	212.66	212.63	212.66	212.65	212.70	212.52	212.55	2

Figure 26. (continued)

- a. Average baseline temperature: 212.69 °F (4.111238 millivolts)
Maximum temperature recorded: 212.85 °F
Minimum temperature recorded: 212.47 °F
Temperature measurement rate: 1532 samples/sec
Sampling time: 1 second
Time of sample: 03:49:10 P.M.

B:DKTST

212.63	212.69	212.73	212.72	212.74	212.73	212.73	212.70	212.74	212.73
212.72	212.69	212.67	212.73	212.70	212.65	212.73	212.73	212.67	212.75
212.57	212.64	212.67	212.69	212.78	212.67	212.70	212.77	212.70	212.70
212.76	212.76	212.90	212.93	212.87	212.74	212.74	212.73	212.75	212.64
212.64	212.61	212.64	212.57	212.60	212.64	212.69	212.75	212.61	212.61
212.63	212.70	212.69	212.70	212.84	212.73	212.72	212.76	212.75	212.76
212.91	212.87	212.74	212.78	212.69	212.64	212.64	212.63	212.69	212.61
212.64	212.66	212.70	212.70	212.72	212.82	212.70	212.77	212.65	212.67
212.77	212.78	212.87	213.02	212.94	212.81	212.75	212.80	212.90	212.89
212.78	212.69	212.56	212.60	212.57	212.63	212.58	212.72	212.73	212.70
212.73	212.77	212.60	212.66	212.73	212.80	212.75	212.75	212.89	212.93
212.86	212.77	212.78	212.87	212.90	212.89	212.74	212.73	212.76	212.65
212.53	212.56	212.65	212.61	212.61	212.66	212.73	212.73	212.75	212.67
212.77	212.72	212.74	212.72	212.75	212.76	212.87	212.93	212.84	212.78
212.72	212.70	212.67	212.64	212.55	212.56	212.60	212.61	212.61	212.67
212.69	212.72	212.70	212.78	212.66	212.75	212.67	212.74	212.73	212.73
212.75	212.75	212.90	212.94	212.94	212.83	212.70	212.74	212.61	212.69
212.70	212.66	212.65	212.64	212.70	212.66	212.73	212.73	212.80	212.70
212.70	212.74	212.80	212.72	212.77	212.70	212.78	212.81	212.92	212.94
212.77	212.78	212.77	212.91	212.87	212.72	212.73	212.77	212.65	212.64
212.58	212.69	212.73	212.75	212.61	212.66	212.70	212.78	212.70	212.74
212.75	212.78	212.94	213.00	212.91	212.78	212.70	212.72	212.67	212.69
212.65	212.64	212.60	212.64	212.64	212.64	212.61	212.70	212.73	212.76
212.59	212.69	212.69	212.77	212.66	212.70	212.81	212.77	212.86	212.95
212.95	212.84	212.76	212.81	212.91	212.89	212.77	212.73	212.64	212.61
212.66	212.61	212.65	212.70	212.75	212.61	212.61	212.61	212.66	212.70
212.73	212.83	212.70	212.74	212.72	212.75	212.70	212.70	212.69	212.70
212.75	212.66	212.64	212.66	212.64	212.61	212.60	212.60	212.61	212.70
212.70	212.73	212.78	212.61	212.64	212.74	212.75	212.72	212.75	212.77
212.91	212.99	212.87	212.75	212.74	212.73	212.70	212.61	212.70	212.64
212.58	212.57	212.61	212.63	212.66	212.70	212.69	212.72	212.75	212.66
212.70	212.70	212.78	212.73	212.66	212.77	212.76	212.87	212.94	212.94
212.77	212.73	212.73	212.70	212.67	212.61	212.61	212.61	212.66	212.69

Figure 27. Temperature Data Obtained in Rapid Temperature Measurement Experiments (T8 Position: 10.5 Inches Below Surface of Liquid)^a.

212.73	212.78	212.60	212.66	212.65	212.70	212.75	212.64	212.70	212.74
212.78	212.74	212.74	212.70	212.75	212.76	212.89	212.90	212.87	212.73
212.66	212.67	212.66	212.70	212.72	212.73	212.60	212.61	212.66	212.69
212.72	212.76	212.61	212.70	212.76	212.72	212.70	212.75	212.82	212.90
213.00	212.87	212.74	212.66	212.76	212.64	212.61	212.57	212.58	212.60
212.64	212.61	212.63	212.72	212.70	212.70	212.78	212.69	212.75	212.70
212.69	212.70	212.73	212.74	212.78	212.80	212.78	212.90	212.87	212.73
212.78	212.69	212.58	212.58	212.60	212.66	212.72	212.73	212.74	212.75
212.57	212.57	212.64	212.66	212.70	212.82	212.76	212.77	212.87	212.90
212.83	212.75	212.73	212.75	212.81	212.99	212.83	212.70	212.73	212.70
212.74	212.74	212.75	212.61	212.66	212.64	212.69	212.70	212.77	212.70
212.73	212.78	212.69	212.70	212.78	212.80	212.90	212.98	212.83	212.78
212.73	212.69	212.66	212.67	212.65	212.61	212.64	212.59	212.64	212.70
212.72	212.75	212.58	212.58	212.65	212.69	212.75	212.66	212.73	212.78
212.77	212.86	212.99	212.91	212.77	212.73	212.69	212.70	212.67	212.66
212.61	212.65	212.64	212.66	212.72	212.75	212.61	212.61	212.58	212.65
212.73	212.78	212.70	212.72	212.74	212.77	212.74	212.72	212.70	212.71
212.72	212.76	212.76	212.76	212.84	212.78	212.69	212.72	212.76	212.64
212.53	212.61	212.61	212.67	212.70	212.75	212.70	212.60	212.65	212.75
212.74	212.70	212.73	212.78	212.75	212.95	212.94	212.87	212.74	212.72
212.73	212.67	212.70	212.70	212.74	212.73	212.78	212.64	212.69	212.70
212.70	212.73	212.84	212.61	212.75	212.70	212.69	212.75	212.76	212.93
212.95	212.90	212.75	212.65	212.69	212.70	212.61	212.61	212.58	212.64
212.60	212.63	212.70	212.69	212.75	212.60	212.55	212.65	212.73	212.78
212.73	212.66	212.73	212.74	212.73	212.70	212.70	212.73	212.73	212.70
212.73	212.74	212.77	212.57	212.61	212.63	212.67	212.60	212.61	212.64
212.66	212.75	212.63	212.67	212.70	212.70	212.78	212.75	212.76	212.87
212.92	212.86	212.73	212.70	212.76	212.67	212.73	212.56	212.64	212.61
212.63	212.64	212.58	212.69	212.69	212.76	212.61	212.58	212.65	212.64
212.70	212.78	212.66	212.76	212.70	212.70	212.72	212.70	212.73	212.73
212.73	212.73	212.77	212.66	212.56	212.61	212.66	212.60	212.61	212.61
212.66	212.66	212.76	212.58	212.63	212.70	212.70	212.73	212.80	212.74
212.73	212.78	212.69	212.69	212.73	212.73	212.74	212.70	212.76	212.64
212.61	212.58	212.61	212.60	212.60	212.66	212.65	212.65	212.69	212.77
212.66	212.61	212.75	212.70	212.66	212.66	212.73	212.78	212.74	212.76
212.81	212.89	212.87	212.72	212.73	212.75	212.61	212.63	212.61	212.64
212.61	212.66	212.70	212.70	212.74	212.78	212.64	212.66	212.72	212.76
212.70	212.66	212.78	212.72	212.70	212.72	212.70	212.75	212.66	212.61
212.60	212.61	212.57	212.61	212.61	212.63	212.66	212.67	212.69	212.71
212.73	212.73	212.76	212.73	212.77	212.66	212.66	212.70	212.74	212.80
212.67	212.70	212.70	212.70	212.66	212.67	212.65	212.72	212.65	212.66
212.75	212.59	212.56	212.60	212.64	212.67	212.70	212.75	212.61	212.63
212.75	212.63	212.66	212.73	212.74	212.73	212.77	212.72	212.70	212.66
212.70	212.63	212.67	212.69	212.66	212.67	212.72	212.71	212.75	212.58
212.60	212.63	212.70	212.77	212.64	212.70	212.69	212.75	212.74	212.67
212.74	212.77	212.73	212.70	212.66	212.66	212.61	212.64	212.64	212.59
212.66	212.61	212.64	212.67	212.70	212.77	212.64	212.66	212.70	212.73
212.78	212.66	212.77	212.70	212.72	212.75	212.80	212.90	212.91	212.78
212.65	212.65	212.73	212.75	212.60	212.60	212.60	212.61	212.58	212.63
212.66	212.63	212.61	212.70	212.75	212.61	212.66	212.69	212.78	212.70
212.70	212.70	212.78	212.78	212.85	212.89	212.87	212.69	212.70	212.70
212.70	212.73	212.78	212.61	212.66	212.66	212.69	212.70	212.76	212.66
212.66	212.64	212.76	212.70	212.67	212.70	212.78	212.78	212.81	212.93
212.87	212.80	212.73	212.72	212.67	212.60	212.63	212.64	212.66	212.61
212.67	212.69	212.67	212.77	212.67	212.67	212.69	212.70	212.74	212.78
212.66	212.78	212.70	212.70	212.77	212.81	212.87	212.90	212.83	212.70
212.66	212.63	212.61	212.64	212.64	212.64	212.69	212.74	212.70	212.72
212.77	212.65	212.76	212.59	212.69	212.74	212.83	212.70	212.76	212.78
212.90	212.86	212.78	212.70	212.66	212.66	212.66	212.60	212.61	212.67
212.69	212.73	212.73	212.74	212.77	212.65	212.70	212.70	212.76	212.70
212.70	212.75	212.69	212.66	212.70	212.75	212.77	212.84	212.98	212.87
212.66	212.69	212.69	212.67	212.69	212.70	212.72	212.74	212.74	212.73
212.78	212.64	212.70	212.75	212.64	212.67	212.75	212.66	212.76	212.75

Figure 27. (continued)

212.87	212.99	212.81	212.72	212.69	212.76	212.66	212.69	212.62	212.59
212.61	212.60	212.65	212.67	212.70	212.66	212.76	212.57	212.61	212.65
212.66	212.74	212.75	212.70	212.81	212.70	212.75	212.78	212.94	212.91
212.77	212.73	212.65	212.66	212.66	212.66	212.66	212.64	212.66	212.67
212.70	212.73	212.74	212.80	212.70	212.67	212.77	212.64	212.73	212.77
212.74	212.75	212.78	212.87	212.89	212.81	212.75	212.72	212.70	212.63
212.63	212.57	212.61	212.59	212.60	212.56	212.58	212.63	212.63	212.74
212.70	212.77	212.66	212.69	212.73	212.78	212.73	212.73	212.75	212.70
212.73	212.72	212.69	212.64	212.60	212.61	212.66	212.60	212.69	212.69
212.70	212.66	212.73	212.74	212.80	212.70	212.75	212.57	212.66	212.76
212.70	212.69	212.70	212.74	212.78	212.69	212.75	212.82	212.90	212.87
212.74	212.67	212.66	212.73	212.69	212.75	212.58	212.57	212.64	212.67
212.65	212.67	212.75	212.70	212.70	212.74	212.78	212.73	212.73	212.74
212.70	212.75	212.70	212.67	212.70	212.61	212.64	212.69	212.61	212.64
212.66	212.70	212.73	212.76	212.61	212.63	212.61	212.69	212.73	212.78
212.69	212.77	212.73	212.67	212.72	212.72	212.75	212.76	212.76	212.87
212.78	212.64	212.67	212.73	212.67	212.69	212.74	212.72	212.75	212.65
212.64	212.69	212.69	212.66	212.81	212.66	212.73	212.78	212.70	212.67
212.78	212.69	212.73	212.70	212.61	212.66	212.66	212.66	212.63	212.63
212.69	212.69	212.67	212.67	212.70	212.72	212.73	212.83	212.70	212.76
212.61	212.70	212.77	212.69	212.72	212.73	212.74	212.75	212.70	212.69
212.70	212.65	212.61	212.61	212.66	212.67	212.64	212.69	212.69	212.73
212.69	212.75	212.63	212.63	212.72	212.77	212.61	212.67	212.75	212.73
212.66	212.75	212.80	212.91	212.93	212.80	212.69	212.67	212.69	212.64
212.61	212.70	212.70	212.69	212.72	212.73	212.75	212.70	212.73	212.66
212.76	212.61	212.69	212.72	212.73	212.76	212.75	212.73	212.74	212.67
212.70	212.70	212.67	212.66	212.70	212.64	212.64	212.64	212.67	212.70
212.70	212.77	212.61	212.60	212.63	212.72	212.74	212.80	212.69	212.70
212.78	212.75	212.80	212.87	212.93	212.82	212.69	212.78	212.74	212.69
212.66	212.57	212.58	212.57	212.60	212.58	212.61	212.60	212.64	212.70
212.73	212.73	212.78	212.72	212.73	212.78	212.74	212.75	212.73	212.72
212.67	212.69	212.70	212.65	212.65	212.70	212.74	212.70	212.67	212.69
212.75	212.58	212.66	212.61	212.64	212.66	212.70	212.75	212.65	212.70
212.73	212.82	212.70	212.69	212.75	212.75	212.90	212.90	212.87	212.76
212.70	212.65	212.60	212.65	212.59	212.58	212.57	212.60	212.64	212.69
212.70	212.75	212.61	212.64	212.69	212.73	212.78	212.69	212.77	2

Figure 27. (continued)

- a. Average baseline temperature: 212.75 °F (4.112548 millivolts)
Maximum temperature recorded: 213.02 °F
Minimum temperature recorded: 212.49 °F
Temperature measurement rate: 1544 samples/sec
Sampling time: 1 second
Time of sample: 03:56:10 P.M.

APPENDIX H

EVALUATION OF THE CRITERIA OF BLANDER AND KATZ FOR PENTANE-WATER AND METHYL SALICYLATE-WATER SYSTEMS

Calculations are given in this appendix for determining the phase in which nucleation occurs when one liquid is superheated in contact with another.

1. Evaluation of the Criteria of Blander and Katz for the Pentane-Water System

The criteria of Blander and Katz have already been discussed in the "Background" section.

- (1) If $\sigma_B > \sigma_A + \sigma_{AB}$, homogeneous nucleation occurs in liquid "A."
- (2) If $\sigma_A \geq \sigma_B + \sigma_{AB}$, homogeneous nucleation occurs within liquid "B."
- (3) If $\sigma_A < \sigma_B + \sigma_{AB}$ and $\sigma_B < \sigma_A + \sigma_{AB}$, heterogeneous nucleation can occur at the interface between liquids "A" and "B."

Values of the surface tensions of pentane and water at 36 °C were obtained from handbooks. An approximate value (27.3 dynes/cm) for the interfacial tension between pentane and water was measured with a Dunoüy interfacial tensiometer. The interfacial tension value was obtained at 32.2 °C, which is slightly below the boiling point (36.1 °C) of pentane.

For pentane-water, the first criterion listed above was satisfied, and nucleation occurs in the pentane phase.

$$\sigma_B > \sigma_A + \sigma_{AB} \quad \text{B: Water} \quad \text{A: Pentane}$$

$$70.2 > 14.3 + 27.3 \quad (\text{at } 36 \text{ } ^\circ\text{C})$$

$$\text{or } 70.2 > 41.6 \quad \text{UNITS: dyne/cm}$$

2. Evaluation of the Criteria of Blander and Katz for the Methyl Salicylate-Water System

Values of the surface tensions at 100 °C for methyl salicylate and water were obtained from handbooks. An approximate value (20.3 dynes/cm) was measured for the interfacial tension between methyl salicylate and water at 93 °C. A measurement at 100 °C was not

attempted because bubbles impacting the interface would affect the measurement.

For methyl salicylate-water, the second criterion is satisfied, and nucleation occurs in the methyl salicylate phase.

$$\sigma_A \geq \sigma_B + \sigma_{AB} \quad \text{A: Water} \quad \text{B: Methyl salicylate}$$

$$61.8 \geq 31.2 + 20.3 \quad (\text{at } 100^\circ\text{C})$$

$$\text{or } 61.8 \geq 51.5 \quad \text{UNITS: dyne/cm}$$

PART II

Development of a Method for the
Measurement of Interfacial Area
in a Direct Contact Boiler

I. INTRODUCTION

In studies of direct contact heat exchangers overall heat transfer coefficients are usually based on volume, rather than on the actual contact area between the phases. For one to compare heat transfer coefficients for direct contact heat exchangers with coefficients obtained for conventional heat transfer devices, it is desirable to base the coefficients on actual heat transfer area. Basing the coefficient on actual contact area also facilitates the use of analogies between heat transfer and mass transfer for comparison of existing data for similar situations.

In the present work, a chemical method is developed for measuring interfacial area in a direct contact boiler. The theoretical basis of the method is given and previous applications of the method for measuring interfacial area in mass transfer equipment are cited. Since it was necessary to measure or to estimate physico-chemical data to evaluate the workability of the method, a discussion of these measurements or calculations is included.

II. BACKGROUND

A. Methods of Measuring Interfacial Area

1. Physical Methods. In an effort to find the most suitable technique for measuring interfacial area in a direct contact boiler, a survey of the literature was conducted. Several physical techniques, such as light transmission and photography were reviewed. For example, Buchlin,¹ et al., used a fluorescence technique to measure local voidage in random packed beds. In this method, a column is packed with a transparent material, such as glass spheres, and the interstitial volumes are filled with a liquid having the same refractive index as the packing material. (Ethyl salicylate was used in this case.) This allows a light beam to cross the bed without being scattered. When a light beam, for example a laser sheet, is passed through the bed, the light excites a fluorescent reemission. The liquid remains visible, but the glass spheres appear as dark spots. Thus, one can determine the voidage distribution within the illuminated part of the bed.

The fluorescence technique is not satisfactory for interfacial area measurement in the direct contact heat exchanger under study because, instead of glass beads, one has vapor bubbles and unvaporized working fluid droplets, as well as the continuous oil phase. Therefore, matching optical properties of the heating fluid with the working fluid liquid and vapor bubbles in addition to satisfying the other constraints, such as density difference and immiscibility, necessary for system operation would be a near impossible task.

Various other physical techniques, such as the one described by Weinstein and Treybal,² have been used to measure interfacial area. In fact, Fernandes and Sharma³ include a summary table of physical methods that have been used to measure interfacial area in agitated vessels.

2. A Chemical Method. Since none of the physical methods appeared to be particularly well-suited for measurement of interfacial area in a direct contact boiler, a search for a chemical method was conducted. Chemical methods of interfacial area determination have been used in the past in mass transfer applications. Danckwerts, et al,⁴ have developed a model of absorption accompanied by chemical reaction to determine interfacial area in a gas-liquid system. Danckwerts' technique involves using a reaction of known kinetics in the contacting device so that measurement of extent of chemical reaction can be used to calculate interfacial area. Many investigators have used Danckwerts' technique to evaluate interfacial area in packed columns, sieve trays, and in two-phase gas-liquid flow in pipes (5, 6, 7).

Nanda and Sharma⁸ have used a model of extraction accompanied by chemical reaction to measure interfacial area in liquid-liquid systems. They determined effective interfacial area in a spray column at various flow rates and have suggested that the theory can be applied for finding effective interfacial area in any type of contactor. They found that under certain conditions the concentration of a reactive species at the interface is practically the same as in the bulk of the dispersed phase, and the rate of extraction per unit area is only a function of the physical and chemical properties of the system and independent of hydrodynamic

factors. A discussion of the criteria and theory applicable to this chemical method is given in the section entitled "Theory."

Many investigators have employed the chemical technique of Nanda and Sharma for measuring interfacial area in various types of liquid-liquid contactors. Fernandes and Sharma measured interfacial area in air-agitated liquid-liquid extraction columns, and evaluated the effects of several parameters on the magnitude of the interfacial area.⁹ Fernandes and Sharma also applied the chemical technique in their study of agitated tanks.³ Puranik and Sharma employed this chemical technique to measure interfacial area in countercurrent, packed, liquid extraction columns.¹⁰ Finally, Shah and Sharma measured interfacial area in horizontal pipeline contactors.¹¹ Bubble and plug flow regimes were studied for co-current flow of several pairs of essentially immiscible liquids.

In the study of packed liquid extraction columns by Puranik and Sharma, mentioned above, liquid-liquid interfacial area was measured by both physical and chemical methods for two liquid-liquid systems. The values of interfacial area obtained by physical and by chemical methods differed by only about 12%. Fernandes and Sharma, who measured liquid-liquid interfacial area in stirred tanks, reported values ranging up to $900 \text{ cm}^2/\text{cm}^3$ for interfacial area per unit volume obtained by the chemical method. Workers using physical methods have obtained values ranging up to about $800 \text{ cm}^2/\text{cm}^3$ for interfacial area per unit volume in stirred tanks, according to Fernandes and Sharma. Consequently, from the good agreement indicated for interfacial area values obtained by physical and by chemical methods, one may conclude that the chemical method of interfacial area measurement discussed herein is valid and reliable.

B. The Search for a Pair of Liquids for Use in Simultaneous Heat Transfer and Interfacial Area Measurements.

1. The Screening Process. Based on the success of the application of the chemical technique for measuring effective interfacial area in various types of contactors, it was decided that this technique is probably the most suitable for measuring interfacial area in a direct contact boiler. The next task was to find a pair of liquids which can satisfy the constraints applicable for satisfactory heat transfer and can also satisfy the constraints applicable to the chemical method of measurement of interfacial area. Because of the safety hazards associated with handling volatile organic liquids, water was selected as the working fluid. A search was then conducted for a suitable organic heat transfer fluid.

In the search for an organic heat transfer fluid, the physical properties of approximately five thousand chemical compounds were reviewed. Consequently, the field of possible heat transfer liquids was greatly narrowed. Further screening was based on the cost of the compounds, and on the results of some shake tests to determine the rate of phase separation from hot water.

2. Selection of Methyl Salicylate. Methyl salicylate was selected as the heat transfer liquid. It has the following desirable characteristics:

- (1) Very low solubility in water (ca. 0.4% by wt. at 100°C)
- (2) Very low toxicity (average lethal dose by ingestion for an adult is 30 ml.)
- (3) Density greater than that of water (sp. gr. $D_4^{25} = 1.1787$)

- (4) Good phase separation from hot or boiling water, even after vigorous agitation
- (5) Boiling point (223°C) much greater than that of water
- (6) Low vapor pressure, even at the boiling point of water (12.5 mm Hg at 100°C)
- (7) The flash point is higher than the boiling point of water (225°F, open cup)
- (8) Methyl salicylate is an ester, and for this reason is a good choice for use in the part of the work dealing with measurement of interfacial contact area.

