24,818

INTERPHASE PHENOMENA AND THE
CONDENSATION OF LIQUID METAL VAPORS.
THE CONDENSATION MECHANISM OF
NITROGEN TETROXIDE VAPOR.

by

Jose Larrain
and
Charles F. Bonilla

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Atomic Energy Commission, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

Liquid Metals Research Laboratory
Department of Chemical Engineering
Columbia University
New York, N. Y. 10027

MASTER

This report constitutes the thesis of
Jose Larrain for the Doctor of Engineer-
ing Science degree in Chemical Engineering.

DISCLAIMER

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

DISCLAIMER

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

ABSTRACT

Theoretical analyses of interphase processes involving vapors and liquids are presented. Monoatomic and reacting vapors were considered in situations such as condensation, evaporation and heat transfer between the vapor and its liquid. These developments are believed to be the most accurate to date in describing such processes.

The implications of the presence of diatomic and heavier molecules in liquid metal vapors in their condensation heat transfer are discussed. It is shown that some assumed detailed mechanisms of condensation of these species can explain the low experimental condensation heat transfer coefficients of liquid metals.

Results of an experimental investigation of the condensation mechanism and condensation heat transfer of nitrogen tetroxide vapor are presented. From measurements of temperature profiles in the vapor near the vapor-liquid interface during condensation it was concluded that both major components of the vapor (nitrogen dioxide and nitrogen tetroxide) condense at comparable rates. This mechanism is in qualitative agreement with the experimental condensation heat transfer coefficients, which were found to be 10 to 20 percent higher than predicted by Nusselt's theory. This is apparently the first determination of a detailed condensation mechanism at moderate pressures where traditional methods (e.g., vacuum evaporation techniques) can not be used.

Acknowledgements.

I would like to express my sincere gratitude to my advisor, Professor Charles F. Bonilla, for his guidance and encouragement throughout the course of this investigation.

I would like to acknowledge the cooperation of the members of the Department of Chemical Engineering and Applied Chemistry, and in particular the invaluable advice in the early design stages and excellent services rendered by Mr. Frank J. Lech of the Machine Shop.

Financial support of the Atomic Energy Commission under AEC Contract Numbers AT(30-1)-2660 and AT(11-1)-3027 made this investigation possible, and is gratefully acknowledged.

Table of Contents.

	<u>Page</u>
I. Introduction	1
II. Condensation of Liquid Metal Vapors	7
III. Interphase Transport Between a Pure Monoatomic Vapor and its Liquid	19
1. General	20
2. Behavior of the vapor	25
3. Boundary conditions at the vapor-liquid interface	30
4. Condensation	34
5. Evaporation	52
6. Heat transfer from the vapor to the liquid	56
IV. Interphase Transport Between a Dimerizing Vapor and its Liquid	60
1. General	60
2. Behavior of the vapor	65
3. Boundary conditions at the vapor-liquid interface	69
4. Condensation	73
5. Evaporation	81
6. Heat transfer from the vapor to the liquid	85
7. Possible structural effects in the condensation of liquid metal vapors	91
V. Experimental Determination of the Condensation Mechanism of Nitrogen Tetroxide Vapor	105
1. Condenser	109
2. Temperature profile and superheat measurements	113
3. Boiler section and vapor temperature control	117
4. Miscellaneous and operation	119
5. Results and discussion	124
VI. Summary and Conclusions	145

	<u>Page</u>
Nomenclature	147
References	154
Appendix	159
A. Physical properties of nitrogen tetroxide . . .	159
B. Physical properties of liquid metals	168
C. Reflection of sound waves by a liquid surface	172
D. Condensation in the presence of a noncondensable gas	181
E. Data reduction	186
F. Digital computer program for the reduction of the condensation heat transfer data	202

List of Tables.

<u>Table</u>	<u>Page</u>
I. Smoothened properties of liquid nitrogen tetroxide	5
II. Smoothened properties of saturated nitrogen tetroxide vapor	6
III. Condensation of liquid metals with a heat flux of 50,000 Btu/hr.ft ² , condensation coefficient of unity (monoatomic vapor)	40
IV. Condensation coefficients calculated from experimental heat transfer data assuming liquid metal vapors to be monoatomic	41
V. Evaporation of liquid metals with a heat flux of 10,000 Btu/hr.ft ² , condensation coefficient of unity (monoatomic vapor)	54
VI. Typical predicted behavior of nitrogen tetroxide vapor during condensation	74
VII. Typical predicted behavior during the steady state evaporation of nitrogen tetroxide	82
VIII. Typical predicted behavior during heat transfer from nitrogen tetroxide vapor to the liquid	89
IX. Acetone experimental data reduction	126
X. Nitrogen tetroxide experimental data and results	127

List of Figures.

<u>Figure</u>	<u>Page</u>
1. Condensation coefficients calculated with Schrage's equation	11
2. Vapor pressure of liquid metals	12
3. Dimer content of saturated liquid metal vapors	13
4. Vapor superheat necessary to have a condensation coefficient of unity (monoatomic vapors).	15
5. Schematic diagram of the postulated details of an interphase process between a pure liquid and its vapor	21
6. Coordinate system and notation	26
7. Typical temperature profiles predicted by the present investigation during the condensation of a pure monoatomic vapor	38
8. Schematic set-up for heat transfer between vapor and liquid	57
9. Temperature profile predicted during heat transfer between a pure monoatomic vapor and its liquid	59
10. Typical predicted temperature profiles during condensation of saturated nitrogen tetroxide vapor	75
11. Typical predicted temperature profiles during condensation of superheated nitrogen tetroxide vapor	76
12. Calculated effect of vapor superheat on the temperature profile during condensation of nitrogen tetroxide vapor when monomer is assumed not to condense	79
13. Typical predicted effect of condensation rate on the temperature profiles during condensation of saturated nitrogen tetroxide vapor at 20 °C when monomer is assumed not to condense	80
14. Typical predicted temperature profiles during evaporation of nitrogen tetroxide	83

<u>Figure</u>	<u>Page</u>
15. Predicted temperature profile during heat transfer between a dimerizing vapor and its liquid when one component does not condense, or heat transfer to a solid, non-catalytic wall	88
16. Typical predicted temperature profiles during heat transfer from nitrogen tetroxide vapor to liquid	90
17. Condensation coefficients of liquid metals calculated with Schrage's equation when monomer and dimer are assumed to condense at the maximum rate	94'
18. Condensation coefficients of liquid metals calculated with Schrage's equation when dimer is assumed not to condense	96
19. Condensation coefficients of liquid metals calculated with Schrage's equation when diatomic molecules striking the liquid surface are assumed to condense with the emission of one atom into the vapor	100
20. Condensation coefficients of liquid metals calculated with Schrage's equation when dimer molecules striking the liquid surface are assumed to dissociate into two atoms which return to the vapor	101
21. Temperature effects when diatomic liquid metal molecules are assumed to condense with the emission of one atom into the vapor	103
22. Diagram of the apparatus	107
23. Schematic diagram of the condenser	111
24. Schematic diagram of the electrical circuit used in the temperature profile measurements . .	116
25. Schematic diagram of the hydraulic circuit . . .	120
26. Experimental results, condensation heat transfer	130

<u>Figure</u>	<u>Page</u>
27. Condensation results as function of the condenser pressure	131
28. Sample results of the data reduction calculations	133
29. Temperature profile in the vapor, run N44 . . .	134
30. Temperature profile in the vapor, run N51 . . .	137
31. Temperature profile in the vapor, run N48 . . .	138
32. Sample temperature profile in the vapor	140
33. Sample temperature profile in the vapor	141

I. Introduction.

The Liquid Metals Research Laboratory at Columbia University has made over the years important contributions in the fields of physical and heat transfer properties of such materials.*

In the present investigation possible explanations were explored of the low condensation heat transfer coefficients of liquid metal vapors that have consistently been reported in the literature since the original experiments of Misra and Bonilla (1) and Engelbrecht and Bonilla (2) in this laboratory.

Such explanations would have considerable practical importance, being directly related to condenser sizing for power generation using liquid metals as thermodynamic working fluids. General explanations would also permit more accurate predictions of condensation heat transfer coefficients for materials for which experimental data are scarce or unavailable.

This problem has prompted many theoretical and experimental studies on all aspects of the condensation process, which have concluded that there is a thermal resistance to condensation at the interface between the vapor and the liquid. This thermal resistance has traditionally been explained in terms of the "temperature jump" predicted by kinetic theory of gases during interphase processes, as first done by Misra and Bonilla (1) to explain the discrepancy between their experimental results and Nusselt's equation for film condensation.

* The designation "liquid metal" is commonly used, for convenience, in referring to fluid properties and phenomena of low-melting metals, including vapor-liquid transformations. Where appropriate in this dissertation it will be understood to refer to the vapor phase or the transformation between the fluid phases.

Temperature jump theory includes as a parameter the "condensation coefficient" of the vapor for which independent values are usually not available and whose prediction from such data as vapor and liquid structures is not possible at present. For these reasons, condensation experiments with liquid metals have (apart from their obvious design value) reduced to just measurements of this property.

As described later, the experimental condensation coefficients of liquid metals are not constant, but show a decreasing trend with temperature while current views on the subject indicate their value should be constant and equal to unity for the full range of experimental conditions.

Most developments to date have assumed liquid metal vapors to be monoatomic, neglecting the effects of dimer (and other possible heavier) molecules in them because of their low concentration (less than 15 mole percent at the boiling point), and also because of the unavailability of theories describing satisfactorily the interphase transport between liquids and such reacting vapors.

As the proportion of dimer molecules in liquid metal vapors increases with temperature (vapor pressure), it has suggested itself as a cause of the apparent decrease of the condensation coefficients with temperature and this possibility was explored in the present study.

General calculations, believed to be the most accurate to date, for interphase transport between monoatomic and multicomponent vapors and their liquids were performed in terms of parameters (such as condensation coefficients for each species present) describing the detailed mechanism of condensation. An important feature of these calculations is that enough equations were developed to solve for all unknowns involved in the processes studied (which included condensation, evaporation and heat transfer between a vapor and its liquid). For instance, during free evaporation both temperature and pressure of the vapor were calculated as

functions of evaporation rate, liquid temperature and physical properties.

These developments were applied to the condensation of liquid metal vapors, assuming (in accordance with current views) that monoatomic molecules condense at the maximum rate (i.e., have a condensation coefficient of unity). Calculations with certain (seemingly reasonable) assumed detailed condensation mechanisms of the diatomic molecules have successfully reproduced the trends of the experimental data. In essence, the processes envisioned consisted of the following: if for some reason the diatomic molecules do not condense at the maximum rate (i.e., their condensation coefficient is smaller than unity) there would be accumulation of dimer near the liquid surface, causing the appearance of a diffusional resistance to the condensation of monomer besides the temperature jump effect.

Low (or even nil) condensation coefficients of dimer may be justified by postulating liquid metals as monoatomic in the liquid form (as generally accepted) and by arguments based on whether heavy diatomic molecules can evaporate from such monoatomic liquids. It should be noted in this respect that evaporation and condensation processes are intimately connected because their mechanism must be identical during thermodynamic equilibrium.

Although the viability of some such explanations was demonstrated analytically, it can not be established conclusively however which (if any) is the true one because of the sensitivity of the calculations to vapor properties that can only be estimated at present (such as reaction rates) and to the assumed mechanism of the condensation of the heavy molecules.

As application and general test of the theoretical calculations the condensation mechanism of nitrogen tetroxide vapor was studied experimentally in an apparatus designed for the measurement of the temperature profile in the vapor while

condensation took place on a vertical wall. Condensation experiments were selected, based on calculations for other possible situations, as being the most practical for the determination of the condensation mechanism. Condensation heat transfer data were obtained simultaneously for comparison with standard correlations (e.g., Nusselt's equation).

Nitrogen tetroxide was chosen for this study because: i) reasonable temperature range (freezing point -11.25°C , boiling point 21.15°C); ii) the vapor consists of the monomer-dimer equilibrium mixture as for liquid metals, presenting a large difference between vapor and liquid compositions; iii) fairly well-known properties, summarized in Tables I and II and Appendix A. However, liquid thermal conductivity data were sparse and more measurements were performed as reported elsewhere (3).

This appears to be the first determination of a condensation mechanism for a multicomponent system at moderate pressures where conventional methods (i.e., vacuum evaporation techniques) can not be applied. Condensation mechanisms are important since they may provide insight into the structure and properties of liquid phases and surfaces, which are not well understood at present.

In the following sections, general background information is presented on the condensation of liquid metal vapors, followed by the theoretical developments on interphase processes involving monoatomic and reacting vapors, with their application to liquid metal and nitrogen tetroxide vapors, and finally, the details of the experimental determination of the condensation mechanism of nitrogen tetroxide vapor. The calculations reported were performed with an IBM model 360/91 digital computer.

Table I

Smoothened Properties of Liquid Nitrogen Tetroxide

Temperature (°C)	-11.25	-10.0	- 5.0	0.0	5.0	10.0	15.0	20.0	21.15
Mole percent NO ₂	0.038	0.042	0.057	0.078	0.106	0.141	0.186	0.244	0.259
Density (gr/cm ³)	1.518	1.515	1.504	1.492	1.480	1.469	1.457	1.446	1.443
Viscosity (10 ⁻² gr/cm.sec)	0.608	0.598	0.561	0.523	0.496	0.468	0.442	0.418	0.413
Thermal Conductivity (10 ⁻³ cal/cm.sec.°K)	0.455	0.450	0.431	0.412	0.392	0.373	0.354	0.335	0.330
Heat Capacity (cal/gr.°K)	0.355	0.356	0.357	0.359	0.361	0.363	0.365	0.368	0.369
Equilibrium Heat of Vaporization (cal/gr)	94.7	94.9	95.8	96.7	97.7	98.8	99.9	101.0	101.3

Table II

Smoothened Properties of Saturated Nitrogen Tetroxide Vapor

Temperature	(°C)	-11.25	-10.0	- 5.0	0.0	5.0	10.0	15.0	20.0	21.15
Pressure	(atm)	0.183	0.197	0.262	0.346	0.451	0.582	0.746	0.948	1.000
Mole Fraction NO ₂		0.164	0.168	0.184	0.201	0.219	0.237	0.255	0.274	0.278
Viscosity	(10 ⁻³ gr/cm.sec)	0.110	0.111	0.114	0.116	0.119	0.121	0.125	0.127	0.128
Diffusion Coefficient	(cm ² /sec)	0.302	0.383	0.221	0.174	0.139	0.111	0.090	0.073	0.070
Heat of Dimerization	(Kcal/g-mole N ₂ O ₄)	-13.7	-13.7	-13.7	-13.7	-13.7	-13.7	-13.7	-13.7	-13.7
Thermal Conductivity										
Frozen		0.029	0.029	0.030	0.031	0.032	0.033	0.034	0.035	0.035
Equilibrium		0.173	0.176	0.187	0.199	0.211	0.223	0.234	0.245	0.247
Heat Capacity	(10 ⁻³ cal/cm.sec.°K)									
Frozen		0.189	0.189	0.191	0.192	0.194	0.195	0.197	0.198	0.198
Equilibrium		0.852	0.862	0.906	0.950	0.993	1.035	1.076	1.117	1.126
A = $\left(\frac{\partial R_2}{\partial Z}\right)_{T,P}$										
(g-mole N ₂ O ₄ /cm ³ sec)		1.96	2.40	5.23	11.1	22.8	45.7	89.3	170.3	196.9

II. Condensation of Liquid Metal Vapors.

The average heat flux during film condensation of a vapor on a vertical wall at temperature T_w may be calculated from the well-known Nusselt equation (4), based on a thin laminar film of condensate flowing down the wall as the only thermal resistance:

$$(Q/A) = \frac{2}{3} \sqrt{2} \, k_L^{3/4} \left[\frac{\rho_L^2 g \Delta H_{\text{vap}}}{L \mu_L} \right]^{1/4} (T_s - T_w)^{3/4} \quad (1)$$

T_s is the temperature of the surface of the liquid film, assumed by Nusselt as equal to the saturation temperature of the vapor.

Experiments with most common liquids agree fairly well with this relationship (5,6). However, experimental condensation heat transfer coefficients of liquid metals are several times lower than predicted by equation 1. Reformulations of the condensation problem and more rigorous derivations including phenomena not considered by Nusselt (such as vapor drag, rippling and turbulence in the film, variable liquid properties, non-linear temperature distribution in the film, contribution of liquid subcooling to heat transfer) have failed to produce significantly better agreement between theory and experiments with liquid metals (7,8,9).

There is general agreement that the available theories (including equation 1) predict satisfactorily the temperature drop across the liquid film, as shown by Sukhatme and Rohsenow (10) in their measurements of the liquid film thickness during condensation of mercury. Because contact thermal resistances between the liquid film and the colder wall are negligible, at least after prolonged operation of the equipment (11) it is believed that the low condensation

heat transfer coefficients of liquid metals are caused by a thermal resistance at the vapor-liquid interface, as discussed at length by Wilhelm (12).

Due to the high thermal conductivity of liquid metals the temperature drop across the liquid film is small, and a large portion of the temperature difference found between the cold wall and the vapor would be due to the interfacial resistance. During film condensation of non-metallic substances (of lower thermal conductivity) the interfacial temperature drop would be negligible compared with the drop across the liquid film, as experiments show agreement with Nusselt's equation or its modifications.

One cause of interfacial resistance is the presence of noncondensable gases, which even in minute amounts are known to reduce condensation heat transfer coefficients significantly (13). Although this explanation has not been discarded, it is thought to be unlikely because of the fair reproducibility of data by investigators using different equipment and techniques. Also, even though more recent (and presumably more careful) experiments have yielded somewhat higher condensation heat transfer coefficients for liquid metals, they are still much lower than predicted by Nusselt's theory. Besides, to compensate for this effect some experimenters (e.g., Misra and Bonilla, 1) have deliberately introduced noncondensables into the liquid metal vapors and extrapolated the results to the no-noncondensables condition, obtaining fair agreement with other data.

The accepted explanation of the vapor-liquid interfacial resistance is that of a general phenomenon associated with non-equilibrium systems, the temperature jump: In condensation there is a net flow of vapor molecules towards the liquid surface and there must be a driving force for it. This driving force would be provided by a difference in temperature between the liquid surface and the vapor, resulting in an

effective thermal resistance at the interface.

The existence of the temperature jump has been clearly established, as by careful measurements of the temperature profile with travelling thermocouples during the condensation of liquid metal vapors at low pressures (14,15).

Kinetic theory of gases was used by Schrage (16) to calculate the temperature jump during interphase mass transfer between a pure liquid and its vapor. Schrage obtained equation 2 relating a dimensionless vapor velocity (ξ_v), the temperature (T_v) and pressure (P_v) of the vapor, and the temperature (T_s) and corresponding vapor pressure (P_s) of the liquid surface.

$$\sqrt{\pi} \xi_v \left[2 - \zeta_c \left[1 - \phi(\xi_v) \right] \right] = \zeta_e \frac{P_s}{P_v} \left(\frac{T_v}{T_s} \right)^{1/2} - \zeta_c e^{-\xi_v^2} \quad (2)$$

ζ_c and ζ_e are the condensation and evaporation coefficients respectively, and are used to characterize the detailed mechanism of the process. The condensation coefficient is defined as the fraction of the vapor molecules striking the liquid surface that actually condense, the rest (the fraction $1 - \zeta_c$) being reflected back into the vapor. The evaporation coefficient is the ratio between the actual number of molecules evaporating from the liquid and the number of molecules that would strike the liquid if it were in equilibrium with vapor at a temperature T_s and pressure P_s .

During thermodynamic equilibrium the evaporation and condensation coefficients must be equal. In general, it is assumed that this equality continues to hold during non-equilibrium conditions, through the argument that the process should be identical at the molecular level whether there is or not net condensation (or evaporation). This assumption was maintained throughout this investigation, with the (equal) coefficients being called just condensation coefficient (ζ)

as commonly done in the literature (which sometimes also refers to it as mass accommodation coefficient).

After some approximations (valid for low vapor velocities) the net condensing mass flux (W) may be obtained from equation 2 in the more familiar form:

$$W = \left[\frac{2M}{\pi R} \right]^{1/2} \frac{\sigma}{(2-\sigma)} \left[\frac{P_v}{T_v^{1/2}} - \frac{P_s}{T_s^{1/2}} \right] \quad (3)$$

In a typical condensation experiment the average heat flux, wall temperature and vapor conditions are determined. Then, by applying Nusselt's equation (equation 1) or a more advanced theory if warranted (such as those in references 7, 17, 18) the temperature of the surface of the liquid is calculated, which permits the determination of the condensation coefficient with Schrage's equation.

Experimental condensation coefficients of liquid metals obtained from condensation heat transfer data are shown in figure 1, with the saturation pressure at the liquid surface temperature (P_s) used as sole correlating variable. This is based on the view (9) that the condensation coefficient should be a function of only the liquid surface conditions (i.e., its temperature), and in fact no correlation with condensation rate is apparent from the data. The molecular weight (M) in equation 2 was taken as the atomic weight of the elements since it is customary to neglect (either explicitly or implicitly) the effects of the heavier molecules in liquid metal vapors. The sodium data of Roth (26) deviate considerably (in the direction of lower condensation heat transfer coefficients) from those of other investigators and has not been included. As reference, figure 2 shows the vapor pressures of mercury, potassium and sodium for which condensation heat transfer data are most abundant, and figure 3 the dimer content of their saturated vapors. Appendix B presents addi-

Figure 1.- Condensation coefficients calculated with Schrage's equation.

Figure 2.- Vapor pressure of liquid metals

Figure 3.- Dimer content of saturated liquid metal vapors.

tional information on the properties of liquid metal vapors.

Experiments are often carried out in a combination boiler-condenser system, with the vapor being generated and condensed in the same container. Because of the experimental difficulties in measuring accurately the pressure (P_v) in these high-temperature systems while avoiding contamination of the vapor, only the temperature of the vapor (T_v) has in general been determined. With the exception of the mercury data of Sukhatme and Rohsenow (10) the vapor was assumed (as is customary in the literature) to be saturated in the calculations leading to figure 1 because of the unavailability of data or theoretical information in this respect (Schrage's equation provides only one relationship between the two unknowns, temperature and pressure of the vapor, during evaporation). This assumption is critical because superheat of the vapor would have a large effect in the calculated condensation coefficient, specially at high pressures. This can be seen in figure 4 which shows the results of calculations of the vapor superheat required to make the condensation coefficients calculated with equation 1 equal to unity. Subsequent chapters will refer back to this assumption when discussing the implications of some possible detailed mechanisms of condensation or evaporation of liquid metals. Briefly stated, the present investigation concluded that during free evaporation (not exactly though the method of generating vapor in these studies, which is mainly pool boiling) the vapor produced may be either subcooled or superheated depending on the condensation mechanism.

In spite of the large scatter present in figure 1, the following is apparent: the condensation coefficients of liquid metals calculated with Schrage's equation are essentially unity at low temperatures (low vapor pressures) and they decrease as the boiling point is approached.

A satisfactory explanation is needed for this apparent

Figure 4.- Vapor superheat necessary to have a condensation coefficient of unity (monoatomic vapors).

behavior of the condensation coefficient of liquid metals. Even though as mentioned earlier the condensation coefficient can not be estimated independently at present, it is accepted (27) that the condensation coefficients of monoatomic vapors on clean liquid surfaces (as the continuously renewed ones in condensation studies) should be unity under all conditions, as evidenced even by liquid metals at low temperatures.

It would seem that the liquid metal data agree with the trend mentioned by Strickland-Constable (28) in his review of condensation coefficients of liquids and solids, i.e., they decrease with increasing pressures. Such trend is not clearly established however, and may have resulted from only the increased difficulty of measurements, as discussed in that work.

In this respect, an experimental error explanation has been proposed to account for the low condensation coefficients of liquid metals at high temperatures. Wilcox and Rohsenow (24) calculated the expected values of the measured condensation coefficients assuming a true condensation coefficient of unity and that investigators would be reluctant to report measurements where the liquid surface temperature (usually calculated by extrapolation from the temperature profile in the condenser wall) is higher than the vapor temperature, or that the thermal conductivity of the condenser materials and thermocouple data used would be biased to insure that such situation would not arise. The expected values follow the general trend of the available data, decreasing at higher pressures when the temperature differences become smaller (because of the higher likelihood that some of the data would be discarded or modified).

The equality of the evaporation and condensation coefficients of liquid metals has also been questioned. Sartor et al. (29) calculated the condensation coefficient from their rubidium data, assuming the evaporation coefficient to be unity, obtaining values very close to unity for it (0.96 on

the average). However, this is due mainly to the high sensitivity of Schrage's equation to the ratio of condensation and evaporation coefficients, with small departures from unity having a very large effect. A condensation coefficient smaller than the evaporation coefficient (which is apparent in data for crystals, 27) has been justified by pointing out that evaporation would proceed unimpeded by many factors that hinder condensation. This is not clear however in a system free of contaminants, and for that reason condensation and evaporation coefficients are assumed equal.

Apart from such treatments based on experimental errors or system contamination, most investigators have accepted the data and taken more fundamental approaches towards their explanation, as done in the present work.

Investigators have questioned the validity of Schrage's equation for the calculation of the condensation coefficient (or conversely, the temperature jump) and have tried to improve on it. The most successful such development (in the sense of taking the calculated value of the condensation coefficient to unity throughout the experimental range) was presented by Meyrial et al. (22) and Fedorovich and Rohsenow (30); however, their analysis contains some unrealistic assumptions as discussed in Chapter III.

In the present investigation, new equations based on kinetic theory of gases were developed for the calculation of the condensation coefficient of a pure monoatomic vapor from condensation heat transfer data and are presented in Chapter III. They disagree with the above results, however, and produce with the most favorable assumptions values of the condensation coefficient only slightly higher than calculated with Schrage's equation, still not equal to unity throughout the experimental range.

Because of this failure of the more accurate equations to yield a constant value of the condensation coefficient at high and low pressures, another explanation (of the type

first suggested by Subbotin and co-workers, 31, 32) based on the possible effects of the structure of liquid metal vapors (i.e., including the effect of dimer and heavier molecules) were explored analytically; results are presented in Chapter IV. In essence, it was postulated that liquid metals are monoatomic the liquid form (as generally accepted). With this assumption it may be concluded that diatomic and heavier vapor molecules do not condense, i.e., the polyatomic molecules must decompose into monomer in the vapor phase before condensation takes place. This would create a reaction zone near the vapor-liquid interface and the appearance of a diffusional resistance to the condensation of the monoatomic molecules.

III. Interphase Transport Between a Pure Monoatomic Vapor and its Liquid.

Throughout the present investigation (and the literature) vapors are assumed to obey the ideal gas law. In this section they are further assumed to consist of monoatomic molecules with only translational energy since additional assumptions are needed to describe the general case of polyatomic molecules with several degrees of freedom.

Two concepts are used to describe the interaction between a liquid surface and vapor molecules: condensation coefficient (σ) and energy accommodation coefficient (α), which is usually defined somewhat loosely by analogies made with a solid wall.

In this investigation σ was taken as the fraction, assumed independent of the molecular energy (velocity) and angle of incidence, of the vapor molecules striking the liquid surface that actually condense (i.e., become indistinguishable from the other molecules in the liquid) in accordance with its usual definition (16). Of the molecules striking the liquid surface that do not condense (the fraction $1 - \sigma$), a fraction α was assumed to be reflected diffusely away from the surface with a mean temperature T_g (regardless of their original energy), and the rest (a fraction $1 - \alpha$) to be reflected specularly by the surface. This definition of energy accommodation coefficient is consistent with the use of this concept during heat transfer between a gas and a solid wall (as in reference 33).

The coefficients σ and α were further assumed to depend only on the temperature of the liquid surface (T_g), and with these definitions condensation and energy accommodation coefficients may take values ranging from zero to unity, independently of each other.

The emissive properties of the surface were also assumed to depend only on the temperature of the liquid surface and could then be calculated from $\bar{v}$ and α by considering the thermodynamic equilibrium situation together with the principle of microscopic reversibility as is customary (16). Equality of condensation and evaporation coefficients ($\bar{v}_c$ and $\bar{v}_e$) is implied. A schematic diagram of an interphase process is shown in figure 5.

It is recognized that these coefficients do not necessarily provide the true description of interphase processes, or that the microscopic properties of the liquid surface may not be described better some other way. However, the concepts of condensation and energy accommodation coefficients and the mechanism they imply are widely accepted and, unlike some possible energy-dependent reflective properties, they give fairly logical and very reasonable emissive properties of the liquid surface when the principle of microscopic reversibility is applied to the equilibrium situation. Also, they are in agreement with the reported reflection of molecular beams by solid substrates as according to the cosine law (34).

III.1. - General

Schrage (16) obtained equation 2 with a material balance at the interface assuming that during condensation the bulk vapor conditions prevail up to the vapor-liquid interface (i.e., that the velocity distribution of the vapor molecules is Maxwellian and constant throughout).

Wilhelm (12) presents a good summary of previous as well as his own efforts towards improving on Schrage's theory. Wilhelm paid particular attention to the inconsistencies in that theory, which derive mainly from the fact that although equation 2 satisfies the material balance at the interface, it does not agree with either momentum or energy balances.

N = Molar flux = Number of moles per unit area and unit time.

$N_{1s} = \left(\frac{P_s}{2\pi M R T_s} \right)^{\frac{1}{2}}$ = Incident molar flux during thermodynamic equilibrium at a temperature T_s and corresponding vapor pressure P_s .

Figure 5. - Schematic diagram of the postulated details of an interphase process between a pure liquid and its vapor.

Along with former investigators, Wilhelm attempted a solution to the condensation problem by assuming the form of the velocity distribution function of the vapor molecules at the interface. The parameters in the assumed velocity distributions were then calculated with the requirement that mass, momentum and energy balances at the interface be satisfied. No consistent solution for a wide range of conditions could be found by Wilhelm with this or other approaches based on setting a limit to the energy of the molecules that condense (in lieu of the condensation coefficient concept).

Another important limitation of Schrage's theory is that when applied to evaporation it provides only one relationship (equation 2) between the temperature and pressure of the vapor, and one additional assumption (usually that the vapor is saturated) must be made in practice.

Bornhorst and Hatsopoulos (35) were the first to give a complete description of interphase processes in the sense of deriving enough equations to solve for all the variables involved. In their analysis they used the methods of irreversible thermodynamics to obtain the conditions at the vapor-liquid interface and concluded that the pressure at the interface is essentially equal to that of the bulk of the vapor, and derived an expression for the interfacial temperature. The theory has shortcomings inherent in the irreversible thermodynamics treatment, as the assumptions of linearity of the process and constancy of the phenomenological coefficients. These coefficients were calculated using Schrage's equation and Kennard's expression (33) for the temperature jump during heat transfer between a gas and a reflecting wall for an energy accommodation coefficient of unity.

Kroger (21) applied the results of Bornhorst and Hatsopoulos to the calculation of the condensation coefficients of liquid metals, using Schrage's equation with T_v substituted by the temperature of the vapor at the interface

(T_o) given by equation 4. The calculated interfacial temperatures are slightly lower than the bulk vapor temperature (indicating subcooling of the vapor at the interface), but Kroger concluded that essentially the same condensation coefficients would be obtained as with Schrage's equation.

$$T_o - T_v = \frac{P_s(v_v - v_L)}{2 c_{p,v}} + \frac{T_s (1 + \gamma) (2 - \gamma)}{\gamma \gamma \left[1 - \frac{2 T_s (P_v - P_s)}{P_s (T_o - T_s)} \right]} \quad (4)$$

Meyrial et al. (22) and Fedorovich and Rohsenow (30) extended the treatment of Bornhorst and Hatsopoulos to include the size (d) of the Knudsen zone as a parameter. Assuming an energy accommodation coefficient of unity they obtained equation 5 giving the temperature of the vapor as also lower than that of the bulk. Agreement with a condensation coefficient of unity was obtained by these investigators with a Knudsen zone size of 10 mean free paths and using Schrage's equation with T_o instead of T_v and taking the saturation pressure at the temperature T_o instead of P_v . The latter assumption about the pressure at the interface being the vapor pressure at the interfacial temperature was justified by Fedorovich and Rohsenow through possible nucleation in the subcooled vapor. This assumption does not however seem realistic because even if nucleation took place in the subcooled vapor the pressure would remain relatively constant, with most of the vapor reaching the liquid surface under a pressure close to P_v (as calculated by Bornhorst and Hatsopoulos) and only a small fraction as liquid droplets. Moreover, both the present investigation and that of Muratova and Labuntsov (36) predict that when the condensation coefficient is unity the vapor at the interface is superheated, in direct opposition with this theory.

$$\frac{T_v - T_o}{T_o - T_s} = \frac{k_v}{W c_{v,v} \left[d + \frac{2 \lambda^*}{P_r} \left(\frac{r}{1+\delta} \right) \right]} \quad (5)$$

A conceptually more direct approach to the problem of interphase transport was followed in the present investigation and the simultaneous developments by Muratova and Labuntsov (36). In theory, a complete description of the processes, at moderate and low pressures where the effects of triple collisions may be neglected, is given by the solution to Boltzmann's integro-differential equation (37) as applied to the vapor and subject to the boundary conditions at the vapor-liquid interface implied by the condensation and energy accommodation coefficients. For condensation and evaporation the boundary condition far from the liquid surface would be a Maxwellian distribution with constant average velocity, temperature T_v and pressure P_v .

Muratova and Labuntsov (36) used a linearized theory with an eight-moment approximation to the velocity distribution function of the vapor molecules to describe condensation and evaporation. Their results agree qualitatively with the present ones for these cases.

In the present study a solution was obtained based on the thirteen-moment expansion by Grad (38) of the solution to Boltzmann equation. The investigation concentrated on three phenomena - condensation, evaporation and heat transfer between the vapor and its liquid - and the theoretical developments are presented below. Results of sample calculations are given relating to the behavior of liquid metal vapors when assumed monoatomic.

It should be noted that the results are in general not applicable to very high rates of mass transfer (with vapor velocities close to the speed of sound), where the hydrodynamic equations associated with the thirteen-moment approxi-

mation are not valid. In such cases (e.g., evaporation into a vacuum) the Hertz-Knudsen equation may provide a better description.

In essence, the method followed consisted of obtaining the general solution to the transport equations associated with the thirteen-moment approximation for each case treated, and using the boundary conditions at the interface (implied by condensation and energy accommodation coefficients) to find the unknown constants involved in such solution.

Because of its possible application to the determination of condensation coefficients, an approximate solution is presented in Appendix C to the reflection of sound waves by a liquid surface.

For polyatomic substances, the approximations and assumptions in Chapter IV can be used to compensate for the additional degrees of freedom of the vapor molecules.

III.2. - Behavior of the vapor.

Consider a liquid whose surface is located perpendicular to the x -direction at $x = 0$, and the steady flow of its vapor in the $+x$ direction with an average velocity u_v (negative for net condensation), temperature T_v and pressure P_v far from the liquid surface (i.e., at $x = +\infty$), as shown in figure 6. Let T_s be the temperature of the liquid surface, P_s the corresponding vapor pressure of the liquid, and the subscript 'o' denote the conditions of the vapor at the vapor-liquid interface ($x = 0$). Orthogonal coordinate axes y and z and corresponding velocity components v and w parallel to the liquid surface are defined for future use, although the state of the system is assumed not to vary in these directions.

In his thirteen-moment approximate solution to Boltzmann

Figure 6.- Coordinate system and notation.

integro-differential equation, Grad (38) describes the condition of a gas for a one-dimensional flow in terms of five variables: ρ (density), $\bar{u}$ (mean velocity), T (absolute temperature), p (a component of the stress tensor) and S (which corresponds to twice the heat flux vector). The pressure P is introduced through the equation of state of the gas (the ideal gas law, $P = \rho R' T$).

For a steady, one-dimensional flow, Grad's equations (38, 39) reduce to:

$$\rho \bar{u} = G \quad (6a)$$

$$G \bar{u} + P + p = C_1 \quad (6b)$$

$$\bar{u} P + \frac{2}{3} C_1 \bar{u} - \frac{1}{3} G \bar{u}^2 + \frac{1}{3} S = C_2 \quad (6c)$$

$$\frac{d}{dx}(\rho \bar{u}) + \frac{4}{3} (p+P) \frac{d\bar{u}}{dx} + \frac{4}{15} \frac{dS}{dx} + \frac{pP}{\mu_v} = 0 \quad (6d)$$

$$\begin{aligned} \bar{u} \frac{dS}{dx} - \frac{2pR'T}{P} \frac{dP}{dx} + R'(5P+7p) \frac{dT}{dx} + 2R'T(1 - \frac{p}{P}) \frac{dP}{dx} + \\ + \frac{16}{5} S \frac{d\bar{u}}{dx} + \frac{5PR'S}{2k_v} = 0 \end{aligned} \quad (6e)$$

where G , C_1 and C_2 are constants.

In terms of the values of the variables at $x = \infty$, equations 6 reduce to equations 7 and the differential equations 8 in terms of only $\bar{u}$ and P .

$$\frac{T}{T_v} = \frac{P}{P_v} \frac{\bar{u}}{u_v} \quad (7a)$$

$$\frac{P}{P_v} = 1 + \beta - \beta \frac{\bar{u}}{u_v} - \frac{P}{P_v} \quad (7b)$$

$$\frac{S}{u_v P_v} = 5 + \beta + \beta \left[\frac{\bar{u}}{u_v} \right]^2 - 2(1+\beta) \frac{\bar{u}}{u_v} - 3 \frac{P}{P_v} \frac{\bar{u}}{u_v} \quad (7c)$$

$$[9(1+\beta) - 14\beta \frac{\bar{u}}{u_v} - 9 \frac{P}{P_v}] \frac{d}{dx} \left[\frac{\bar{u}}{u_v} \right] - 9 \frac{\bar{u}}{u_v} \frac{d}{dx} \left[\frac{P}{P_v} \right] - 5 \frac{\mu_v u_v}{P_v} \frac{P}{P_v} \left[\frac{P}{P_v} + \beta \frac{\bar{u}}{u_v} - 1 - \beta \right] = 0 \quad (8a)$$

$$\begin{aligned} & \left[\frac{16}{5} \beta \frac{\bar{u}}{u_v} \left[\beta \frac{\bar{u}}{u_v} - 2(1+\beta) \right] + \frac{P}{P_v} \left[7(1+\beta) - 2 \frac{P}{P_v} - \frac{118}{5} \beta \frac{\bar{u}}{u_v} \right] + \right. \\ & \left. + \frac{16}{5} \beta(5+\beta) \right] \frac{d}{dx} \left[\frac{\bar{u}}{u_v} \right] + \\ & + \left[\frac{\bar{u}}{u_v} \left[7(1+\beta) - 10\beta \frac{\bar{u}}{u_v} \right] - 4 \frac{\bar{u}}{u_v} \frac{P}{P_v} \right] \frac{d}{dx} \left[\frac{P}{P_v} \right] + \\ & + \beta P_v \frac{\mu_v u_v}{P_v} \frac{P}{P_v} \left[5 + \beta + \beta \left[\frac{\bar{u}}{u_v} \right]^2 - 2(1+\beta) \frac{\bar{u}}{u_v} - 3 \frac{\bar{u}}{u_v} \frac{P}{P_v} \right] = 0 \end{aligned} \quad (8b)$$

where $\beta = 2 \xi_v^2$ and with the boundary conditions:

$$P(x \rightarrow \infty) = P_v \quad (9a)$$

$$\bar{u}(x \rightarrow \infty) = u_v \quad (9b)$$

As further refinements do not seem warranted, viscosity and Prandtl number were taken as constant, and the general solution to the differential equations 8 was expanded in exponential power series of the form:

$$\frac{P}{P_v} = 1 + \sum_{n=1}^{\infty} p_n e^{nax} \quad (10a)$$

$$\frac{\bar{u}}{u_v} = 1 + \sum_{n=1}^{\infty} u_n e^{nax} \quad (10b)$$

where a is required by convergence criteria and boundary conditions 9 to be negative.

In fact, the solution contains only one arbitrary parameter, chosen as the first coefficient (u_1) of the expansion of the velocity profile of the vapor (equation 10b). With the coefficient a given by the negative root of equation 11, the velocity and pressure profiles take the form of equation 12,

with constants given by the simultaneous recurrence formulas 13.

$$\frac{3}{5} \left\{ 3 - \frac{26}{5} \beta + \beta^2 \right\} P_r \beta \left[\frac{k_v a}{G_{c_{p,v}}} \right]^2 + \left[1 - 2\beta - \frac{9}{5} \beta^2 (1 + P_r^2) \right] \frac{k_v a}{G_{c_{p,v}}} - \left(1 - \frac{3}{5} \beta \right) = 0 \quad (11)$$

$$\frac{u}{u_v} = 1 + \sum_{j=1}^{\infty} b_j u_1^j e^{j a x} \quad (12a)$$

$$\frac{p}{p_v} = 1 + \sum_{j=1}^{\infty} c_j u_1^j e^{j a x} \quad (12b)$$

$$b_0 = c_0 = b_1 = 1 \quad (13a)$$

$$c_1 = - \frac{\beta \left[1 + P_r \beta \frac{k_v a}{G_{c_{p,v}}} \right]}{1 + 1.8 P_r \beta \frac{k_v a}{G_{c_{p,v}}}} \quad (13b)$$

$$\begin{aligned} & \beta b_j \left[1 + P_r \beta \frac{k_v a}{G_{c_{p,v}}} j \right] + c_j \left[1 + 1.8 P_r \beta \frac{k_v a}{G_{c_{p,v}}} \right] = \\ & = - \sum_{\substack{m+n=j \\ m,n \neq j}} \left[c_m c_n + 1.4 P_r \beta^2 \frac{k_v a}{G_{c_{p,v}}} j b_m b_n + \right. \\ & \quad \left. + \beta \left[1 + 0.2 P_r \frac{k_v a}{G_{c_{p,v}}} \right] b_m c_n \right] \quad (13c) \end{aligned}$$

$$\begin{aligned} & b_j \left[(1 - 1.4\beta) \frac{k_v a}{G_{c_{p,v}}} j - 1 \right] + 0.6 c_j \left[(1 - \beta) \frac{k_v a}{G_{c_{p,v}}} j - 1 \right] = \\ & = (1 + \beta) \sum_{\substack{m+n=j \\ m,n \neq j}} \left[j \frac{k_v a}{G_{c_{p,v}}} (0.64 \beta b_m - 1.4 c_m) b_n + 0.4 b_m c_n \right] + \\ & + \sum_{\substack{r+m+n=j \\ r,m,n \neq j}} \left[n \frac{k_v a}{G_{c_{p,v}}} (0.4 c_r c_m b_n + 0.8 b_r c_m c_n - \right. \\ & \quad \left. - 0.64 \beta b_r b_m b_n + 4.72 \beta c_r b_m b_n + 2 \beta b_r b_m c_n) - \right. \\ & \quad \left. - c_r b_m (3 c_n - \beta b_n) \right] \quad (13d) \end{aligned}$$

The series converge very rapidly, with the coefficients b_j and c_j decreasing approximately according to powers of β , which is usually much smaller than one (being of the order of the square of the Mach number of the vapor).

The series solution (equations 10) and equations 7 give a complete description of the behavior of the vapor as a function of only one arbitrary parameter (u_1), to be determined by the boundary conditions at the vapor-liquid interface.

III.3. - Boundary conditions at the vapor-liquid interface.

The emissive properties of the liquid surface were assumed to depend only on the liquid surface temperature (T_s) and can then be calculated by considering the thermodynamic equilibrium situation.

During equilibrium, the velocity distribution function (f_s) of the vapor molecules is Maxwellian throughout, with zero mean velocity and temperature T_s . The velocity distribution function of the vapor molecules that strike the liquid and condense is $\bar{\sigma} f_s$, and because of the principle of microscopic reversibility the molecules emitted by the liquid must have the same velocity distribution ($\bar{\sigma} f_s$).

Calling f_0 the velocity distribution function of the vapor molecules at the vapor-liquid interface ($x=0$), the general boundary condition for the distribution function is, according to the definitions of the coefficients $\bar{\sigma}$ and α , given by:

$$\begin{aligned}
 f_0(u>0, v, w) = & \underbrace{(1-\alpha)(1-\bar{\sigma})f_0(-u, v, w)}_{\text{molecules leaving the surface}} + \underbrace{\bar{\sigma} f_s}_{\text{molecules reflected specularly by the liquid surface}} + \underbrace{\alpha(1-\bar{\sigma}) f_s}_{\text{molecules emitted by the liquid}} \times \left[\begin{array}{l} \text{ratio of incident molecular} \\ \text{flux to the flux emitted by} \\ \text{the liquid surface} \end{array} \right] \\
 & \underbrace{\text{molecules reflected diffusely by the}}_{\text{liquid surface.}}
 \end{aligned} \tag{14}$$

Grad (38) gives the velocity distribution function associated with the thirteen-moment approximation, and for a one-dimensional flow in the x-direction it reduces to:

$$f = \frac{\rho}{(2\pi R'T)^{3/2}} \left[1 + \frac{p}{2P'R'T} \left\{ (u-\bar{u})^2 - \frac{v^2}{2} - \frac{w^2}{2} \right\} - \frac{S(u-\bar{u})}{2P'R'T} \left[1 - \frac{(u-\bar{u})^2 + v^2 + w^2}{5R'T} \right] \right] e^{-\frac{(u-\bar{u})^2 + v^2 + w^2}{2R'T}} \quad (15)$$

By direct integration, the ratio of incident to emitted molecular fluxes is:

$$\frac{-\int_{-\infty}^0 u f_o du}{\int_0^{\infty} u f_s du} = \frac{P_o}{P_s} \sqrt{\frac{T_s}{T_o}} \left[e^{-\xi_o^2} - \xi_o \sqrt{\pi} [1 - \Phi(\xi_o)] + \frac{P_o}{P_o} \frac{e^{-\xi_o^2}}{2} - \frac{\xi_o^2 S_o T_v}{5P_v u_v T_o} e^{-\xi_o^2} \right] \quad (16)$$

and boundary condition 14 reduces to equation 17, where $u > 0$.

$$\begin{aligned} & \frac{\rho_o}{(2\pi R'T_o)^{3/2}} \left[1 - \frac{P_o}{2P_o R'T_o} \left\{ (u-u_o)^2 - \frac{v^2}{2} - \frac{w^2}{2} \right\} - \frac{S_o(u-u_o)}{2P_o R'T_o} \left[1 - \frac{(u-u_o)^2 + v^2 + w^2}{5R'T_o} \right] \right] e^{-\frac{(u-u_o)^2 + v^2 + w^2}{2R'T_o}} \\ & - \frac{(1-\alpha)(1-\sigma) \rho_o}{(2\pi R'T_o)^{3/2}} \left[1 - \frac{P_o}{2P_o R'T_o} \left\{ (u+u_o)^2 - \frac{v^2}{2} - \frac{w^2}{2} \right\} + \frac{S_o(u+u_o)}{2P_o R'T_o} \left[1 - \frac{(u+u_o)^2 + v^2 + w^2}{5R'T_o} \right] \right] e^{-\frac{(u+u_o)^2 + v^2 + w^2}{2R'T_o}} \\ & + \frac{P_s}{(2R'T_s)^{3/2}} \left[\sigma + \alpha(1-\sigma) \left[e^{-\xi_o^2} - \xi_o \sqrt{\pi} [1 - \Phi(\xi_o)] + \frac{P_o}{P_o} \frac{e^{-\xi_o^2}}{2} - \frac{\xi_o^2 S_o T_v}{5P_v u_v T_o} e^{-\xi_o^2} \right] \frac{P_o}{P_s} \sqrt{\frac{T_s}{T_o}} \right] e^{-\frac{u^2 + v^2 + w^2}{2R'T_s}} \end{aligned} \quad (17)$$

Equation 14 (and similarly, equation 17) is an exact boundary condition derived only from the physical assumptions of the problem. However, as discussed by Grad (38), boundary conditions can not be expected to be satisfied exactly by the thirteen moment approximation (which is not an exact solution to Boltzmann's integro-differential equation) because they place too many (and in general incompatible) constraints on the parameters of the approximation. In fact, equation 17 represents an infinite number of constraints on the five parameters. Grad found by analogy with the case of a perfectly reflecting wall (energy accommodation coefficient equal to zero) that the boundary conditions in the general case ($\alpha \neq 0$) were the two moments of the exact boundary condition with respect to $(u-\bar{u})$ and $(u-\bar{u})[(u-\bar{u})^2 + v^2 + w^2]$, which represent mass and energy balances respectively. Since the reflecting wall is a special case of condensation (zero condensation coefficient), Grad's reasoning that the same boundary conditions apply to special and general cases yields the boundary conditions to use in interphase transport as mass and energy balances that can be derived from boundary condition 17.