3. Additional Physico-Chemical Data for Methyl Salicylate. To confirm the suitability of methyl salicylate for use in measurement of interfacial area in the direct contact boiler, additional physico-chemical data were needed. The literature was searched for these data, especially data relating to the rate of alkaline hydrolysis of methyl salicylate, since that type of reaction will be utilized in the boiler for the measurement of interfacial area. The reaction rate data obtained from the literature is discussed in the following paragraphs.

Alkaline hydrolysis of methyl salicylate has been studied previously by Goldschmidt and Scholz¹² and by Pal, Lahiri, and Aditya.¹³ Goldschmidt and Scholz indicate that the true reaction rate coefficient for the second order, bimolecular reaction between aqueous sodium hydroxide (0.05 to 0.2N solutions) and methyl salicylate is between 6 and 7 liters per gm-mole minute (100-110 cm³/gm-mole sec) at 25°C.

Goldschmidt and Scholz also found that the solubility of methyl salicylate in water is so low at 25°C that 0.005N solutions could barely be obtained. Consequently, their experiments were conducted in such a way that weighted amounts of the ester were inserted via small tubes into sodium hydroxide solutions of known concentration. Samples of the aqueous phase were removed and were analyzed by titration.

The only other study found in the literature concerning alkaline hydrolysis of methyl salicylate was published by Pal, Lahiri, and Aditya in 1974.¹³ In that study, a spectrophotometric technique was used to study the reaction. In agreement with Goldschmidt and Scholz, those workers indicate that the overall reaction between methyl salicylate and sodium hydroxide is second order; however, the statement is made that methyl salicylate reacts almost instantaneously to form methyl salicylate anion. Consequently, the concentration of methyl salicylate is very small compared to the sodium hydroxide present, and determination of the second order rate constant is difficult. Therefore, Pal and his co-workers chose to follow the decomposition of methyl salicylate anion, which is a pseudo-first order reaction.

Pal, et al. measured the pseudo-first order reaction rate coefficients for decomposition of methyl salicylate anion at several temperatures. Entropy of activation and activation energy were also determined. The reactions were conducted in methanol-water media because of the low solubility of methyl salicylate in water.

Toward the end of the Pal, et al. paper, the statement is made that the reaction rate diminishes with increasing methanol concentrations, indicating that the reaction follows an intermolecular mechanism.

One would therefore expect that reaction rate coefficients for hydrolysis in aqueous media should be higher than the values obtained in methanol-water media.

4. The Need for an Improved Technique for Measuring Reaction Rate Coefficients for Compounds Having Low Water Solubility.

The literature search for kinetic data on the alkaline hydrolysis of methyl salicylate revealed that little work on the hydrolysis of aromatic acid esters has been conducted with water as the only solvent, primarily because of the low solubility of the esters in water. Usually a solvent, such as methanol or acetone, is added to enhance the solubility, but the cosolvent usually diminishes the reaction rate, often as much as an order of magnitude.¹⁴ Therefore, the need for an improved technique for determining reaction rate coefficients for reactions of esters in water is apparent, and the present research is an effort aimed in that direction.

In certain environmental applications the need to determine the hydrolysis rates of organic compounds, such as pesticides, in natural waters is very important because hydrolysis is often the dominant route of degradation of anthropogenic chemicals in the environment. For example, 2-4-D is a widely used herbicide that may be formulated as an ester (e.g., as the 2-Butoxyethyl ester or as the methyl ester). These compounds have very low water solubility. In the pH range of 5 to 9, which is typical of natural waters, hydrolysis is an important breakdown process for these compounds, and is the dominant removal process at a pH of 9. Hydrolysis, photolysis and evaporation are the mechanisms being compared in this case.¹⁵

III. THEORY

A. Theoretical Basis for the Chemical Method of Interfacial Area Measurement.

1. Differential Equations for the Film Model. The theoretical basis for this chemical method of interfacial area measurement is discussed in Danckwert's book entitled Gas-Liquid Reactions.⁴ In the discussion below, only second order and pseudo-first order irreversible chemical reactions will be considered.

To begin the discussion of this chemical technique of interfacial area measurement, consider the situation described in Figure 1:

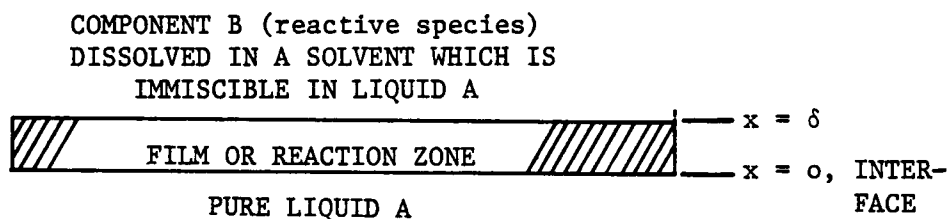


Figure 1. The Physical Situation.

A pure liquid "A" is in contact with an essentially immiscible liquid solvent containing reactive component "B." For example, phase "A" could be methyl salicylate (an ester) and the other phase could be an aqueous solution of sodium hydroxide. The two phases may be in any type of contacting device. Both phases are at the same constant temperature.

For the sake of simplicity, the film model will be used initially to describe the mass transfer between "A" and "B" phases. In any type of contacting device, the resistance to mass transfer of "A" into "B" is considered to be confined to a thin film on the "B" side of the interface. Since liquid "A" is pure, there is no mass transfer resistance

on the "A" side of the interface. Transport of "A" into "B" at the interface and in the film occurs only by diffusion.

To complete the description of the problem, some additional assumptions are necessary:

- (1) Assume steady-state conditions exist; i.e., at a given depth, x , in the "B" phase, the molar concentrations of "A" and "B" are constant with time.
- (2) Assume that the reaction between "A" and "B" occurs only in the "B" phase, and the reaction between "A" and "B" occurs according to the equation $A + B \xrightarrow{k_2} \text{PRODUCTS}$. Also, the rate of reaction is given by $r_A = k_2 C_A C_B$.

If one does mass balances on components "A" and "B" in the film near the interface, one obtains the following equations:

$$D_{AB} \frac{d^2 C_A}{dx^2} - k_2 C_A C_B = 0 \quad (1)$$

$$D_{BB} \frac{d^2 C_B}{dx^2} - Z k_2 C_A C_B = 0 \quad (2)$$

2. Boundary Conditions for the Film Model. The appropriate boundary conditions for the solution are:

$$\text{At } x = 0 \quad C_A = C_A^*, \quad (3)$$

$$\frac{dC_B}{dx} = 0.$$

At $x = \delta$,

$$\begin{cases} C_A = A^\circ = \text{bulk conc. of "A"} \\ C_B = B^\circ = \text{bulk conc. of "B."} \end{cases} \quad (4)$$

3. Approximate Solution of the Film Model. As indicated by Danckwerts,⁴ the analytical solution of this set of equations is not

available, but an approximate solution was developed by Van Krevelen and Hoftijzer for the case in which $A^\circ = 0$. (i.e., The concentration of "A" in the bulk of the "B" phase is zero.) This condition, $A^\circ = 0$, implies that the reaction is so fast that it occurs only in the film.

The approximate solution is given in the following form:

$$E = \frac{\sqrt{M \frac{E_1 - E}{E_1 - 1}}}{\tanh \sqrt{M \frac{E_1 - E}{E_1 - 1}}}, \quad (5)$$

Danckwerts gives a plot of E as a function of $\sqrt{M}$ for several values of the parameter E_1 . Figure 2 illustrates the solution.

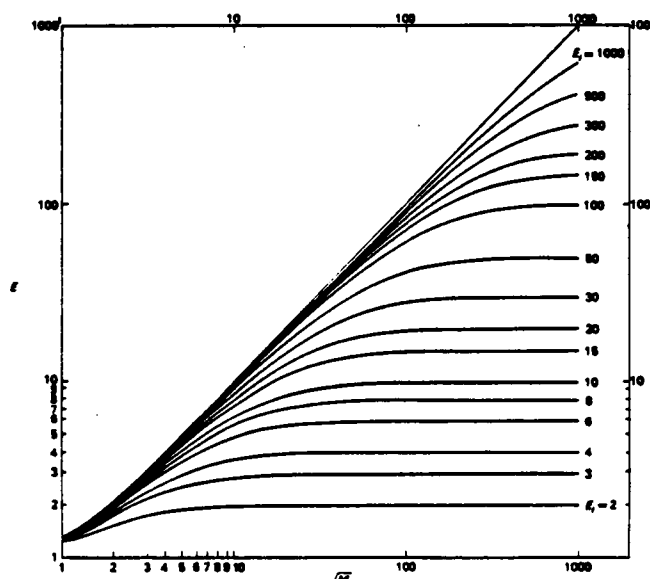


Figure 2.^a Enhancement factors for second-order reaction; for quiescent liquid or agitated liquid (film or Higbie models).

a. Taken from Danckwerts, P.V., Gas-Liquid Reactions, McGraw-Hill, New York, N.Y., 1970, p. 117.

4. Pseudo-First Order Criterion Based on the Film Model. A couple of interesting points can be made about the solution:

- (1) If $\sqrt{M} < \frac{1}{2}E_1$ the corresponding value of E is very close to the main diagonal, and the reaction may be treated as pseudo-first order. This means that either the reaction is slow enough or the mass transfer of "A" into phase "B" is fast enough that the concentration of "B" is approximately equal to B^0 all the way to the interface. (i.e., The depletion of "B" in the film is small.)
- (2) If $\sqrt{M} < \frac{1}{2}E_1$ and $\sqrt{M} > 3$, the rate of chemical reaction is much greater than the rate of mass transfer, and $E \approx \sqrt{M}$. In other words, the reaction is a "fast, pseudo-first order reaction," and the average rate of extraction per unit area is given by:

$$\bar{R} = C^* \sqrt{D_{AB} k_2 B^0} . \quad (6)$$

5. Pseudo-First Order Criterion Based on Danckwerts' Model. Up to this point, the film model has been used as the model of the mass transfer at the interface. Danckwerts' surface-rejuvenation model is probably more descriptive of the actual mass transfer situation. For the second-order irreversible reaction discussed above, the criterion for the reaction to be pseudo-first order, according to the Danckwerts model is:

$$\sqrt{1 + M} - 1 \ll \frac{B^0}{2C^*} . \quad (7)$$

This is the same as the criterion given above for the film model if $M \gg 1$ and if $D_{AB} = D_{BB}$ (i.e., $M \gg 1 \rightarrow \frac{D_{AB} k_2 B^0}{k_L^2} \gg 1$ or that

$$D_{AB} K_2 B^0 \gg k_L^2).$$

6. Expression For the Average Rate of Extraction per Unit

Area Based on Danckwerts Model. The average rate of extraction per unit area according to the Danckwerts model is given by⁴:

$$\bar{R} = s \int_0^\infty R e^{-st} dt, \text{ where} \quad (8)$$

$$R = -D_{AB} \left(\frac{\partial C_A}{\partial x} \right)_{x=0}. \quad (9)$$

$$\bar{R} = s \int_0^\infty -D_{AB} \left(\frac{\partial C_A}{\partial x} \right)_{x=0} e^{-st} dt. \quad (10)$$

To obtain an expression for $\frac{\partial C_A}{\partial x}$, one solves the species conservation equation for component "A", given that the reaction kinetics are first order or pseudo-first order.

$$D_{AB} \frac{\partial^2 C_A}{\partial x^2} = \frac{\partial C_A}{\partial t} + k_1 C_A \quad (11)$$

The boundary conditions are:

$$\begin{cases} C_A = 0, x > 0, t = 0 \\ C_A = C^*, x = 0, t > 0 \\ C_A = 0, x = \infty, t > 0 \end{cases} \quad (12)$$

(i.e. $C_A = 0$ in bulk of B phase and reaction occurs only in the region near the interface.)

The Laplace transform technique was used to reduce equation (11) to an ordinary differential equation. The ordinary differential equation was then solved to yield the solution in the Laplace domain. This result

was used to obtain the expression for the average rate of extraction per unit area, $\bar{R}$, for an irreversible, first order or pseudo-first order reaction. The result is given below:

$$\bar{R} = k_L C^* \sqrt{1+M}, \quad \text{where } M = \frac{D_{AB} k_2 B^0}{k_L^2} \quad (13)$$

$$\therefore \bar{R} = C^* \sqrt{D_A k_2 B^0 + k_L^2} \quad (14)$$

If $M \gg 1$, then the reaction is a "fast, pseudo-first order" reaction, and one can approximate $\bar{R}$ by:

$$\bar{R} = C^* \sqrt{D_A k_2 B^0} \quad (15)$$

In Appendix A, the pseudo-first order criterion is evaluated for the case of methyl salicylate reacting with sodium hydroxide. The magnitude of the terms in equation (14) are also assessed.

7. The Danckwerts Plot. Usually, the equation for the average rate of extraction per unit area is multiplied (on both sides) by "a," the interfacial area per unit volume, to yield the expression:

$$\bar{R}a = aC^* \sqrt{D_{AB} k_2 B^0 + k_L^2} \quad (16)$$

If one squares both sides,

$$(\bar{R}a)^2 = (aC^*)^2 D_{AB} k_2 B^0 + (aC^*)^2 k_L^2 \quad (17)$$

Therefore, if one plots $(\bar{R}a)^2$ as a function of $k_2 B^0$, the equation is that of a straight line with slope of $(aC^*)^2 D_{AB}$ and intercept of $(aC^*)^2 k_L^2$. Given D_{AB} and C^* and the slope of the line, one calculates "a"; and from "a," C^* , and the intercept k_L is calculated. The plot described above is called a "Danckwerts plot" and is illustrated in Figure 3.

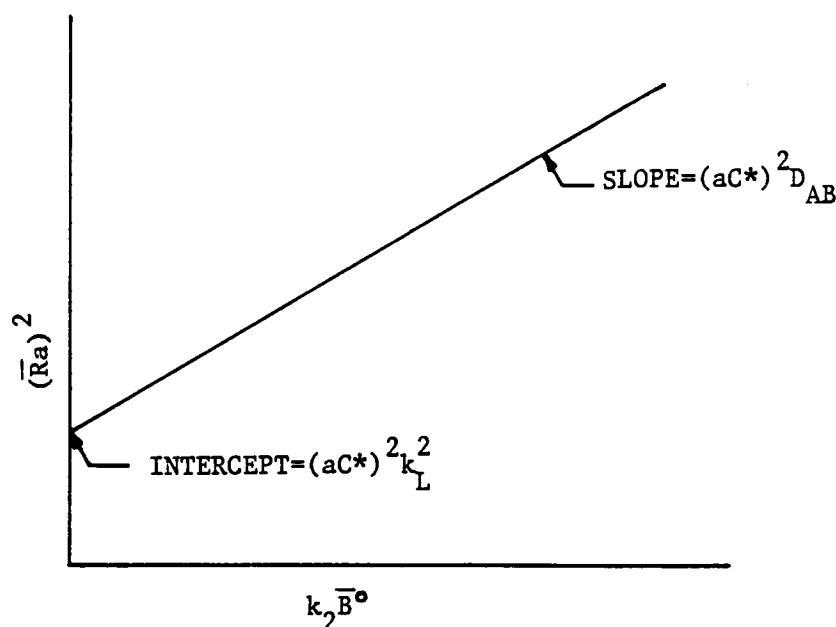


Figure 3. The Danckwerts Plot.

To obtain experimental data for the Danckwerts plot, experimental runs must be conducted to measure $\bar{Ra}$ values for several values of sodium hydroxide concentration. For a direct contact boiler column, the rate of extraction per unit volume of dispersion, $\bar{Ra}$, may be calculated from the relationship:

$$\bar{Ra} = \frac{\left(B^{\circ} \text{column inlet} - B^{\circ} \text{column outlet} \right) Q_d}{\left(\frac{\pi D^2}{4} \right) L} \quad (18)$$

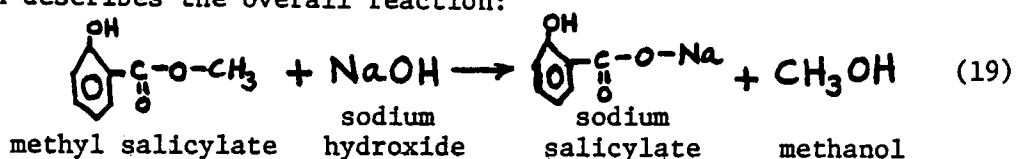
B. Determination of Physico-Chemical Properties for

Use in the Measurement of Interfacial Area

The chemical method of interfacial area measurement requires some physico-chemical property data. Values of reaction rate coefficient, diffusivity, mass transfer coefficient and solubility are needed to determine whether the criteria for a pseudo-first order or fast,

pseudo-first order reaction are satisfied. Solubility data and diffusivities are needed for use of the Danckwerts plot for determination of interfacial area and mass transfer coefficient. In this section, the equations used for the determination of physico-chemical data are given.

1. Reaction Rate Coefficients. Saponification of methyl salicylate is bimolecular, second order and irreversible. The following equation describes the overall reaction:

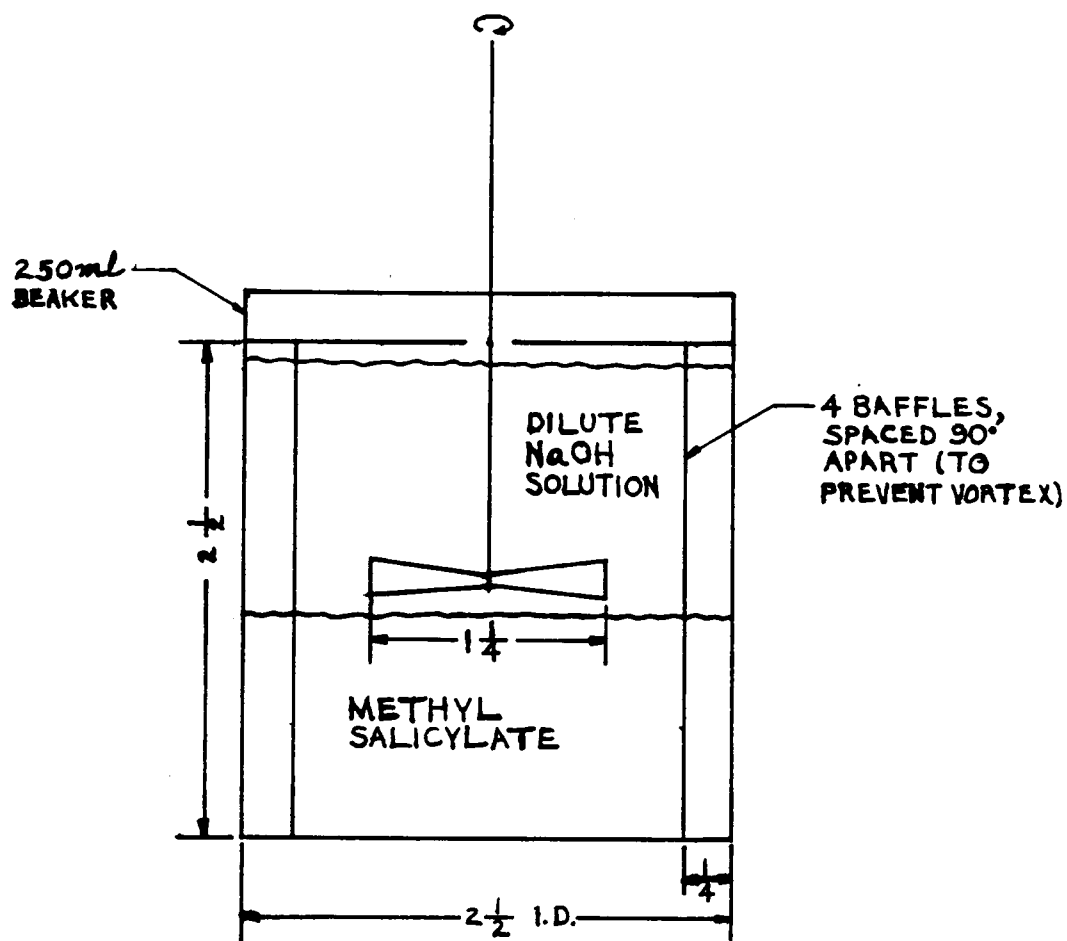


Consequently, the rate of consumption of either reactant is given by the expression

$$-r = k_2 C_A C_B \quad (20)$$

One of the objectives of this study was to obtain values of the second order reaction rate coefficient, k_2 , at several temperatures. These coefficients were determined with two basic pieces of information: a computer model of a stirred cell containing separate layers of methyl salicylate (bottom layer) and aqueous sodium hydroxide (top layer) and experimental values of hydroxyl ion concentration as a function of time for the top layer. Measurement of the concentration profile data is described in a later section, and development of the computer model is discussed below.

The stirred cell is illustrated schematically in Figure 4. A mathematical model of the cell was developed by treating it as a semi-batch reactor. Reaction occurs only in the aqueous layer, and the bottom layer serves as a source of methyl salicylate feed. One can visualize the bottom layer as an infinite number of discrete methyl salicylate feed lines.



- NOTES: 1. THE AGITATOR IS A TWO-BLADED, 10° INCLINED PADDLE AGITATOR.
 2. DIMENSIONS ARE IN INCHES.

Figure 4. Illustration of Stirred Cell.

If a component mass balance is made for the sodium hydroxide in the aqueous layer, the following equation is obtained:

$$-r_B = \frac{-dC_B}{dt} = k_2 C_A C_B \quad (21)$$

A balance for methyl salicylate in the aqueous phase yields:

$$-r_A = \frac{-dC_A}{dt} = \frac{-K_L A_i}{V} (C^* - C_A) + k_2 C_A C_B \quad (22)$$

In both equations, perfect mixing of the aqueous phase has been assumed. Equations (21) and (22) constitute a system of first order, coupled, ordinary, nonlinear differential equations with constant coefficients.

To solve equations (21) and (22) numerically, a set of initial conditions and values of the coefficients in the equations must be specified. The initial conditions that best fit the physical situation in this case are given below as equations (23) and (24):

$$\text{At } t = 0, C_A = C^* \quad (23)$$

$$\text{At } t = 0, C_B = C_{B0} \quad (24)$$

2. Mass Transfer Coefficients. An estimate of the mass transfer coefficient for the stirred cell was needed for solving equations (21) and (22). To obtain an expression for k_2 , the reaction term in equation (22) is set equal to zero, and the resulting differential equation was solved analytically. In this case, the required initial condition is given by equation (25):

$$\text{At } t = 0, C_A = 0 \quad (25)$$

The resulting analytical solution is given in equation (26):

$$\frac{C_A}{C^*} = 1 - e^{-k_L \frac{A_i}{V} t} \quad (26)$$

Equation (26) can be rearranged and solved for the mass transfer coefficient, k_L , to give:

$$k_L = -\frac{V}{A_i t} \ln \left(1 - \frac{C_A}{C^*} \right) \quad (27)$$

Equation (27) and experimental data relating C_A at a point in time were utilized to calculate values of the mass transfer coefficient for the case of mass transfer in a stirred cell containing a lower methyl salicylate layer and an upper layer consisting only of distilled water. A sample calculation of the mass transfer coefficient from experimental data is given in Appendix B.

Values of the mass transfer coefficient were also calculated from a correlation developed by Brown for transfer of an electrolyte in a stirred cell having an upper layer of aqueous electrolyte solution and a lower layer of mercury¹⁶. Brown's correlation is given below:

$$N_{Sh} = [0.029 \text{ EXP } (3.3 \times 10^{-6} N_{Re_m})] N_{Re_w}^{0.81} N_{Sc_w}^{0.52} \quad (28)$$

$$\text{for } 100 < N_{Sh} < 160,000$$

If the lower layer is not agitated, one obtains:

$$N_{Sh} = 0.029 N_{Re_w}^{0.81} N_{Sc_w}^{0.52} \quad (29)$$

Equation (29) was utilized to calculate mass transfer coefficient values

for comparison with values determined in the present work. A sample calculation illustrating the use of Brown's correlation is given in Appendix C.

3. Diffusivities. Values of diffusivities used in this work were calculated from the well-known Wilke-Chang correlation, which is valid for dilute solutions. The correlation is given below in equation (30).

$$D_{AB} = \frac{(7.4 \times 10^{-8})(\phi M_B)^{0.5} T}{\mu \left(v_A \right)^{0.6}} \quad (30)$$

Since the quantities in the Wilke-Chang correlation are tied to a specific set of units, these quantities and their units are listed below:

D_{AB}	Diffusivity of component "A" in component "B"	$\frac{\text{cm}^2}{\text{sec}}$
T	Absolute temperature	K
μ	Viscosity of solution	Centipoises
M_B	Molecular weight of component B	$\frac{\text{grams}}{\text{gm-mole}}$
ϕ	Association factor for solvent ($\phi=2.6$ for water)	---
v_A	Molar volume of species A	$\frac{\text{cm}^3}{\text{gm-mole}}$

Based on a comparison of experimentally determined diffusivity values in the literature with values calculated from the Wilke-Chang correlation for the same temperature, the correlation should yield diffusivity estimates that are in error by no more than about 15%.

IV. EXPERIMENTAL EQUIPMENT AND PROCEDURE

A. Measurement of Sodium Hydroxide Concentration Versus Time Data for Calculating Reaction Rate Coefficients.

In this section, a discussion is given of experimental equipment and procedure applicable to the measurement of the physico-chemical data needed in connection with the determination of interfacial area in a direct contact boiler. Equipment and procedure used for measuring reaction rate coefficients, solubility data, and mass transfer coefficients are discussed.

As indicated earlier, the method for determining values of the reaction rate coefficient and mass transfer coefficient relies on experimental concentration versus time data. In a typical run for obtaining concentration data, the baffled 250 ml stirred cell containing 100 ml of methyl salicylate was placed into a constant temperature bath. A lightly stoppered Erlenmeyer flask containing 120 ml of approximately 0.1N aqueous sodium hydroxide solution was also put into the constant temperature bath. When both solutions had reached the desired temperature, the agitator in the beaker was turned on at the approximate speed. In all runs, the agitator was centered in the beaker, and its bottom tip was at the 125 ml mark. A calibrated speed controller was used for precise agitator speed control. With the agitator in motion, the sodium hydroxide solution and container were momentarily removed from the bath, and the sodium hydroxide solution was added as rapidly as possible to the reaction vessel. The layers soon became well defined and clear again after the addition, and sampling of the aqueous phase was begun after about one minute.

During an experimental run, a total of about seven, 2 ml samples were taken, and these were analyzed by titration. Sampling was performed with a 2 ml pipet and a suction bulb. As soon as a sample was taken, it was transferred rapidly to a 250 ml Erlenmeyer flask containing 2 drops of phenolphthalein solution and excess aqueous hydrochloric acid solution (about 50 ml of distilled water and enough 0.1 N HCl solution to consume all the sodium hydroxide present plus a slight excess of HCl).

The hydrochloric acid serves to "quench" the alkaline hydrolysis reaction. Acid catalyzed hydrolysis of methyl salicylate was neglected, since data for similar compounds indicate that acid catalyzed hydrolysis is generally much slower than alkaline hydrolysis.¹⁴ The reverse reaction, esterification of the salicylic acid product by hydrochloric acid, has also been neglected. Data on the rate of esterification of salicylic acid by hydrochloric acid are given in the literature.^{17,18,19}

After the quenching step, the excess hydrochloric acid, and the salicylic acid formed in the quench were titrated with approximately 0.01N aqueous sodium hydroxide solution to a faint pink phenolphthalein endpoint. Great care was taken to prevent overrunning the endpoint. Using the stoichiometric relationships and the data obtained, the concentration of sodium hydroxide in the original sample was calculated. A sample calculation for determining the sodium hydroxide concentration from the titration data is given in Appendix D.

The constant temperature bath that was used for this work is a Hewlett Packard Model No. 5910A. A silicone oil, Dow Corning 200 Fluid (dimethyl polysiloxane) was the heat transfer medium in the bath.

Agitator speed control in the semibatch reactor was achieved through the use of a Cole Parmer Master Servodyne controller. A General Radio Strobotac tachometer (model no. 1531-AB) was used to calibrate the speed controller. The agitator speed controller calibration curve is given in Appendix E.

In all experiments of the present work, Aldrich technical grade methyl salicylate (98% purity) was used (lot no. CD032397). Fisher certified grade sodium hydroxide pellets (97.4% NaOH) was used to make the solutions used as the aqueous phase. Sodium hydroxide solutions were standardized against Aldrich gold label, primary standard grade potassium hydrogen phthalate (99.95 - 100.05% KHP).

B. Measurement of the Solubility of Methyl Salicylate in Water at Various Temperatures.

Another part of the experimental work was the determination of the solubility of methyl salicylate in water at various temperatures. These values are required in the differential equations which were solved numerically to obtain concentration versus time information for the aqueous phase of the stirred cell.

To determine the solubility of methyl salicylate in water, the stirred cell was again employed. About 100 ml of methyl salicylate and 120 ml of distilled water were placed into the breaker, and the cell and its contents were transferred to a constant temperature bath. The agitator was run at 200 RPM. Since approximate measurements of mass transfer coefficients had revealed that the aqueous phase rapidly approaches the saturation concentration, only one hour was allowed for equilibration. At the end of the equilibration period, a 50 ml sample

of the aqueous phase was taken with a pipet. The sample was immediately transferred to a 250 ml Erlenmeyer flask containing excess sodium hydroxide for saponification of the methyl salicylate in the sample. The Erlenmeyer flask was then put back into the constant temperature bath for about 30 minutes.

The technique for sample preparation and analysis from this point on was essentially the same as was described earlier. Hydrochloric acid was utilized to convert the sodium salicylate to salicylic acid, and the excess HCl and salicylic acid were titrated with sodium hydroxide (0.1N in this case) to a phenolphthalein endpoint. Given the stoichiometric relationships and the sample preparation and titration data, the solubility of methyl salicylate in water was determined at a given temperature. A sample calculation of methyl salicylate solubility from titration data is given in Appendix F.

Figure 5 is a titration curve showing the pH of the sample being titrated with 0.1N sodium hydroxide as a function of the volume of sodium hydroxide added. The phenolphthalein color change occurs at a pH of 8.19 in this case. The almost vertical portion of the curve occurring between pH values of 4.5 and 8.5 was traversed by addition of only 0.11 ml of 0.1N sodium hydroxide solution. Consequently, phenolphthalein appears to be a suitable indicator for the titration.

C. Measurement of Sodium Hydroxide Concentration Data for Determining Mass Transfer Coefficients.

In the third part of the experimental work, approximate values were measured for the mass transfer coefficient for transport of methyl

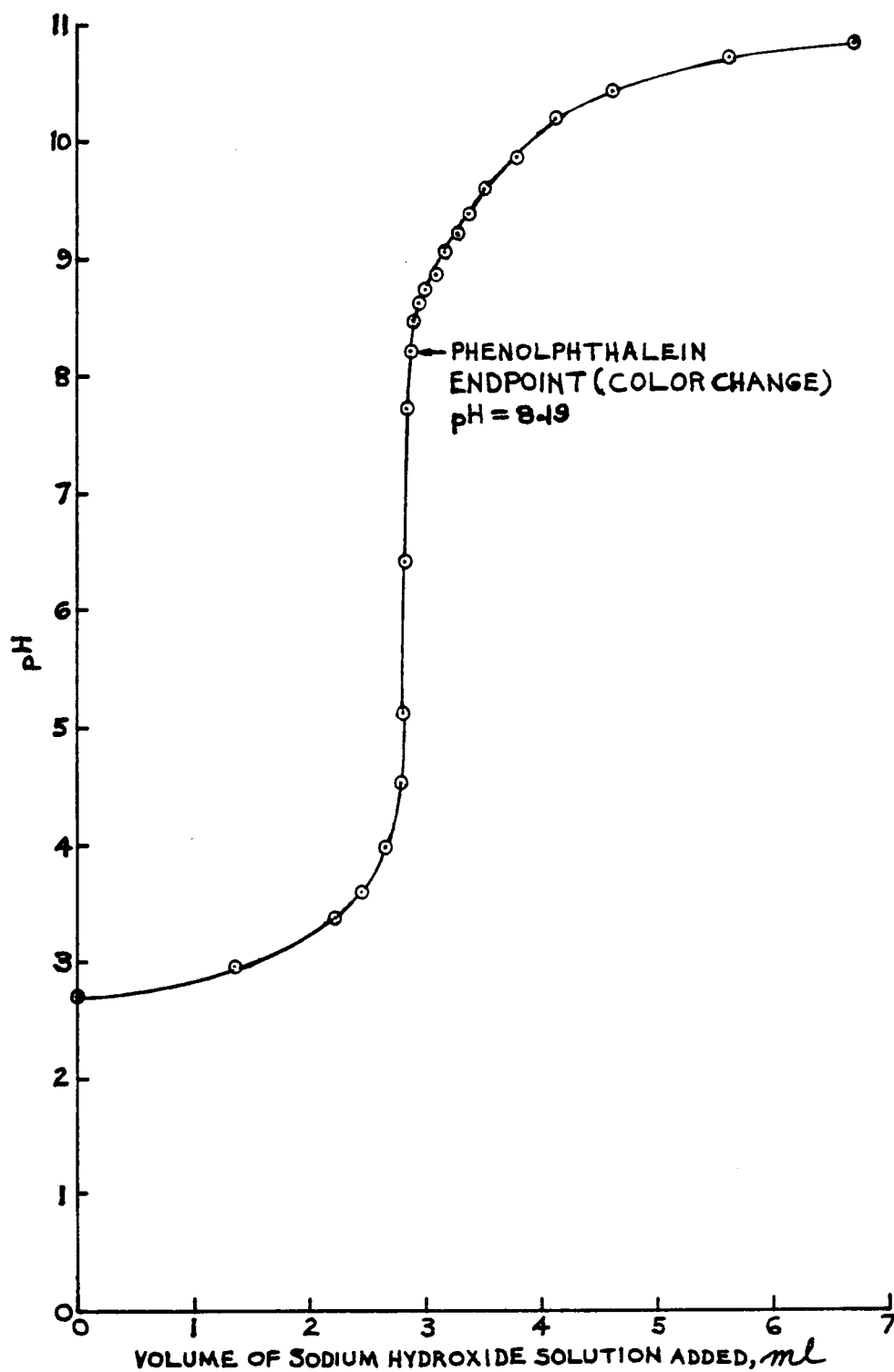


Figure 5. Titration Curve for Titration of Salicylic Acid and Hydrochloric Acid Solution with 0.09504 N Sodium Hydroxide.

salicylate into an upper layer consisting only of distilled water in the stirred cell. These experiments were conducted at 30°C and at 61°C. In all cases, the agitation rate was 200 RPM.

For these mass transfer coefficient measurements, 100 ml of methyl salicylate was placed into the 250 ml baffled beaker and the beaker and its contents were placed into the constant temperature bath. A 120 ml quantity of distilled water in a 250 ml Erlenmeyer flask was also put into the bath. As soon as the temperature of both liquids had stabilized at the desired value, the agitator was turned on at the desired rate. The flask containing the water was momentarily removed from the bath, and the water was added slowly to the stirred cell containing the methyl salicylate. After approximately one minute, a 50 ml sample of the aqueous phase was removed and was added to a 250 ml flask containing aqueous sodium hydroxide solution. As in the solubility experiments, the sample was then put back into the constant temperature bath and heated for 30 to 45 minutes to saponify the methyl salicylate in the sample. After this, the sample was analyzed in the same way as in the solubility experiments to determine the concentration of methyl salicylate in the sample. The concentration of methyl salicylate was then used in the calculation of the mass transfer coefficient.

V. ANALYSIS OF EXPERIMENTAL DATA

A. Determination of Mass Transfer Coefficient and Reaction Rate Coefficient by Using CSMP.

The mathematical model of the stirred cell, defined by equations (21) and (22) and conditions (23) and (24), contains two unknown parameters, k_L and k_2 . Values for the other constants (A_1 , V , and C^*) were available. Therefore, to determine values for k_L and k_2 , a trial and error technique was used. Estimates of k_L and k_2 were made and the model was solved to obtain values for the sodium hydroxide concentration as a function of time. These concentration values were compared with concentration data obtained in experiments with the stirred cell, and a new estimate of k_L and k_2 was made. The model was solved repeatedly until satisfactory agreement was obtained between concentration versus time values generated by the model and experimental concentration versus time data. Computer model solutions were matched with experimental $C_B(t)$ data obtained at temperatures of 30, 61, and 80°C. The computer solutions of best agreement with the data are illustrated in the "Discussion of Results" section.

Numerical solutions were obtained on an IBM System/370 digital computer by employing the Continuous System Modeling Program (CSMP III Program Number 5734-X59). For simulation of low temperature runs, the integration technique used for solving the differential equations was the Fourth Order Runge-Kutta with variable step size. For simulation of the stirred cell at high temperatures, difficulties were encountered in numerical integration due to the steep rate of descent of the $C_B(t)$ curve, and trapezoidal rule integration was specified and worked well.

Figure 6 gives the computer input statements which were used for the 30°C case and Table 1 is a sample of the computer output generated by that input.

B. A Nonlinear Least Squares Program for Determining Optimum Values of Mass Transfer Coefficient and Reaction Rate Coefficient.

An effort was made to find values of the parameters, k_L and k_2 , which yield the optimum computer generated solution curve through the experimental concentration data. A nonlinear least squares optimization program was employed in this effort. This program is entitled "Nonlinear Parameter Estimation and Programming" (360D 13.6.003, Dec. 1967), and at one time was furnished by IBM Corporation to its users. The printed program output for the 30°C case is given in Appendix G. The results are discussed in the next section.

```

$$$CONTINUOUS SYSTEM MODELING PROGRAM III VIN3 TRANSLATOR OUTPUT$$$

TITLE HYDROL
INITIAL
  CA0=4.86E-6
  CBO=9.504E-5
  AI=31.67
  CSTAR=4.86E-6
  V=120.
  KL=.011
PARAM Z=(17.4,100.,110.)
DYNAMIC
  DCADT=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA-Z*CA*CB
  CA=INTGRL(CA0,DCADT)
  DCBDT=-Z*CA*CB
  CB=INTGRL(CBO,DCBDT)
  TRANS=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA
TERMINAL
TIMER DELT=0.5, FINTIM=1860., PROEL=30.
PRINT CA, CB, DCADT, DCBDT, TRANS
END
STOP

OUTPUT VARIABLE SEQUENCE
CA0  CBO  AI  CSTAR  V  KL  DCADT  CA  DCBDT  CB
TRANS

$$$ TRANSLATION TABLE CONTENTS $$$          CURRENT          MAXIMUM

MACRO AND STATEMENT OUTPUTS                  17                  600
STATEMENT INPUT WORK AREA                    50                  1900
INTEGRATORS+MEMORY BLOCK OUTPUTS             2 + 0                  300
PARAMETERS+FUNCTION GENERATORS              4 + 0                  400
STORAGE VARIABLES+INTEGRATOR ARRAYS          0 + 0/2                 50
HISTORY AND MEMORY BLOCK NAMES               21                   50
MACRO DEFINITIONS AND NESTED MACROS           6                   50
MACRO STATEMENT STORAGE                      13                  125
LITERAL CONSTANT STORAGE                     0                   100
SORT SECTIONS                                2                   20
MAXIMUM STATEMENTS IN SECTION                 6                   600

$$$END OF TRANSLATOR OUTPUT$$$

```

Figure 6. Typical Computer Input for Model of Stirred Cell.

TABLE 1

Sample of Computer Output Generated by
the Program Input Statements
Shown in Figure 6

TIME	CA	CB	DCADT	DCBDT	TRANS
.0	4.8600E-06	9.5040E-05	-4.6189E-08	-4.6189E-08	-7.1054E-15
30.0000	3.7097E-06	9.3836E-05	-3.1471E-08	-3.4811E-08	3.3393E-09
60.0000	2.9241E-06	9.2914E-05	-2.1549E-08	-2.7169E-08	5.6201E-09
90.0000	2.3852E-06	9.2182E-05	-1.4803E-08	-2.1988E-08	7.1844E-09
120.0000	2.0147E-06	9.1579E-05	-1.0190E-08	-1.8450E-08	8.2602E-09
150.0000	1.7595E-06	9.1064E-05	-7.0213E-09	-1.6022E-08	9.0011E-09
180.0000	1.5836E-06	9.0610E-05	-4.8374E-09	-1.4349E-08	9.5116E-09
210.0000	1.4625E-06	9.0198E-05	-3.3283E-09	-1.3192E-08	9.8632E-09
240.0000	1.3793E-06	8.9815E-05	-2.2833E-09	-1.2388E-08	1.0105E-08
270.0000	1.3223E-06	8.9452E-05	-1.5583E-09	-1.1828E-08	1.0270E-08
300.0000	1.2836E-06	8.9103E-05	-1.0546E-09	-1.1437E-08	1.0383E-08
330.0000	1.2575E-06	8.8764E-05	-7.0410E-10	-1.1162E-08	1.0458E-08
360.0000	1.2403E-06	8.8433E-05	-4.5986E-10	-1.0968E-08	1.0508E-08
390.0000	1.2292E-06	8.8106E-05	-2.8945E-10	-1.0830E-08	1.0541E-08
420.0000	1.2224E-06	8.7782E-05	-1.7037E-10	-1.0731E-08	1.0560E-08
450.0000	1.2186E-06	8.7442E-05	-8.7027E-11	-1.0658E-08	1.0571E-08
480.0000	1.2169E-06	8.7143E-05	-2.8606E-11	-1.0605E-08	1.0576E-08
510.0000	1.2167E-06	8.6825E-05	1.2434E-11	-1.0564E-08	1.0577E-08
540.0000	1.2176E-06	8.6509E-05	4.1336E-11	-1.0533E-08	1.0574E-08
570.0000	1.2191E-06	8.6193E-05	6.1757E-11	-1.0508E-08	1.0570E-08
600.0000	1.2212E-06	8.5878E-05	7.6231E-11	-1.0487E-08	1.0564E-08
630.0000	1.2237E-06	8.5564E-05	8.6551E-11	-1.0470E-08	1.0557E-08
660.0000	1.2264E-06	8.5250E-05	9.3959E-11	-1.0455E-08	1.0549E-08
690.0000	1.2293E-06	8.4936E-05	9.9309E-11	-1.0441E-08	1.0540E-08
720.0000	1.2323E-06	8.4623E-05	1.0324E-10	-1.0428E-08	1.0531E-08
750.0000	1.2355E-06	8.4311E-05	1.0617E-10	-1.0416E-08	1.0522E-08
780.0000	1.2387E-06	8.3998E-05	1.0837E-10	-1.0405E-08	1.0513E-08
810.0000	1.2419E-06	8.3686E-05	1.1008E-10	-1.0393E-08	1.0503E-08
840.0000	1.2453E-06	8.3375E-05	1.1143E-10	-1.0382E-08	1.0494E-08
870.0000	1.2486E-06	8.3063E-05	1.1255E-10	-1.0372E-08	1.0484E-08
900.0000	1.2520E-06	8.2752E-05	1.1349E-10	-1.0361E-08	1.0474E-08
930.0000	1.2554E-06	8.2442E-05	1.1430E-10	-1.0350E-08	1.0464E-08
960.0000	1.2589E-06	8.2131E-05	1.1503E-10	-1.0339E-08	1.0454E-08
990.0000	1.2623E-06	8.1821E-05	1.1570E-10	-1.0329E-08	1.0444E-08
1020.00	1.2658E-06	8.1512E-05	1.1633E-10	-1.0318E-08	1.0434E-08
1050.00	1.2693E-06	8.1202E-05	1.1693E-10	-1.0307E-08	1.0424E-08
1080.00	1.2728E-06	8.0893E-05	1.1752E-10	-1.0296E-08	1.0414E-08
1110.00	1.2764E-06	8.0585E-05	1.1809E-10	-1.0286E-08	1.0404E-08
1140.00	1.2799E-06	8.0276E-05	1.1865E-10	-1.0275E-08	1.0393E-08
1170.00	1.2835E-06	7.9968E-05	1.1920E-10	-1.0264E-08	1.0383E-08
1200.00	1.2871E-06	7.9660E-05	1.1975E-10	-1.0253E-08	1.0373E-08
1230.00	1.2907E-06	7.9353E-05	1.2031E-10	-1.0242E-08	1.0362E-08
1260.00	1.2943E-06	7.9046E-05	1.2085E-10	-1.0231E-08	1.0352E-08
1290.00	1.2979E-06	7.8739E-05	1.2140E-10	-1.0220E-08	1.0341E-08
1320.00	1.3016E-06	7.8433E-05	1.2195E-10	-1.0208E-08	1.0330E-08
1350.00	1.3052E-06	7.8126E-05	1.2250E-10	-1.0197E-08	1.0320E-08
1380.00	1.3089E-06	7.7821E-05	1.2307E-10	-1.0186E-08	1.0309E-08
1410.00	1.3126E-06	7.7515E-05	1.2362E-10	-1.0175E-08	1.0298E-08
1440.00	1.3163E-06	7.7210E-05	1.2419E-10	-1.0163E-08	1.0288E-08
1470.00	1.3201E-06	7.6905E-05	1.2475E-10	-1.0152E-08	1.0277E-08
1500.00	1.3238E-06	7.6601E-05	1.2532E-10	-1.0141E-08	1.0266E-08
1530.00	1.3276E-06	7.6297E-05	1.2589E-10	-1.0129E-08	1.0255E-08
1560.00	1.3314E-06	7.5993E-05	1.2647E-10	-1.0117E-08	1.0244E-08
1590.00	1.3352E-06	7.5690E-05	1.2704E-10	-1.0106E-08	1.0233E-08
1620.00	1.3390E-06	7.5387E-05	1.2762E-10	-1.0094E-08	1.0222E-08

VI. DISCUSSION OF RESULTS

A. Determination of Reaction Rate Coefficients and Mass Transfer Coefficients

As indicated in the "Analysis of Experimental Data" section, differential equations (21) and (22) in the "Theory" section were solved subject to initial conditions (23) and (24) for several values of the parameters, k_L and k_2 . Values of the parameters which yield computer generated concentration values agreeing well with experimental $C_B(t)$ data at 30, 61 and 80°C were determined and are summarized in Table 2. The computer solutions for $C_B(t)$ were drawn through the experimental data, and these curves are shown in Figure 7. The computer input statements and printouts are given in Appendix H, and experimental sodium hydroxide concentration data that are shown in Figure 7 are tabulated in Appendix I.