Equations 18 and 19 are the boundary conditions at the vapor-liquid interphase implied by the assumed mechanism of condensation (condensation and energy accommodation coefficients) consistent with the thirteen-moment approximation. They were obtained by multiplying equation 17 by $(u-u_0)$ and $(u-u_0)[(u-u_0)^2 + v^2 + w^2]$ respectively, followed by integration between the limits 0 to ∞ for u and $-\infty$ to $+\infty$ for v and w .

$$\begin{aligned}
& \frac{P_o}{\sqrt{T_o}} \left[2 \xi_o \sqrt{\pi} (1-c) [1-\phi(\xi_o)] + 2 \frac{P_o}{P_o} \xi_o^2 e^{-\xi_o^2} + \right. \\
& \quad + \frac{2 S_o T_v \xi_o^2 (1-2 \xi_o^2)}{5 P_v u_v T_o} e^{-\xi_o^2} + c e^{-\xi_o^2} \left[1 + \right. \\
& \quad \left. \left. + \frac{P_o}{P_o} \left(\frac{1}{2} - \xi_o^2 \right) - \frac{2 S_o T_v \xi_o^2 (1-\xi_o^2)}{5 P_v u_v T_o} \right] \right] - \quad (18) \\
& = \frac{P_s}{\sqrt{T_s}} (1 - \xi_s \sqrt{\pi}) \left[\Gamma + \alpha (1-\Gamma) \left[e^{-\xi_o^2} - \xi_o \sqrt{\pi} [1-\phi(\xi_o)] + \right. \right. \\
& \quad \left. \left. + \frac{P_o}{2 P_o} e^{-\xi_o^2} - \frac{S_o T_v \xi_o^2}{5 P_v u_v T_o} e^{-\xi_o^2} \right] \frac{P_o}{P_s} \sqrt{\frac{T_s}{T_o}} \right]
\end{aligned}$$

$$\begin{aligned}
& \frac{P_o}{P_v} \sqrt{\frac{T_o}{T_v}} \left[\xi_o \sqrt{\pi} [1-\phi(\xi_o)] (5+8 \xi_o^2) - 3 \xi_o^2 e^{-\xi_o^2} \right] + \\
& \quad + \frac{P_o}{P_v} \sqrt{\frac{T_o}{T_v}} \left[\xi_o \sqrt{\pi} [1-\phi(\xi_o)] + \xi_o^2 (1+\xi_o^2) e^{-\xi_o^2} \right] + \\
& \quad + \frac{S_o \xi_o}{5 u_v P_v} \frac{P_o}{P_v} \sqrt{\frac{T_v}{T_o}} \left[\frac{5}{2} \sqrt{\pi} - \xi_o (4-3 \xi_o^2-2 \xi_o^4) e^{-\xi_o^2} \right] + \\
& \quad + c \left[\frac{P_o}{P_v} \sqrt{\frac{T_o}{T_v}} \left[\left(1 + \frac{7}{2} \xi_o^2 \right) e^{-\xi_o^2} - \right. \right. \\
& \quad \quad \left. \left. - \frac{\sqrt{\pi}}{2} \xi_o (5+8 \xi_o^2) [1-\phi(\xi_o)] \right] + \right. \\
& \quad + \frac{P_o}{P_v} \sqrt{\frac{T_o}{T_v}} \left[(3+\xi_o^2-2 \xi_o^4) \frac{e^{-\xi_o^2}}{4} - \xi_o \sqrt{\pi} [1-\phi(\xi_o)] \right] - \\
& \quad - \frac{S_o \xi_o}{5 u_v P_v} \frac{P_o}{P_v} \sqrt{\frac{T_v}{T_o}} \left[\frac{5 \sqrt{\pi}}{4} [1-\phi(\xi_o)] - \right. \\
& \quad \quad \left. \left. - \frac{\xi_o}{2} (3-10 \xi_o^2-6 \xi_o^4) e^{-\xi_o^2} \right] \right] - \\
& = \frac{P_s}{P_v} \sqrt{\frac{T_s}{T_v}} \left[1 - \frac{\xi_s \sqrt{\pi}}{4} (5+2 \xi_s^2) + \frac{3}{2} \xi_s^2 \right] \left[\Gamma + \alpha (1-\Gamma) \left[e^{-\xi_o^2} - \right. \right. \\
& \quad \left. \left. - \xi_o \sqrt{\pi} [1-\phi(\xi_o)] + \frac{P_o}{2 P_o} e^{-\xi_o^2} - \frac{S_o T_v \xi_o^2}{5 P_v u_v T_o} e^{-\xi_o^2} \right] \frac{P_o}{P_s} \sqrt{\frac{T_s}{T_o}} \right]
\end{aligned} \quad (19)$$

III.4. - Condensation.

During condensation of a pure vapor the liquid surface temperature (T_s) is determined only by condensation rate (i.e., u_v), the conditions of the bulk of the vapor (T_v , P_v), and liquid and vapor properties. The two relationships presented (equations 18 and 19) can be used to solve simultaneously for the parameter u_1 which determines the conditions of the vapor (according to equations 7 and 12) and the liquid surface temperature in this case. Alternatively, they can be used to solve for u_1 and the condensation coefficient $\bar{\sigma}$ when all other condensation parameters are known (as in condensation experiments).

For small condensation rates, the behavior of the vapor is given by the following approximations to equations 7 and 12:

$$\frac{u}{u_v} \approx 1 + u_1 e^{Gc_{p,v}x/k_v} \quad (20a)$$

$$\frac{P}{P_v} \approx 1 - \beta u_1 e^{Gc_{p,v}x/k_v} \quad (20b)$$

$$\frac{T}{T_v} \approx 1 + (1-\beta) u_1 e^{Gc_{p,v}x/k_v} \quad (20c)$$

$$\frac{P}{P_v} \approx 0 \quad (20d)$$

$$\frac{S}{u_v P_v} \approx - (5-3\beta) u_1 e^{Gc_{p,v}x/k_v} \quad (20e)$$

Boundary conditions 18 and 19 reduce with these approximations to:

$$2 \epsilon_v \sqrt{\pi} (1-c) + c(1 - \frac{u_1}{2}) \approx \left[1 - \epsilon_v \sqrt{\frac{\pi T_v}{T_s}} \right] \left[\sigma \frac{p_s}{p_v} \sqrt{\frac{T_v}{T_s}} + \alpha(1-\sigma) \left(1 - \frac{u_1}{2} - \epsilon_v \sqrt{\pi} \right) \right] \quad (21)$$

$$\begin{aligned} \frac{5}{2} \epsilon_v \sqrt{\pi} + c \left(1 + \frac{u_1}{2} \right) \left(1 - \frac{5}{2} \epsilon_v \sqrt{\pi} \right) &\approx \\ &\approx \sigma \frac{p_s}{p_v} \sqrt{\frac{T_s}{T_v}} \left[1 - \frac{5}{4} \epsilon_v \sqrt{\frac{\pi T_v}{T_s}} \right] + \\ &+ \alpha(1-\sigma) \sqrt{\frac{T_s}{T_v}} \left[1 - \epsilon_v \sqrt{\pi} \left(1 + \frac{5}{4} \sqrt{\frac{T_v}{T_s}} \right) - \frac{u_1}{2} \right] \end{aligned} \quad (22)$$

The treatment and some of the conclusions reached may be illustrated with these approximations to the full set of equations:

i) The vapor conditions approach the bulk ones with almost the same exponential decay predicted by Navier-Stokes' equations for heat conduction in a homogeneous flowing medium (as in approximations 20). To a first approximation, which Muratova and Labuntsov (36) took as exact:

$$T - T_v \approx (T_0 - T_v) e^{-Wc_{p,v} x / k_v} \quad (23)$$

where x is the distance from the liquid surface.

ii) The pressure of the vapor is practically constant, as the predicted variations are close to what Bernoulli's equation would predict for the changes in density associated with just the temperature variations (as in approximation 20b). The behavior of the vapor is described by only one unknown parameter, u_1 or conversely, the temperature at the

interface (T_0), as in approximation 23.

(iii) Boundary conditions at the interface, which consist of material and energy balances derived by Grad (38), yield one relationship between the condensation rate and vapor and liquid temperatures, and an expression for the unknown temperature of the vapor at the interface, in terms of the assumed mechanism of condensation. The following approximations (obtained from approximations 20, 21 and 22) show the results of this process for the two extreme values of the energy accommodation coefficient ($\alpha=0$ and $\alpha=1$). For comparison purposes, similar approximations to Schrage's equation are provided, along with the results of Muratova and Labuntsov (36).

$$\sqrt{\pi} \mathcal{E}_v \approx \frac{8}{9} \frac{\sigma}{(2-\sigma)} \frac{(P_v - P_s)}{P_v}, \quad \alpha = 0 \quad (24a)$$

$$\approx \frac{\sigma}{(2-0.875\sigma)} \frac{(P_v - P_s)}{P_v}, \quad \alpha = 1 \quad (24b)$$

$$\approx \frac{\sigma}{(2-\sigma)} \left[\frac{P_v - P_s}{P_v} - \frac{T_v - T_s}{2 T_v} \right], \quad \text{Schrage (ref. 16)} \quad (24c)$$

$$= \frac{\sigma}{(1.997-0.7970\sigma)} \frac{(P_v - P_s)}{P_s}, \quad \alpha = 1, \text{ ref. 36.} \quad (24d)$$

$$T_0 \approx T_s + \frac{2}{9} \frac{(P_v - P_s)}{P_v} T_s, \quad \alpha = 0 \quad (25a)$$

$$\approx T_s + \frac{\sigma}{(8-3.5\sigma)} \frac{(P_v - P_s)}{P_v} T_s, \quad \alpha = 1 \quad (25b)$$

$$= T_v, \quad \text{Schrage (ref. 16)} \quad (25c)$$

$$= T_s + \frac{\sigma}{(7.812-3.117\sigma)} \frac{(P_v - P_s)}{P_s} T_s, \quad \alpha = 1, \text{ ref. 36.} \quad (25d)$$

Mutual support as to the correctness of the solutions is provided by the similarity between the results of Muratova and Labuntsov (equations 24d and 25d) and the present ones (in the approximate form of 24b and 25b). Also, comparison provides an estimate of the accuracy of the present solution by considering that the results of the 8-moment approach are not markedly different from those of the 13-moment one, showing an apparently fast convergence of the method to the true solution.

Nucleation and fog formation were assumed not to take place in cases where the vapor was calculated as subcooled at the interface (as implicit in approximation 23). This possibility is apparent in approximation 25b (for $\alpha=1$) when the condensation coefficient is small.

Predicted temperature profiles during condensation of a pure vapor are shown schematically in figure 7, and the following generalizations apply:

i) When the condensation coefficient is close to unity and the vapor is saturated or only slightly superheated, the temperature of the vapor at the interface (T_0) is higher than the bulk vapor temperature (T_v).

ii) When the condensation coefficient is close to unity and the vapor is substantially superheated, T_0 is less than T_v , but the vapor is still superheated throughout.

iii) When the condensation coefficient is small ($\sigma \ll 1$) and depending on the value of the energy accommodation coefficient the temperature of the vapor at the interface may be higher (small α) or lower (α close to unity) than the bulk vapor temperature.

Bulk vapor superheat acts in the expected direction, i. e., to hinder condensation by requiring lower liquid surface temperatures for the same condensation rates and at the same total pressures. The effect is small (being not evident in

Figure 7.- Typical temperature profiles predicted by the present investigation during the condensation of a pure monoatomic vapor.

the first order approximations given above, or in the linearized theory of Muratova and Labuntsov), as is the increase of the temperature of the vapor at the interface with superheat. This is shown in Table III for constant mass condensation rates corresponding to condensation heat fluxes of $50,000 \text{ Btu/hr.ft}^2$ for saturated vapors, and assuming liquid metal vapors to be monoatomic with condensation coefficients of unity and Prandtl number of 0.667 (rigid, elastic spheres). Predicted pressure variations are very small, making the vapor superheat at the interface equal to the difference between T_0 and the saturation temperature of the vapor within the given number of figures.

Table IV shows the condensation coefficients calculated from available liquid metal data, assuming the vapors are monoatomic with Prandtl numbers of 0.667. With the exception of the mercury data of Sukhatme and Rohsenow (10) the bulk vapor was assumed saturated in the calculations as for figure 1. The condensation coefficients obtained are slightly larger (up to 10 percent) than the ones calculated with Schrage's theory (equation 2) when the energy accommodation coefficient is taken as zero (i.e., if the reflected molecules have not exchanged energy with the liquid) mainly because of the higher interfacial temperatures then predicted. When α is large this investigation predicts condensation coefficients slightly smaller than those calculated with Schrage's equation when $\bar{\sigma}$ is small (mainly because then $T_v > T_0 > T_s$ as expected), and slightly larger when $\bar{\sigma}$ is close to unity (yielding then $T_0 > T_v$).

It is apparent from Table IV that similarly to Schrage's theory the present approach fails to yield constant values of the condensation coefficients of liquid metals when their vapors are assumed monoatomic.

Table III. - Condensation of liquid metals with a heat flux of 50,000 Btu/hr.ft², condensation coefficient of unity (monoatomic vapor).
 T_{sat} = Saturation temperature of the vapor.

		Vapor superheat	Superheat at $x = 0$.
	P_v	$T_v - T_{sat}$	$T_{sat} - T_s$
	(atm)	(°K)	(°K)
Mercury	0.010	0.0	2.79
	0.010	2.0	2.79
	0.010	4.0	2.80
	0.010	6.0	2.80
	0.010	8.0	2.81
	0.010	10.0	2.81
	0.100	0.0	0.42
	0.100	1.0	0.42
	0.100	2.0	0.42
	0.100	3.0	0.42
	0.100	4.0	0.42
	1.000	0.0	0.07
	1.000	1.0	0.07
	1.000	2.0	0.07
	1.000	3.0	0.07
Potassium	0.010	0.0	2.02
	0.010	2.0	2.02
	0.010	4.0	2.03
	0.010	6.0	2.03
	0.010	8.0	2.03
	0.010	10.0	2.03
	0.100	0.0	0.33
	0.100	1.0	0.33
	0.100	2.0	0.33
	0.100	3.0	0.33
	0.100	4.0	0.33
	1.000	0.0	0.06
	1.000	1.0	0.06
	1.000	2.0	0.06
	1.000	3.0	0.06
Sodium	0.010	0.0	1.48
	0.010	2.0	1.48
	0.010	4.0	1.48
	0.010	6.0	1.48
	0.010	8.0	1.48
	0.010	10.0	1.48
	0.100	0.0	0.22
	0.100	1.0	0.22
	0.100	2.0	0.22
	0.100	3.0	0.22
	0.100	4.0	0.22
	1.000	0.0	0.04
	1.000	1.0	0.04
	1.000	2.0	0.04
	1.000	3.0	0.04

Table IV

Condensation Coefficients Calculated from
Experimental Heat Transfer Data Assuming
Liquid Metal Vapors to be Monoatomic.

Mercury data of Ivanovskii, Milovanov and Subbotin (19),
 saturated vapor.

T_V (°K)	Q/A ($\frac{\text{cal}}{\text{cm}^2 \text{sec}}$)	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_O - T_S)/(T_V - T_S)$	
			Schrage ($\alpha=0$)	($\alpha=1$)		($\alpha=0$)	($\alpha=1$)
353.6	0.28	16.7	0.807	0.830	0.807	4.05	2.10
352.6	0.25	17.5	0.772	0.796	0.770	4.12	1.94
352.1	0.24	18.0	0.755	0.813	0.794	4.11	2.09
351.6	0.24	15.2	0.819	0.841	0.820	4.07	2.22
372.1	0.31	8.2	0.729	0.756	0.733	4.19	2.20
373.1	0.37	7.1	0.806	0.832	0.815	4.13	2.63
389.1	0.60	4.0	0.946	0.974	0.970	3.91	3.66
391.1	0.53	5.0	0.758	0.789	0.768	4.04	2.44
398.1	0.24	1.2	0.884	0.923	0.914	4.02	3.41
398.1	0.17	0.9	0.874	0.915	0.905	4.04	3.38
398.1	0.17	1.2	0.716	0.754	0.732	4.06	2.41
365.1	0.24	4.5	0.973	0.996	0.996	4.02	3.98
365.1	0.18	4.5	0.832	0.861	0.847	4.26	3.02
369.1	0.18	3.7	0.822	0.854	0.839	4.26	3.01
375.1	0.20	3.5	0.771	0.805	0.785	4.23	2.70
375.1	0.19	2.5	0.907	0.936	0.928	4.18	3.61
388.1	0.21	2.0	0.798	0.825	0.807	4.13	2.82
408.1	0.22	2.0	0.921	0.956	0.951	3.87	3.52
408.9	0.62	2.5	0.803	0.839	0.823	3.90	2.74
353.6	0.14	7.0	0.817	0.842	0.825	4.31	2.78
354.1	0.14	6.2	0.851	0.876	0.863	4.27	3.03
355.1	0.15	6.5	0.837	0.862	0.848	4.28	2.93
376.1	0.24	2.5	0.990	1.021	1.024	4.08	4.29
377.1	0.24	2.5	0.970	1.001	1.001	4.09	4.11
379.1	0.24	2.1	1.008	1.040	1.045	4.06	4.47
354.1	0.15	7.0	0.811	0.837	0.820	4.31	2.75
355.1	0.09	6.4	0.620	0.651	0.623	4.45	1.89
390.1	0.25	2.4	0.747	0.784	0.763	4.11	2.56
390.1	0.25	2.7	0.697	0.732	0.709	4.12	2.28

Table IV (cont.)

Mercury data of Misra and Bonilla (1), saturated vapor.

T_V (°K)	Q/A ($\frac{\text{cal}}{\text{cm}^2\text{sec}}$)	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_O - T_S)/(T_V - T_S)$	
			Schrage	($\alpha=0$)	($\alpha=1$)	($\alpha=0$)	($\alpha=1$)
630.6	30.49	139.2	0.018	0.020	0.016	2.04	0.02
630.4	36.32	159.4	0.021	0.023	0.018	1.95	0.02
630.4	46.77	144.4	0.027	0.030	0.024	2.02	0.02
630.4	38.28	155.0	0.022	0.024	0.019	1.97	0.02
630.4	35.26	133.9	0.021	0.023	0.018	2.06	0.02
630.4	48.89	140.6	0.028	0.032	0.025	2.04	0.03
577.6	31.04	113.9	0.049	0.054	0.044	2.17	0.05
561.9	25.17	108.2	0.055	0.061	0.050	2.20	0.05
506.3	25.41	60.9	0.218	0.235	0.206	2.73	0.28
500.0	32.10	38.6	0.367	0.389	0.355	3.06	0.57
631.4	41.79	157.2	0.024	0.026	0.020	1.96	0.02
485.9	31.96	22.2	0.624	0.648	0.617	3.28	1.26
495.4	34.81	25.6	0.522	0.547	0.514	3.22	0.96
630.4	51.10	140.6	0.030	0.033	0.026	2.04	0.03
504.4	36.13	34.1	0.392	0.414	0.381	3.09	0.64
617.0	39.02	143.3	0.028	0.032	0.025	2.01	0.03
590.9	38.13	118.9	0.046	0.051	0.041	2.14	0.04
547.6	37.06	76.7	0.117	0.127	0.108	2.48	0.14
494.3	33.75	27.3	0.500	0.524	0.490	3.21	0.90
490.4	33.68	22.2	0.598	0.623	0.592	3.26	1.19
507.0	37.07	33.9	0.381	0.403	0.370	3.07	0.62
627.0	48.90	135.6	0.030	0.034	0.027	2.06	0.03
597.0	45.61	112.2	0.049	0.055	0.044	2.18	0.05
560.4	42.04	81.1	0.100	0.109	0.092	2.43	0.11
509.8	36.32	37.8	0.336	0.357	0.325	3.01	0.52
628.7	53.98	131.7	0.033	0.036	0.029	2.08	0.03
514.3	44.53	31.7	0.398	0.420	0.387	3.06	0.65
504.8	38.73	29.4	0.442	0.465	0.431	3.13	0.76
513.1	40.16	36.1	0.349	0.371	0.338	3.02	0.55
504.3	36.77	32.2	0.410	0.433	0.399	3.11	0.68
504.8	35.41	25.6	0.445	0.469	0.436	3.15	0.79
504.3	32.25	18.9	0.498	0.523	0.491	3.18	0.96
500.5	28.78	16.8	0.525	0.551	0.519	3.21	1.05
508.7	34.51	27.8	0.387	0.410	0.378	3.10	0.66
514.8	37.90	27.8	0.372	0.394	0.362	3.07	0.62
629.3	51.39	126.1	0.031	0.034	0.028	2.11	0.03
592.0	44.83	98.9	0.055	0.061	0.050	2.27	0.06
562.0	40.31	78.3	0.094	0.103	0.087	2.44	0.11
527.0	33.15	50.0	0.191	0.206	0.182	2.78	0.26
482.0	19.14	28.3	0.413	0.436	0.403	3.23	0.72
508.7	31.95	33.9	0.327	0.348	0.316	3.04	0.52
509.3	32.55	32.2	0.337	0.358	0.327	3.05	0.54
629.8	9.34	5.0	0.062	0.067	0.060	2.57	0.09
574.8	6.34	13.9	0.039	0.042	0.037	2.75	0.06
496.5	3.53	5.6	0.229	0.246	0.224	3.22	0.44
497.6	4.17	5.6	0.259	0.278	0.254	3.22	0.50
499.3	5.32	6.7	0.275	0.294	0.270	3.21	0.53
500.4	7.90	7.2	0.342	0.365	0.337	3.21	0.68
630.4	5.57	17.2	0.012	0.013	0.011	2.51	0.02

Table IV (cont.)