Solution of equations (21) and (22) for the 30°C case was based on experimental values for the parameters, k_L and k_2 . The value of the parameter k_2 in this case was the value estimated by Goldschmidt and Scholz at 25°C. The computer solution that was obtained with these experimentally determined parameters is the uppermost curve in Figure 7. This curve fits the experimental $C_B(t)$ data reasonably well, but one may ask whether or not these parameters yield the optimum fit.

A non-linear least squares optimization program, which was described in an earlier section, was used to obtain optimum values for parameters k_L and k_2 . In the case of the 30°C run discussed above, the optimization program determined $k_L = 0.00806$ cm/sec and $k_2 = 243.1$ cm³/gm-mole sec as the parameter values which describe the curve of best fit through

TABLE 2
Summary of Parameter Values, k_L and k_2 ,
Defining the Curves in Figure 7

Temp., °C	$k_L, \frac{\text{cm}}{\text{sec}}$	$k_2, \frac{\text{cm}^3}{\text{gm-mole sec}}$
30	0.011	100
61	0.10	350
80	0.30	1000

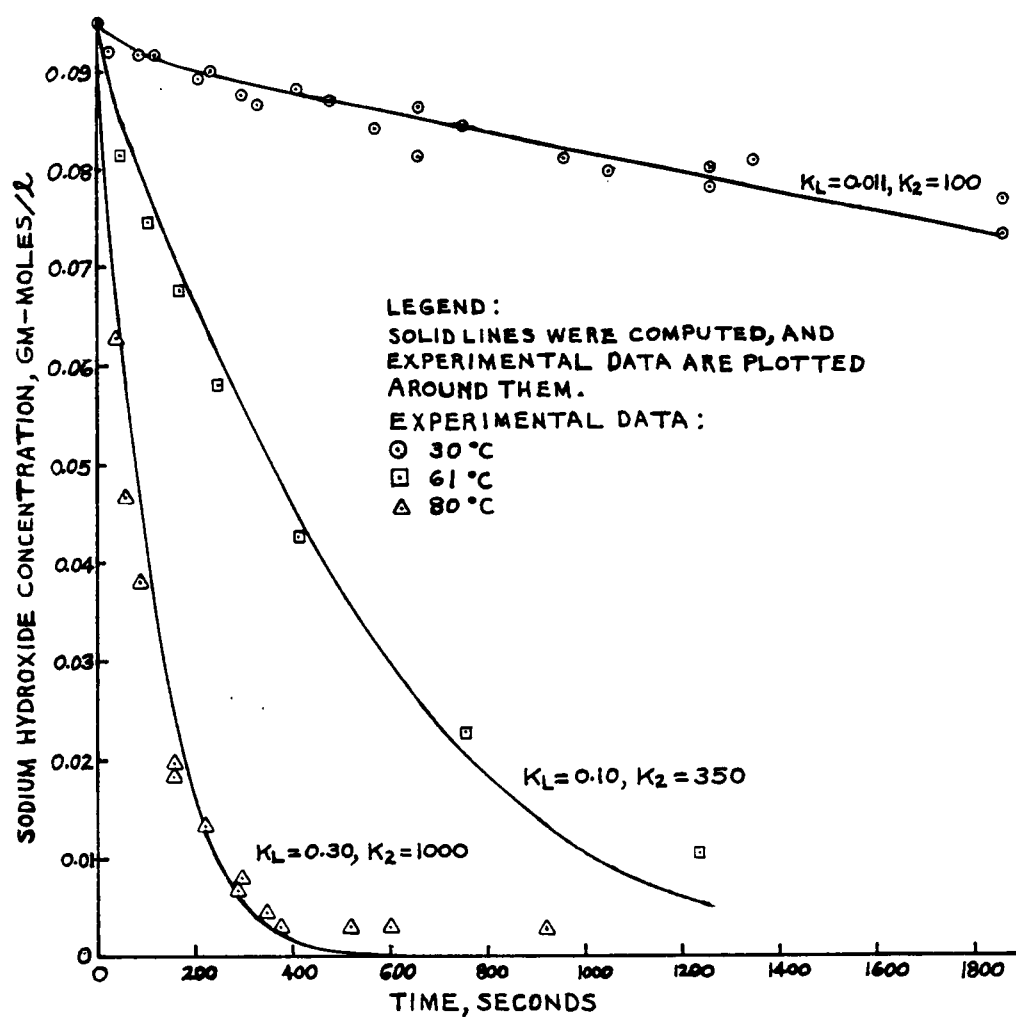


Figure 7. Alkaline Hydrolysis of Methyl Salicylate: Sodium Hydroxide Concentration as a Function of Time at Various Temperatures Based on Visual Comparison of Data and CSMP Solution Curves.

the experimental data. The optimization program output for the 30°C case is given in Appendix G and the corresponding CSMP program input and output are given in Appendix J. Figure 8 (uppermost curve) shows this computer solution of best fit through the experimental data, and it appears that the fit is very good. On the other hand, if one superimposes Figure 7 over Figure 8, it is apparent that the former values of $k_L = 0.011$ cm/sec and $k_2 = 100$ cm³/gm-mole sec give a computer generated curve not much different from the computer curve determined by the optimized parameters.

An attempt was made to run the optimization program for the 61°C and the 80°C data, but the optimization program would not converge. This difficulty appears to have been caused by the inability of the integration technique in the optimization program to handle the "stiff" concentration curves defined by the data at 61°C and 80°C. Therefore, to optimize the values of the parameters for equations (21) and (22) subject to (23) and (24), solutions via CSMP were generated for many values of k_L and k_2 . The sum of the squares of the deviations of the experimental data points from computer generated $C_p(t)$ data points was calculated for each set of parameters. Consequently, sets of k_L and k_2 values were determined at 61°C and at 80°C that minimize the sum of the squares of the deviations. The resulting computer generated curves based on these k_L and k_2 values were drawn through the experimental data and are the middle and lower curves in Figure 8. The computer input and corresponding pertinent output are given in Appendix K.

For the 80°C curve in Figure 8 one may question whether or not the optimum fit of the data has been obtained, since the computer generated curve does not appear to fit the experimental data very well near the

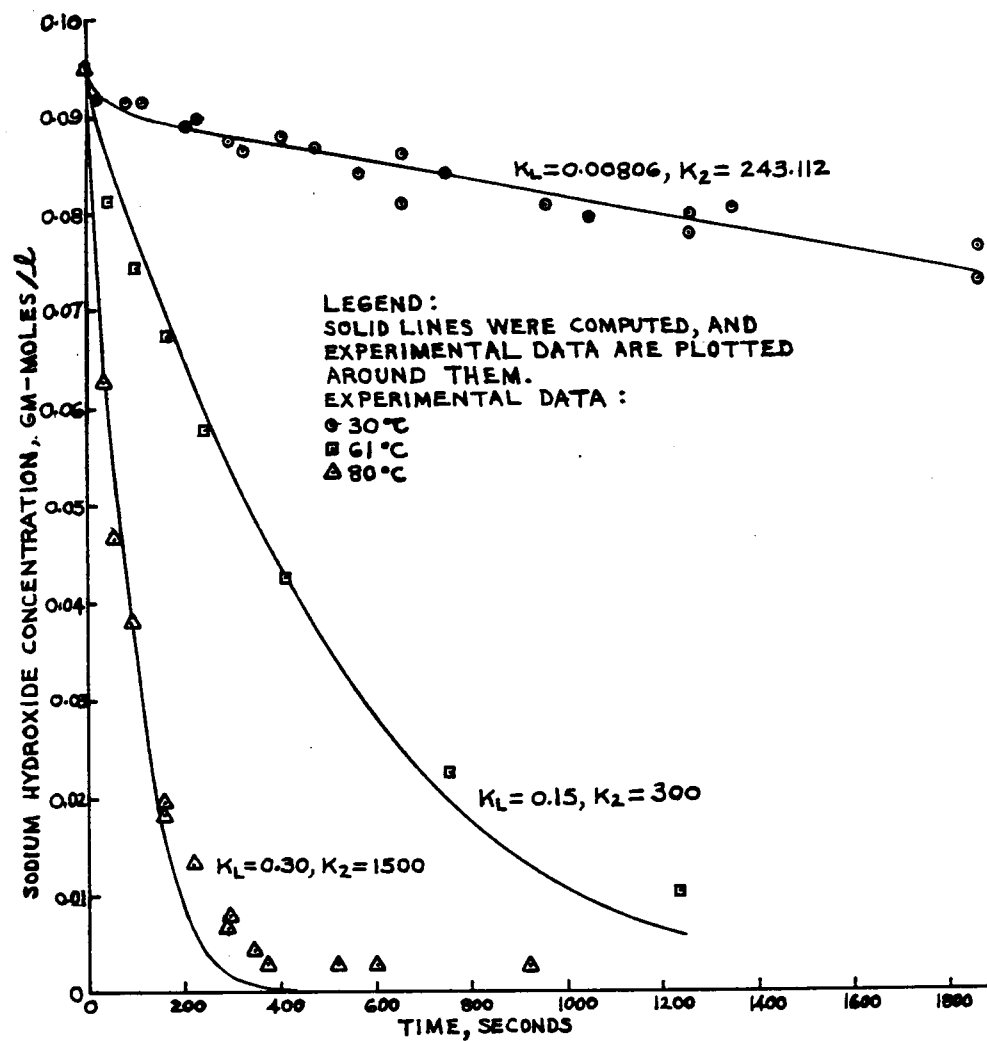


Figure 8. Alkaline Hydrolysis of Methyl Salicylate: Sodium Hydroxide Concentration as a Function of Time at Various Temperatures Based on Statistical Fitting of Computer Solution Curves Through Data.

"knee" of the curve. The reason for the poor least squares fit is that it was obtained relative to the sodium hydroxide concentration values, which are represented by vertical distances on the graph. Perhaps optimization of the fit in some other way would yield a better fit of the data near the "knee" of the curve.

Figure 9 is an Arrhenius plot of k_2 values versus reciprocal absolute temperature and is based upon values from Table 2. From the slope of the straight line in Figure 9, the activation energy was found to be 9.58 kilocalories per gram mole. This calculation was based on the assumption that the activation energy does not vary with temperature. Figure 10 is an Arrhenius plot of the k_2 values determined at 30°C by the optimization program and by least squares fitting of the data, as described above, for the 61°C and 80°C cases. It is readily apparent that the k_2 data for the latter case define a poor straight line fit of the data, and the activation energy obtained from the slope of this line is only 6.91 kilocalories per gram mole. Consequently, since the data in Table 2 determine a good statistical straight line fit on the Arrhenius plot, and the activation energy of 9.58 kilocalories per gram mole is close to activation energy values given by Mabey and Mill¹⁴ for similar compounds, it is felt that the values in Table 2 are the more accurate and consistent set of k_L and k_2 values.

If one uses the 9.58 k-cal/gm-mole value for the activation energy, and the k_2 value given in Table 2 for 30°C, one can calculate a value of k_2 for 25°C to compare with the literature value of Goldschmidt and Scholz. This was done, and based upon the assumption that the literature value is correct, the value that was taken from Table 2 is in error by 23.4%. This calculation gives further justification for the

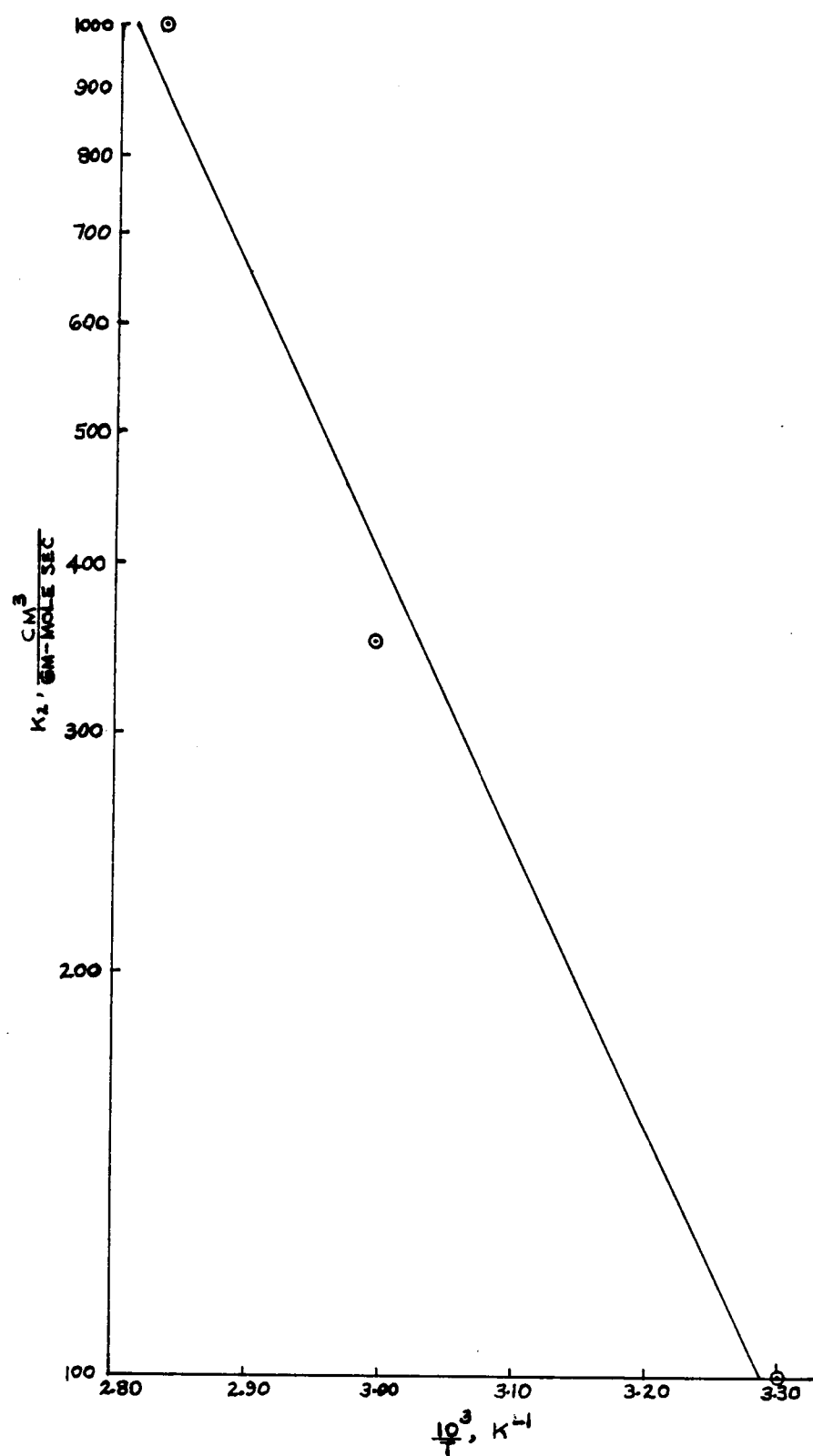


Figure 9. Arrhenius Plot Based on k_2 Values in Table 2, p. 184.

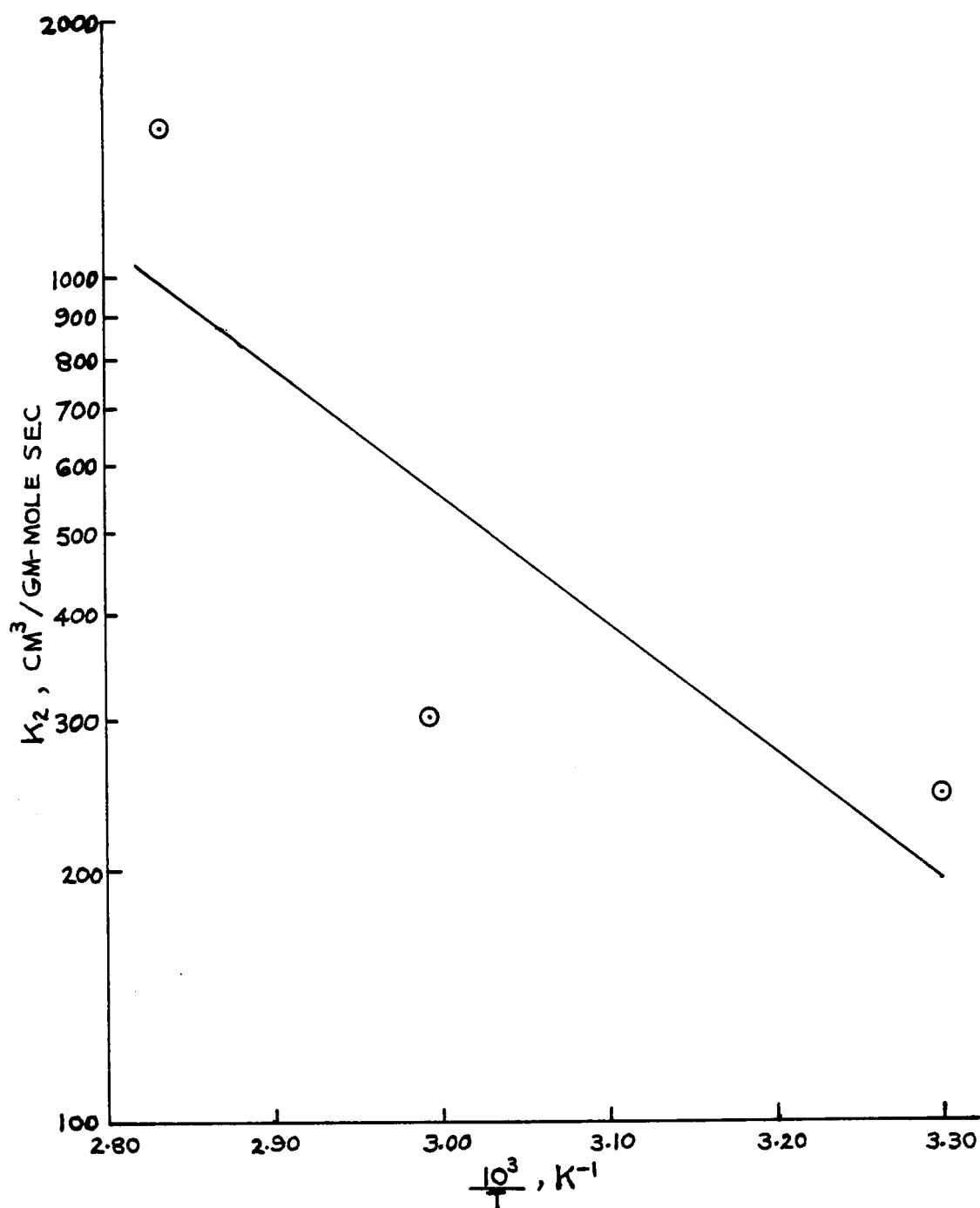


Figure 10. Arrhenius Plot Based on k_2 Values Obtained by Optimization Program or Least Squares Fit of Data.

preference of the k_2 values shown in Table 2, p. 184 and provides an estimate of the experimental error associated with the values of k_2 reported in Table 2, p. 184.

B. Solubility of Methyl Salicylate in Water at Various Temperatures

Figure 11 shows the effect of temperature on the solubility of methyl salicylate in water. The data defining the solubility curve are tabulated in Appendix L. Two literature values are given at 30°C for comparison. One value is from Seidell,²⁰ and the other is from Lange's Handbook of Chemistry.²¹ If the value given by Seidell is assumed to be correct, then the solubility value determined in the present work is slightly low (i.e. 15.6% error).

C. Effect of Agitator Speed on the Sodium Hydroxide Concentration Versus Time Data

It was discovered early in the experimental work that the agitator speed affects the shape of the sodium hydroxide concentration versus time curves. One reason for this effect is that the mass transfer coefficient depends on the agitator speed, as indicated in Brown's correlation and other similar correlations.

Figure 12 illustrates the order of magnitude of the effect of the agitator speed on the sodium hydroxide concentration. Experimental data that are shown in Figure 12 are given in Appendix J. At an agitator speed of 200 RPM a well-mixed condition is approached for the aqueous phase. It should be noted here that 200 RPM was chosen as an upper limit on the agitator speed because at higher speeds droplets or globules of the bottom layer of methyl salicylate become entrained in the aqueous phase.

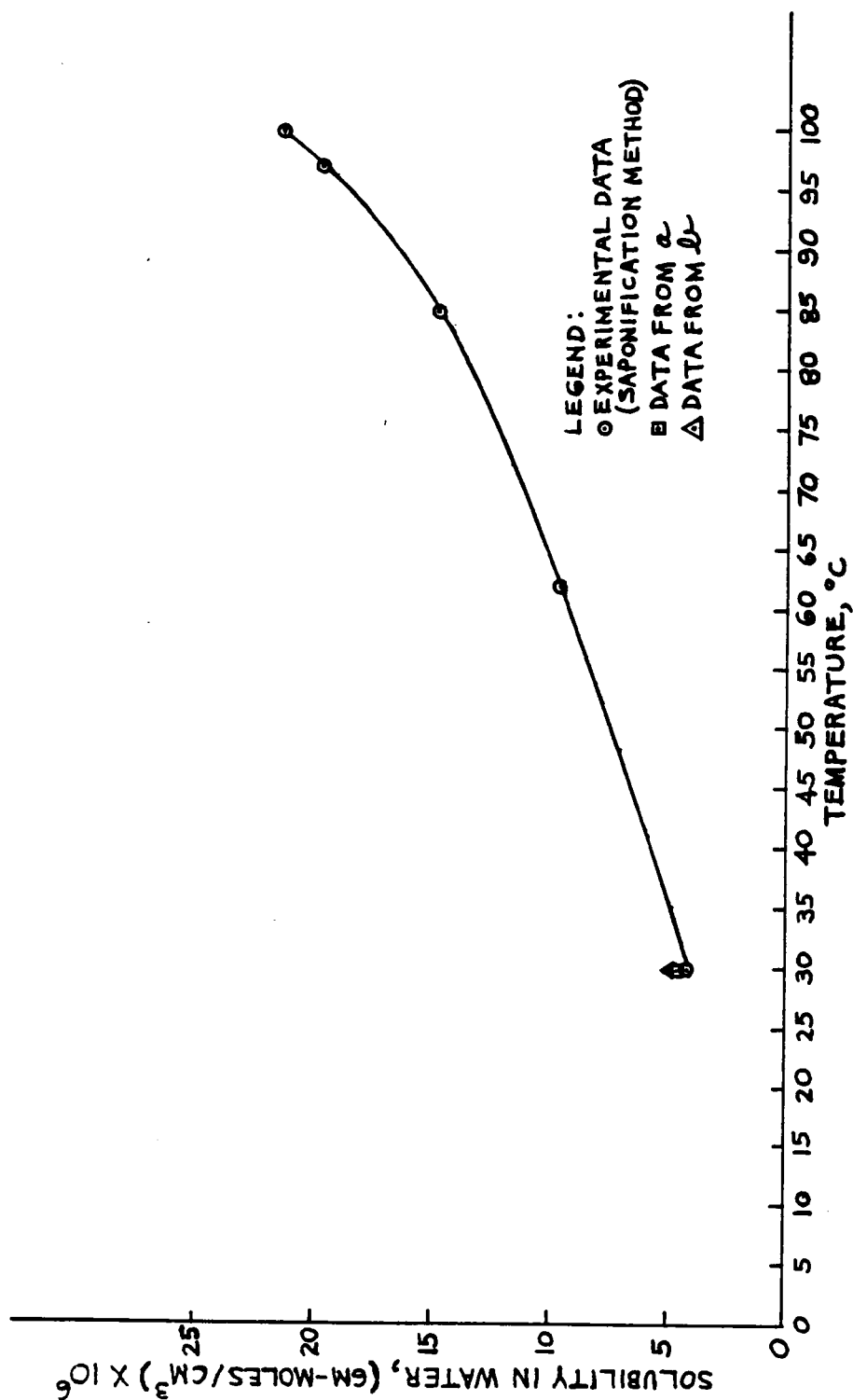


Figure 11. Solubility of Methyl Salicylate in Water as a Function of Temperature.

a. Dean, John A., Ed., Lange's Handbook of Chemistry, 12th Ed., McGraw-Hill, New York, N.Y., 1978.

b. Seidell, A., Solubilities of Organic Compounds, Vol. 2., 3rd Ed., D. Van Nostrand Co., New York, N.Y., 1941.

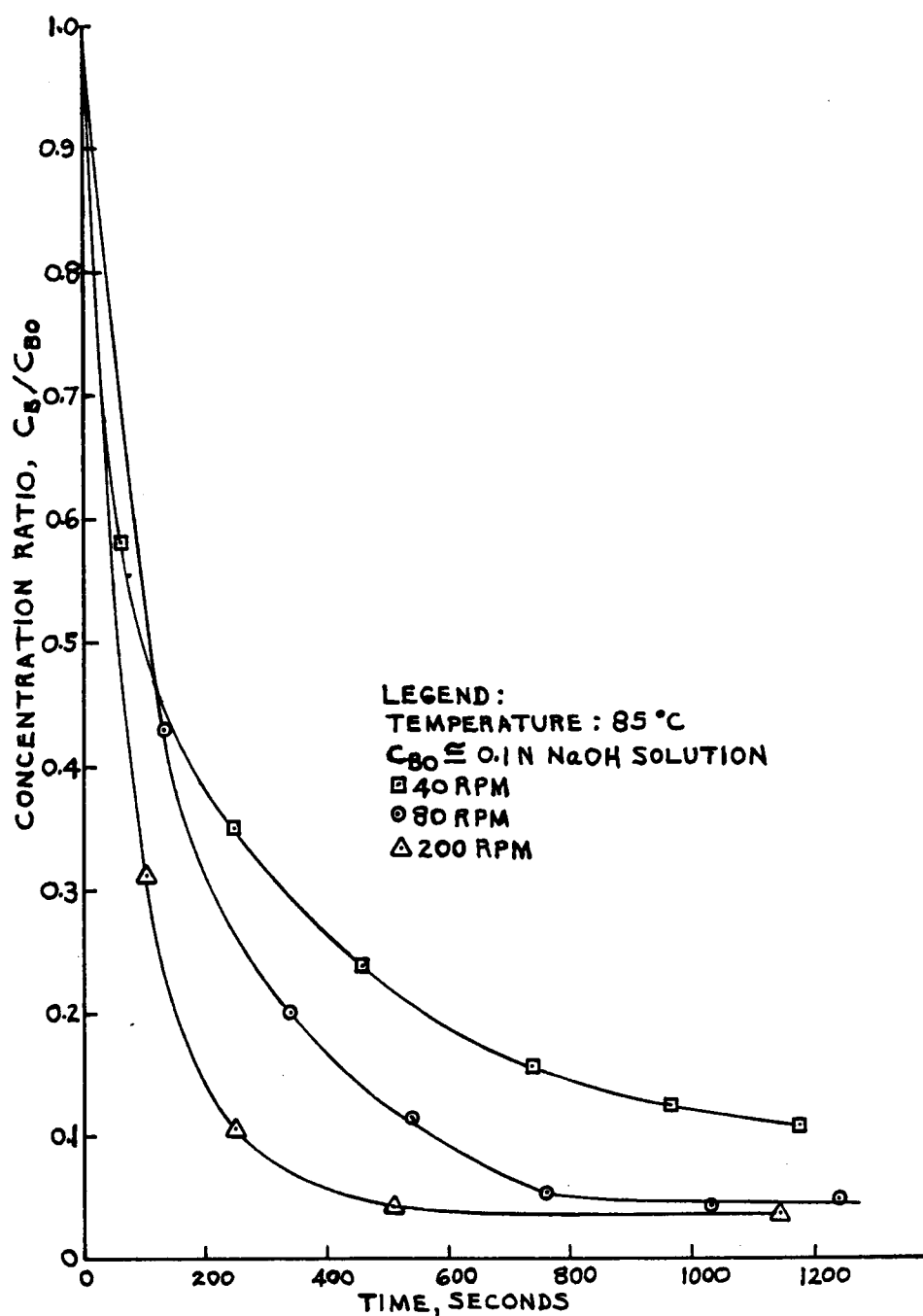


Figure 12. Effect of Agitation Rate on the Rate of Alkaline Hydrolysis of Methyl Salicylate at Constant Temperature.

D. Mass Transfer Coefficient Measurements for the Stirred Cell

Equation (27) of the "Theory" section and experimental data relating the concentration of methyl salicylate in the aqueous phase at a point in time were utilized to estimate values of the mass transfer coefficient, k_L . Measurements at 30°C fixed k_L at 0.011 cm/sec. The agitation rate was 200 RPM. Equation (27) was only used to estimate k_L for the 30°C case. At 61°C it was found that the aqueous phase becomes saturated much more rapidly and meaningful results could not be obtained.

The value of the mass transfer coefficient, k_L , that was based on experimental measurements at 30°C agrees well with the value of 0.00806 obtained by using the optimization program (see Figure 8, p. 187). On the other hand, the experimental value for k_L (0.011 cm/sec) is much greater than the 2.38×10^{-3} cm/sec value for the k_L estimated from Brown's correlation. One can conclude, based on the comparisons above, that Brown's correlation does not apply to the methyl salicylate-water system.

E. Evaluation of Danckwerts' Pseudo-First Order and Fast, Pseudo-First Order Criteria for the Reaction Between Methyl Salicylate and Sodium Hydroxide

Given the values of the physico-chemical properties, the Danckwerts criteria for pseudo-first order reaction and fast, pseudo-first order reaction were evaluated for the reaction between methyl salicylate and sodium hydroxide in a spray column at 100°C. As indicated earlier, the calculations are in Appendix A. It was found from the calculations that the reaction is pseudo-first order, but not fast, pseudo-first order when the sodium hydroxide concentration in the aqueous phase is 0.1 molar. If the sodium hydroxide concentration is increased to

about 0.7 molar, the reaction becomes fast, pseudo-first order.

F. Supplementary Sodium Hydroxide Concentration Versus Time Data

Finally, it should be noted that some extraction runs in the stirred cell were conducted with an aqueous phase having an initial sodium hydroxide concentration of about 1 molar. The data were not used for any calculations, but have been included in Appendix M for the sake of completeness.

VII. CONCLUSIONS

1. Since the chemical method of liquid-liquid interfacial area measurement has been successfully applied to a three phase system in the air-agitated contactor study of Fernandes and Sharma,⁹ the method definitely appears to be applicable to the determination of interfacial area in a direct contact boiler. Also, the good agreement which has been obtained between physical and chemical methods of interfacial area measurement in various types of contacting devices is additional evidence to indicate that the chemical method of interfacial area measurement discussed herein is both valid and reliable.
2. The reaction between methyl salicylate and approximately 0.1 molar sodium hydroxide in a spray column at 100°C is a pseudo-first order reaction, but is not a fast, pseudo-first order reaction unless the sodium hydroxide concentration is increased to about 0.7 molar.
3. Values of the solubility of methyl salicylate in water were obtained at several temperatures. At 30°C agreement with literature values was within about 15%.
4. To summarize the effectiveness of determining k_L and k_2 by the method proposed in this research, one can conclude the following:
 - a) From a comparison of the computer curve generated by parameters specified by the optimization program with the computer curve based on approximate experimental values of the parameters at 30°C, one can conclude that a relatively large change in the value of k_2 (from 243.1 to 100 cm³/gm mole sec in this case) does not change the position of the computer generated curve through the data very much. Therefore, the differential equations are not always extremely sensitive to changes in k_2 .

- b) Reliable experimental concentration versus time data are required to minimize the uncertainty in the determination of k_2 with the computer model.
- c) It has been observed through the many CSMP runs that a fairly small change in the value of the k_L causes a substantial shift of the computer generated curves through the data. In other words, the differential equations are fairly sensitive to changes in k_L .
- d) It is very helpful to use an Arrhenius plot to assist in selecting trial values of k_2 for the computer model to determine k_L and k_2 .
- e) The technique described herein for the determination of k_L and k_2 should yield sufficiently accurate values of k_2 for use in the chemical method of measuring interfacial area. Based upon a comparison with limited data from the literature, values of k_2 obtained by using the proposed technique are not likely to be in error by more than about 25%.

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PART II: LIST OF REFERENCES

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APPENDICES

APPENDIX A

EVALUATION OF THE DANCKWERTS CRITERIA FOR PSEUDO-FIRST

ORDER REACTION AND FAST, PSEUDO-FIRST

ORDER REACTION

The following calculation verifies that the reaction between methyl salicylate and approximately 0.1 molar sodium hydroxide in a spray column at 100°C is a "pseudo-first order" reaction, but is not a fast, pseudo-first order reaction unless the sodium hydroxide concentration is increased to about 0.7 molar. The pseudo-first order criterion based on the Danckwerts surface-rejuvenation model of mass transfer was used for the calculation.

The criterion for a pseudo-first order reaction is given in equation (7):

$$\sqrt{1 + M} - 1 \ll \frac{B^\circ}{ZC^*}$$

$$M = \frac{D_{AB} k_2 B^\circ}{k_L^2}$$

If, in addition,

$$\frac{D_{AB} k_2 B^\circ}{k_L^2} > 10 ,$$

the reaction is a fast, pseudo-first order reaction.

CASE I: 0.1 molar NaOH

Evaluate the above criteria for the reaction between 0.1 molar sodium hydroxide and methyl salicylate in a spray column heat exchanger at 100°C.

PHYSICAL PROPERTY DATA:

$$C^* = 2.13 \times 10^{-5} \frac{\text{gm-moles}}{\text{cm}^3} \text{ at } 100^\circ\text{C} \text{ (from Appendix M)}$$

$$D_{AB} = 3.05 \times 10^{-5} \frac{\text{cm}^2}{\text{sec}} \text{ at } 100^\circ\text{C} \text{ (from Wilke-Chang Correlation)}$$

A: Methyl Salicylate B: Aqueous Sodium Hydroxide

$$Z = 1$$

$$B^\circ = 0.1 \frac{\text{gm-moles}}{\ell} \text{ or } 1.0 \times 10^{-4} \frac{\text{gm-moles}}{\text{cm}^3}$$

Calculate k_2 at 100°C, given k_2 at 80°C and the activation energy.

Use the Arrhenius equation.

$$k_2 \text{ at } 100^\circ\text{C} = \left(k_2 \text{ at } 80^\circ\text{C} \right) \text{EXP} \left(\frac{E_a}{R} \frac{(T_2 - T_1)}{T_2 T_1} \right)$$

$$T_2 = 100^\circ\text{C or } 373 \text{ K} \quad T_1 = 80^\circ\text{C or } 353 \text{ K}$$

$$R = 1.987 \text{ cal/gm-mole K}$$

$$E_a = 9.58 \times 10^3 \text{ cal/gm-mole}$$

$$k_2 = 1000 \text{ cm}^3/\text{gm-mole sec at } 80^\circ\text{C}$$

$$k_2 \text{ at } 100^\circ\text{C} = (1000) \text{EXP} \left(\frac{9.58 \times 10^3}{1.987} \frac{(373 - 353)}{(373)(353)} \right)$$

$$k_2 \text{ at } 100^\circ\text{C} = 2080 \frac{\text{cm}^3}{\text{gm-mole sec}}$$

Evaluate k_L at 100°C from Vermuelen's correlation. Since it has been observed that the droplets of the aqueous phase near the bottom of the spray column are about 1/16 inch in diameter and in many cases smaller, the correlation of Vermuelen for rigid drops will be used to calculate k_L . The Vermuelen correlation and other correlations applicable to mass transfer in spray towers are summarized by Knight and Perona.²²

$$k_L = \frac{-r_d}{3t} \ln \left[1 - \left(1 - \text{EXP} \left(-\frac{\pi D_{AB}^2 t}{r_d^2} \right) \right)^{\frac{1}{2}} \right]$$

$$r_d = \frac{1}{32} \text{ inch or } 0.0794 \text{ cm, radius of drop}$$

$$D_{AB} = 3.05 \times 10^{-5} \frac{\text{cm}^2}{\text{sec}} \text{ at } 100^\circ\text{C}$$

The value of t , the contact time, was calculated from the column height between dispersed phase inlet and outlet and the rise velocity of the drop. The Klee and Treybal correlation²³ was used to calculate the terminal rise velocity of a water droplet rising in methyl salicylate.

$$U_t = \begin{array}{l} \text{terminal} \\ \text{rise velocity} \\ \text{of a water drop} \end{array} = 5.70 \frac{\text{cm}}{\text{sec}}$$

The continuous phase velocity was calculated from the methyl salicylate flow rate to the column and the column cross-sectional area.

$$V_c = \begin{array}{l} \text{velocity of} \\ \text{continuous phase} \end{array} = \frac{Q_c}{\frac{\pi D^2}{4}}$$

$$Q_c = 250 \frac{\text{cm}^3}{\text{min}}, \text{ a typical methyl salicylate flowrate}$$

$$D = 4 \text{ inches or } 10.16 \text{ cm, column inside diameter}$$

$$V_c = 0.0514 \frac{\text{cm}}{\text{sec}}$$

The slip velocity of a rising drop, is given by:

$$U_s = U_t - V_c$$

$$U_s = 5.70 - 0.0514 = 5.65 \frac{\text{cm}}{\text{sec}} .$$

$$t = \frac{L}{U_s} \quad L = \text{column length} = 41 \frac{3}{8} \text{ inches or } 105.1 \text{ cm}$$

$$t = \frac{105.1}{5.65} = 18.6 \text{ sec}$$

$$k_L = \frac{-0.0794}{3(18.6)} \ln \left[1 - \left(1 - \exp \left(\frac{-\pi^2 (3.05 \times 10^{-5}) (18.6)}{(0.0794)^2} \right) \right)^{\frac{1}{2}} \right]$$

$$k_L = 2.07 \times 10^{-3} \frac{\text{cm}}{\text{sec}} \text{ at } 100^\circ\text{C}$$

dispersed
phase

Now, the pseudo-first order criterion may be calculated:

$$M = \frac{(3.05 \times 10^{-5})(2080)(1.0 \times 10^{-4})}{(2.07 \times 10^{-3})^2}$$

$$M = 1.48$$

$$\sqrt{1+1.48} - 1 \ll \frac{1.0 \times 10^{-4}}{(1.0)(2.13 \times 10^{-5})}$$

$$0.57 \ll 4.69$$

The pseudo-first order criterion is satisfied.

$$M = 1.48 \neq 10$$

The reaction is not a fast reaction when the sodium hydroxide concentration in the aqueous phase is 0.1 molar.

CASE II: 0.7 molar NaOH

Evaluate the above criteria again for 0.7 molar NaOH as the aqueous phase:

$$M = \frac{(3.05 \times 10^{-5})(2080)(7.0 \times 10^{-4})}{(2.07 \times 10^{-3})^2} = 10.4$$

$$\sqrt{1+10.4} - 1 \ll \frac{5.0 \times 10^{-4}}{(1.0)(2.13 \times 10^{-5})}$$

$$2.38 \ll 23.47$$

The pseudo-first order criterion is satisfied.

$$M = 10.4 > 10$$

The reaction is a fast, pseudo-first order reaction.

Evaluate the magnitude of the terms of the equation for the average rate of extraction per unit area:

$$\bar{R} = C^* \sqrt{D_{AB} k_2 B^o + K_L^2}$$

$$\bar{R} = C^* \sqrt{(3.05 \times 10^{-5})(2080)(7.0 \times 10^{-4}) + (2.07 \times 10^{-3})^2}$$

$$\bar{R} = C^* \sqrt{4.44 \times 10^{-5} + 4.28 \times 10^{-6}}$$

From the calculations given above, it appears that the reaction between methyl salicylate and 0.7N sodium hydroxide can be used for interfacial area measurements in the direct contact boiler at 100°C.

APPENDIX B

CALCULATION OF THE MASS TRANSFER COEFFICIENT IN A STIRRED CELL FROM EXPERIMENTAL DATA

The following calculation illustrates the use of equation (27) and experimental data to determine a mass transfer coefficient for the stirred cell.

equation (27) $k_L = \frac{-V}{A_i t} \ln \left(1 - \frac{C_A}{C^*} \right)$

Use data obtained at 30°C. Agitation rate was 200 RPM.

$$C^* = 4.86 \times 10^{-6} \frac{\text{gm-moles}}{\text{cm}^3}$$

$$V = \text{volume of aqueous phase} = 120 \text{ cm}^3$$

$$C_A = \text{concentration of methyl salicylate in aqueous phase after contact time, } t = 1.28 \times 10^{-6} \frac{\text{moles}}{\text{cm}^3}$$

$$t = 105 \text{ sec, contact time}$$

$$A_i = \text{interfacial area (i.e. cross-sectional area of stirred cell)} = 31.67 \text{ cm}^2$$

$$k_L = \frac{-(120)}{(31.67)(105)} \ln \left(1 - \frac{1.28 \times 10^{-6}}{4.86 \times 10^{-6}} \right) \frac{\text{cm}}{\text{sec}}$$

$$k_L = 0.0110 \frac{\text{cm}}{\text{sec}}$$

APPENDIX C

SAMPLE CALCULATION ILLUSTRATING THE USE OF BROWN'S CORRELATION

This appendix contains a calculation illustrating the use of Brown's correlation for obtaining mass transfer coefficients for a stirred cell.

Problem: Calculate k_L at 30°C and 200 RPM for mass transfer in the stirred cell illustrated in Figure 4, p. 169. The top layer is distilled water and the bottom layer is methyl salicylate.

$$N_{Sh} = 0.029 N_{Re_w}^{0.81} N_{Sc_w}^{0.52}$$

$$N_{Sh} = \frac{k_L Da}{D_{AB}} ; N_{Re_w} = \frac{Da^2 n \rho}{\mu}$$

$$N_{Sc_w} = \frac{\mu}{\rho D_{AB}}$$

$$D_a = 1.25 \text{ in or } 0.1042 \text{ ft or } 0.0318 \text{ m}$$

$$\mu = 0.8007 \text{ centipoise or } 1.94 \frac{\text{lb}_m}{\text{ft hr}}$$

$$\rho = 62.2 \frac{\text{lb}_m}{\text{ft}^3}$$

$$n = 200 \frac{\text{rev}}{\text{min}} \text{ or } 12,000 \frac{\text{rev}}{\text{hr}}$$

$$N_{Re_w} = \frac{(0.1042)^2 ((12,000)(62.2))}{1.94}$$

$$N_{Re_w} = 4177 \text{ rev}$$

Note: Brown's correlation requires that n must have units of revolutions per time. The conversion of revolutions to radians has apparently been taken into account by the constant, 0.029, in the correlation.