Mercury data of Sukhatme and Rohsenow (10).

T_V (°K)	P_V (mm Hg)	Q/A ($\frac{\text{cal}}{\text{cm}^2\text{sec}}$)	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_O - T_S)/(T_V - T_S)$	
				Schrage	$(\alpha=0)$	$(\alpha=1)$	$(\alpha=0)$	$(\alpha=1)$
411.5	1.0	2.77	121.1	0.605	0.638	0.564	2.23	0.56
416.5	1.4	2.61	60.1	0.511	0.537	0.491	2.89	0.67
434.3	2.4	3.70	144.2	0.426	0.451	0.391	1.97	0.34
439.3	3.2	4.12	85.3	0.378	0.402	0.354	2.48	0.41
437.6	3.0	3.99	68.2	0.406	0.429	0.285	2.67	0.49
449.8	6.8	3.59	12.2	0.534	0.558	0.527	2.57	0.90
437.0	2.9	4.68	137.8	0.439	0.465	0.397	2.03	0.37
433.7	2.7	4.60	110.7	0.458	0.484	0.424	2.27	0.44
448.7	3.5	5.47	144.3	0.434	0.459	0.390	2.00	0.36
447.0	4.9	5.61	46.7	0.417	0.440	0.401	2.82	0.58
454.3	6.7	5.58	26.8	0.467	0.489	0.454	2.59	0.69
459.3	8.4	5.44	20.4	0.485	0.507	0.473	2.40	0.71
466.5	11.3	5.51	16.5	0.466	0.487	0.455	2.32	0.67
473.1	14.2	5.46	14.9	0.445	0.465	0.433	2.16	0.60
449.3	4.6	7.37	139.8	0.442	0.467	0.400	2.04	0.37
450.9	5.0	7.49	97.2	0.428	0.452	0.399	2.41	0.44
473.1	13.1	7.62	24.3	0.415	0.436	0.402	2.39	0.57
477.6	17.0	7.52	21.0	0.338	0.358	0.328	2.66	0.51
459.8	5.2	9.57	140.2	0.493	0.520	0.451	2.09	0.43
439.8	5.5	9.57	89.8	0.470	0.497	0.443	2.55	0.51
468.7	8.0	11.00	145.7	0.407	0.427	0.362	2.02	0.34
459.3	6.0	10.77	104.4	0.490	0.517	0.460	2.40	0.50
470.9	8.7	10.55	110.1	0.368	0.391	0.339	2.26	0.36

Table IV (cont.)

Potassium data of Aladyed, Kondratyev et al. (20),
saturated vapor.

T_V (°K)	Q/A ($\frac{\text{cal}}{\text{cm}^2 \text{sec}}$)	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_O - T_S)/(T_V - T_S)$	
			Schrage	$(\alpha=0)$	$(\alpha=1)$	$(\alpha=0)$	$(\alpha=1)$
778.1	4.78	3.5	0.356	0.379	0.352	2.89	0.67
778.1	4.78	3.8	0.332	0.354	0.327	2.89	0.61
781.1	4.78	3.9	0.315	0.336	0.310	2.88	0.57
827.1	5.74	2.9	0.290	0.309	0.284	2.71	0.49
824.1	5.74	3.1	0.290	0.310	0.285	2.72	0.49
826.1	5.74	3.2	0.276	0.295	0.271	2.72	0.46
873.1	6.69	3.2	0.201	0.215	0.195	2.56	0.31
878.1	6.69	3.6	0.174	0.186	0.169	2.55	0.26
881.1	6.69	3.4	0.177	0.189	0.171	2.54	0.26
981.1	7.41	2.7	0.109	0.116	0.105	2.26	0.14
981.1	7.41	3.4	0.087	0.092	0.083	2.26	0.11
1008.1	8.37	2.8	0.099	0.106	0.095	2.20	0.12
1013.1	8.37	2.7	0.104	0.111	0.100	2.17	0.13
1015.1	8.37	2.9	0.090	0.096	0.086	2.18	0.11
1023.1	8.37	2.6	0.095	0.102	0.091	2.16	0.12
788.1	4.54	3.1	0.342	0.364	0.337	2.85	0.63
783.1	4.54	4.1	0.284	0.304	0.279	2.87	0.51
828.1	5.50	3.4	0.243	0.260	0.238	2.71	0.40
828.1	5.50	3.7	0.228	0.244	0.222	2.71	0.37
833.1	5.50	3.9	0.209	0.224	0.203	2.69	0.33
863.1	6.45	3.6	0.193	0.206	0.187	2.59	0.29
863.1	6.45	3.7	0.187	0.200	0.182	2.59	0.29
869.1	6.45	3.8	0.174	0.186	0.169	2.57	0.26
876.1	6.45	3.9	0.158	0.169	0.153	2.55	0.23
923.1	7.41	2.9	0.158	0.168	0.152	2.41	0.22
928.1	7.41	3.2	0.140	0.150	0.135	2.40	0.19
978.1	8.37	2.6	0.130	0.138	0.125	2.27	0.17
981.1	8.37	2.7	0.120	0.128	0.115	2.26	0.15
978.1	8.37	2.9	0.117	0.124	0.112	2.27	0.15
981.1	8.37	3.0	0.110	0.118	0.106	2.26	0.14
978.1	8.37	3.2	0.105	0.112	0.101	2.27	0.14
981.1	8.37	3.2	0.103	0.110	0.099	2.26	0.13
1015.1	8.37	3.2	0.082	0.088	0.079	2.18	0.10
1023.1	8.37	2.9	0.086	0.091	0.082	2.16	0.10
1048.1	24.86	8.4	0.076	0.081	0.073	2.12	0.09
1055.1	25.34	8.7	0.073	0.077	0.069	2.10	0.08
978.1	21.51	8.5	0.105	0.112	0.100	2.28	0.13
883.1	17.93	11.3	0.148	0.158	0.142	2.54	0.21
1026.1	5.38	1.9	0.084	0.089	0.080	2.15	0.10
1023.1	5.38	1.9	0.085	0.090	0.081	2.16	0.10
1028.1	5.38	2.2	0.072	0.077	0.069	2.15	0.09
1008.1	5.26	2.1	0.081	0.086	0.077	2.20	0.10

Table IV (cont.)

Potassium data of Engelbrecht and Bonilla (2), saturated vapor.

T_V (°K)	Q/A $\left(\frac{\text{cal}}{\text{cm}^2 \text{sec}}\right)$	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_O - T_S)/(T_V - T_S)$	
			Schrage ($\alpha=0$)	($\alpha=1$)		($\alpha=0$)	($\alpha=1$)
706.5	0.35	7.5	0.043	0.047	0.042	3.16	0.08
696.5	0.33	9.3	0.040	0.044	0.039	3.20	0.07
961.9	0.76	9.1	0.007	0.008	0.007	2.31	0.01
790.4	0.47	4.7	0.027	0.029	0.026	2.83	0.04
790.4	0.47	5.1	0.025	0.027	0.024	2.83	0.04
797.1	0.48	4.1	0.029	0.031	0.028	2.81	0.04
834.1	0.60	3.1	0.031	0.034	0.030	2.68	0.05
732.0	0.39	8.3	0.029	0.031	0.028	3.05	0.05
763.5	0.42	21.0	0.009	0.010	0.008	2.88	0.01
733.1	0.39	58.1	0.006	0.007	0.006	2.76	0.01
789.4	0.46	31.3	0.005	0.005	0.005	2.76	0.01
734.8	0.16	2.4	0.037	0.040	0.036	3.06	0.06
727.6	1.08	3.4	0.188	0.202	0.183	3.09	0.34
717.2	0.85	3.4	0.175	0.188	0.171	3.14	0.32
756.1	1.29	0.4	0.809	0.847	0.831	2.98	2.19
769.3	0.19	1.0	0.069	0.074	0.066	2.92	0.11
743.6	1.25	2.0	0.273	0.293	0.269	3.03	0.51
748.2	1.75	0.3	1.208	1.244	1.283	3.00	4.96
688.4	0.27	15.4	0.024	0.027	0.024	3.19	0.04
749.6	0.35	42.2	0.005	0.006	0.005	2.82	0.01
815.3	0.44	9.6	0.009	0.010	0.009	2.74	0.01
787.5	0.40	14.1	0.008	0.009	0.008	2.82	0.01
827.1	0.46	40.4	0.002	0.003	0.002	2.63	0.00
843.1	0.48	42.1	0.002	0.002	0.002	2.59	0.00
718.8	0.31	1.5	0.141	0.152	0.137	3.14	0.26
747.5	0.35	1.7	0.091	0.099	0.089	3.01	0.16
711.2	0.30	2.1	0.115	0.124	0.112	3.17	0.21
689.1	0.28	2.9	0.112	0.121	0.109	3.27	0.21
498.3	0.10	13.7	0.790	0.814	0.794	4.25	2.44
599.4	0.18	0.9	0.851	0.892	0.880	3.78	3.02
834.3	1.34	7.8	0.028	0.030	0.027	2.68	0.04
750.8	1.22	17.9	0.035	0.038	0.033	2.94	0.05
761.1	1.09	7.1	0.061	0.066	0.059	2.94	0.10
802.8	1.26	6.2	0.047	0.050	0.045	2.79	0.07
782.2	1.76	5.0	0.103	0.111	0.100	2.87	0.17
764.6	1.79	8.0	0.093	0.101	0.090	2.93	0.15
677.8	0.81	3.7	0.286	0.307	0.282	3.33	0.59
653.5	1.51	2.3	0.860	0.897	0.886	3.43	2.76
652.1	0.99	4.5	0.429	0.457	0.427	3.47	0.99

Table IV (cont.)

Potassium data of Subbotin, Ivanovskii et al. (14),
saturated vapor.

T_V (°K)	Q/A $\left(\frac{\text{cal}}{\text{cm}^2 \text{sec}}\right)$	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_O - T_S)/(T_V - T_S)$	
			Schrage	$(\alpha=0)$	$(\alpha=1)$	$(\alpha=0)$	$(\alpha=1)$
621.6	2.36	5.7	0.977	1.004	1.005	3.45	3.49
913.1	4.72	1.5	0.205	0.219	0.199	2.44	0.30
631.6	2.36	4.3	1.005	1.034	1.039	3.42	3.71
648.1	2.36	2.8	1.045	1.077	1.088	3.37	4.00
660.1	2.39	2.0	1.098	1.131	1.150	3.31	4.42
660.1	2.53	2.6	1.000	1.034	1.038	3.34	3.60
646.6	2.44	3.5	0.970	1.003	1.003	3.40	3.42
640.6	2.14	3.4	0.979	1.012	1.013	3.43	3.52
640.6	2.28	3.3	1.022	1.054	1.061	3.40	3.84
637.1	2.11	3.6	0.980	1.012	1.014	3.44	3.54
636.1	2.14	3.6	0.996	1.028	1.032	3.43	3.66
632.6	2.19	4.0	0.994	1.025	1.028	3.44	3.64
622.1	2.86	8.3	0.894	0.920	0.911	3.48	2.85
609.1	2.39	6.7	1.038	1.059	1.067	3.36	3.94
631.6	2.22	4.2	0.987	1.018	1.020	3.44	3.59
632.1	2.28	4.2	0.994	1.024	1.027	3.43	3.63
640.1	2.53	3.5	1.049	1.079	1.089	3.37	4.04
647.6	2.42	3.0	1.028	1.060	1.068	3.37	3.86
655.6	2.58	3.0	0.984	1.018	1.020	3.36	3.50
671.6	2.61	2.4	0.949	0.985	0.983	3.31	3.21
665.1	2.53	2.7	0.935	0.971	0.967	3.35	3.14
670.6	2.61	1.9	1.070	1.105	1.119	3.28	4.12
675.1	2.97	1.8	1.118	1.152	1.174	3.24	4.52
675.1	2.56	1.7	1.073	1.109	1.124	3.27	4.13

Potassium data of Meyrial, Morin and Rohsenow (22), saturated
vapor.

713.9	6.82	7.3	0.559	0.590	0.560	3.17	1.26
718.0	5.42	4.9	0.592	0.624	0.596	3.14	1.38
725.7	3.49	3.1	0.554	0.586	0.557	3.11	1.26
766.9	7.88	3.9	0.547	0.577	0.548	2.94	1.17
837.0	6.88	7.1	0.144	0.155	0.140	2.68	0.22
842.5	6.00	5.6	0.148	0.158	0.143	2.66	0.23
845.4	8.79	2.6	0.392	0.416	0.387	2.65	0.69
859.4	7.40	5.2	0.164	0.175	0.158	2.61	0.25
872.0	5.20	8.4	0.066	0.071	0.063	2.56	0.09
881.1	5.23	9.2	0.056	0.060	0.054	2.54	0.08
918.4	4.84	6.1	0.055	0.059	0.053	2.43	0.07
972.0	9.02	9.4	0.043	0.046	0.041	2.29	0.05

Table IV (cont.)

Potassium data of Sawochka (23), saturated vapor.

T_V (°K)	Q/A $\left(\frac{\text{cal}}{\text{cm}^2\text{sec}}\right)$	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_0 - T_S)/(T_V - T_S)$	
			Schrage	$(\alpha=0)$	$(\alpha=1)$	$(\alpha=0)$	$(\alpha=1)$
868.7	2.34	0.9	0.262	0.279	0.256	2.57	0.42
889.8	2.31	0.8	0.220	0.234	0.214	2.51	0.33
918.7	2.06	0.6	0.209	0.223	0.203	2.43	0.30
953.7	1.82	0.4	0.236	0.251	0.229	2.33	0.34
921.5	3.63	1.3	0.168	0.179	0.162	2.42	0.24
869.3	3.63	1.4	0.246	0.262	0.239	2.57	0.39
1035.4	4.14	1.0	0.116	0.123	0.111	2.13	0.14
1034.3	4.67	1.1	0.113	0.120	0.108	2.14	0.14
981.5	5.37	1.7	0.124	0.132	0.119	2.26	0.16
943.1	5.46	2.1	0.137	0.146	0.132	2.36	0.18
910.9	6.80	2.6	0.175	0.187	0.170	2.45	0.25
1029.3	6.80	2.0	0.096	0.102	0.092	2.15	0.12
978.7	9.07	2.7	0.134	0.143	0.129	2.27	0.17
948.7	9.14	3.6	0.128	0.137	0.124	2.35	0.17
1038.7	10.86	3.5	0.084	0.089	0.080	2.13	0.10
973.7	12.91	5.3	0.104	0.111	0.099	2.28	0.13
958.7	16.85	6.0	0.133	0.142	0.128	2.32	0.18
929.3	21.96	8.2	0.161	0.171	0.155	2.41	0.22
899.8	18.69	7.6	0.189	0.201	0.183	2.49	0.27
871.5	3.30	1.0	0.304	0.323	0.298	2.57	0.49
891.5	3.12	0.9	0.279	0.297	0.273	2.50	0.44
953.7	2.29	0.6	0.168	0.179	0.163	2.33	0.23
924.3	5.12	1.1	0.262	0.278	0.255	2.41	0.39
894.3	5.79	1.8	0.242	0.258	0.236	2.50	0.37
877.6	5.92	1.8	0.280	0.298	0.274	2.55	0.44
880.9	7.25	2.2	0.274	0.292	0.268	2.54	0.43
899.3	6.86	2.0	0.246	0.262	0.240	2.48	0.37
923.7	6.48	1.9	0.200	0.213	0.193	2.41	0.29
1035.9	5.19	1.0	0.077	0.082	0.073	2.13	0.09
930.4	7.84	2.8	0.164	0.175	0.158	2.39	0.23
1033.7	10.99	3.6	0.085	0.091	0.082	2.14	0.10
981.5	11.86	4.0	0.118	0.126	0.113	2.26	0.15
957.6	12.54	4.5	0.132	0.140	0.126	2.32	0.17
1040.9	13.73	4.4	0.083	0.089	0.080	2.13	0.10
1040.9	16.41	4.0	0.108	0.114	0.103	2.13	0.13
985.4	17.84	3.7	0.180	0.191	0.173	2.25	0.24
973.1	19.94	2.8	0.271	0.288	0.264	2.28	0.38
955.9	19.05	4.2	0.207	0.221	0.201	2.33	0.29
844.8	9.37	19.2	0.074	0.079	0.071	2.64	0.11
825.9	7.99	15.5	0.093	0.101	0.090	2.71	0.14
746.5	3.41	20.9	0.088	0.095	0.084	2.96	0.14

Table IV (cont.)

Potassium data of Kroger (21), saturated vapor.

T_V (°K)	Q/A ($\frac{\text{cal}}{\text{cm}^2\text{sec}}$)	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_O - T_S)/(T_V - T_S)$	
			Schrage	($\alpha=0$)	($\alpha=1$)	($\alpha=0$)	($\alpha=1$)
840.1	2.59	1.3	0.260	0.277	0.254	2.67	0.43
841.5	4.07	2.3	0.230	0.246	0.224	2.66	0.37
884.7	2.71	1.4	0.170	0.182	0.165	2.52	0.25
892.5	5.01	2.8	0.146	0.156	0.141	2.50	0.21
922.9	3.09	2.1	0.095	0.101	0.091	2.41	0.13
912.0	3.20	1.2	0.175	0.187	0.170	2.44	0.25
940.6	3.43	3.1	0.062	0.066	0.059	2.36	0.08
977.6	3.76	2.0	0.079	0.084	0.075	2.27	0.10
980.4	7.45	4.7	0.065	0.069	0.062	2.27	0.08
702.9	3.32	3.4	0.649	0.683	0.657	3.21	1.63
705.9	6.10	5.6	0.679	0.712	0.687	3.19	1.70
728.0	3.46	3.8	0.462	0.490	0.460	3.10	0.98
763.1	6.10	6.1	0.332	0.354	0.327	2.95	0.62
759.0	3.25	2.6	0.404	0.430	0.401	2.97	0.80
820.5	3.12	2.7	0.195	0.209	0.190	2.73	0.32
932.2	2.22	1.1	0.117	0.125	0.112	2.39	0.16

Potassium data of Wilcox and Rohsenow (24), saturated vapor.

729.7	3.01	1.2	0.893	0.931	0.924	3.08	2.68
723.7	2.88	1.1	0.938	0.976	0.973	3.10	2.95
731.2	3.89	1.5	0.873	0.911	0.901	3.07	2.55
804.4	4.74	0.7	0.900	0.937	0.930	2.78	2.45
790.9	4.47	0.6	1.002	1.040	1.045	2.83	3.07
800.5	4.50	0.7	0.883	0.921	0.912	2.80	2.39
798.5	4.49	0.6	0.983	1.020	1.023	2.80	2.92
735.5	3.68	1.2	0.916	0.954	0.948	3.05	2.77
725.4	3.36	1.4	0.903	0.940	0.933	3.09	2.74
729.0	3.25	1.3	0.873	0.911	0.901	3.08	2.57
728.0	3.25	1.2	0.927	0.965	0.960	3.08	2.87
729.3	4.14	1.5	0.937	0.974	0.971	3.07	2.91
693.8	3.72	2.2	0.973	1.009	1.011	3.21	3.27
678.3	3.34	2.6	0.991	1.026	1.029	3.26	3.45
764.0	4.51	1.0	0.901	0.930	0.932	2.94	2.59
796.0	4.82	0.8	0.882	0.910	0.910	2.82	2.40
730.1	3.34	1.2	0.912	0.950	0.944	3.07	2.77
723.3	3.42	1.3	0.946	0.983	0.981	3.10	2.99
767.9	3.67	1.0	0.709	0.836	0.819	2.93	2.09
805.9	3.90	0.6	0.851	0.888	0.876	2.78	2.22
805.0	3.90	0.5	0.970	1.003	1.009	2.78	2.83
865.5	4.37	0.5	0.674	0.707	0.682	2.59	1.41

Table IV (cont.)

Sodium data of Barry (25), saturated vapor.

T_V (°K)	Q/A ($\frac{\text{cal}}{\text{cm}^2\text{sec}}$)	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_O - T_S)/(T_V - T_S)$	
			Schrage	$(\alpha=0)$	$(\alpha=1)$	$(\alpha=0)$	$(\alpha=1)$
987.0	37.15	30.0	0.099	0.107	0.095	2.72	0.15
992.0	39.33	25.6	0.114	0.123	0.110	2.72	0.17
994.3	37.67	25.5	0.107	0.116	0.103	2.71	0.16
1023.7	43.93	34.5	0.074	0.080	0.071	2.62	0.10
1037.6	42.42	33.3	0.065	0.070	0.062	2.59	0.09
1056.5	42.12	35.0	0.053	0.057	0.050	2.55	0.07
1052.0	42.12	30.6	0.061	0.066	0.058	2.56	0.08
1074.3	42.57	28.9	0.054	0.058	0.051	2.51	0.07
1089.3	43.47	25.5	0.054	0.059	0.052	2.48	0.07
1102.6	39.10	22.8	0.049	0.053	0.047	2.45	0.06
1090.4	36.39	20.6	0.055	0.059	0.052	2.48	0.07
1084.3	26.57	18.5	0.047	0.051	0.045	2.49	0.06
1090.4	34.06	23.9	0.045	0.049	0.043	2.48	0.06
1093.1	22.38	13.9	0.048	0.051	0.046	2.47	0.06
1042.6	16.20	13.3	0.055	0.059	0.052	2.59	0.08
1030.9	20.27	15.0	0.067	0.073	0.065	2.62	0.10
1019.8	20.42	11.7	0.094	0.101	0.090	2.65	0.14
1016.5	19.67	12.2	0.090	0.095	0.086	2.66	0.13
1000.4	19.21	13.3	0.094	0.101	0.090	2.70	0.14
993.1	20.64	12.8	0.111	0.120	0.107	2.72	0.17
982.6	20.34	11.1	0.137	0.148	0.133	2.75	0.21
977.0	21.17	15.0	0.116	0.124	0.111	2.77	0.18
970.9	21.32	13.3	0.137	0.147	0.132	2.79	0.21
968.5	20.42	14.4	0.128	0.138	0.124	2.80	0.20
959.8	21.25	16.7	0.125	0.135	0.121	2.81	0.20
957.0	21.55	15.0	0.143	0.154	0.138	2.82	0.23
954.3	21.55	14.4	0.152	0.163	0.147	2.83	0.24
944.3	21.85	15.0	0.165	0.177	0.160	2.86	0.27
962.0	29.76	17.8	0.150	0.171	0.154	2.81	0.25
957.0	29.23	15.6	0.183	0.197	0.178	2.83	0.30
983.1	22.30	12.8	0.132	0.141	0.127	2.75	0.20
1003.7	22.63	13.9	0.103	0.110	0.099	2.69	0.15
1032.0	26.97	15.0	0.088	0.095	0.084	2.62	0.13
1042.6	32.02	16.1	0.089	0.096	0.085	2.59	0.13
1042.0	33.68	18.3	0.084	0.090	0.080	2.59	0.12
1033.7	36.69	19.5	0.092	0.099	0.089	2.61	0.13
1030.9	38.65	17.8	0.108	0.116	0.103	2.62	0.16
1020.9	40.23	21.1	0.105	0.113	0.101	2.65	0.15
1007.0	39.18	18.3	0.131	0.141	0.126	2.69	0.20

Table IV (cont.)

Sodium data of Bakulin, Ivanovskii et al. (15), saturated vapor.