Calculate D_{AB} from the Wilke-Chang correlation:

$$D_{AB} = \frac{(7.4 \times 10^{-8}) (\phi_B^M)^{0.5} T}{\mu v_A^{0.6}}$$

$$M_B = \text{molecular weight of water} = 18.02 \frac{\text{grams}}{\text{gm-mole}}$$

$$T = 303 \text{ K}$$

$$\phi = 2.6 \text{ for water}$$

$$v_A = \text{molar volume of methyl salicylate, } C_8H_8O_3$$

$$v_A = (14.8) 8 + (3.7)(8) + (7.4)(3) = 170.2 \frac{\text{cm}^3}{\text{gm-mole}}$$

$$\mu = 0.8007 \text{ centipoises}$$

$$D_{AB} = \frac{(7.4 \times 10^{-8}) [(2.6)(18.02)]^{0.5} (303)}{(0.8007)(170.2)^{0.6}}$$

$$D_{AB} = 8.79 \times 10^{-6} \frac{\text{cm}^2}{\text{sec}} \quad \text{or} \quad 8.79 \times 10^{-10} \frac{\text{m}^2}{\text{sec}}$$

$$D_{AB} = (8.79 \times 10^{-6})(3.87) = 3.40 \times 10^{-5} \frac{\text{ft}^2}{\text{hr}}$$

$$N_{Sc_w} = \frac{\mu}{\rho D_{AB}} = \frac{1.94}{(62.2)(3.40 \times 10^{-5})} = 917.3$$

$$N_{Sh} = (0.029)(4177)^{0.81} (917.3)^{0.52}$$

$$N_{Sh} = 862.6$$

$$k_L = \frac{(D_{AB})(862.6)}{Da} = \frac{(8.79 \times 10^{-10} \frac{\text{m}^2}{\text{sec}})(862.6)}{(0.0318\text{m})}$$

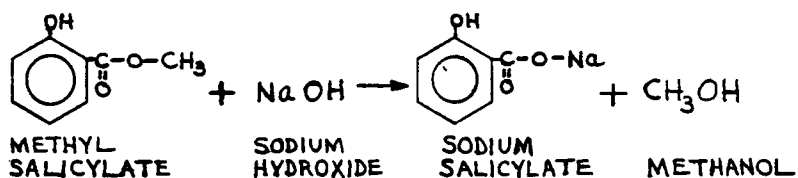
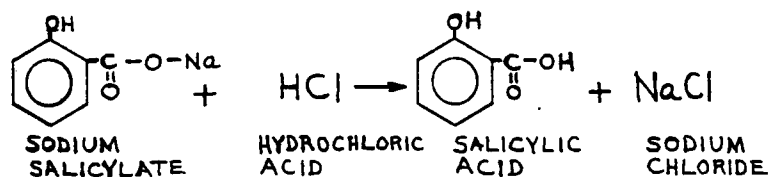
$$k_L = 2.38 \times 10^{-5} \frac{\text{m}}{\text{sec}} \quad \text{or} \quad 2.38 \times 10^{-3} \frac{\text{cm}}{\text{sec}}$$

APPENDIX D

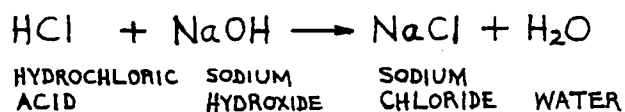
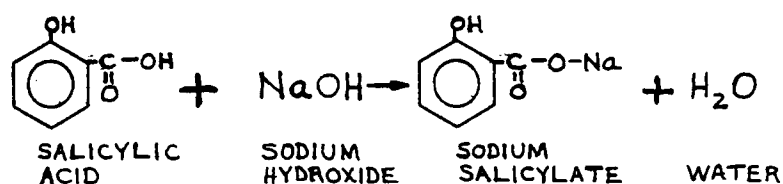
SAMPLE CALCULATION FOR OBTAINING THE SODIUM HYDROXIDE CONCENTRATION FROM TITRATION DATA

During the extraction runs, which were performed in the stirred cell, samples of the aqueous phase were taken and were analyzed by titration to determine the sodium hydroxide concentration. This appendix contains a sample calculation for obtaining the sodium hydroxide concentration from the titration data. The stoichiometric relationships that were utilized are also described.

CHEMICAL EQUATIONS:

CHEMICAL
REACTION
IN STIRRED CELL:CHEMICAL
REACTIONS
IN "QUENCH":

NOTE: THE HYDROCHLORIC ACID WAS SLIGHTLY IN EXCESS IN THE "QUENCH" REACTION.

CHEMICAL
REACTIONS
IN TITRATION:

STOICHIOMETRIC RELATIONSHIPS:

Let "meq" abbreviate the word "milliequivalents."

meq NaOH	-	meq NaOH	=	meq excess NaOH
put into		reacted to		
stirred cell		form		
initially		sodium salicylate		
↑				↑
THIS QUANTITY IS KNOWN.				THIS QUANTITY IS DESIRED.

meq HCl	=	HCl reacted with	+	HCl reacted	+	HCl
used for		sodium salicylate		with excess		excess
"quench"		to form salicylic acid		NaOH to form		
↑				sodium		
THIS QUANTITY IS KNOWN.				chloride		

meq NaOH	=	meq HCl	+	meq HCl
consumed in		excess		reacted with
titration				salicylic acid
↑				
THIS QUANTITY IS KNOWN.				

meq HCl used - meq	=	meq excess
for quench NaOH		sodium hydroxide
consumed		in stirred cell sample
in titration		

$\frac{\text{meq excess NaOH}}{\text{Sample volume, ml}}$	=	$\frac{\text{meq}}{\text{ml}}$ NaOH	=	$\frac{\text{moles}}{\ell}$ NaOH
				↑
				DESIRED RESULT

SAMPLE CALCULATION:

(Extraction Run No. 26, Sample No. 1)

At $t = 0$, a 120 ml quantity of 0.09504N NaOH solution was added as the aqueous phase of the stirred cell. After 25 seconds, a 2 ml sample was taken with a 2 ml pipet and was added to an Erlenmeyer flask containing 5 ml of 0.0957N hydrochloric acid, about 50 ml of distilled water, and 2 drops of phenolphthalein indicator solution. Titration to a phenolphthalein endpoint required 7.79 ml of 0.03782N NaOH solution.

$$(120)(0.09504) = 11.4048 \text{ meq NaOH initially charged to stirred cell.}$$

$$(5 \text{ ml HCl})(0.0957 \text{ N}) = 0.4785 \text{ meq HCl added in quench}$$

$$(7.79 \text{ ml})(0.03782 \text{ N}) = 0.2946 \text{ meq NaOH added in titration}$$

$$0.1839 \text{ meq excess NaOH in stirred cell sample.}$$

$$\frac{0.1839 \text{ meq}}{2 \text{ ml sample}} = 0.0919 \frac{\text{moles}}{\ell} \text{ NaOH concentration in stirred cell at the time sample No. 1 was taken.}$$

$$0.0919 \frac{\text{moles}}{\ell} \times \frac{1 \ell}{1000 \text{ cm}^3} = 9.19 \times 10^{-5} \frac{\text{gm-moles NaOH}}{\text{cm}^3}$$

This is one of the results given in Table 11 of Appendix I .

APPENDIX E

CALIBRATION CURVE FOR AGITATOR SPEED

CONTROLLER

Figure 13 is the calibration curve for the speed controller used to regulate the agitator speed in the stirred cell.

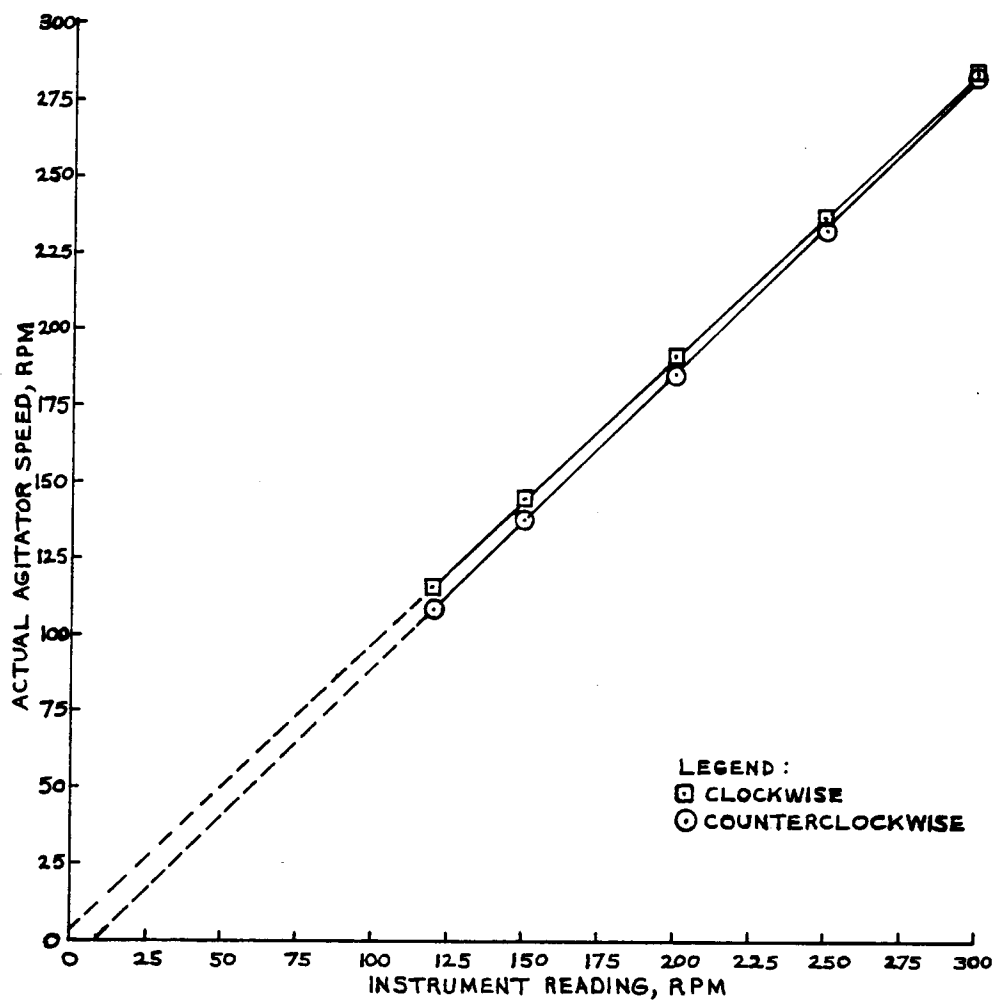


Figure 13. Calibration Curve for Agitator Speed Controller.

APPENDIX F

SAMPLE CALCULATION OF METHYL SALICYLATE SOLUBILITY

IN WATER FROM TITRATION DATA

The following is a sample of the calculations for obtaining the solubility of methyl salicylate in water from titration data.

SAMPLE CALCULATION:

A 120 ml quantity of distilled water was added to a stirred cell containing 100 ml of methyl salicylate. At the end of the one hour equilibration period, a 50 ml sample was taken with a pipet. The sample was transferred immediately to an Erlenmeyer flask containing 23 ml of 0.09504N NaOH solution. The sample was heated for 30 minutes before a 24 ml quantity of 0.0957N HCl was added to convert the sodium salicylate to salicylic acid and to neutralize the excess NaOH. The sample was then titrated immediately with 0.09504N NaOH, and 11.55 ml was required to reach the phenolphthalein endpoint.

$$\begin{aligned} (24 \text{ ml})(0.0957\text{N}) &= 2.2968 \text{ meq HCl used in quench} \\ (11.55 \text{ ml})(0.09504\text{N}) &= 1.0977 \text{ meq for titration} \end{aligned}$$

$$1.9991 \text{ meq excess NaOH}$$

$$\begin{aligned} (23 \text{ ml})(0.09504\text{N}) &= 2.1859 \text{ meq NaOH added for saponification} \\ &\quad \text{of sample} \\ &- 1.9991 \text{ meq excess NaOH} \end{aligned}$$

$$0.9868 \text{ meq NaOH consumed in saponification of sample}$$

$$\frac{0.9868 \text{ meq}}{50 \text{ ml sample}} \times \frac{1 \frac{\text{mole}}{\ell}}{1 \frac{\text{meq}}{\text{ml}}} \times \frac{1 \ell}{1000 \text{ cm}^3} = 1.97 \times 10^{-5} \frac{\text{gm-moles}}{\text{cm}^3}$$

solubility of methyl
salicylate in water
at 97°C.

APPENDIX G

PRINTED COMPUTER OUTPUT FOR NONLINEAR

LEAST SQUARES OPTIMIZATION PROGRAM

Tables 3, 4 and 5 contain the printed output obtained from a non-linear least squares optimization program for obtaining values of k_L and k_2 at 30°C.

TABLE 3

Experimental Sodium Hydroxide Concentration Input Data
and Initial Conditions for Use in Optimization Program

KINETICS TEST PROBLEM

MODEL 1

RUN	EXP.	TIME	OBSERVATIONS
1		INIT. COND.	0.950400E-04 0.426000E-05
	1	0.0	0.950400E-04
	2	0.250000E+02	0.919000E-04
	3	0.650000E+02	0.915500E-04
	4	0.120000E+03	0.916000E-04
	5	0.210000E+03	0.891000E-04
	6	0.235000E+03	0.899000E-04
	7	0.300000E+03	0.875000E-04
	8	0.330000E+03	0.865000E-04
	9	0.410000E+03	0.880000E-04
	10	0.480000E+03	0.868000E-04
	11	0.570000E+03	0.841000E-04
	12	0.660000E+03	0.835500E-04
	13	0.750000E+03	0.842000E-04
	14	0.960000E+03	0.808000E-04
	15	0.105000E+04	0.795000E-04
	16	0.126000E+04	0.788000E-04
	17	0.135000E+04	0.805000E-04
	18	0.186000E+04	0.746500E-04

PARAMETER	LOWER BOUND	UPPER BOUND	PENALTY COEFFICIENT
1	0.0	0.100000E+03	0.120000E-05
2	0.0	0.100000E+07	0.100001E-01

PARAMETER INITIAL GUESSES
0.110000E-01 0.100000E+03

MAXIMUM OF OBJECTIVE FUNCTION 0.2467105E+03

PARAMETERS
0.8056372E-02 0.2431117E+03

FUNCTION EVALUATIONS 30 DERIVATIVE EVALUATIONS 10

TABLE 4

Difference Between Computer Generated Solution
Values for $C_B(t)$ and Experimental Values of $C_B(t)$

KINETICS TEST PROBLEM	
MODEL	1
RESIDUALS (COMPUTED-OBSERVED)	
1	-0.145519E-10
2	0.101607E-05
3	-0.865373E-06
4	-0.152817E-05
5	-0.610453E-07
6	-0.110644E-05
7	0.673870E-06
8	0.139148E-05
9	-0.858461E-06
10	-0.313230E-06
11	0.154585E-05
12	0.125571E-05
13	-0.233558E-06
14	0.121158E-05
15	0.167525E-05
16	0.427419E-06
17	-0.210584E-05
18	-0.958447E-06

COVARIANCE MATRIX OF RESIDUALS

0.140007E-11

STANDARD DEVIATIONS OF RESIDUALS

0.118325E-05

TABLE 5

Optimized Values of Parameters, k_L and k_2 , Obtained
by Program and Various Statistical Information

LOG PROBABILITY	0.2211696E+03
LOG LIKELIHOOD	0.2211696E+03
LOG PRIOR	0.0
SUM OF SQUARES OF RESIDUALS	0.2240177E-10
PARAMETERS	
0.805637E-02	0.243112E+03
STANDARD DEVIATIONS OF PARAMETERS	
0.690089E-03	0.690254E+02
COVARIANCE MATRIX OF PARAMETERS	
0.476222E-06	-0.528076E-01
-0.528076E-01	0.792552E+04
EIGENVALUES OF CORRELATION MATRIX	
0.185956E+01	0.140438E+00
PRINCIPAL COMPONENTS	
0.102466E+04	-0.794275E-02
0.102466E+04	0.794275E-02
EXPECTED VALUES	
0.632407E+01	0.101860E+02
STANDARD DEVIATIONS	
0.136366E+01	0.374750E+00

APPENDIX H

COMPUTER INPUT STATEMENTS AND CORRESPONDING NUMERICAL OUTPUT USED TO PLOT CURVES IN

FIGURE 7, p. 185

Figures 14, 15 and 16 contain computer input statements, and Tables 6, 7 and 8 are the corresponding pertinent output values which were used to plot the curves in Figure 7, p. 185.

```

$$$CONTINUOUS SYSTEM MODELING PROGRAM III VIN3 TRANSLATOR OUTPUT$$$

TITLE HYDROL
INITIAL
  CAO=4.86E-6
  CBO=9.504E-5
  AI=31.67
  CSTAR=4.86E-6
  V=120.
  KL=.011
PARAM Z=(17.4,100.,110.)
DYNAMIC
  DCADT=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA-Z*CA*CB
  CA=INTGRL(CAO,DCADT)
  DCBDT=-Z*CA*CB
  CB=INTGRL(CBO,DCBDT)
  TRANS=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA
TERMINAL
TIMER DELT=0.5, FINTIM=1860., PRDEL=30.
PRINT CA, CB, DCADT, DCBDT, TRANS
END
STOP

OUTPUT VARIABLE SEQUENCE
CAO CBO AI CSTAR V KL DCADT CA DCBDT CB
TRANS

$$$ TRANSLATION TABLE CONTENTS $$$
CURRENT MAXIMUM
MACRO AND STATEMENT OUTPUTS 17 600
STATEMENT INPUT WORK AREA 50 1900
INTEGRATORS+MEMORY BLOCK OUTPUTS 2 + 0 300
PARAMETERS+FUNCTION GENERATORS 4 + 0 400
STORAGE VARIABLES+INTEGRATOR ARRAYS 0 + 0/2 50
HISTORY AND MEMORY BLOCK NAMES 21 50
MACRO DEFINITIONS AND NESTED MACROS 6 50
MACRO STATEMENT STORAGE 13 125
LITERAL CONSTANT STORAGE 0 100
SORT SECTIONS 2 20
MAXIMUM STATEMENTS IN SECTION 6 600

```

\$\$\$END OF TRANSLATOR OUTPUT\$\$\$

Figure 14. Input Statements for CSMP Simulation No. 32.

TABLE 6

Results for CSMP Simulation
No. 32 ($k_L = 0.011$, $k_2 = 100$)

TIME	CA	CB	DCADT	DCBDT	TRANS
.0	4.8600E-06	9.5040E-05	-4.6189E-08	-4.6189E-08	-7.1054E-15
30.0000	3.7097E-06	9.3836E-05	-3.1471E-08	-3.4811E-08	3.3393E-09
60.0000	2.9241E-06	9.2914E-05	-2.1549E-08	-2.7169E-08	5.6201E-09
90.0000	2.3852E-06	9.2182E-05	-1.4803E-08	-2.1988E-08	7.1844E-09
120.000	2.0147E-06	9.1579E-05	-1.0190E-08	-1.8450E-08	8.2602E-09
150.000	1.7595E-06	9.1064E-05	-7.0213E-09	-1.6022E-08	9.0011E-09
180.000	1.5836E-06	9.0610E-05	-4.8374E-09	-1.4349E-08	9.5116E-09
210.000	1.4625E-06	9.0198E-05	-3.3283E-09	-1.3192E-08	9.8632E-09
240.000	1.3793E-06	8.9815E-05	-2.2833E-09	-1.2388E-08	1.0105E-08
270.000	1.3223E-06	8.9452E-05	-1.5583E-09	-1.1828E-08	1.0270E-08
300.000	1.2836E-06	8.9103E-05	-1.0546E-09	-1.1437E-08	1.0383E-08
330.000	1.2575E-06	8.8764E-05	-7.0410E-10	-1.1162E-08	1.0458E-08
360.000	1.2403E-06	8.8433E-05	-4.5986E-10	-1.0968E-08	1.0508E-08
390.000	1.2292E-06	8.8106E-05	-2.8945E-10	-1.0830E-08	1.0541E-08
420.000	1.2224E-06	8.7782E-05	-1.7037E-10	-1.0731E-08	1.0560E-08
450.000	1.2186E-06	8.7462E-05	-8.7027E-11	-1.0658E-08	1.0571E-08
480.000	1.2169E-06	8.7143E-05	-2.8606E-11	-1.0605E-08	1.0576E-08
510.000	1.2167E-06	8.6825E-05	1.2434E-11	-1.0564E-08	1.0577E-08
540.000	1.2176E-06	8.6509E-05	4.1336E-11	-1.0533E-08	1.0574E-08
570.000	1.2191E-06	8.6193E-05	6.1757E-11	-1.0508E-08	1.0570E-08
600.000	1.2212E-06	8.5878E-05	7.6231E-11	-1.0487E-08	1.0564E-08
630.000	1.2237E-06	8.5564E-05	8.6551E-11	-1.0470E-08	1.0557E-08
660.000	1.2264E-06	8.5250E-05	9.3959E-11	-1.0455E-08	1.0549E-08
690.000	1.2293E-06	8.4936E-05	9.9309E-11	-1.0441E-08	1.0540E-08
720.000	1.2323E-06	8.4623E-05	1.0324E-10	-1.0428E-08	1.0531E-08
750.000	1.2355E-06	8.4311E-05	1.0617E-10	-1.0416E-08	1.0522E-08
780.000	1.2387E-06	8.3998E-05	1.0837E-10	-1.0405E-08	1.0513E-08
810.000	1.2419E-06	8.3686E-05	1.1008E-10	-1.0393E-08	1.0503E-08
840.000	1.2453E-06	8.3375E-05	1.1143E-10	-1.0382E-08	1.0494E-08
870.000	1.2486E-06	8.3063E-05	1.1255E-10	-1.0372E-08	1.0484E-08
900.000	1.2520E-06	8.2752E-05	1.1349E-10	-1.0361E-08	1.0474E-08
930.000	1.2554E-06	8.2442E-05	1.1430E-10	-1.0350E-08	1.0464E-08
960.000	1.2589E-06	8.2131E-05	1.1503E-10	-1.0339E-08	1.0454E-08
990.000	1.2623E-06	8.1821E-05	1.1570E-10	-1.0329E-08	1.0444E-08
1020.00	1.2658E-06	8.1512E-05	1.1633E-10	-1.0318E-08	1.0434E-08
1050.00	1.2693E-06	8.1202E-05	1.1693E-10	-1.0307E-08	1.0424E-08
1080.00	1.2728E-06	8.0893E-05	1.1752E-10	-1.0296E-08	1.0414E-08
1110.00	1.2764E-06	8.0585E-05	1.1809E-10	-1.0286E-08	1.0404E-08
1140.00	1.2799E-06	8.0276E-05	1.1865E-10	-1.0275E-08	1.0393E-08
1170.00	1.2835E-06	7.9968E-05	1.1920E-10	-1.0264E-08	1.0383E-08
1200.00	1.2871E-06	7.9660E-05	1.1975E-10	-1.0253E-08	1.0373E-08
1230.00	1.2907E-06	7.9353E-05	1.2031E-10	-1.0242E-08	1.0362E-08
1260.00	1.2943E-06	7.9046E-05	1.2085E-10	-1.0231E-08	1.0352E-08
1290.00	1.2979E-06	7.8739E-05	1.2140E-10	-1.0220E-08	1.0341E-08
1320.00	1.3016E-06	7.8433E-05	1.2195E-10	-1.0208E-08	1.0330E-08
1350.00	1.3052E-06	7.8126E-05	1.2250E-10	-1.0197E-08	1.0320E-08
1380.00	1.3089E-06	7.7821E-05	1.2307E-10	-1.0186E-08	1.0309E-08
1410.00	1.3126E-06	7.7515E-05	1.2362E-10	-1.0175E-08	1.0298E-08
1440.00	1.3163E-06	7.7210E-05	1.2419E-10	-1.0163E-08	1.0288E-08
1470.00	1.3201E-06	7.6905E-05	1.2475E-10	-1.0152E-08	1.0277E-08
1500.00	1.3238E-06	7.6601E-05	1.2532E-10	-1.0141E-08	1.0266E-08
1530.00	1.3276E-06	7.6297E-05	1.2589E-10	-1.0129E-08	1.0255E-08
1560.00	1.3314E-06	7.5993E-05	1.2647E-10	-1.0117E-08	1.0244E-08
1590.00	1.3352E-06	7.5690E-05	1.2704E-10	-1.0106E-08	1.0233E-08
1620.00	1.3390E-06	7.5387E-05	1.2762E-10	-1.0094E-08	1.0222E-08

```

$$$CONTINUOUS SYSTEM MODELING PROGRAM III   VIM3   TRANSLATOR OUTPUT$$$

TITLE HYDROL
INITIAL
    CAO=9.38E-6
    CBO=9.504E-5
    AI=31.67
    V=120.
    CSTAR=9.38E-6
    KL=.10
PARAM Z=(450.,400.,350.,300.,250.)
METHOD TRAPZ
DYNAMIC
    DCADT=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA-Z*CA*CB
    CA=INTGRL(CAO,DCADT)
    DCBDT=-Z*CA*CB
    CB=INTGRL(CBO,DCBDT)
    TRANS=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA
TERMINAL
TIMER DELT=0.5, FINTIM=1260., PRDEL=30.
PRINT CA, CB, DCADT, DCBDT, TRANS
END
STOP

OUTPUT VARIABLE SEQUENCE
CAO  CBO  AI  V  CSTAR  KL  DCADT  CA  DCBDT  CB
TRANS

$$$ TRANSLATION TABLE CONTENTS $$$

MACRO AND STATEMENT OUTPUTS          17          600
STATEMENT INPUT WORK AREA            50          1900
INTEGRATORS+MEMORY BLOCK OUTPUTS      2 + 0          300
PARAMETERS+FUNCTION GENERATORS        4 + 0          400
STORAGE VARIABLES+INTEGRATOR ARRAYS    0 + 0/2          50
HISTORY AND MEMORY BLOCK NAMES        21           50
MACRO DEFINITIONS AND NESTED MACROS     6           50
MACRO STATEMENT STORAGE               13          125
LITERAL CONSTANT STORAGE               0           100
SORT SECTIONS                         2            20
MAXIMUM STATEMENTS IN SECTION          6           600

$$$END OF TRANSLATOR OUTPUT$$$

```

Figure 15. Input Statements for CSMP Simulation No. 46.