T_V (°K)	Q/A ($\frac{\text{cal}}{\text{cm}^2\text{sec}}$)	$T_V - T_S$ (°K)	Condensation Coeff.			$(T_D - T_S)/(T_V - T_S)$	
			Schrage	$(\alpha=0)$	$(\alpha=1)$	$(\alpha=0)$	$(\alpha=1)$
785.1	4.45	1.8	1.093	1.128	1.147	3.39	4.47
756.6	3.75	3.1	0.988	1.023	1.026	3.52	3.70
754.1	3.63	3.6	0.924	0.959	0.954	3.55	3.25
735.1	3.13	3.5	1.036	1.069	1.078	3.56	4.17
737.6	3.11	3.4	1.024	1.057	1.064	3.57	4.05
706.6	2.80	5.3	1.059	1.085	1.096	3.56	4.41
685.6	2.37	7.6	1.029	1.051	1.058	3.58	4.11
685.6	2.53	7.4	1.070	1.089	1.101	3.47	4.47
664.1	2.58	12.3	1.072	1.081	1.093	3.10	4.24
650.6	2.72	14.1	1.072	1.078	1.091	2.93	4.11
657.1	2.87	17.3	1.048	1.054	1.064	2.86	3.72
674.6	2.17	8.5	1.054	1.071	1.081	3.49	4.31
704.6	2.01	4.1	1.044	1.074	1.083	3.66	4.36
704.1	1.72	4.0	0.988	1.021	1.023	3.73	3.91
718.1	1.84	3.3	0.972	1.007	1.007	3.70	3.76
718.1	1.94	3.2	1.010	1.044	1.050	3.68	4.06
734.1	2.06	2.3	1.044	1.080	1.091	3.62	4.31
734.1	1.84	2.2	1.012	1.049	1.056	3.64	4.05
684.1	2.01	7.1	1.002	1.026	1.029	3.67	3.93
746.1	2.34	2.5	0.957	0.994	0.993	3.60	3.55
1172.1	4.66	1.5	0.050	0.053	0.048	2.29	0.06

Sodium data of Gahman, Sartor and Balzhiser (25), saturated vapor.

1071.5	23.51	26.7	0.033	0.036	0.032	2.51	0.04
1070.9	21.77	20.6	0.039	0.042	0.037	2.52	0.05
1068.1	21.55	18.9	0.042	0.046	0.041	2.52	0.06
1076.5	22.98	23.3	0.035	0.038	0.033	2.50	0.05
1068.1	23.51	21.7	0.041	0.044	0.039	2.52	0.06
1063.1	21.55	20.6	0.041	0.044	0.039	2.54	0.06
1070.9	23.56	23.9	0.037	0.040	0.035	2.52	0.05
1079.3	18.46	15.5	0.040	0.043	0.038	2.50	0.05
1067.6	21.93	22.2	0.037	0.040	0.036	2.52	0.05
1086.5	23.66	16.7	0.045	0.048	0.043	2.48	0.06
1108.1	32.85	28.3	0.033	0.035	0.031	2.44	0.04
1107.6	33.53	25.0	0.037	0.040	0.036	2.44	0.05
1094.3	29.76	18.9	0.047	0.051	0.045	2.47	0.06
1084.8	31.87	18.9	0.054	0.059	0.052	2.49	0.07
1082.6	28.63	20.0	0.047	0.051	0.045	2.49	0.06
1084.8	28.33	20.0	0.046	0.050	0.044	2.49	0.06
1084.8	25.62	21.7	0.039	0.042	0.037	2.49	0.05
1074.8	21.10	16.1	0.046	0.049	0.043	2.51	0.06

Table IV (cont.)

Sodium data of Misra and Bonilla (1), saturated vapor.

T_v (°K)	Q/A ($\frac{\text{cal}}{\text{cm}^2\text{sec}}$)	$T_v - T_s$ (°K)	Condensation Coeff.			$(T_o - T_s)/(T_v - T_s)$	
			Schrage	($\alpha=0$)	($\alpha=1$)	($\alpha=0$)	($\alpha=1$)
904.3	4.17	2.6	0.254	0.272	0.249	3.00	0.47
938.3	4.69	2.9	0.182	0.195	0.177	2.89	0.31
956.1	4.83	3.0	0.151	0.162	0.147	2.83	0.25
933.3	4.31	2.7	0.188	0.201	0.183	2.90	0.32
953.8	4.63	2.9	0.153	0.164	0.148	2.84	0.25
975.1	4.79	3.0	0.126	0.135	0.122	2.77	0.20
1033.1	4.95	3.1	0.073	0.078	0.070	2.61	0.11
1059.1	5.17	3.2	0.059	0.064	0.057	2.54	0.08
1071.3	5.26	3.4	0.052	0.055	0.049	2.51	0.07
1086.7	5.49	3.3	0.050	0.053	0.047	2.48	0.07
1098.1	5.58	3.4	0.045	0.048	0.043	2.45	0.06
1113.1	5.80	3.5	0.041	0.044	0.039	2.42	0.05
1125.1	5.98	3.6	0.038	0.040	0.036	2.39	0.05
1141.5	6.34	3.7	0.034	0.036	0.032	2.35	0.04
960.3	4.45	2.7	0.148	0.159	0.144	2.82	0.24
973.1	4.71	3.0	0.125	0.135	0.121	2.78	0.20
993.9	4.93	3.2	0.103	0.110	0.099	2.72	0.16
1016.5	5.22	3.2	0.086	0.092	0.083	2.66	0.13
1040.9	5.72	3.4	0.074	0.079	0.071	2.59	0.11
1084.9	6.07	3.5	0.053	0.057	0.051	2.48	0.07
1099.1	6.53	3.9	0.045	0.049	0.043	2.45	0.06
1115.3	6.75	3.7	0.044	0.047	0.042	2.41	0.06
1129.6	7.14	3.8	0.041	0.044	0.039	2.38	0.05
1139.1	7.40	3.9	0.039	0.041	0.037	2.36	0.05
973.6	4.70	2.9	0.130	0.140	0.126	2.78	0.21
998.1	5.35	3.2	0.106	0.114	0.103	2.71	0.16
1053.1	5.76	3.3	0.068	0.073	0.065	2.56	0.10
1101.9	5.92	3.9	0.040	0.043	0.039	2.44	0.05
1126.9	6.20	3.7	0.037	0.040	0.035	2.39	0.05
1133.1	6.32	4.1	0.033	0.036	0.032	2.37	0.04
1080.4	6.46	4.0	0.051	0.054	0.048	2.49	0.07
1108.1	6.78	4.4	0.040	0.043	0.038	2.43	0.05
1135.3	7.12	4.6	0.033	0.035	0.031	2.37	0.04

III.5.- Evaporation.

Equations 7, 8 and boundary conditions 9 apply to the steady-state evaporation from a liquid surface. In the expansion of the solution in a series of exponential terms (equations 10) the exponents are given by the negative root of equation 11. Because G , $\bar{u}$ and $\bar{c}$ are positive, this root is very large, and, for small vapor velocities, the exponents are approximately equal to:

$$-\frac{5}{9} \frac{n P_v x}{\mu_v \bar{u}_v} = -\frac{5\sqrt{\pi}}{12} \frac{n x}{\lambda \bar{c}_v} \quad (26)$$

Departures from the bulk vapor conditions would then die out over distances from the interface much smaller than the mean free path λ , with these distances decreasing for smaller evaporation rates. The thirteen-moment approximation is not valid over such small distances, and the only consistent solution is given by constant vapor conditions up to the vapor-liquid interface (i.e., $u_1 = 0$ in equations 12), as in the solution to Navier-Stokes' equations for this situation:

$$\bar{u} = u_v \quad (27a)$$

$$P = P_v \quad (27b)$$

$$T = T_v \quad (27c)$$

$$p = 0 \quad (27d)$$

$$S = 0 \quad (27e)$$

Boundary conditions 18 and 19 give with this solution two relationships (equations 28 and 29) between the evaporation rate, liquid surface temperature, vapor pressure, and the temperature and pressure of the vapor, which constitute the complete description of the evaporation process.

$$2 \xi_v \sqrt{\pi} (1-c) [1 - \Phi(\xi_v)] + c e^{-\xi_v^2} = \quad (28)$$

$$= \frac{P_s}{P_v} \sqrt{\frac{T_v}{T_s}} (1 - \xi_s \sqrt{\pi}) \left[\bar{v} + \alpha (1 - \bar{v}) \left[e^{-\xi_v^2} - \xi_v \sqrt{\pi} [1 - \Phi(\xi_v)] \right] \right] \frac{P_v}{P_s} \sqrt{\frac{T_s}{T_v}}$$

$$\xi_v \frac{\sqrt{\pi}}{2} (5 + 8 \xi_v^2) [1 - \Phi(\xi_v)] + c \left[\left(1 + \frac{7}{2} \xi_v^2 \right) e^{-\xi_v^2} - \right. \\ \left. - \xi_v \frac{\sqrt{\pi}}{2} (5 + 8 \xi_v^2) [1 - \Phi(\xi_v)] - 3 \xi_v^2 e^{-\xi_v^2} \right] = \quad (29)$$

$$= \frac{P_s}{P_v} \sqrt{\frac{T_s}{T_v}} \left[1 - \xi_s \frac{\sqrt{\pi}}{4} (5 + 2 \xi_s^2) + \frac{3}{2} \xi_s^2 \right] \left[\bar{v} + \right. \\ \left. + \alpha (1 - \bar{v}) \left[e^{-\xi_v^2} - \xi_v \sqrt{\pi} [1 - \Phi(\xi_v)] \right] \right] \frac{P_v}{P_s} \sqrt{\frac{T_s}{T_v}}$$

It should be noted that there is implied in these equations an extra relationship (because of the absence of the unknown u_1) for evaporation when compared with condensation. This is necessary because during condensation the pressure of the vapor far from the liquid surface is an independent variable while in evaporation that pressure is determined only by evaporation rate and liquid surface temperature, and the added relationship serves to solve for it.

A sample calculation for the steady-state evaporation of liquid metals (taken as monoatomic) assuming a condensation coefficient of unity and a heat flux of 10,000 Btu/hr.ft² supplied to the liquid is shown in Table V for a variable liquid surface temperature. In the numerical calculations, P_s was taken as the thermodynamic equilibrium vapor pressure of the liquid at the temperature T_s . If it is assumed that the Poynting effect correction can be applied when the total pressure over the liquid is lower than the vapor pressure, essentially the same results are obtained.

Table V. - Evaporation of liquid metals with a heat flux of 10,000 Btu/hr.ft², condensation coefficient of unity (monoatomic vapor).

	T_s (°K)	P_s (atm)	$T_s - T_v$ (°K)	$100 \times \frac{P_s - P_v}{P_s}$	Vapor Subcooling (°K)
Mercury	450.0	0.010	1.98	1.98	1.43
	475.0	0.024	0.92	0.87	0.65
	500.0	0.052	0.46	0.42	0.32
	525.0	0.103	0.25	0.21	0.17
	550.0	0.192	0.14	0.12	0.09
	575.0	0.339	0.09	0.07	0.06
	600.0	0.570	0.06	0.04	0.03
	625.0	0.918	0.04	0.03	0.02
	650.0	1.424	0.03	0.02	0.01
	650.0	0.003	3.61	2.49	2.57
Potassium	675.0	0.006	2.14	1.42	1.50
	700.0	0.010	1.32	0.85	0.91
	725.0	0.016	0.85	0.53	0.57
	750.0	0.026	0.56	0.34	0.37
	775.0	0.040	0.38	0.22	0.25
	800.0	0.061	0.27	0.15	0.17
	825.0	0.089	0.19	0.11	0.12
	850.0	0.127	0.14	0.08	0.09
	875.0	0.178	0.11	0.05	0.07
	900.0	0.245	0.08	0.04	0.05
	925.0	0.331	0.06	0.03	0.04
	950.0	0.440	0.05	0.02	0.03
	975.0	0.576	0.04	0.02	0.02
	1000.0	0.743	0.03	0.01	0.02
	1025.0	0.947	0.03	0.01	0.01
	1050.0	1.192	0.02	0.01	0.01
Sodium	750.0	0.003	2.73	1.64	1.98
	775.0	0.006	1.68	0.98	1.21
	800.0	0.009	1.07	0.60	0.76
	825.0	0.015	0.71	0.38	0.49
	850.0	0.023	0.48	0.25	0.33
	875.0	0.035	0.23	0.17	0.22
	900.0	0.051	0.23	0.12	0.16
	925.0	0.074	0.17	0.08	0.11
	950.0	0.104	0.12	0.06	0.08
	975.0	0.145	0.09	0.04	0.06
	1000.0	0.198	0.07	0.03	0.04
	1025.0	0.266	0.06	0.02	0.03
	1050.0	0.352	0.04	0.02	0.03
	1075.0	0.461	0.03	0.01	0.02
	1100.0	0.595	0.03	0.01	0.02
	1125.0	0.760	0.02	0.01	0.01
	1150.0	0.959	0.02	0.01	0.01
	1175.0	1.199	0.02	0.01	0.01

The results show, as expected, that the temperature and pressure of the vapor are lower than the temperature of the liquid surface and its vapor pressure at this temperature, respectively. Furthermore, it was found that the vapor is slightly subcooled during steady-state evaporation from a liquid surface under these conditions.

It is also possible for the vapor to be superheated. This could happen if the condensation coefficient were very small ($\sigma \ll 1$) and the energy accommodation coefficient large (close to unity), and also depending on the slope of the vapor pressure curve of the liquid. This may be observed from first order approximations to the solution:

When the evaporation rate is small, the same relationships as during condensation (equations 7a and 7b, where ϵ_v is now positive) apply. Furthermore, the pressure and temperature of the vapor are then related by the approximations:

$$\frac{P_s - P_v}{T_s - T_v} \approx \frac{\sigma}{2} \frac{P_s}{T_s}, \quad \alpha = 0 \quad (30a)$$

$$\approx \frac{(8 - 3.5\sigma)}{\sigma} \frac{P_s}{T_s}, \quad \alpha = 1 \quad (30b)$$

These results are presented as an illustration of the order of magnitude of the kinetic effects at the interface during evaporation, and no attempt has been made to answer the question posed before about the pressure of the vapor in condensation experiments with a combination boiler-condenser system. To solve the bubble-growth problem, the present analysis could be repeated for a spherical geometry under unsteady-state conditions, including heat transfer and liquid and vapor dynamics as done by Bornhorst and Hatsopoulos (40) for their kinetic expression.

III.6. - Heat transfer from the vapor to the liquid.

Consider a monoatomic liquid in contact with its pure vapor in a container with a heated top and a cooled bottom, so that heat flows from the vapor to the liquid as shown in figure 8.

Neglecting gravitational effects, Grad's equations (38) reduce in this situation to:

$$\bar{u} = 0 \quad (31a)$$

$$p = 0 \quad (31b)$$

$$P = \text{constant} \quad (31c)$$

$$S = \text{constant} \quad (31d)$$

$$\mu_v R' \frac{dT}{dx} = - \frac{2}{15} S \quad (31e)$$

The temperature difference between the vapor at the interface and the liquid surface was calculated with boundary condition 19 as a function of the heat flux [represented by $\lambda \frac{dT}{dx}|_{x=0}$ = temperature drop over one mean free path of the vapor molecules at the interface] as:

$$T_0 - T_s = \frac{5}{4} \left(\frac{2-c}{c} \right) \lambda \frac{dT}{dx} \Big|_{x=0} \quad (32)$$

where $c = \bar{v} + \alpha - \bar{v}\alpha$.

This result is identical to the temperature jump obtained by other investigators (e.g., reference 41) for the case of heat transfer between a gas and a reflecting wall (corresponding to $\bar{v} = 0$), lending additional support to the present approach.

Figure 8.- Schematic set-up for heat transfer between vapor and liquid.

Only when the condensation coefficient is different from zero boundary condition 18 yields an additional equation, allowing the calculation of the pressure of the vapor over the liquid as:

$$P = P_s \sqrt{\frac{T_o}{T_s}}, \quad \sigma \neq 0 \quad (33)$$

The calculated temperature profile is shown schematically in figure 9, and although the pressure of the vapor predicted by equation 33 is higher than the vapor pressure of the liquid at the temperature T_s , the temperature jump at the vapor-liquid interface is such that the vapor is always superheated throughout.

Figure 9.- Temperature profile predicted during heat transfer between a pure monoatomic vapor and its liquid.

IV. - Interphase Transport Between a Dimerizing Vapor and its Liquid.

IV.1. - General.

Investigations of condensation and evaporation mechanisms of complex or dissociating molecules are few and often conflicting as shown in general reviews of the subject (e.g., references 28, 34, 42). Experimental methods to date apparently reduce to vacuum evaporation techniques which are applicable only at low pressures. Apart from the more recent application of mass spectrometry to the direct determination of the evaporating species, measurements have traditionally consisted of the rate of weight loss and recoil pressure of samples placed under high vacuum, followed by the calculation of a mean molecular weight of the molecules emitted by the surface and an apparent evaporation coefficient by equations given by kinetic theory of gases for free molecular flow.

Substances which have a vapor phase of different chemical composition than the condensed phase (such as alumina, aluminum and boron nitrides, ammonium chloride) are reported to have very small apparent evaporation coefficients.

Experiments with one-component materials which can undergo polymerization reactions are scarce, reducing to the vacuum evaporation of some solids. Small apparent condensation coefficients have sometimes been found in this case, along with reported differences in the evaporation rates of the different species. Of special interest are the following: Solid selenium reportedly evaporates as Se_2 and Se_6 with an apparent evaporation coefficient close to unity, and in proportions corresponding to the composition of the saturated vapor. Solid arsenic and red phosphorus have been reported to evaporate with low apparent condensation coefficients as

dimer (As_2 and P_2 , respectively) or a mixture of dimer-tetramer by some investigators, while others report that they evaporate as tetramer (As_4 and P_4), which is the main species present in their equilibrium vapors. Graphite has been reported to evaporate as C , C_2 and C_3 with low (and different) evaporation coefficients for each species.

Outside the molecular flow region some evaporating molecules are expected to be reflected back into the condensed phase after colliding with other vapor molecules. Interphase processes with multicomponents vapors have then in general been analyzed with Schrage's (16) theory writing equation 2 for each component in terms of partial pressures and temperature at the vapor-liquid interface, with diffusion equations describing the composition of the vapor, as done by Wilcox and Rohsenow (24) in their analysis of condensation in the presence of noncondensable gases.

One problem evident in these treatments is the lack of equations to solve for all the unknowns in the processes, and the need to make additional assumptions to compensate for it.

Condensation in the presence of a certain (fixed) amount of a noncondensable gas clearly illustrates this point: The physical process is completely determined once the temperature and pressure of the bulk of the vapor, the liquid surface temperature and the amount of noncondensable are specified. The only information provided by Schrage's equation when applied to the noncondensable (which would have a condensation coefficient equal to zero) is that its net velocity at the interface is zero (i.e., it behaves as a stagnant layer of gas through which the condensing vapor must diffuse). By applying Schrage's equation to the condensing vapor at the interfacial conditions only one relationship is obtained between the two basic unknowns, condensation rate and temperature of the vapor at the interface (since partial pressures are related by diffusion equations to the condensation rate

and the total amount of noncondensable). Results of the present analysis for this case are shown in Appendix D.

Previous theoretical work on reacting vapors apparently reduces to that of Subbotin et al. (31, 32) who also sought an explanation of the low apparent condensation coefficients of liquid metals at high temperature in terms of the dimer content of their vapors. Their method is similar to the one used in the present investigation for the calculation of the vapor conditions (linearized diffusion equations), with less accuracy since they did not include the temperature dependence of the reaction rate, and used an approximate form of Schrage's equation as sole boundary condition at the vapor-liquid interface, with diffusional and interfacial effects taken as additive. They considered only the possibility that dimer does not condense, obtaining discouraging results with their approximate approach.

The present treatment was based on the solution in Chapter III for pure, monoatomic vapors with some simplifying assumptions which however kept its essential characteristics. The behavior of the vapor was described in terms of linearized Navier-Stokes' equations which were solved to obtain general expressions for the temperature and composition profiles. The unknown constants in these expressions were then calculated with the boundary conditions associated with the thirteen-moment approximation for a pure gas, with small corrections to compensate for the additional degrees of freedom of the (now in general polyatomic) molecules.

In view of its possible application to the condensation of liquid metal and nitrogen tetroxide vapors, the present study concentrated on liquids whose vapors undergo a dimerization reaction of the type:

Extension of these developments to other multicomponent systems can readily be accomplished.

The interaction between the liquid surface and the vapor molecules was described in terms of condensation and energy accommodation coefficients for each species (denoted $\bar{\sigma}_1, \bar{\sigma}_2, \alpha_1, \alpha_2$ in the case of a dimerizing vapor), with identical definitions for each type of molecule as in the pure, monoatomic gas case: $\bar{\sigma}_i$ is the fraction (assumed independent of velocity and angle of incidence) of the molecules of type i striking the liquid surface that actually condense; α_i is the fraction of the reflected molecules of type i that leave the liquid surface diffusely with a mean temperature T_s , the rest being reflected specularly. Very fast equilibrium between all the degrees of freedom of the molecules was assumed, along with equality of energy accommodation coefficients for all types of molecular energies as done by Kennard (23).

The emissive properties of the liquid surface were assumed to depend only on its temperature (T_s) and were calculated by reference to the equilibrium situation, with the liquid composition at the surface assumed to be the equilibrium one. This may be justified, at least for nitrogen tetroxide, because the liquid phase reaction is very fast, with a relaxation time of 0.2×10^{-8} seconds at 10°C as given by Chardon and Theobald (43) compared with 0.2×10^{-6} seconds for the gas phase reaction at 30°C measured by Blend (44), and the liquid has essentially always the equilibrium composition.

In a more general case, the diffusion equation for the liquid could be written, and the emissive properties expressed as functions of the composition of the liquid at the surface (e.g., through Raoult's law).

With the aim of designing an experiment to determine its mechanism of condensation the analyses were applied to nitro-

gen tetroxide in the simple situations treated - condensation, evaporation and heat transfer between the vapor and the liquid - and the results are presented in the following sections. Since liquid nitrogen tetroxide is practically pure dimer (99.9 percent N_2O_4 at the boiling point, 45), a high condensation coefficient of dimer is probable and only the extreme case is considered in the examples (i.e., $\bar{U}_2 = 1$) along with the two possible extreme values ($\bar{U}_1 = 0$ and $\bar{U}_1 = 1$) of the condensation coefficient of monomer (NO_2).

If the liquid were pure dimer, it could be stated that the monomer molecules (NO_2) do not condense or evaporate (i.e., $\bar{U}_1 = 0$) through the following reasoning: For monomer to evaporate, dimer molecules at the liquid surface would have to dissociate into monomer prior to the evaporation. Because of the principle of microscopic reversibility, the exact reverse must take place, at least during thermodynamic equilibrium. In condensation then, two monomer molecules should meet on the surface to form dimer and thus be incorporated into the liquid. This process is unlikely, with a very low probability of occurrence.

The possible effects of other species in nitrogen tetroxide vapor were neglected in the analysis because of their small concentration (NO and O_2 less than 0.01 mole percent at the boiling point, 46).

The last section discusses the possible effects of the structure of liquid metal vapors on their condensation heat transfer, and presents results of sample calculations based on simple assumed condensation mechanisms of the dimer molecules.

IV.2. - Behavior of the vapor.

Coordinate system and notation are the same as in Chapter III (figure 6), with y_1 and y_2 representing the mole fractions of monomer and dimer respectively in the vapor. The vapor far from the liquid surface (at $x = +\infty$) is assumed to be moving with an average velocity u_v in the x-direction (negative during net condensation) and having a temperature T_v , pressure P_v and the corresponding equilibrium composition (y_{1v} , y_{2v}). Only ideal gas behavior is considered.

Since diffusional effects were expected to be more important than some other kinetic effects, Navier-Stokes equations were assumed to describe satisfactorily the behavior of the vapor. These equations give good approximations for small vapor velocities to the results presented in Chapter III.

The Navier-Stokes equations (4), neglecting the effect of composition and stress on pressure, thermal diffusion and Dufour effects, reduce to:

$$P = P_v \quad (35a)$$

$$N_1 + 2 N_2 = N \quad (35b)$$

$$N_2 - y_2 (N_1 + N_2) = - \frac{P}{R T} \frac{dy_2}{dx} \quad (35c)$$

$$k_v \frac{dT}{dx} = (N_1 C_{p1} + N_2 C_{p2})(T - T_v) + \Delta H_{dim}(N_2 - N_{2v}) \quad (35d)$$

$$\frac{dN_2}{dx} = R_2 \quad (35e)$$

where N_1 and N_2 are the molar fluxes of monomer and dimer respectively and N is a constant. R_2 is the net molar rate of production of dimer and ΔH_{dim} the enthalpy change of the dimerization reaction per mole of dimer. N_{2v} represents the

molar flux of dimer far from the liquid surface ($u_v y_{2v} P_v / RT_v$) and D the binary diffusion coefficient for the monomer-dimer mixture.

Composition was expressed in terms of the variable $Z = (1+y_2)^{-1}$ and because relatively small variations in temperature and composition (expressed in Z -units) were expected, the reaction rate was linearized around the vapor conditions far from the liquid surface, taking the form:

$$R_2 = A (Z - Z_v) - A B (T - T_v) \quad (36)$$

where $Z_v = (1+y_{2v})^{-1}$ and constant pressure is implied. B can be calculated by the requirement that at equilibrium the net rate of production of dimer be zero, yielding through a thermodynamic reasoning:

$$B = - \frac{\Delta H_{dim}}{R T_v^2} Z_v (1 - Z_v) (2Z_v - 1) \quad (37)$$

Introducing a new variable V defined by equation 38c, equations 35 reduce to:

$$A (Z - Z_v) - A B (T - T_v) = - N \frac{dZ}{dx} - \frac{PD}{RT} \frac{dV}{dx} \quad (38a)$$

$$k_v \frac{dT}{dx} = (N_1 C_{p1} + N_2 C_{p2}) (T - T_v) - \Delta H_{dim} [N (Z - Z_v) + \frac{PD}{RT} V] \quad (38b)$$

$$\frac{dZ}{dx} = - VZ \quad (38c)$$

As a good approximation, which still preserves the basic properties of the differential equations, equation 39c was used instead of 38c. Furthermore, it was assumed that the term $N_1 C_{p1} + N_2 C_{p2}$ could be approximated by an average value [the arithmetic average between the values at $x=0$ and $x=\infty$ was used in the actual calculations], denoted (NC_p) .

Assuming constant physical properties, the system of equations 38 takes the approximate linearized form:

$$- N \frac{d\theta}{dx} - \frac{PD}{RT_v} \frac{dv}{dx} = A\theta - AB\tau \quad (39a)$$

$$k_v \frac{d\tau}{dx} = (NC_p)\tau - \Delta H_{dim} [N\theta + \frac{PD}{RT_v} v] \quad (39b)$$

$$\frac{d\theta}{dx} = -Z_v v \quad (39c)$$

with boundary conditions:

$$\theta(x = \infty) = 0 \quad (40a)$$

$$\tau(x = \infty) = 0 \quad (40b)$$

$$v(x = \infty) = 0 \quad (40c)$$

where $\theta = Z - Z_v$ and $\tau = T - T_v$.

Taking the Laplace transform of equations 39, the following are obtained:

$$s \bar{v} - v_o = \frac{NRT_v Z_v}{PD} \bar{v} - \frac{ART_v}{PD} [\bar{\theta} - B \bar{\tau}] \quad (41a)$$

$$s \bar{\tau} - \tau_o = \frac{(NC_p)}{k_v} \bar{\tau} - \frac{\Delta H_{dim}}{k_v} [N \bar{\theta} + \frac{PD}{RT_v} \bar{v}] \quad (41b)$$

$$s \bar{\theta} - \theta_o = -Z_v \bar{v}$$

where a bar (̄) denotes the transform of a function and the subscript 'o' the value of the function at $x = 0$.

The transform of the function τ giving the temperature profile in the vapor can be obtained from equations 41 as:

$$\bar{\tau} = \frac{\varphi(s)}{F(s)} \quad (42)$$

with the functions $\varphi(s)$ and $F(s)$ given by equations 43 and 44.

$$\begin{aligned}
\varphi(s) = & \tau_o s^2 - \left[\frac{NRT_v Z_v}{PD} \tau_o + \frac{N\Delta H_{dim}}{k_v} \theta_o + \frac{PD\Delta H_{dim}}{RT_v k_v} V_o \right] s + \\
& + \left[\frac{N^2 RT_v \Delta H_{dim} Z_v}{PD k_v} + \frac{A\Delta H_{dim}}{k_v} \right] \theta_o + \\
& + \frac{N\Delta H_{dim} Z_v}{k_v} V_o - \frac{ART_v Z_v}{PD} \tau_o
\end{aligned} \quad (43)$$

$$\begin{aligned}
F(s) = & s^3 - \left[\frac{(NC_p)}{k_v} + \frac{NRT_v Z_v}{PD} \right] s^2 + \\
& + \left[\frac{(NC_p)NRT_v Z_v}{k_v PD} - \frac{ART_v Z_v}{PD} + \frac{A\Delta H_{dim}}{k_v} \right] s + \\
& + \frac{ART_v Z_v}{k_v PD} [(NC_p) - N\Delta H_{dim}]
\end{aligned} \quad (44)$$

It should be noted that $F(s)$ depends only on the condensation rate and physical properties of the vapor (not on the boundary conditions). Denoting s_1 , s_2 and s_3 the roots of the equation $F(s) = 0$, the polynomial $F(s)$ can be expressed as in equation 45, and the general solution for the temperature profile in the vapor takes the form of equation 46.

$$F(s) = (s-s_1)(s-s_2)(s-s_3) \quad (45)$$

$$\begin{aligned}
\tau = T - T_v = & \frac{\varphi(s_1)}{(s_1-s_2)(s_1-s_3)} e^{s_1 x} + \frac{\varphi(s_2)}{(s_2-s_1)(s_2-s_3)} e^{s_2 x} + \\
& + \frac{\varphi(s_3)}{(s_3-s_1)(s_3-s_2)} e^{s_3 x}
\end{aligned} \quad (46)$$

Similar expressions can be obtained for θ and V ; the expressions for τ are sufficient however for the subsequent discussion because of the linearity of equations 41.

For low vapor velocities and high reaction rates, the three roots of $F(s) = 0$ are given by approximations 47:

$$s_1 \approx \frac{G c_{p, \text{equil}}}{k_{\text{equil}}} \quad (47a)$$

$$s_2, s_3 \approx \pm \sqrt{\frac{ART_v Z_v k_{\text{equil}}}{PD k_v}} \quad (47b)$$

where $G = \rho_v u_v$ is the mass flux of the vapor, $k_{\text{equil}} = k_v - B\Delta H_{\text{dim}} PD/RT_v Z_v$ is the equilibrium thermal conductivity of the vapor and $c_{p, \text{equil}} = c_{p, v} + y_{1v} y_{2v} Z_v^3 (\Delta H_{\text{dim}})^2 / M_1 RT_v^2$ is the equilibrium heat capacity of the vapor.

IV.3.- Boundary conditions at the vapor-liquid interface.

In essence, mass balances (similar to equation 18) for monomer and dimer molecules, plus an energy balance (as in equation 19) including both classes of molecules were used as boundary conditions at the interface.

Because chemical reactions do not affect appreciably the distribution functions or the expressions for the fluxes (c.f., Hirschfelder et al., 39), equation 48 was used as the mass velocity distribution function of each component:

$$f_i = \frac{\rho_i}{(2\pi R_i T)^{3/2}} \left[1 - \frac{s_i (u - \bar{u}_i)}{2 P_i R_i T} \left[1 - \frac{(u - \bar{u}_i)^2 + v^2 + w^2}{5 R_i T} \right] \right] \cdot e^{-\frac{(u - \bar{u}_i)^2 + v^2 + w^2}{2 R_i T}} \quad (48)$$

where the subscript 'i' denotes either monomer or dimer molecules and the stress term p in equation 15 was neglected.

The average velocity $\bar{u}_i$ of component i is given by the average velocity (defined as the ratio between the net mass flux and density) less the diffusion velocity, and take the form of equations 49, which are consistent with the already made approximations.

$$\bar{u}_1 = \frac{NRTZ}{P} + \frac{2DV}{y_1} \quad (49a)$$

$$\bar{u}_2 = \frac{NRTZ}{P} - \frac{DV}{y_2} \quad (49b)$$

The term S_i is related to the heat carried by the translational motion of each type of molecule. The total heat flux due to molecular motion is given approximately by the product of the frozen thermal conductivity (k_v) and the temperature gradient, and as a simplifying assumption the heat carried by each type of molecule was taken as proportional to the product of its mole fraction times the thermal conductivity of the pure gas (k_i). The contribution of the translational motion of each type of molecule to heat transfer then yields:

$$S_i = \frac{3Ry_i k_i}{C_{v1}(y_1 k_1 + y_2 k_2)} k_v \frac{dT}{dx} \quad (50)$$

Material balances at the vapor-liquid interface give the two boundary conditions 51, analogous to equation 18, in terms of the condensation and energy accommodation coefficients of each type of molecule.

$$2\epsilon_{10}\sqrt{\pi}(1-c_1)[1-\Phi(\epsilon_{10})] + e^{-\epsilon_{10}^2} \left[c_1 - \frac{2S_{10}\epsilon_{10}}{5P_{10}\sqrt{2R_1T_0}} [c_1(1-\epsilon_{10}^2) + \epsilon_{10}^2 - 1] \right] = \quad (51)$$

$$= \frac{P_{1s}\sqrt{T_0}}{P_{10}\sqrt{T_s}} [1-\epsilon_{1s}\sqrt{\pi}] \left[\bar{u}_1 + \alpha_1(1-\bar{u}_1) \left[e^{-\epsilon_{10}^2} - \epsilon_{10}\sqrt{\pi}[1-\Phi(\epsilon_{10})] - \frac{S_{10}\epsilon_{10}}{5P_{10}\sqrt{2R_1T_0}} e^{-\epsilon_{10}^2} \right] \frac{P_{10}\sqrt{T_s}}{P_{1s}\sqrt{T_0}} \right]$$

where $\xi_{io} = \bar{u}_{io} [2R'_i T_o]^{-1/2}$, $\xi_{is} = \bar{u}_{io} [2R'_i T_s]^{-1/2}$,

$$c_i = \bar{u}_i + \alpha_i - \bar{u}_i \alpha_i$$

The subscript 'o' refers to the conditions of the vapor at the interface ($x=0$), and the subscript 'i' denotes either monomer ($i=1$) or dimer ($i=2$). When one of the components does not condense (e.g., $\bar{u}_j=0$) this boundary condition reduces to zero mean velocity at the interface for that component (i.e., $\bar{u}_{jo} = 0$).

The third boundary condition is the energy balance at the interface (as in equation 19), given by equation 52, where the molar heat capacities at constant volume were introduced to account for the internal degrees of freedom of the vapor molecules, and fast equilibrium between all degrees of freedom is assumed. This is equivalent to the assumption made by Kennard (33) of equality of accommodation coefficients for all types of molecular energies.

In the integration leading to equation 19 the square root of R' appears as divisor of both sides of the equal sign and subsequently drops out. That factor is included in equation 52 as the square root of the molecular weight ratio ($M_2/M_1 = 2$).

$$\sqrt{2} C_{v1} E_1 + C_{v2} E_2 = 0 \quad (52)$$

where:

$$\begin{aligned}
 E_i = P_{i0} \sqrt{T_0} & \left[\epsilon_{i0} \frac{\sqrt{\pi}}{2} (1-c_i) [1-\Phi(\epsilon_{i0})] (5+8\epsilon_{i0}^2) + \right. \\
 & + e^{-\epsilon_{i0}^2} [c_i (1+\frac{7}{2}\epsilon_{i0}^2) - 3\epsilon_{i0}^2] + \\
 & + \frac{s_{i0}}{5P_{i0} \sqrt{2R_i' T_0}} \left[\frac{5}{2}\sqrt{\pi} - \frac{5}{4}\sqrt{\pi} c_i [1-\Phi(\epsilon_{i0})] - \right. \\
 & - \epsilon_{i0} e^{-\epsilon_{i0}^2} [4-3\epsilon_{i0}^2-2\epsilon_{i0}^4] + \\
 & \left. \left. + \frac{c_i}{2} \epsilon_{i0} e^{-\epsilon_{i0}^2} [3-10\epsilon_{i0}^2-6\epsilon_{i0}^4] \right] \right] - \\
 & - P_{is} \sqrt{T_s} \left[1 - \frac{\sqrt{\pi}}{4} \epsilon_{is} (5+2\epsilon_{is}^2) + \frac{3}{2} \epsilon_{is}^2 \right] \left[\tilde{\sigma}_i + \right. \\
 & + \alpha_i (1-\tilde{\sigma}_i) \frac{P_{i0} \sqrt{T_s}}{P_{is} \sqrt{T_0}} \left[e^{-\epsilon_{i0}^2} - \right. \\
 & - \epsilon_{i0} \sqrt{\pi} [1-\Phi(\epsilon_{i0})] - \\
 & \left. \left. - \frac{s_{i0} \epsilon_{i0}}{5P_{i0} \sqrt{2R_i' T_0}} e^{-\epsilon_{i0}^2} \right] \right]
 \end{aligned}$$

IV.4. - Condensation.

For net condensation, the equation $F(s)=0$ has always one positive real root (denoted s_+) since N is negative. The other two roots are real and negative for small condensation rates (complex conjugate roots with negative real part can be calculated for very large N , implying an oscillatory behavior of the solution), as can be observed with approximations 47.

Boundary conditions 40 require the vanishing of the coefficient of e^{s_+x} in equation 46, and equation 53 is obtained as a constraint to be satisfied by the values of τ_0 , V_0 and θ_0 .

$$\varphi(s_+) = 0 \quad (53)$$

This equation together with boundary conditions 51 and 52 constitute four relationships that determine fully the condensation process in terms of physical properties. The vapor conditions are determined only by the three values τ_0 , V_0 and θ_0 (being the three boundary conditions required by the linear differential equations 39), with the fourth relationship serving to solve for the liquid surface temperature when the condensation rate is specified, or the condensation rate for a given liquid surface temperature, in terms of the conditions of the vapor far from the liquid surface.

It should be noted that P_{is} in equations 51 and 52 is a function of only T_s since very fast equilibrium in the liquid was assumed. In the general case, when the liquid surface composition becomes an independent variable, other relationships (such as diffusion equations for the liquid) and boundary conditions compensate for the additional unknowns.

Table VI and figures 10 and 11 show the predicted behavior of nitrogen tetroxide vapor during condensation for a net

Table VI.

Typical Predicted Behavior of Nitrogen
Tetroxide Vapor During Condensation.

T_{sat} = Saturation temperature of the vapor
 $\bar{G}_2 = 1.0$, $W = 0.00893 \text{ gr/cm}^2 \text{ sec}$

Vapor Conditions		Case	$\bar{G}_1$	α_1	$T_{sat}-T_s$ (°K)	$T_{sat}-T_o$ (°K)	T_o-T_s (°K)	$100 \times$ $(y_{2o}-y_{2v})$
$T_{sat}=293.15 \text{ } ^\circ\text{K}$ (20°C)	Saturated	1	1	-	0.005	-0.010	0.015	0.002
		2	0	1	0.120	0.083	0.037	-0.342
	$y_{2v}=0.7264$	3	0	0	0.125	0.071	0.054	-0.354
$P_v = 0.9475 \text{ atm}$	2 °K	7	1	-	0.005	-0.013	0.018	1.882
	Superheat	8	0	1	0.113	0.075	0.038	1.560
	$y_{2v}=0.7076$	9	0	0	0.118	0.061	0.057	1.547
$T_{sat}=278.15 \text{ } ^\circ\text{K}$ (5°C)	Saturated	4	1	-	0.009	-0.020	0.029	0.005
		5	0	1	0.226	0.163	0.063	-0.790
	$y_{2v}=0.7814$	6	0	0	0.231	0.145	0.086	-0.806
$P_v = 0.4505 \text{ atm}$	2 °K	10	1	-	0.009	-0.022	0.031	1.755
	Superheat	11	0	1	0.226	0.160	0.066	0.960
	$y_{2v}=0.7639$	12	0	0	0.231	0.141	0.090	0.943

Figure 10.- Typical predicted temperature profiles during condensation of saturated nitrogen tetroxide vapor.
 Conditions are listed in Table VI.
 Note the expanded scales at the interface.

Figure 11.- Typical predicted temperature profiles during condensation of superheated nitrogen tetroxide vapor.

Conditions are listed in Table VI.
Note the expanded scale at the liquid.

condensing mass flux $W = 0.00893 \text{ gr/cm}^2\text{sec}$, which is the average predicted by Nusselt's equation for condensation of saturated vapor at 20°C on a vertical plate 10 cm high at 5°C .

Cases 1 and 4 in figure 10 correspond to $\bar{\sigma}_1 = \bar{\sigma}_2 = 1$, i.e., all monomer and dimer molecules striking the liquid surface condense, when the vapor far from the condenser is saturated ($T_v = T_{\text{sat}}$ = saturation temperature of the vapor). Because of its higher diffusion velocity (due to its smaller mass) there is a slight depletion of monomer (accumulation of dimer) near the interface, with the vapor phase reaction proceeding from dimer to monomer with absorption of heat. This accounts for the temperature of the vapor in the vicinity of the liquid surface being lower than the saturation temperature (nucleation and fog formation were assumed not to occur). The temperature of the vapor at the interface (T_0) is higher than T_v due to kinetic effects as during the condensation of a pure monoatomic vapor (figure 7).

Cases 3 and 6 correspond to $\bar{\sigma}_1 = 0$, $\bar{\sigma}_2 = 1$, $\alpha_1 = 0$ (i.e., only dimer condenses, and monomer molecules are reflected specularly by the liquid surface) and because of the required dimerization reaction the temperature of the vapor close to the liquid is higher than T_v , reaching substantial levels. The sharp drop in the temperature of the vapor at the interface is caused by kinetic effects similar to those in condensation of a superheated vapor (figure 7). Because of the diffusional resistance of monomer the liquid surface temperature is much lower (relatively) than in the first cases. When monomer molecules are reflected diffusely by the surface at a temperature T_s (cases 2 and 5) the interfacial temperature is lower and accordingly the liquid surface temperature is slightly higher than for cases 3 and 6, but still much lower than for cases 1 and 4.

Figure 11 shows the effect of 2 °K superheat ($T_v - T_{\text{sat}} = 2$ °K) on the condensation of nitrogen tetroxide vapor under the same pressures and same condensation rate as in figure 10. As for the condensation of a pure, monoatomic vapor (Table III) superheat was found to have a very small effect on the temperature of the surface of the liquid. However, the surface temperature was calculated as slightly higher than during the condensation of a saturated vapor (for the same mass condensation rate), which may not be significant since it is due in part to the different properties used in the calculations (reaction rate, diffusion coefficient, composition of the bulk of the vapor). When the bulk of the vapor is substantially superheated (as in these examples) its temperature decreases steadily as it approaches the liquid, without exhibiting the extremes shown in figure 10 for the condensation of a saturated vapor. Figure 12 shows this effect more clearly, by giving the calculated temperature profiles of the vapor for different superheats when monomer is assumed not to condense.

Condensation rate was found to have a two-fold effect on the temperature profiles predicted for the condensation of saturated or only slightly superheated vapor: high rates tend to "compress" the profiles towards the liquid surface (in a fashion similar to that described by approximations 23 and 47a), and the higher amounts of reactants entering then the reaction zone per unit time make the temperature extremes larger. This is shown in figure 13 for saturated nitrogen tetroxide vapor at 20 °C and condensation rates one-half and twice those of figure 10 when monomer is assumed not to condense ($\tilde{G}_1 = 0$) and dimer is assumed to condense at the maximum rate ($\tilde{G}_2 = 1$).

Figure 12.- Calculated effect of vapor superheat on the temperature profile during condensation of nitrogen tetroxide vapor when monomer is assumed not to condense.

$$\tilde{\sigma}_1 = 0, \quad \alpha_1 = \tilde{\sigma}_2 = 1$$

$$W = 0.00893 \text{ gr/cm}^2\text{sec}$$

$$T_{\text{sat}} = 293.15^\circ\text{K} (20^\circ\text{C}) = \text{saturation temperature of the vapor.}$$

Note the expanded scale at the liquid.

Figure 13.- Typical predicted effect of condensation rate on the temperature profiles during condensation of saturated nitrogen tetroxide vapor at 20°C when monomer is assumed not to condense.

$$\alpha_1 = \sigma_1 = 0, \quad \sigma_2 = 1$$

Note the expanded scale at the liquid.

IV.5. - Evaporation.

For net evaporation, the equation $F(s)=0$ always has one real negative root since N is positive. The other two roots (denoted s_{+1} and s_{+2}) are real and positive for small condensation rates (as in approximations 47) and complex conjugate with positive real part for large N .

Boundary conditions 40 require the vanishing of the coefficients of $e^{s_{+1}x}$ and $e^{s_{+2}x}$ in equation 46, and equations 54 are two constraints that should be satisfied by ζ_0 , V_0 and θ_0 .

$$\varphi(s_{+1}) = 0 \quad (54a)$$

$$\varphi(s_{+2}) = 0 \quad (54b)$$

Equations 54 and boundary conditions 51 and 52 provide five relationships that completely determine the evaporation process. As in condensation, the vapor conditions are determined by only the three values ζ_0 , V_0 and θ_0 , with the other two relationships serving to solve, for instance, for the temperature and pressure of the vapor when the liquid surface temperature and the evaporation rate are given. It is interesting to note that the calculated pressures are always lower than the vapor pressure at the liquid surface temperature, and that apparently the present developments do not violate the laws of thermodynamics.

Table VII and figure 14 show typical results for evaporation of nitrogen tetroxide at a net mass flux $W = 0.00893$ gr/cm²sec. As for condensation, only condensation coefficients of unity for dimer are considered. Because of the high rates of the dimerization reaction in the vapor, essentially constant conditions are encountered at a very small distance

Table VII.

Typical Predicted Behavior During the Steady
State Evaporation of Nitrogen Tetroxide.

$$\bar{G}_2 = 1.0 \quad , \quad W = 0.00893 \text{ gr/cm}^2 \text{ sec}$$

Liquid Surface Conditions	Case	$\bar{G}_1$	α_1	$T_s - T_v$ (°C)	$T_s - T_o$ (°C)	$100 \times \frac{P_s - P_v}{P_s}$	$100 \times (y_{2v} - y_{2s})$	$100 \times (y_{2o} - y_{2s})$	Vapor Subcooling $T_{sat} - T_v$ (°C)
$T_s = 293.15^\circ \text{K}$ (20°C)	1	1	-	0.003	0.014	0.023	0.001	-0.001	-0.002
$P_s = 0.9475 \text{ atm}$	2	0	1	0.422	0.036	0.558	0.325	0.384	0.304
$y_{2s} = 0.7264$	3	0	0	0.439	0.054	0.579	0.338	0.397	0.316
$T_s = 278.15^\circ \text{K}$ (5°C)	4	1	-	0.007	0.028	0.046	0.001	-0.002	-0.002
$P_s = 0.4505 \text{ atm}$	5	0	1	0.954	0.063	1.129	0.708	0.844	0.738
$y_{2s} = 0.7814$	6	0	0	0.974	0.083	1.151	0.723	0.859	0.753

Figure 14.- Typical predicted temperature profiles during evaporation of nitrogen tetroxide. Conditions are listed in Table VII.

from the liquid surface as shown in the figure. For the same reason, the pressure of the vapor is not too different from the equilibrium vapor pressure at the liquid surface temperature (P_s).