TABLE 7

Results for CSMP Simulation
No. 46 ($k_L = 0.10$, $k_2 = 350$)

TIME	CA	CB	DCADT	DCBDT	TRANS
.0	9.3800E-06	9.5040E-05	-3.1202E-07	-3.1202E-07	5.6843E-14
30.0000	5.1479E-06	8.8639E-05	-4.8015E-08	-1.5971E-07	1.1169E-07
60.0000	4.5255E-06	8.4339E-05	-5.4662E-09	-1.3359E-07	1.2812E-07
90.0000	4.5027E-06	8.0449E-05	1.9367E-09	-1.2678E-07	1.2872E-07
120.000	4.5872E-06	7.6702E-05	3.3430E-09	-1.2315E-07	1.2649E-07
150.000	4.6935E-06	7.3055E-05	3.6774E-09	-1.2001E-07	1.2369E-07
180.000	4.8060E-06	6.9501E-05	3.8108E-09	-1.1691E-07	1.2072E-07
210.000	4.9217E-06	6.6040E-05	3.9028E-09	-1.1376E-07	1.1766E-07
240.000	5.0400E-06	6.2675E-05	3.9834E-09	-1.1056E-07	1.1454E-07
270.000	5.1606E-06	5.9406E-05	4.0581E-09	-1.0730E-07	1.1136E-07
300.000	5.2833E-06	5.6237E-05	4.1271E-09	-1.0399E-07	1.0812E-07
330.000	5.4081E-06	5.3167E-05	4.1901E-09	-1.0064E-07	1.0483E-07
360.000	5.5346E-06	5.0198E-05	4.2464E-09	-9.7240E-08	1.0149E-07
390.000	5.6627E-06	4.7332E-05	4.2950E-09	-9.3810E-08	9.8105E-08
420.000	5.7922E-06	4.4569E-05	4.3353E-09	-9.0353E-08	9.4688E-08
450.000	5.9227E-06	4.1910E-05	4.3661E-09	-8.6878E-08	9.1244E-08
480.000	6.0540E-06	3.9356E-05	4.3877E-09	-8.3391E-08	8.7778E-08
510.000	6.1858E-06	3.6906E-05	4.3984E-09	-7.9902E-08	8.4300E-08
540.000	6.3177E-06	3.4560E-05	4.3976E-09	-7.6420E-08	8.0818E-08
570.000	6.4495E-06	3.2319E-05	4.3855E-09	-7.2955E-08	7.7341E-08
600.000	6.5807E-06	3.0182E-05	4.3615E-09	-6.9517E-08	7.3878E-08
630.000	6.7110E-06	2.8147E-05	4.3252E-09	-6.6114E-08	7.0439E-08
660.000	6.8400E-06	2.6214E-05	4.2769E-09	-6.2757E-08	6.7034E-08
690.000	6.9674E-06	2.4381E-05	4.2166E-09	-5.9455E-08	6.3671E-08
720.000	7.0929E-06	2.2645E-05	4.1443E-09	-5.6217E-08	6.0361E-08
750.000	7.2159E-06	2.1006E-05	4.0607E-09	-5.3053E-08	5.7113E-08
780.000	7.3363E-06	1.9461E-05	3.9662E-09	-4.9969E-08	5.3936E-08
810.000	7.4538E-06	1.8006E-05	3.8616E-09	-4.6975E-08	5.0837E-08
840.000	7.5679E-06	1.6640E-05	3.7479E-09	-4.4077E-08	4.7824E-08
870.000	7.6785E-06	1.5360E-05	3.6260E-09	-4.1280E-08	4.4906E-08
900.000	7.7853E-06	1.4162E-05	3.4963E-09	-3.8590E-08	4.2086E-08
930.000	7.8882E-06	1.3043E-05	3.3611E-09	-3.6011E-08	3.9372E-08
960.000	7.9869E-06	1.2000E-05	3.2210E-09	-3.3546E-08	3.6767E-08
990.000	8.0813E-06	1.1029E-05	3.0775E-09	-3.1196E-08	3.4274E-08
1020.00	8.1714E-06	1.0127E-05	2.9315E-09	-2.8964E-08	3.1896E-08
1050.00	8.2572E-06	9.2904E-06	2.7844E-09	-2.6849E-08	2.9634E-08
1080.00	8.3385E-06	8.5151E-06	2.6371E-09	-2.4851E-08	2.7488E-08
1110.00	8.4153E-06	7.7981E-06	2.4907E-09	-2.2968E-08	2.5459E-08
1140.00	8.4879E-06	7.1359E-06	2.3462E-09	-2.1199E-08	2.3545E-08
1170.00	8.5561E-06	6.5250E-06	2.2045E-09	-1.9540E-08	2.1744E-08
1200.00	8.6201E-06	5.9623E-06	2.0662E-09	-1.7989E-08	2.0055E-08
1230.00	8.6800E-06	5.4446E-06	1.9321E-09	-1.6541E-08	1.8473E-08
1260.00	8.7360E-06	4.9688E-06	1.8027E-09	-1.5193E-08	1.6996E-08

```

$$$CONTINUOUS SYSTEM MODELING PROGRAM   III   VIM3   TRANSLATOR OUTPUT$$$

TITLE HYDROL
INITIAL
    CAO=1.32E-5
    CBO=9.504E-5
    AI=31.67
    V=120.
    CSTAR=1.32E-5
PARAM Z=(2700.,2500.,1500.,1000.,500.)
    KL=.3
METHOD TRAPZ
DYNAMIC
    DCADT=(KL*AI*CSTAR/V)-(KL*AI/V)*CA-Z*CA*CB
    CA=INTGRL(CAO,DCADT)
    DCBDT=-Z*CA*CB
    CB=INTGRL(CBO,DCBDT)
    TRANS=(KL*AI*CSTAR/V)-(KL*AI/V)*CA
TERMINAL
    TIMER DELT=0.5, FINTIM=1260., PRDEL=30.
    PRINT CA, CB, DCADT, DCBDT, TRANS
END
STOP

OUTPUT VARIABLE SEQUENCE
CAO    CBO    AI    V    CSTAR  KL    DCADT  CA    DCBDT  CB
TRANS

$$$ TRANSLATION TABLE CONTENTS $$$          CURRENT          MAXIMUM

MACRO AND STATEMENT OUTPUTS                17                600
STATEMENT INPUT WORK AREA                   50                1900
INTEGRATORS+MEMORY BLOCK OUTPUTS            2 + 0                300
PARAMETERS+FUNCTION GENERATORS              4 + 0                400
STORAGE VARIABLES+INTEGRATOR ARRAYS         0 + 0/2              50
HISTORY AND MEMORY BLOCK NAMES              21                 50
MACRO DEFINITIONS AND NESTED MACROS          6                 50
MACRO STATEMENT STORAGE                     13                125
LITERAL CONSTANT STORAGE                    0                 100
SORT SECTIONS                               2                 20
MAXIMUM STATEMENTS IN SECTION               6                 600

$$$END OF TRANSLATOR OUTPUT$$$

```

Figure 16. Input Statements for CSMP Simulation No. 44.

TABLE 8

Results for CSMP Simulation No. 44
 $(k_L = 0.3, k_2 = 1000)$

TIME	CA	CB	DCADT	DCBDT	TRANS
.0	1.3200E-05	9.5040E-05	-1.2545E-06	-1.2545E-06	9.0949E-13
30.0000	6.6737E-06	7.5443E-05	1.3237E-08	-5.0348E-07	5.1672E-07
60.0000	7.2827E-06	6.1227E-05	2.2674E-08	-4.4587E-07	4.6854E-07
90.0000	7.9849E-06	4.8709E-05	2.4032E-08	-3.8887E-07	4.1290E-07
120.000	8.7162E-06	3.7909E-05	2.4574E-08	-3.3043E-07	3.5500E-07
150.000	9.4497E-06	2.8866E-05	2.4151E-08	-2.7278E-07	2.9693E-07
180.000	1.0155E-05	2.1509E-05	2.2683E-08	-2.1842E-07	2.4110E-07
210.000	1.0801E-05	1.5704E-05	2.0286E-08	-1.6963E-07	1.8991E-07
240.000	1.1366E-05	1.1259E-05	1.7264E-08	-1.2797E-07	1.4523E-07
270.000	1.1835E-05	7.9482E-06	1.4015E-08	-9.4066E-08	1.0808E-07
300.000	1.2208E-05	5.5404E-06	1.0907E-08	-6.7637E-08	7.8544E-08
330.000	1.2493E-05	3.8242E-06	8.1868E-09	-4.7776E-08	5.5963E-08
360.000	1.2704E-05	2.6201E-06	5.9693E-09	-3.3286E-08	3.9256E-08
390.000	1.2856E-05	1.7854E-06	4.2550E-09	-2.2954E-08	2.7209E-08
420.000	1.2964E-05	1.2120E-06	2.9827E-09	-1.5712E-08	1.8695E-08
450.000	1.3039E-05	8.2048E-07	2.0658E-09	-1.0698E-08	1.2764E-08
480.000	1.3090E-05	5.5441E-07	1.4173E-09	-7.2574E-09	8.6748E-09
510.000	1.3126E-05	3.7414E-07	9.6722E-10	-4.9108E-09	5.8781E-09
540.000	1.3150E-05	2.5226E-07	6.5730E-10	-3.3172E-09	3.9745E-09
570.000	1.3166E-05	1.6998E-07	4.4498E-10	-2.2380E-09	2.6830E-09
600.000	1.3177E-05	1.1450E-07	3.0117E-10	-1.5087E-09	1.8099E-09
630.000	1.3185E-05	7.7099E-08	2.0402E-10	-1.0165E-09	1.2205E-09
660.000	1.3190E-05	5.1907E-08	1.3754E-10	-6.8464E-10	8.2218E-10
690.000	1.3193E-05	3.4943E-08	9.2878E-11	-4.6100E-10	5.5388E-10
720.000	1.3195E-05	2.3521E-08	6.3436E-11	-3.1037E-10	3.7380E-10
750.000	1.3197E-05	1.5832E-08	4.3003E-11	-2.0893E-10	2.5193E-10
780.000	1.3198E-05	1.0656E-08	2.9445E-11	-1.4063E-10	1.7008E-10
810.000	1.3199E-05	7.1716E-09	1.9942E-11	-9.4655E-11	1.1460E-10
840.000	1.3199E-05	4.8266E-09	1.3600E-11	-6.3707E-11	7.7307E-11
870.000	1.3199E-05	3.2484E-09	9.8741E-12	-4.2877E-11	5.2751E-11
900.000	1.3200E-05	2.1862E-09	6.6131E-12	-2.8857E-11	3.5470E-11
930.000	1.3200E-05	1.4714E-09	5.1349E-12	-1.9421E-11	2.4556E-11
960.000	1.3200E-05	9.9024E-10	3.3000E-12	-1.3071E-11	1.6371E-11
990.000	1.3200E-05	6.6644E-10	3.0265E-12	-8.7969E-12	1.1823E-11
1020.00	1.3200E-05	4.4852E-10	2.2651E-12	-5.9204E-12	8.1855E-12
1050.00	1.3200E-05	3.0185E-10	1.4726E-12	-3.9844E-12	5.4570E-12
1080.00	1.3200E-05	2.0315E-10	1.8660E-12	-2.6815E-12	4.5475E-12
1110.00	1.3200E-05	1.3672E-10	1.8333E-12	-1.8047E-12	3.6380E-12
1140.00	1.3200E-05	9.2013E-11	1.5139E-12	-1.2146E-12	2.7285E-12
1170.00	1.3200E-05	6.1925E-11	1.9111E-12	-8.1741E-13	2.7285E-12
1200.00	1.3200E-05	4.1676E-11	2.1784E-12	-5.5012E-13	2.7285E-12
1230.00	1.3200E-05	2.8048E-11	1.4488E-12	-3.7073E-13	1.8190E-12
1260.00	1.3200E-05	1.8876E-11	1.5698E-12	-2.4917E-13	1.8190E-12

APPENDIX I

EXPERIMENTAL SODIUM HYDROXIDE CONCENTRATION VERSUS

TIME DATA FOR FIGURES 7 AND 8, PP. 185 AND 187

Tables 9 through 14 contain the original sodium hydroxide concentration versus time data that have been plotted in Figures 7 and 8, pp. 185 and 187. The data were obtained from experiments with the stirred cell at an agitation rate of 200 RPM and at the temperatures indicated in the tables.

TABLE 9

Sodium Hydroxide Concentration as a Function
of Time at 30°C (Extraction Run No. 21)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.504
85	9.15
210	8.91
330	8.65
570	8.41
750	8.42
1050	7.95
1350	8.05

TABLE 10

Sodium Hydroxide Concentration as a Function
of Time at 30°C (Extraction Run No. 22)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.504
120	9.16
300	8.75
480	8.68
660	8.10
960	8.08
1260	7.78
1860	7.29

TABLE 11

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Sodium Hydroxide Concentration as a Function
of Time at 30°C (Extraction Run No. 26)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.504
25	9.19
85	9.16
235	8.99
410	8.80
660	8.61
1260	7.98
1860	7.64

TABLE 12

Sodium Hydroxide Concentration as a Function
of Time at 61°C (Extraction Run No. 24)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.504
50	8.14
105	7.45
170	6.75
250	5.79
415	4.26
755	2.27
1235	1.04

TABLE 13

Sodium Hydroxide Concentration as a Function
of Time at 80°C (Extraction Run No. 23)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.504
60	4.67
160	1.84
290	0.670
373	0.290
520	0.290
920	0.270

TABLE 14

Sodium Hydroxide Concentration as a Function
of Time at 80°C (Extraction Run No. 25)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.504
40	6.28
95	3.80
160	1.97
220	1.33
295	0.800
345	0.440
600	0.290

APPENDIX J

EXPERIMENTAL SODIUM HYDROXIDE CONCENTRATION

VERSUS TIME DATA FOR FIGURE 12, p. 193

Tables 15 through 17 contain the original sodium hydroxide concentration versus time data that have been plotted in Figure 12, p. 193. The data were obtained from experiments with the stirred cell at a temperature of 85°C and at the agitation rates indicated in the tables.

TABLE 15

Sodium Hydroxide Concentration as a Function
of Time at 40 RPM, (Extraction Run No. 19)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.820
65	5.71
250	3.44
460	2.34
740	1.54
965	1.23
1175	1.06

TABLE 16

Sodium Hydroxide Concentration as a Function
of Time at 80 RPM (Extraction Run No. 15)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.820
135	4.22
340	1.97
540	1.13
760	0.517
1030	0.411
1240	0.469

TABLE 17

Sodium Hydroxide Concentration as a Function
of Time at 200 RPM (Extraction Run No. 16)

TIME, sec	Sodium Hydroxide Concentration $\times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.820
105	3.07
250	1.05
510	0.426
780	0.830
1146	0.349
1350	0.565

APPENDIX K

CSMP INPUT STATEMENTS AND PRINTED OUTPUT FOR COMPUTER SIMULATIONS USING k_L AND k_2 VALUES GENERATED BY THE OPTIMIZATION PROGRAM

The values of k_L and k_2 that were selected by the nonlinear least squares optimization program were used in this CSMP program. The CSMP input statements are shown in Figure 17, and the corresponding output is given in Table 18.

```

$$$CONTINUOUS SYSTEM MODELING PROGRAM III  VIM3  TRANSLATOR OUTPUT$$$

TITLE HYDROL
INITIAL
  CAO=.00000486
  CBO=.00009504
  AI=31.67
  CSTAR=.00000486
  V=120.
  KL=.00805637
  Z=243.112
DYNAMIC
  DCADT=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA-Z*CA*CB
  CA=INTGRL(CAO,DCADT)
  DCBDT=-Z*CA*CB
  CB=INTGRL(CBO,DCBDT)
  TRANS=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA
TERMINAL
  TIMER DELT=0.5, FINTIM=1860., PRDEL=30.
  PRINT CA, CB, DCADT, DCBDT, TRANS
END
STOP

OUTPUT VARIABLE SEQUENCE
CAO  CBO  AI  CSTAR  V  KL  Z  DCADT  CA  DCBDT
CB  TRANS

$$$ TRANSLATION TABLE CONTENTS $$$

MACRO AND STATEMENT OUTPUTS          18          600
STATEMENT INPUT WORK AREA             50          1900
INTEGRATORS+MEMORY BLOCK OUTPUTS      2 + 0          300
PARAMETERS+FUNCTION GENERATORS        3 + 0          400
STORAGE VARIABLES+INTEGRATOR ARRAYS    0 + 0/2          50
HISTORY AND MEMORY BLOCK NAMES         21          50
MACRO DEFINITIONS AND NESTED MACROS     6          50
MACRO STATEMENT STORAGE                13          125
LITERAL CONSTANT STORAGE               0          100
SORT SECTIONS                          2          20
MAXIMUM STATEMENTS IN SECTION          7          600

$$$END OF TRANSLATOR OUTPUT$$$

```

Figure 17. Input Statements for CSMP Simulation No. 48.