When both monomer and dimer can evaporate and condense at the maximum rate ($\tilde{G}_1 = \tilde{G}_2 = 1$) the vapor far from the liquid surface is slightly superheated due to the dimerization reaction caused by the faster emission of monomer by the liquid due to its smaller mass.

When monomer does not evaporate ($\tilde{G}_1 = 0$) the vapor is substantially subcooled because of the endothermic dissociation of the dimer emitted by the liquid surface necessary to meet the equilibrium requirements in the bulk of the vapor. Nucleation and fog formation (which would eventually take place, but probably farther away from the liquid surface) were assumed not to occur.

In a situation where only monomer can be emitted by the liquid ($\tilde{G}_2 = 0$), as is thought possible for liquid metals, the vapor far from the liquid surface may be substantially superheated (depending on physical properties and the values of $\tilde{G}_1$, α_1 , and α_2) due to the exothermic dimerization reaction that would then take place in the vapor. The temperature rise of pure monoatomic liquid metal vapor allowed to react and reach equilibrium adiabatically at 1 atmosphere pressure can be calculated as 20 °C for mercury, more than 150 °C for potassium and close to 400 °C for sodium. These figures give the possible order of magnitude of these effects when it is assumed that only monomer can evaporate and that the reaction rate is so low that dimerization occurs far from the liquid surface and there is no exchange of heat between the (superheated) vapor and the liquid surface.

IV.6.- Heat transfer from the vapor to the liquid.

For the steady-state heat transfer between a heated vapor and its liquid shown in figure 8, the Navier-Stokes' equations reduce approximately to:

$$P = P_v \quad (55a)$$

$$N_1 + 2 N_2 = 0 \quad (55b)$$

$$\frac{dN_2}{dx} = R_2 \quad (55c)$$

$$N_2 = - \frac{PD}{RT(1+y_2)} \frac{dy_2}{dx} \quad (55d)$$

$$q = - k_v \frac{dT}{dx} + \Delta H_{dim} N_2 \quad (55e)$$

where P_v is a constant, q is the total heat flux (a negative constant) and k_v is the frozen thermal conductivity of the vapor.

For the sake of simplicity, and in order to obtain an asymptotic solution not including the effect of the large variation of effective thermal conductivity with temperature, the following approximations, valid for small fluxes and gradients were used:

$$\frac{dy_2}{dx} = - \left[\frac{RT}{PD} (1+y_2) \right] N_2 \quad (56a)$$

$$\frac{dN_2}{dx} = - A' (y_2 - y_{2o}^*) - A'B' (T - T_o) \quad (56b)$$

$$\frac{dT}{dx} = - \left[\frac{q}{k_v} \right] + \left[\frac{\Delta H_{dim}}{k_v} \right] N_2 \quad (56c)$$

The quantities in brackets $[]$ and the properties of the vapor were taken as constants, to be evaluated at the inter-

facial conditions ($x=0$, denoted by the subscript 'o'). The reaction rate was linearized around the interfacial conditions, with y_{2o}^* denoting the equilibrium mole fraction of dimer at P_v and temperature T_o . The constants A' and B' are related to A and B used in equation 36 by:

$$A = A' / Z^2 \quad (57a)$$

$$B = B' Z^2 \quad (57b)$$

A Laplace transform analysis of the differential equations 56 yields the temperature profile of the vapor as in equation 58, and the additional relationship 59.

$$T = T_o - \frac{1}{1+aB'} [a(y_{2o}-y_{2o}^*)(1-e^{-bx}) + \frac{q}{k_v} x] \quad (58)$$

$$\frac{B'q}{k_v} + \frac{N_{2o}b^2}{A'} = b(y_{2o}-y_{2o}^*) \quad (59)$$

where

$$a = - \frac{\Delta H_{dim} P_v D}{k_v R T_o (1+y_{2o})}, \quad b = \sqrt{- \frac{A' \Delta H_{dim} (1+aB')}{k_v a}}$$

The product $k_v(1+aB')$ is the effective thermal conductivity of the vapor (k_{eff} , which corresponds approximately to the equilibrium thermal conductivity in the case of nitrogen tetroxide because of its high dimerization rate).

In a typical experiment, the temperature of the liquid surface (T_s) and the heat flux (q) would be specified. The unknown temperature profile in the vapor and pressure over the liquid (given by T_o , P_v , N_{2o} and y_{2o} ; y_{2o}^* is a known function of T_o and P_v) can be obtained as the solution to equation 59 and boundary conditions 51 and 52. The dimensionless velocities to use in the boundary conditions are obtained by introducing $N=0$ in equations 49, yielding:

$$\xi_{10} = - \frac{N_{20}}{y_{10} P_v} [2M_1 RT_0]^{1/2} \quad (60a)$$

$$\xi_{20} = \frac{N_{20}}{y_{20} P_v} [M_1 RT_0]^{1/2} \quad (60b)$$

When component 1 does not condense (i.e., $\sigma_1=0$), boundary condition 51 reduces to $\xi_{j0}=0$, and therefore the molar fluxes of both components vanish at the surface (i.e., $N_{10} = N_{20} = 0$). In this case the temperature profile of the vapor takes the shape shown schematically in figure 15. The other equations can be used to determine the temperature at the interface (T_0) and the total pressure P_v .

When both components do not condense ($\sigma_1 = \sigma_2 = 0$) as in heat transfer to a solid wall, the temperature profile is again that shown in figure 15. However, boundary condition 51 provides no additional information and only the temperature difference $T_0 - T_s$ can be determined with equation 52 because the total pressure becomes then an independent variable.

The results of the present analysis are similar to the ones presented by Brokaw (47) for heat transfer between a reacting gas mixture and a solid wall. Apart from the method followed in the linearization of the Navier-Stokes equations, the main difference is that Brokaw used an extension of Kennard's (33) expression for the temperature jump at the wall instead of the energy balance in equation 52.

Table VIII and figure 16 show results of the analysis for heat transfer from nitrogen tetroxide vapor to liquid for a very large heat flux ($q = -0.245 \text{ cal/cm}^2 \text{ sec}$, yielding a temperature gradient in the vapor of approximately $1,000 \text{ }^\circ\text{C/cm}$ for a liquid surface temperature of $20 \text{ }^\circ\text{C}$). It can be seen that the effects of the condensation mechanism are very small due to the relatively high calculated pressure in the examples and the fast reaction rates in the vapor. T_{A0} in Table

Figure 15.- Predicted temperature profile during heat transfer between a dimerizing vapor and its liquid when one component does not condense, or heat transfer to a solid, non-catalytic wall.

Table VIII.

Typical predicted behavior during heat transfer
from nitrogen tetroxide vapor to the liquid.

T_{Ao} = Interfacial temperature obtained by
extrapolation of the asymptotic
vapor temperature profile.

y_{2o}^* = Equilibrium mole fraction of dimer
(N_2O_4) at the interfacial conditions.

$$G_2 = 1.0 \quad , \quad q = - 0.245 \text{ cal/cm}^2\text{sec}$$

Liquid Surface Conditions	Case	G_1	α_1	$T_o - T_s$ (°C)	$T_{Ao} - T_s$ (°C)	$100 \times \frac{P_v - P_s}{P_s}$	$100 \times (y_{2s} - y_{2o})$	$100 \times (y_{2o}^* - y_{2o})$
$T_s = 293.15^\circ K$ (20 °C)	1	1	-	0.002	0.001	-0.001	0.001	-0.001
$P_s = 0.9475 \text{ atm}$	2	0	1	0.025	0.415	0.531	0.380	0.419
$y_{2s} = 0.7264$	3	0	0	0.041	0.432	0.552	0.393	0.419
$T_s = 278.15^\circ K$ (5 °C)	4	1	-	0.005	0.003	-0.002	0.002	-0.002
$P_s = 0.4505 \text{ atm}$	5	0	1	0.050	1.228	1.423	1.088	1.182
$y_{2s} = 0.7814$	6	0	0	0.078	1.255	1.453	1.109	1.182

Figure 16.- Typical predicted temperature profiles during heat transfer from nitrogen tetroxide vapor to liquid. Conditions are listed in Table VIII.

VIII denotes the temperature of the vapor at the interface obtained by extrapolation to the liquid surface of the asymptotic profile far from the surface of the liquid.

It is interesting to note that when $\bar{G}_1 = \bar{G}_2 = 1$ the temperature of the vapor near the liquid surface is slightly higher than that obtained by extrapolation of the asymptotic profile ($T_0 > T_{Ao}$). This is caused by the higher condensation rate of monomer, causing its diffusion velocity towards the liquid to be higher at the interface than far from it.

IV.7. - Possible structural effects in the condensation of liquid metal vapors.

The condensation coefficients calculated with Schrage's equation (equation 2, with equal condensation and evaporation coefficients, $\bar{G}_c = \bar{G}_e = \bar{G}$) are used in this section as a standard basis of comparison with the experimental data (figure 1) with the following procedure: The temperature of the liquid surface was calculated as in section IV.4 with the conditions of the bulk of the vapor, condensation rate and assumed detailed condensation mechanisms. The liquid surface temperature was used then to calculate the condensation coefficient with Schrage's equation, assuming then liquid metal vapors to be monoatomic as in figure 1. The results are only slightly sensitive to condensation heat flux at normal operating conditions, and the condensation rates were standardized as the ones giving a value of -10^{-3} for the dimensionless velocity $\bar{G}_v$ in Schrage's equation. Only at higher values of this parameter the strongly nonlinear character of the theoretical calculations becomes noticeable.

The aim has been to find a simple mechanism that would explain the general trend of the data in figure 1. As the calculations are very sensitive to some properties of the liquid metal vapors which can only be estimated at present,

the results should not be taken as definite. The predicted trends and implications are significant however.

The vapor pressure and dimer content of liquid metal vapors shown in figures 2 and 3 were taken from the literature (Appendix B). The vapor pressure equations used are reliable, with only a small uncertainty. There is however some controversy in the literature about the composition of liquid metal vapors, specially at low pressures, with the values shown being the most recently available. They were derived (for potassium and sodium) from fits to high-temperature PVT data assuming a constant heat of dimerization.

An important property needed is the rate of the gas phase reaction. The accepted mechanism (31, 32, 48) involves the collision of three molecules, with the third body serving to remove excess energy and stabilize the diatomic molecule formed by the other two. The rate of the dimerization reaction was estimated with Tolman's technique (48), and may be expressed as: Whenever two liquid metal atoms are within 1 Angstrom of a third one, a dimer molecule is formed. This implies an efficiency factor of unity for collisions between three atoms; the contribution of dimer molecules as third bodies to the dimerization reaction was neglected because of their low concentration and their possible low efficiencies, as done by Subbotin et al. (32).

Because measurements have failed to detect other species in them, it is generally accepted that in the liquid form liquid metals are monoatomic. Liquid metal vapors contain dimer (and possibly heavier) molecules and this discussion centers upon whether or not these polyatomic molecules evaporate from such monoatomic liquids. It is possible that they do not as first suggested by Subbotin and co-workers (31, 32), i.e., during evaporation only atoms would escape from the monoatomic liquid, with the heavier molecules appearing later through a gas phase reaction between the atoms.

At thermodynamic equilibrium, if a certain species does not evaporate, it can not condense (with the principle of microscopic reversibility). It may also be assumed that this situation continues to hold during non-equilibrium conditions, and it could then be stated that polyatomic molecules may have (as an extreme case) a condensation coefficient equal to zero. The low condensation coefficients of liquid metal vapors might then be explained through the reasoning that if some molecules do not condense there would be a reaction zone at the vapor-liquid interface, and a diffusional resistance to the condensing molecules.

Some simple possibilities of such hypothesis were tested analytically since the experimental data can not be explained if both monomer and dimer condense (and evaporate) at the maximum rate. Figure 17 shows the condensation coefficients that would be calculated with Schrage's equation for the condensation of saturated vapors for such situation ($\sigma_1 = \sigma_2 = 1$). The condensation coefficients obtained increase slowly with pressure, reaching eventually values higher than unity because the heavier (dimer) molecules would not be included in Schrage's equation. It is interesting to note that at low pressure the limit is not a value of unity, but come close to 0.94 as predicted by approximations 24 for monoatomic vapors. Many points in figure 1 and data in the literature for other substances (e.g., reference 27) show condensation coefficients not equal to unity, but slightly less, which may be caused by the kinetic effects discussed in Chapter III.

Reaction rates affect only slightly the curves in figure 17, with lower rates yielding lower condensation coefficients. The effect increases with pressure and calculations for a zero reaction rate differ from those for the figure by a maximum of 0.5 percent for sodium at 1 atmosphere.

When this mechanism is analyzed for evaporation with the developments in section IV.5, subcooled vapors are predicted;

Figure 17.- Condensation coefficients of liquid metals calculated with Schrage's equation when monomer and dimer are assumed to condense at the maximum rate.

$$\tilde{v}_1 = \tilde{v}_2 = 1, \quad \epsilon_v = -0.001$$

Saturated vapor.

this is caused by their relatively low dimer content (when compared for instance with nitrogen tetroxide and the results in Table VII).

Figure 18 considers the condensation of saturated liquid metal vapors when dimer is assumed not to condense ($\tilde{\sigma}_2 = 0$) and monomer condenses at the maximum rate ($\tilde{\sigma}_1 = 1$). Only mercury is seen to present a trend that would successfully reproduce that of the liquid metal data in figure 1. For instance, by using lower efficiency factors, or in fact proportionally lower reaction rates, the higher pressure end of the curve would be lowered the most, with the low pressure end remaining at a value close to unity.

Potassium and sodium fail to agree with the trend of the experimental data, due mainly to their relatively slowly varying dimer content (figure 3) compared with the variation of the triple collision reaction rate with pressure.

Subbotin et al. (31, 32) found similar results for sodium and concluded that the condensation coefficient of dimer in sodium vapor is different from zero, at least over a range of low pressures, and that this ($\tilde{\sigma}_2 = 0$) was not then the explanation of its low condensation coefficient; the present results support their views. Because they did not consider the effect of temperature on the equilibrium and of the different approach to the problem, their results show however a much more marked effect at low pressures than the present ones.

Because of the relatively low dimer content, the energy accommodation coefficient of dimer has a very small effect on the curves in figure 18, with condensation coefficients calculated with $\alpha_2 = 1$ being slightly larger than when $\alpha_2 = 0$, with the difference becoming more evident at higher pressures when more dimer is present.

The temperature of the vapor at the interface was calculated in some cases (at the higher pressures) as lower than

Figure 18.- Condensation coefficients of liquid metals calculated with Schrage's equation when dimer is assumed not to condense.

$$\bar{C}_1 = 1, \quad \bar{C}_2 = 0, \quad \epsilon_v = -0.001$$

Saturated vapor.

the liquid surface temperature. The effect is more apparent for sodium and is caused by the endothermic dissociation of dimer required in the vapor near the interface when $\tilde{v}_2 = 0$. The heat transfer at the interface is unable to compensate for it when the dimer content of the vapor is high. In such cases, condensation in the vapor was assumed not to occur.

With this mechanism also, the vapor was calculated as substantially superheated during evaporation of potassium and sodium. Calculations with a value $\xi_v = 0.001$ yielded vapor superheats of 1 °K for potassium and 2 °K for sodium at a pressure of 1 atmosphere, which compares with differences in temperature between the bulk (saturated) vapor and the liquid surface of 0.3 °K and 0.5 °K respectively for condensation at the same conditions (with $\xi_v = -0.001$ as for figure 18).

The effects of unknown property data can be seen in the following: The potassium dimer compositions in figure 3 were calculated from the results of the compilation of Ewing et al. (49), and at low pressures they are about twice as high as the ones compiled by Lee (50). The difference is actually sufficient to make potassium vapor behave like mercury in figure 18.

However, with the property data used in the calculations, it should be concluded that for sodium and potassium the condensation coefficient of dimer must be greater than zero, at least at low pressures. Variable condensation coefficients of dimer (unity at low pressure, and decreasing with increasing temperature) and collision efficiency factors for the dimerization reaction can be fitted to obtain good agreement with figure 1. Such behavior, although possible, appears unlikely.

The analysis may be applied to heavier molecules. Tetramers (K_4 and Na_4) have been reported by some authors (49, 51) but because of their low concentration (less than 0.2 mole percent at the boiling point) they would affect the

calculated condensation coefficients significantly with only extreme assumptions.

Of many other possible mechanisms, a very promising one was analyzed theoretically: It seems in fact unlikely that the heavier dimer molecules would just be reflected by the liquid surface without really interacting with it, as implied when $\zeta_2 = 0$. Instead, the liquid surface was assumed to catalyze the dissociation of the dimer molecules striking it. In its simplest form, it was assumed that all diatomic molecules striking the liquid surface condense with the emission of a certain number (Ω) of atoms into the vapor.

One important characteristic of this mechanism is that, contrary to the assumption $\zeta_2 = 0$, it allows steady-state condensation to take place even when the dimerization reaction has zero rate.

For simplicity also, it was assumed that the atoms were emitted diffusely at the temperature of the liquid surface.

The principle of microscopic reversibility yields as implication of this mechanism the fact that whenever atoms condense a certain number of dimer molecules are emitted. In the results below it was assumed that Ω and the ratio (ω) of emitted dimers to incident atoms were constant.

This situation can be calculated readily with the same procedure as in sections IV.4 (condensation) and IV.5 (evaporation) by using in boundary conditions 51 and 52 condensation coefficients of unity for both monomer and dimer and the pressures P_{1s}^* and P_{2s}^* given below instead of the thermodynamic equilibrium pressures P_{1s} and P_{2s} respectively.

The mass balance during thermodynamic equilibrium: [evaporating mass flux of dimer] = 2ω [incident mass flux of monomer] yields:

$$\omega = \frac{P_{2s}}{\sqrt{2} P_{1s}} \quad (61)$$

The equivalent vapor pressures P_{1s}^* and P_{2s}^* are then obtained as in equations 62 from the following mass balances: [evaporating mass flux of dimer] = 2ω [incident mass flux of monomer] and [evaporating mass flux of monomer] = [mass flux of monomer emitted at equilibrium] + Ω [incident mass flux of dimer]/2, which can be evaluated by direct integration of expression 48.

$$P_{1s}^* = P_{1s} + \frac{\Omega}{\sqrt{2}} \left[e^{-\xi_{2o}^2} - \xi_{2o} \sqrt{\pi} [1 - \Phi(\xi_{2o})] - \frac{s_{2o} \xi_{2o}}{5P_{2o} \sqrt{2R_2 T_o}} e^{-\xi_{2o}^2} \right] P_{2o} \sqrt{\frac{T_s}{T_o}} - P_{2s} \quad (62a)$$

$$P_{2s}^* = P_{2s} \frac{P_{1o}}{P_{1s}} \sqrt{\frac{T_s}{T_o}} \left[e^{-\xi_{1o}^2} - \xi_{1o} \sqrt{\pi} [1 - \Phi(\xi_{1o})] - \frac{s_{1o} \xi_{1o}}{5P_{1o} \sqrt{2R_1 T_o}} e^{-\xi_{1o}^2} \right] \quad (62b)$$

Figure 19 shows the condensation coefficients that would be calculated with Schrage's equation when it is assumed that whenever one dimer molecule strikes the liquid surface it dissociates into two atoms, one of which condenses and the other is ejected back into the vapor.

Figure 20 shows the same calculations (for comparison purposes) for the case when dimer striking the liquid surface dissociate into two atoms, both of which return to the vapor. This mechanism is very unlikely actually since microscopic reversibility at equilibrium would require the exact reverse to take place, i.e., two atoms would have to strike the liquid surface at practically the same position to form a dimer that would return to the vapor.

Figure 19.- Condensation coefficients of liquid metals calculated with Schrage's equation when diatomic molecules striking the liquid surface are assumed to condense with the emission of one atom into the vapor.
Saturated vapor, $\epsilon_v = -0.001$

Figure 20.- Condensation coefficients of liquid metals calculated with Schrage's equation when dimer molecules striking the liquid surface are assumed to dissociate into two atoms which return to the vapor.

Saturated vapor, $\ell_v = -0.001$

Dimerization rate has only a small effect on figures 19 and 20, with the condensation coefficients calculated with a zero reaction rate differing from those in the figures by just a few percent at high pressures, where the effect is more evident.

Figures 19 and 20 do not in fact seem to present such a pronounced trend at high pressures as the experimental data. However, the generation of the vapor in the experiments should also be considered. During free evaporation from a liquid surface the above mechanisms predict that at low pressures the vapor of potassium and sodium would be subcooled and that at higher pressures (over about 0.1 atm for potassium and 0.01 atm for sodium) the vapor would be superheated, and significantly so. With the high dimerization rates employed (efficiency factors of unity for triple collisions) mercury vapor was calculated as subcooled at all pressures in the figures, with the superheat decreasing however at higher temperatures.

The calculated temperature effects are shown in figure 21 for the most likely case of one dimer condensing with the emission of one atom into the vapor, for an evaporation rate yielding $\epsilon_v = 0.001$. For comparison purposes, the temperature differences between the bulk of the (saturated) vapor and the liquid surface ($T_v - T_s$) calculated for condensation for the conditions of figure 19 are also shown.

The unaccounted for possible superheat of the vapors in the experiments at high pressures would be sufficient to make the described mechanism agree with the data.

The possibility that when one diatomic molecule strikes the liquid surface one (or close to one) atom condenses while another is emitted into the vapor may be justified by reasoning that when a dimer splits the two atoms produced would travel in opposite directions, with one then entering the liquid and another being ejected into the vapor. Also,

Figure 21.- Temperature effects when diatomic liquid metal molecules are assumed to condense with the emission of one atom into the vapor.

the energy requirements of this type of mechanism are low, and calculation with the heats of vaporization and heats of dimerization yielded the following: no energy is required (i.e., $\Delta H = 0$) to convert 1 g-mole of dimer into about 1 g-atom (0.93 for mercury, 1.21 for sodium and 1.32 for potassium) of pure monoatomic gas, and the rest into liquid.

V. Experimental Determination of the Condensation Mechanism of Nitrogen Tetroxide Vapor.

There are many technical problems associated with the determination of the condensation mechanism of a reacting mixture such as nitrogen tetroxide as shown by the theoretical predictions in the preceeding chapter for the simplest cases. Experiments such as measurements of vapor quality (Table VII) or temperature profiles (figure 14) during evaporation, or the temperature profiles during heat transfer from the vapor to the liquid (figure 16) would be extremely difficult because of the high accuracies required. The calculated effects are actually surprisingly small in view of the properties of nitrogen tetroxide, underscoring the need for the more accurate prediction of the interfacial effects. The magnitude of the effects that may have been expected on evaporation with some possible mechanisms is shown by the following results obtained from thermodynamic data (46) for a constant pressure of 1 atmosphere: a temperature drop of about 20 °C would be obtained if pure N_2O_4 at 300 °K were allowed to reach equilibrium adiabatically; if pure NO_2 at 300 °K were allowed to reach equilibrium the temperature would rise by more than 50 °C.