TABLE 18

Results for CSMP Simulation No. 48
 $(k_L = 0.00806, k_2 = 243.1)$

TIME	CA	CB	DCADT	DCBDT	TRANS
.0	4.8600E-06	9.5040E-05	-1.1229E-07	-1.1229E-07	-3.5527E-15
30.0000	2.5210E-06	9.2617E-05	-5.1791E-08	-5.6764E-08	4.9731E-09
60.0000	1.4298E-06	9.1337E-05	-2.4456E-08	-3.1749E-08	7.2933E-09
90.0000	9.1160E-07	9.0582E-05	-1.1680E-08	-2.0075E-08	8.3951E-09
120.0000	6.6347E-07	9.0073E-05	-5.6058E-09	-1.4528E-08	8.9227E-09
150.0000	5.4431E-07	8.9682E-05	-2.6914E-09	-1.1867E-08	9.1761E-09
180.0000	4.8720E-07	8.9347E-05	-1.2853E-09	-1.0583E-08	9.2975E-09
210.0000	4.6009E-07	8.9040E-05	-6.0426E-10	-9.9594E-09	9.3551E-09
240.0000	4.4752E-07	8.8747E-05	-2.7343E-10	-9.6553E-09	9.3819E-09
270.0000	4.4202E-07	8.8459E-05	-1.1227E-10	-9.5058E-09	9.3935E-09
300.0000	4.3997E-07	8.8175E-05	-3.3527E-11	-9.4314E-09	9.3979E-09
330.0000	4.3961E-07	8.7893E-05	5.0910E-12	-9.3936E-09	9.3987E-09
360.0000	4.4008E-07	8.7612E-05	2.4126E-11	-9.3735E-09	9.3977E-09
390.0000	4.4097E-07	8.7331E-05	3.3591E-11	-9.3622E-09	9.3958E-09
420.0000	4.4205E-07	8.7050E-05	3.8369E-11	-9.3551E-09	9.3935E-09
450.0000	4.4325E-07	8.6769E-05	4.0838E-11	-9.3501E-09	9.3909E-09
480.0000	4.4449E-07	8.6489E-05	4.2185E-11	-9.3461E-09	9.3883E-09
510.0000	4.4577E-07	8.6208E-05	4.2970E-11	-9.3426E-09	9.3856E-09
540.0000	4.4707E-07	8.5928E-05	4.3485E-11	-9.3393E-09	9.3828E-09
570.0000	4.4838E-07	8.5648E-05	4.3862E-11	-9.3362E-09	9.3800E-09
600.0000	4.4970E-07	8.5368E-05	4.4174E-11	-9.3330E-09	9.3772E-09
630.0000	4.5103E-07	8.5088E-05	4.4452E-11	-9.3299E-09	9.3744E-09
660.0000	4.5237E-07	8.4808E-05	4.4718E-11	-9.3268E-09	9.3715E-09
690.0000	4.5371E-07	8.4528E-05	4.4977E-11	-9.3237E-09	9.3687E-09
720.0000	4.5506E-07	8.4249E-05	4.5233E-11	-9.3206E-09	9.3658E-09
750.0000	4.5643E-07	8.3969E-05	4.5496E-11	-9.3174E-09	9.3629E-09
780.0000	4.5779E-07	8.3690E-05	4.5748E-11	-9.3143E-09	9.3600E-09
810.0000	4.5917E-07	8.3410E-05	4.6011E-11	-9.3111E-09	9.3571E-09
840.0000	4.6055E-07	8.3131E-05	4.6271E-11	-9.3079E-09	9.3541E-09
870.0000	4.6195E-07	8.2852E-05	4.6530E-11	-9.3046E-09	9.3512E-09
900.0000	4.6335E-07	8.2573E-05	4.6796E-11	-9.3014E-09	9.3482E-09
930.0000	4.6475E-07	8.2294E-05	4.7066E-11	-9.2981E-09	9.3452E-09
960.0000	4.6617E-07	8.2015E-05	4.7333E-11	-9.2949E-09	9.3422E-09
990.0000	4.6759E-07	8.1736E-05	4.7606E-11	-9.2916E-09	9.3392E-09
1020.00	4.6903E-07	8.1457E-05	4.7880E-11	-9.2882E-09	9.3361E-09
1050.00	4.7047E-07	8.1179E-05	4.8157E-11	-9.2849E-09	9.3331E-09
1080.00	4.7192E-07	8.0900E-05	4.8438E-11	-9.2815E-09	9.3300E-09
1110.00	4.7337E-07	8.0622E-05	4.8718E-11	-9.2782E-09	9.3269E-09
1140.00	4.7484E-07	8.0343E-05	4.8999E-11	-9.2748E-09	9.3238E-09
1170.00	4.7631E-07	8.0065E-05	4.9283E-11	-9.2713E-09	9.3206E-09
1200.00	4.7780E-07	7.9787E-05	4.9575E-11	-9.2679E-09	9.3175E-09
1230.00	4.7929E-07	7.9509E-05	4.9862E-11	-9.2644E-09	9.3143E-09
1260.00	4.8079E-07	7.9231E-05	5.0154E-11	-9.2610E-09	9.3111E-09
1290.00	4.8230E-07	7.8953E-05	5.0452E-11	-9.2575E-09	9.3079E-09
1320.00	4.8381E-07	7.8676E-05	5.0751E-11	-9.2539E-09	9.3047E-09
1350.00	4.8534E-07	7.8398E-05	5.1049E-11	-9.2504E-09	9.3014E-09
1380.00	4.8688E-07	7.8121E-05	5.1354E-11	-9.2468E-09	9.2982E-09
1410.00	4.8842E-07	7.7843E-05	5.1656E-11	-9.2432E-09	9.2949E-09
1440.00	4.8998E-07	7.7566E-05	5.1966E-11	-9.2396E-09	9.2916E-09
1470.00	4.9154E-07	7.7289E-05	5.2275E-11	-9.2360E-09	9.2883E-09
1500.00	4.9311E-07	7.7012E-05	5.2587E-11	-9.2323E-09	9.2849E-09
1530.00	4.9470E-07	7.6735E-05	5.2903E-11	-9.2286E-09	9.2815E-09
1560.00	4.9629E-07	7.6458E-05	5.3220E-11	-9.2249E-09	9.2782E-09
1590.00	4.9789E-07	7.6181E-05	5.3543E-11	-9.2212E-09	9.2748E-09
1620.00	4.9950E-07	7.5905E-05	5.3866E-11	-9.2175E-09	9.2713E-09
1650.00	5.0112E-07	7.5628E-05	5.4193E-11	-9.2137E-09	9.2679E-09
1680.00	5.0275E-07	7.5352E-05	5.4523E-11	-9.2099E-09	9.2644E-09
1710.00	5.0439E-07	7.5076E-05	5.4857E-11	-9.2061E-09	9.2609E-09
1740.00	5.0604E-07	7.4800E-05	5.5191E-11	-9.2022E-09	9.2574E-09
1770.00	5.0770E-07	7.4524E-05	5.5529E-11	-9.1984E-09	9.2539E-09
1800.00	5.0937E-07	7.4248E-05	5.5870E-11	-9.1945E-09	9.2503E-09
1830.00	5.1106E-07	7.3972E-05	5.6215E-11	-9.1905E-09	9.2468E-09
1860.00	5.1275E-07	7.3696E-05	5.6559E-11	-9.1866E-09	9.2432E-09

APPENDIX L

COMPUTER INPUT STATEMENTS AND CORRESPONDING NUMERICAL OUTPUT USED TO PLOT MIDDLE AND LOWER CURVES IN FIGURE 8, P. 187

Figures 18 and 19 are the computer input statements, and Tables 19 and 20 are the corresponding pertinent output values.

The computer input statements and the corresponding pertinent output used to plot the middle and lower curves in Figure 8, p. 187 are given in this appendix.

```

$$$CONTINUOUS SYSTEM MODELING PROGRAM III  VIM3  TRANSLATOR OUTPUT$$$

TITLE HYDRQL
INITIAL
    CAO=.00000938
    CBO=.00009504
    AI=31.67
    CSTAR=.00000938
    V=120.
    KL=.15
PARAM Z=(200.,300.,350.,400.,780.)
METHOD TRAPZ
DYNAMIC
    DCADT=(KL*AI*CLSTAR/V)-(KL*AI/V)*CA-Z*CA*CB
    CA=INTGRL(CAO,DCADT)
    DCBDT=-Z*CA*CB
    CB=INTGRL(CBO,DCBDT)
    TRANS=(KL*AI*CLSTAR/V)-(KL*AI/V)*CA
TERMINAL
TIMER DELT=0.5, FINTIM=1260., PRDEL=30.
PRINT CA, CB, DCADT, DCBDT, TRANS
END
STOP

OUTPUT VARIABLE SEQUENCE
CAO  CBO  AI  CSTAR  V  KL  DCADT  CA  DCBDT  CB
TRANS

$$$ TRANSLATION TABLE CONTENTS $$$          CURRENT          MAXIMUM

MACRO AND STATEMENT OUTPUTS                  17                      600
STATEMENT INPUT WORK AREA                     50                      1900
INTEGRATORS+MEMORY BLOCK OUTPUTS              2 + 0                      300
PARAMETERS+FUNCTION GENERATORS                4 + 0                      400
STORAGE VARIABLES+INTEGRATOR ARRAYS           0 + 0/2                     50
HISTORY AND MEMORY BLOCK NAMES                21                      50
MACRO DEFINITIONS AND NESTED MACROS            6                      50
MACRO STATEMENT STORAGE                      13                      125
LITERAL CONSTANT STORAGE                     0                      100
SORT SECTIONS                                2                      20
MAXIMUM STATEMENTS IN SECTION                 6                      600

$$$END OF TRANSLATOR OUTPUT$$$

```

Figure 18. Input Statements to Obtain Middle Curve in Figure 8, p. 187 (CSMP Simulation No. 51).

TABLE 19

Results for CSMP Simulation No. 51
 $(k_L = 0.15, k_2 = 300)$

TIME	CA	CB	DCADT	DCBDT	TRANS
0.0	9.3800E-06	9.5040E-05	-2.6744E-07	-2.6744E-07	-5.6843E-14
30.0000	6.0644E-06	8.9100E-05	-3.0845E-08	-1.6210E-07	1.3126E-07
60.0000	5.7308E-06	8.4547E-05	-8.9653E-10	-1.4536E-07	1.4446E-07
90.0000	5.7828E-06	8.0284E-05	3.1206E-09	-1.3528E-07	1.4240E-07
120.000	5.8677E-06	7.6178E-05	3.6995E-09	-1.3455E-07	1.3825E-07
150.000	6.0005E-06	7.2209E-05	3.7985E-09	-1.2999E-07	1.3379E-07
180.000	6.1149E-06	6.8377E-05	3.8228E-09	-1.2544E-07	1.2926E-07
210.000	6.2297E-06	6.4682E-05	3.8297E-09	-1.2088E-07	1.2471E-07
240.000	6.3445E-06	6.1123E-05	3.8277E-09	-1.1634E-07	1.2017E-07
270.000	6.4592E-06	5.7701E-05	3.8175E-09	-1.1181E-07	1.1563E-07
300.000	6.5734E-06	5.4414E-05	3.7993E-09	-1.0731E-07	1.1111E-07
330.000	6.6870E-06	5.1261E-05	3.7730E-09	-1.0284E-07	1.0661E-07
360.000	6.7997E-06	4.8243E-05	3.7386E-09	-9.8410E-08	1.0215E-07
390.000	6.9112E-06	4.5356E-05	3.6961E-09	-9.4038E-08	9.7734E-08
420.000	7.0213E-06	4.2599E-05	3.6453E-09	-8.9730E-08	9.3375E-08
450.000	7.1298E-06	3.9970E-05	3.5870E-09	-8.5494E-08	8.9081E-08
480.000	7.2364E-06	3.7468E-05	3.5211E-09	-8.1339E-08	8.4860E-08
510.000	7.3409E-06	3.5088E-05	3.4481E-09	-7.7274E-08	8.0722E-08
540.000	7.4432E-06	3.2829E-05	3.3684E-09	-7.3306E-08	7.6675E-08
570.000	7.5429E-06	3.0688E-05	3.2827E-09	-6.9443E-08	7.2726E-08
600.000	7.6400E-06	2.8661E-05	3.1912E-09	-6.5691E-08	6.8882E-08
630.000	7.7343E-06	2.6745E-05	3.0948E-09	-6.2055E-08	6.5150E-08
660.000	7.8256E-06	2.4936E-05	2.9943E-09	-5.8541E-08	6.1535E-08
690.000	7.9138E-06	2.3230E-05	2.8898E-09	-5.5152E-08	5.8042E-08
720.000	7.9989E-06	2.1624E-05	2.7823E-09	-5.1892E-08	5.4674E-08
750.000	8.0807E-06	2.0115E-05	2.6730E-09	-4.8762E-08	5.1435E-08
780.000	8.1592E-06	1.8697E-05	2.5625E-09	-4.5765E-08	4.8327E-08
810.000	8.2344E-06	1.7367E-05	2.4508E-09	-4.2901E-08	4.5352E-08
840.000	8.3062E-06	1.6120E-05	2.3389E-09	-4.0170E-08	4.2509E-08
870.000	8.3747E-06	1.4954E-05	2.2272E-09	-3.7571E-08	3.9799E-08
900.000	8.4398E-06	1.3865E-05	2.1164E-09	-3.5104E-08	3.7221E-08
930.000	8.5016E-06	1.2847E-05	2.0073E-09	-3.2766E-08	3.4773E-08
960.000	8.5602E-06	1.1897E-05	1.9004E-09	-3.0553E-08	3.2453E-08
990.000	8.6156E-06	1.1012E-05	1.7962E-09	-2.8463E-08	3.0260E-08
1020.00	8.6680E-06	1.0188E-05	1.6947E-09	-2.6493E-08	2.8188E-08
1050.00	8.7173E-06	9.4215E-06	1.5962E-09	-2.4639E-08	2.6235E-08
1080.00	8.7637E-06	8.7087E-06	1.5011E-09	-2.2896E-08	2.4397E-08
1110.00	8.8073E-06	8.0466E-06	1.4096E-09	-2.1261E-08	2.2670E-08
1140.00	8.8483E-06	7.4320E-06	1.3218E-09	-1.9728E-08	2.1050E-08
1170.00	8.8866E-06	6.8619E-06	1.2378E-09	-1.8294E-08	1.9532E-08
1200.00	8.9225E-06	6.3334E-06	1.1576E-09	-1.6953E-08	1.8111E-08
1230.00	8.9561E-06	5.8438E-06	1.0813E-09	-1.5701E-08	1.6783E-08
1260.00	8.9874E-06	5.3904E-06	1.0090E-09	-1.4534E-08	1.5543E-08

\$\$\$CONTINUOUS SYSTEM MODELING PROGRAM III VIM3 TRANSLATOR OUTPUT\$\$\$

TITLE HYDROL

INITIAL

CA0=1.32E-5

CB0=9.504E-5

AI=31.67

V=120.

CSTAR=1.32E-5

PARAM Z=(2700.,2500.,1500.,1000.,500.)

KL=.3

METHOD TRAPZ

DYNAMIC

DCADT=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA-Z*CA*CB

CA=INTGRL(CA0,DCADT)

DCBDT=-Z*CA*CB

CB=INTGRL(CB0,DCBDT)

TRANS=(KL*AI*CSSTAR/V)-(KL*AI/V)*CA

TERMINAL

TIMER DELT=0.5, FINTIM=1260., PRDEL=30.

PRINT CA, CB, DCADT, DCBDT, TRANS

END

STOP

OUTPUT VARIABLE SEQUENCE

CA0	CB0	AI	V	CSTAR	KL	DCADT	CA	DCBDT	CB
TRANS									

\$\$\$ TRANSLATION TABLE CONTENTS \$\$\$

CURRENT

MAXIMUM

MACRO AND STATEMENT OUTPUTS

17

600

STATEMENT INPUT WORK AREA

50

1900

INTEGRATORS+MEMORY BLOCK OUTPUTS

2 + 0

300

PARAMETERS+FUNCTION GENERATORS

4 + 0

400

STORAGE VARIABLES+INTEGRATOR ARRAYS

0 + 0/2

50

HISTORY AND MEMORY BLOCK NAMES

21

50

MACRO DEFINITIONS AND NESTED MACROS

6

50

MACRO STATEMENT STORAGE

13

125

LITERAL CONSTANT STORAGE

0

100

SORT SECTIONS

2

20

MAXIMUM STATEMENTS IN SECTION

6

600

\$\$\$END OF TRANSLATOR OUTPUT\$\$\$

Figure 19. Input Statements to Obtain Lower Curve in Figure 8, p. 187 (CSMP Simulation No. 44).

TABLE 20
Results for CSMP Simulation No. 44
($k_L = 0.3$, $k_2 = 1500$)

TIME	CA	CB	DCADT	DCBDT	TRANS
.0	1.3200E-05	9.5040E-05	-1.8818E-06	-1.8818E-06	9.0949E-13
30.0000	5.5020E-06	7.1219E-05	2.1731E-08	-5.8776E-07	6.0949E-07
60.0000	6.3010E-06	5.4646E-05	2.9422E-08	-5.1665E-07	5.4607E-07
90.0000	7.2463E-06	4.0304E-05	3.3305E-08	-4.3808E-07	4.7139E-07
120.000	8.2867E-06	2.8424E-05	3.5706E-08	-3.5331E-07	3.8901E-07
150.000	9.3624E-06	1.9108E-05	3.5498E-08	-2.6834E-07	3.0384E-07
180.000	1.0385E-05	1.2248E-05	3.2124E-08	-1.9079E-07	2.2291E-07
210.000	1.1264E-05	7.5205E-06	2.6205E-08	-1.2707E-07	1.5327E-07
240.000	1.1947E-05	4.4576E-06	1.9314E-08	-7.9883E-08	9.9197E-08
270.000	1.2429E-05	2.5739E-06	1.3032E-08	-4.7988E-08	6.1020E-08
300.000	1.2744E-05	1.4601E-06	8.2067E-09	-2.7910E-08	3.6117E-08
330.000	1.2937E-05	8.1896E-07	4.9185E-09	-1.5893E-08	2.0811E-08
360.000	1.3051E-05	4.5627E-07	2.8530E-09	-8.9322E-09	1.1785E-08
390.000	1.3117E-05	2.5320E-07	1.6213E-09	-4.9816E-09	6.6029E-09
420.000	1.3154E-05	1.4019E-07	9.1106E-10	-2.7660E-09	3.6771E-09
450.000	1.3174E-05	7.7524E-08	5.0802E-10	-1.5320E-09	2.0400E-09
480.000	1.3186E-05	4.2839E-08	2.8229E-10	-8.4730E-10	1.1296E-09
510.000	1.3192E-05	2.3664E-08	1.5656E-10	-4.6826E-10	6.2482E-10
540.000	1.3196E-05	1.3069E-08	8.6933E-11	-2.5868E-10	3.4561E-10
570.000	1.3198E-05	7.2165E-09	4.8133E-11	-1.4286E-10	1.9099E-10
600.000	1.3199E-05	3.9846E-09	2.7523E-11	-7.8888E-11	1.0641E-10
630.000	1.3199E-05	2.2001E-09	1.5558E-11	-4.3559E-11	5.9117E-11
660.000	1.3200E-05	1.2147E-09	8.6908E-12	-2.4051E-11	3.2742E-11
690.000	1.3200E-05	6.7068E-10	4.9106E-12	-1.3279E-11	1.8190E-11
720.000	1.3200E-05	3.7030E-10	3.5821E-12	-7.3318E-12	1.0914E-11
750.000	1.3200E-05	2.0445E-10	2.3185E-12	-4.0480E-12	6.3665E-12
780.000	1.3200E-05	1.1288E-10	1.4030E-12	-2.2350E-12	3.6380E-12
810.000	1.3200E-05	6.2322E-11	1.4945E-12	-1.2340E-12	2.7285E-12
840.000	1.3200E-05	3.4409E-11	2.0472E-12	-6.8130E-13	2.7285E-12
870.000	1.3200E-05	1.8998E-11	1.4428E-12	-3.7615E-13	1.8190E-12
900.000	1.3200E-05	1.0489E-11	1.6113E-12	-2.0768E-13	1.8190E-12
930.000	1.3200E-05	5.7911E-12	1.7043E-12	-1.1466E-13	1.8190E-12
960.000	1.3200E-05	3.1974E-12	1.7557E-12	-6.3308E-14	1.8190E-12
990.000	1.3200E-05	1.7653E-12	1.7840E-12	-3.4953E-14	1.8190E-12
1020.00	1.3200E-05	9.7466E-13	1.7997E-12	-1.9299E-14	1.8190E-12
1050.00	1.3200E-05	5.3813E-13	1.8083E-12	-1.0655E-14	1.8190E-12
1080.00	1.3200E-05	2.9711E-13	1.8131E-12	-5.8828E-15	1.8190E-12
1110.00	1.3200E-05	1.6404E-13	1.8157E-12	-3.2480E-15	1.8190E-12
1140.00	1.3200E-05	9.0568E-14	1.8172E-12	-1.7932E-15	1.8190E-12
1170.00	1.3200E-05	5.0004E-14	1.8180E-12	-9.9007E-16	1.8190E-12
1200.00	1.3200E-05	2.7608E-14	1.8184E-12	-5.4664E-16	1.8190E-12
1230.00	1.3200E-05	1.5243E-14	1.8187E-12	-3.0181E-16	1.8190E-12
1260.00	1.3200E-05	8.4158E-15	1.8188E-12	-1.6663E-16	1.8190E-12

APPENDIX M

EXPERIMENTAL SOLUBILITY DATA

FOR FIGURE 11, P. 192

Table 21 gives the experimentally determined solubility values for methyl salicylate in water at various temperatures.

TABLE 21

Solubility of Methyl Salicylate in Water
at Various Temperatures

$C^* \times 10^5$, $\frac{\text{gram-moles}}{\text{cm}^3}$	TEMP., °C
0.460	30 ^a
0.486	30 ^b
0.410	30
0.962	62
1.45	85
1.97	97
2.13	100 ^c

a. Dean, John A., Ed., Lange's Handbook of Chemistry, 12th Edition, McGraw-Hill, New York, N.Y., 1978.

b. Seidell, A., Solubilities of Organic Compounds, Vol. 2, 3rd Edition, D. Van Nostrand Company, New York, N.Y., 1941.

c. In this experiment, the water was boiling.

APPENDIX N

SODIUM HYDROXIDE CONCENTRATION VERSUS TIME

DATA FOR 1 MOLAR NaOH EXTRACTION RUNS

Tables 22 and 23 contain sodium hydroxide concentration versus time data which were obtained for runs in which the initial aqueous phase concentration was approximately 1 molar. These data were not used in any calculations or figures but have been included for the sake of completeness.

TABLE 22

Sodium Hydroxide Concentration as a Function of Time
at 84°C (Extraction Run No. 17, ~1N NaOH)

Agitation Rate: 80 RPM

Temperature of Aqueous Phase: 84°C

Initial Sodium Hydroxide Concentration
in Aqueous Phase of Stirred Cell: 0.98011 molar

TIME, sec	Sodium Hydroxide Concentration $\times 10^4$, $\frac{\text{gram-mole}}{\text{cm}^3}$
0	9.8011
120	2.40
320	1.56
570	1.40
852	0.768
1020	0.630
1230	0.458

TABLE 23

Sodium Hydroxide Concentration as a Function of Time
at 96.7°C (Extraction Run No. 18, ~1N NaOH)

Agitation Rate: 80 RPM

Temperature of Aqueous Phase: 96.7°C

Initial Sodium Hydroxide Concentration:
in Aqueous Phase of Stirred Cell: 0.98011 molar

TIME, sec	Sodium Hydroxide Concentration $\times 10^4$, $\frac{\text{gram-moles}}{\text{cm}^3}$
0	9.8011
70	2.29
230	0.974
395	0.772
606	0.326
816	0.139
1002	0.0899

VITA

Walter David Bruce was born on September 13, 1946, in Knoxville, Tennessee. He attended elementary and secondary schools in Knoxville, graduating from Rule High School in June 1964. After high school, the author studied at The University of Tennessee for three quarters. He then entered the United States Marine Corps Reserve and spent six months on active duty. The author worked in industry for about six months before reentering The University of Tennessee from which he received the Bachelor of Science in Chemical Engineering in March, 1970.

Upon graduation, the author worked as a chemical engineer in the development department of the Holston Defense Corporation in Kingsport, Tennessee for over two years. He returned to The University of Tennessee for full-time graduate study in September, 1972, and was awarded the Master of Science in December, 1973.

After receiving his Master's Degree, the author worked as a staff engineer for the Mead Corporation at the papermill in Kingsport, Tennessee for almost a year. The author then worked as an environmental engineer for Hydrosience, Inc. (a subsidiary of the Dow Chemical Company) until September, 1978. In September, 1978, the author began full-time graduate study toward the Doctor of Philosophy and received that degree in December, 1981.

The author is a Registered Professional Engineer in Tennessee and is a member of the American Institute of Chemical Engineers. He is also a member of Phi Kappa Phi and an associate member of Sigma Xi.