Condensation experiments were chosen in this study because they appear to be the most sensitive to the mechanism of the interaction between the vapor and liquid phases. Temperature profiles near the vapor-liquid interface were measured while film condensation of nitrogen tetroxide vapor took place on a vertical wall, and a mechanism fitted to them as in figures 10 to 13.

The designed experiment had enough sensitivity to detect whether nitrogen dioxide condenses or not, which were the two extreme possibilities in view of the liquid composition. De-

termination of energy accommodation coefficients did not seem possible because of the small effect they have on the temperature profiles in condensation.

Any temperature increase detected in the vapor near the interface would provide positive proof that monomer (NO_2) did not condense at the maximum rate. The reverse situation (a large decrease in temperature near the interface) would not be as desirable since it might be due to interfacial effects such as dimer (N_2O_4) not condensing at the maximum rate, or to contamination of the vapor with noncondensables, making the evaluation of the data more difficult.

Consideration was initially given to measurements of the density distribution near the interface by optical means (e. g., interferometry or shadowgraph methods) but they were discarded because of the impractically long optical paths calculated for adequate sensitivity.

A diagram of the apparatus is shown in figure 22. It consists of a 4 x 4 inches square stainless steel (SS 304) tube, with walls 0.125-inch thick, 18 inches high, sealed by two 0.125-inch thick heliarc-welded stainless steel plates, with the top plate inclined to avoid the possible dripping of condensed vapor on the condenser and vapor temperature probe.

Liquid was boiled at the bottom of the apparatus and the vapor condensed on a vertical aluminum plate near the top. Windows on both sides of the condenser allowed visual observation of the process. The windows cover circular openings 2 inches in diameter and consist of 3-inch diameter, 0.75-inch thick Pyrex glass plates sealed to the wall with Teflon gaskets (0.062-inch thick, 0.25-inch wide) and back-up rubber O-rings (1/16-inch nominal thickness). Tightening pressure is provided by 4-inch diameter, 0.50-inch thick machined aluminum plates held in place by 8 stainless steel threaded studs heliarc-welded to the wall of the apparatus.

The temperature profiles were determined with a movable

Figure 22.- Diagram of the apparatus.

hot-wire anemometer probe used as a resistance thermometer. Provision was also made to measure the superheat of the vapor near the condenser with the same probe. High vapor superheat is undesirable because of the decreased sensitivity of the temperature profile to the condensation mechanism (as shown by comparison of figures 10 and 11, or in figure 12).

The effect on the temperature profile of vapor drag caused by the downward liquid velocity would be small since at the location of the vapor temperature probe (near the center of the condensing plate) film thickness and local heat flux were expected to change slowly with vertical distance [after processing the data, variations of less than 5 percent per centimeter were calculated], making the temperature profiles around the probe position fairly similar considering the effect of condensation rate on simple one-dimensional flow shown in figure 13.

Condensation heat transfer data (e.g., average heat fluxes and wall temperatures) were obtained simultaneously with the temperature profile measurements for comparison with Nusselt's equation. To compensate for unknown effects, the condenser was calibrated by means of the condensation of acetone vapor, and the experiments were performed at low Reynolds numbers (i.e., low heat fluxes).

Previous work on the condensation of nitrogen tetroxide apparently reduces to the recent investigation of Kovalev et al. (52) who investigated the high pressure (0.6 to 11 atm) and high heat flux range (1 to 19 Watts/cm²) because of the possible use of dissociating liquids as thermodynamic working fluids for power generation (apart from the intrinsic value of such study). They condensed nitrogen tetroxide vapor on a horizontal tube and report fair agreement of the data with Nusselt's equation (experimental heat transfer coefficients were apparently 10 to 30 percent higher than calculated). They attributed the discrepancies to uncertainties in

the physical properties used with the theory and the formation of ripples and turbulence in the condensate film, concluding that in fact nitrogen tetroxide behaves like other fluids during condensation. The theoretical findings in the previous chapter would tend to confirm this view since the calculated effect of the interfacial phenomena on liquid surface temperature is relatively small and may not be apparent in overall condensation heat transfer data for nitrogen tetroxide.

Nitrogen tetroxide came in contact only with corrosion resistant materials in the apparatus; the main components are described next.

V.1. - Condenser.

Nitrogen tetroxide was condensed on a vertical plate 2.500 inches high and 1.500 inches wide [in the tabulated results a condenser height $L = 2.375$ inches is used, being the effective length over which heat flow was measured]. The condenser was machined from a 0.750-inch thick aluminum plate, and the condensing surface protruded through a rectangular opening near the top of one wall of the apparatus. It was bolted in place by means of 14 stainless steel threaded studs welded on 1-inch centers to the wall of the apparatus, with Teflon (0.062-inch thick, 0.25-inch wide) and back-up rubber O-ring (nominal 1/16-inch thick) gaskets providing a corrosion resistant and vacuum tight seal.

No provision was made to control heat flux directly. The use however of a constant temperature coolant supply together with high coolant flow rates (about 1.5 gallons per minute, giving the coolant temperature rise after going through the condenser as less than 0.5°C for the average operating conditions) assured having constant condensation rates and a desirable heat flux distribution.

The local condensation mass flux at the position of the

vapor temperature probe and the degree of agreement of the condensation of nitrogen tetroxide vapor with Nusselt's equation were obtained from measurements with an extended copper-nickel-copper differential thermocouple electrodeposited on the coolant side of the condensing plate as shown schematically in figure 23a. This couple was chosen because of its high electromotive power, with the relatively low thermal conductivity of nickel providing a high temperature drop across it.

In the construction of the condenser a copper cyanide strike was first electrodeposited on the aluminum base form after a double zincate treatment as described in reference 53. The thickness of the intermediate zinc deposit is negligible (estimated as between 2 and 3×10^{-6} inches, 54). Subsequent copper and nickel plating was done from conventional acid and Watts baths (53) respectively. Dimensional accuracy of the deposits was estimated as just $\pm 5\%$ due mainly to the difficulty of machining (actually, grinding) the soft copper deposits. Direct calibration of the condenser compensated for this uncertainty. By blanking-off the aluminum sides of the coolant cavity with Teflon tape, the deposits obtained were insulated from them, which would improve the accuracy of the measurements. The void (estimated as about 0.01-inch wide) left after removal of this tape was filled with epoxi cement prior to machining the deposits to their final thickness. A thin layer of nickel (about 0.002 inches) was electrodeposited on the last copper layer to protect the thermocouple against corrosion by the coolant.

Connections to the electrodeposits were made by thin enameled wires (0.010 inches diameter copper and 0.020 inches nickel) of the same materials attached by peening inside grooves cut into the deposits after electroplating approximately one half of the desired thicknesses of the layers. The lead wires were protected by thin spaghetti tubing and epoxi

- 1.- Lower copper layer (.114-inch thick)
- 2.- Nickel layer (.058-inch thick)
- 3.- Upper copper layer (.060-inch thick)

Scale 1 : 1 All measurements in inches.

Figure 23.- Schematic diagram of the condenser.

- a) Cross-section showing the Cu-Ni-Cu differential thermocouple.
- b) View from the coolant side showing the location of the leads to the thermocouple.

cement and run through small holes (with a side opening at the bottom) in the sides of the coolant cavity. The leads are distributed as shown in figure 23b around the position of the vapor temperature probe at the center of the condenser (to minimize the error in the condensation mass flux measured at that location), but not too close to interfere with each other or distort the temperature field significantly.

The condenser was calibrated prior to final assembly. First, the thermoelectric properties of the leads were correlated against temperature by measurements of the electromotive forces developed against reference junctions with the condenser immersed in a constant temperature bath. A constant heat flux calibration performed by attaching to the condenser a thick copper block heated electrically yielded unreliable results due to non-uniform contact resistances as discussed in Appendix E. Instead, the condensation of acetone was used as calibration after assembly of the apparatus. This had the added advantage of compensating for unknown hydrodynamic effects because of the similarity of the Prandtl numbers of acetone and nitrogen tetroxide.

During condensation heat flux is not uniform and decreases towards the bottom of the condenser due to the increasing thickness of the condensate film. The varying temperature gradients cause the development of electric currents within the extended thermocouple, affecting its performance. A digital computer program was written to correct for this effect and to obtain the heat flux and condensing wall temperature at any desired location in the condenser from the information supplied by the thermocouple. This program (Appendix F) solved numerically the basic equations of thermoelectricity yielding both temperature and electric potential fields in the thermocouple as described in Appendix E. The boundary conditions used were a modified form of Nusselt's equation (including interfacial resistance) at the vapor side

and a film coefficient of heat transfer at the coolant side.

The data reduction calculations showed that even with the selected location of the leads, the corrections to the heat flux measurements at the probe position due to this effect were significant (about 20 percent), and the overall uncertainty of the reported heat flux measurements is estimated as 5 percent, which compares favorably with the accuracies of other condensation experiments.

After assembling the condenser, and using the window openings, a close-fitting Teflon mask (0.062 inches thick, 0.5-inch wide) was placed around the condenser inside the apparatus, flush with the condensing surface. This prevented possible condensation on the protruding horizontal edge of the condenser and its subsequent uneven running down the vertical surface. No condensation was apparent on the Teflon mask, probably due to its low thermal conductivity.

V.2.- Temperature profile and superheat measurements.

A hot-wire anemometer probe was used as resistance thermometer in the measurements. The probe selected was Flow Corporation model B-24-ED4 and consists of two parallel platinum - 20 % iridium wires (0.10 inches long, 0.00025 inches diameter, 0.030 inches apart) individually welded to a set of four stainless steel needles which serve as supports and connecting leads. The probe body is a 0.250-inch OD stainless steel (SS 304) tube through which pass the leads to the two wires. Insulation and a corrosion resistant seal are provided by Kel-F cemented internally to the probe body.

The probe was sealed to the inclined top of the apparatus by means of a 0.25-inch Conax gland with Teflon sealant. The gland follower was modified to accept two 1/16-inch backup O-rings, one between the probe and the follower and the other between the follower and the gland body. This arrange-

ment made possibly excessive tightening of the gland unnecessary. Also, the follower was threaded to accept the probe protection tube supplied by the manufacturer, to serve as guide during insertion in the apparatus.

The gland was attached to the apparatus by a heliarc welded bellows and was designed to pivot about a horizontal axis as shown in figure 22. A screw mechanism (80 threads per inch) pushing against a plate attached to the gland assembly permitted accurate angular positioning of the probe while obtaining the temperature profile near the vapor-liquid interface. Position measurement and recording were made (with only a correction for geometric factors) with a Pickering model 7304y DC-DC LVDT (range ± 0.050 inches, 0.1 % linearity) displacement transducer arranged similarly to the micrometer screw.

Proper probe alignment was effected by visual comparison of the wires with their images reflected by the condenser wall. The probe described an arc of radius 3.35 inches, with the wire closest to the condenser reaching it at a vertical distance of 1.38 inches from the top edge of the condenser, with the probe forming then an angle of 33° with the vertical. The other wire was lower because of this angle, but the difference in mass flux for each wire was not significant (calculated as less than 0.4 percent). Variations in the local mass condensation rate over the arc described by the probe (less than 1.5° for the graphs presented later) were also negligible (less than 0.3 percent).

At the end of its travel away from the condenser, the probe dipped into liquid contained in a shallow (0.19-inch deep) stainless steel tray. The temperature measured with the probe in that position was the saturation temperature of the vapor; significant temperature gradients in the liquid were not found even when the vapor was substantially superheated. The tray was replenished intermittently with liquid (when

warranted) by running coolant through a secondary cold-finger type condenser (0.25-inch OD, 0.125-inch OD inner tube and 3-inch effective cooled length) located so as to drip condensate on it.

The temperature profile in the vapor was not obtained directly. Instead, the difference in temperature (actually, resistance) between the two platinum alloy wires with one trailing the other in the vapor was determined as a function of their distance from the liquid surface. From such information the temperature profile can be reconstructed, and with this procedure an average temperature profile was obtained, cancelling the effects of possible fluctuations of the temperature of the vapor caused by uneven boiling.

The electrical circuit for the measurements is in a three-legged Kelvin bridge configuration, with the probe wires in separate legs of the bridge as shown in figure 24. For maximum sensitivity (i.e., to minimize self-heating of the wires by the electric current) the resistors in the fixed leg are in a 1 : 1 ratio, and their resistance (23.87 ohms) is approximately equal to that of the wires. The bridge resistors are precision, wire-wound in a series-parallel arrangement and include as main components two Amphenol model No. 205 10-turn potentiometers (2.9 ohms nominal resistance, 0.1 % linearity) and two Helipot 100 ohm, 10-turn potentiometers for fine adjustment. Mercury batteries (Mallory, 1.35 Volt, type RM-4-R) were used to provide a stable bridge voltage. A Keithley, model 150B microvolt-ammeter (with $0.3 \mu\text{V}$ full scale sensitivity, 2 percent accuracy, 10^6 ohms internal resistance) and suitably connected to the bridge through a low-noise rotary switch (Leeds & Northrup model No. 01-02-00-01) was used as both null detector and voltmeter in the measurements.

The bridge was housed in a heavy aluminum box (sides 0.25-inch thick) providing shielding and temperature equali-

S_1 , S_2 = Sensor wires, represented as:

A , B , C = Switch-selectable points
for voltage measurements

Figure 24.- Schematic diagram of the electrical circuit used in the temperature profile measurements.

zation for the components to minimize noise pick-up and thermoelectric effects. For the same reason, special Keithley low noise solder and pure copper wires were used throughout.

The supporting needles of the sensing wires are each connected to two identical copper leads (which would be used as current and potential leads in a general application) and were connected as shown in the diagram to minimize the effects of lead resistance and temperature gradients in them.

During the measurements the probe legs of the bridge were balanced against the fixed resistors (and each other) while far from the condenser (where the temperature of the two wires can be taken as equal). The bridge unbalance (voltage between A and B in figure 24) measured with the microvoltmeter across the legs with the sensing wires was a direct measure of the difference in temperature between the wires. Connection of the output of the displacement transducer and the calibrated recorder output of the microvoltmeter to an x-y recorder provided the temperature profile.

The design had a sensitivity of better than 0.01°C with a small current (typically 0.2 mA) resulting in less than 0.01°C of temperature rise of the wires by self-heating (as calculated with standard correlations, 55) during the experiments. The temperature coefficient of resistance of the probe wires was obtained by an in-place calibration as described in Appendix E.

V.3.- Boiler section and vapor temperature control.

Vapor was generated in the apparatus by heating electrically the bottom plate on which liquid was collected. To prevent some possible interference with the temperature profile measurements, direct current provided by a power supply was used. The heater consisted of 4 feet of 21-gauge nichrome wire wound on a mica form in a flat zig-zag pattern covering

a 3 x 3 inches square, with electrical insulation provided by oversize mica sheets at each side of the winding. It was held against the bottom of the apparatus by two welded threaded studs and a 3.75 x 3.75 inches aluminum pressure plate, 0.25-inch thick.

The heater was protected by a leak-proof aluminum form cemented to the sides of the apparatus, with the electrical leads running through a copper tube cemented to this enclosure.

During any one run, the electrical power to the heater was held constant. This, together with the constancy of the coolant temperature does not however assure the constancy of the vapor temperature because instabilities or uneven boiling may develop. The most common method of control of the vapor conditions is the use of a large volume of cover gas over an auxiliary condenser connected to the boiler-condenser system. The large volume and low inertia of the cover gas provide positive control of the pressure in the system by letting the level of the condensation ring in the auxiliary condenser (and therefore the condenser area) fluctuate with variations in the vapor supply.

A cover gas was not used in the present experiments because of possible contamination of the vapor by it (either by diffusion through the vapor or by being carried to the boiler dissolved in the condensate at the auxiliary condenser), acting then as a noncondensable gas and greatly affecting the phenomena to be studied. Instead, the apparatus was submerged for about 10 inches in a constant temperature bath, and the power to the boiler adjusted to make the temperature of the vapor slightly higher than that of the bath. The walls of the apparatus would act as an auxiliary condenser with large area, necessitating small temperature differences to operate effectively and dampen the temperature fluctuations. This arrangement worked satisfactorily for the condensation of acetone.

It was however practically impossible to obtain saturated vapor during the nitrogen tetroxide experiments, perhaps due to interfacial effects during evaporation.

The auxiliary condenser in figure 22 has a 7.5 inches cooled length and consisted of a thin-walled stainless steel (SS 316) tube (0.625-inch OD, 0.028-inch wall thickness) welded to the apparatus. It was surrounded by a 0.875-inch OD jacket through which coolant was run and was used during charging and to rid the equipment of noncondensables.

V.4.- Miscellaneous and operation.

The coolant consisted of water-ethylene glycol anti-freeze mixture (Prestone, manufactured by Union Carbide Corporation) maintained in an insulated four-gallon metal container, with the expansion coil of a refrigeration unit of about 600 Watts cooling capacity being submerged in the liquid. Centrifugal pumps were used to circulate coolant to the different pieces of equipment (condenser, cold-finger-type secondary condenser, auxiliary condenser and cooling coil for the bath where the apparatus was submerged) as shown in figure 25.

During a run the refrigeration unit was operated continuously at reduced capacity by adjusting the setting of the expansion valve, so as to have only a small drift of temperature with time (about 1 °C every 10 minutes typically). The use of immersion-type electric heaters with a temperature controller was contemplated initially to maintain the coolant temperature constant while operating the unit at optimum capacity. This refinement was found unwarranted during actual operation because of the large thermal inertia of the cooling system and the speed of the measurements. Another factor in the decision was the desire to use as little electrical equipment as possible to avoid noise pick-up by the bridge

Figure 25.- Schematic diagram of the hydraulic circuit.

instrumentation.

The liquid bath where the apparatus was submerged had a capacity of 4 gallons and was fitted with a stirrer, a cooling coil (0.25-inch OD copper tubing, 8 feet long) through which coolant was run and electric immersion heaters (200 Watts capacity). With a constant flow of coolant through the coil, the bath temperature was held at the desired level ($\pm 0.05^{\circ}\text{C}$) by varying the power to the heaters with a Brookstat automatic temperature controller (thermometer pick-up type). Fiberfrax insulation was placed on the exposed low temperature surfaces to decrease the load on the refrigeration unit.

Temperature measurements were performed with sheathed, 0.062-inch OD copper-constantan thermocouples as shown in figure 22. Two such thermocouples (with grounded measuring junctions) were located in the coolant cavity to determine average coolant temperatures at the top and bottom of the condenser. One ungrounded thermocouple, sealed by means of a 1/16-inch Conax gland with Teflon sealant welded to the apparatus was used to measure the vapor temperature.

Electromotive force measurements were made with a Leeds & Northrup type K2 potentiometer, with a Keithley, model 150A microvolt-ammeter ($1/\mu\text{V}$ full-scale sensitivity) used as null detector.

Prior to assembly of the condenser, the stainless steel and Teflon parts of the apparatus were degreased with trichloro ethylene followed by rinsing with acetone and distilled water, followed by a final cleaning with concentrated nitric acid and distilled water rinse. The condenser was degreased with trichloro ethylene followed by acetone and water rinses, then cleaned with Alconox detergent and rinsed with distilled water. After assembly, the apparatus was again degreased with trichloro ethylene followed by several rinses with spectrophotometric grade acetone.

Spectrophotometric grade acetone manufactured by the J.T. Baker Chemical Co. was used in the acetone tests. About 8 ounces of acetone were charged by suction into the previously evacuated apparatus through a 0.25-inch stainless steel tube connected to the main valve. After the tests, the main valve was dismantled. This allowed the introduction of a long thin-walled 0.062-inch OD stainless steel capillary into the apparatus and the elimination by suction of most of the acetone (and possibly impurities) collected on the bottom plate. The remaining acetone was eliminated by evacuation.

Nitrogen tetroxide supplied by The Matheson Company (99.9⁺ percent purity, with 600 parts per million of water as main contaminant) was used in the condensation experiments. Nitrogen tetroxide was charged into the apparatus with the following procedure: With the apparatus first evacuated to a vacuum better than 10 μ Hg nitrogen tetroxide vapor distilled off the supply cylinder (with gentle heating with an electric heating tape) was condensed in the apparatus with all coolant lines running at full capacity. The vapor passed first through a 0.5-inch ID stainless steel tube, 14 inches long, packed with phosphorous pentoxide used as desiccant (56). Further drying was accomplished in a second stainless steel tube, 0.75-inch ID, 16 inches long, packed with Dryerite desiccant. The operation was stopped after 3.5 hours when 1 pound of nitrogen tetroxide was charged into the apparatus as determined by the weight loss of the supply cylinder.

The thermocouple circuits were built with special care because of the small temperature differences expected during the measurements. Individual thermocouple cold junctions were made by twisting together and soft soldering the thermocouple wires and copper leads, and placing the junction inside a glass tube filled with mercury to a depth of 1 inch and covered with silicone oil for an additional 1 inch to prevent absorption of moisture. The cold junctions were placed in a

deep Dewar flask containing a mixture of crushed ice (0.25-inch average size) and water, with an immersion length of about 6 inches, as recommended in the literature (57).

The operation of the equipment entailed supplying ice to the thermocouple cold junctions, turning the refrigeration unit and pumps on, and waiting until the desired operating temperature levels were reached, which usually took about 40 minutes.

The condensation measurements were performed speedily since only measurements with the potentiometer were involved. The superheat measurements took the longest because they involved the setting of bridge current, balancing of the bridge, and measuring and recording the bridge unbalance corresponding to the saturation temperature. Also, for high vapor superheats, the superheat often showed fluctuations, making the determinations unreliable. Another factor in this respect was the effect of the colder liquid tray on the temperature of the vapor. Specially at low condensation rates and high superheat a continuous temperature variation was found in the vapor along the travel of the temperature probe, preventing the accurate determination of the superheat.

Film condensation took place readily in the equipment with both acetone and nitrogen tetroxide, as soon as the coolant supply was turned on. Noncondensables were evident after initial charge of the equipment and also after overnight shut down. Noncondensables were removed by running coolant through the auxiliary condenser and cracking open the main valve connected to a vacuum pump. The sudden increase in condensation heat flux observed by Misra and Bonilla (1) was evident then.

For most reported runs actually, possible noncondensables were eliminated continuously by bleeding through the auxiliary condenser a small amount of gas from the apparatus, as regulated with a needle valve connected in series with the vacuum supply.

V.5. - Results and discussion.

Details of the data reduction procedure are presented in Appendix E. In summary, a digital computer program was used to find the Seebeck coefficient of the nickel deposit consistent with the electromotive force measurements during the condensation of acetone, assuming that Nusselt's equation applied exactly. The results showed a rather large scatter (common to all condensation experiments) and the calculated values for the best runs (i.e., those yielding the highest condensation heat transfer coefficients, indicating the least possible effect of noncondensables) were averaged to obtain the Seebeck coefficient. This coefficient was used in the reduction of the nitrogen tetroxide data, by finding then, with essentially the same digital computer program the factor C defined below, equal to the ratio between the actual heat flux and that predicted by Nusselt's equation, consistent with the measurements. Since in the calculations interfacial effects were considered (at least approximately) values of C different from unity are due mainly to effects (hydrodynamic or otherwise) in the liquid film (in the absence of noncondensables).

$$C = \frac{Q/A}{\frac{2}{3} \sqrt{2} \left[\frac{\rho_L^2 g \Delta H_{\text{vap}}^*}{L \mu_L} \right]^{1/4} k_L^{3/4} (T_s - T_w)^{3/4}} \quad (63)$$

where ΔH_{vap}^* is the heat of vaporization corrected for liquid subcooling, and the average temperature between the liquid surface and the wall is used.

For comparison purposes, the same calculation of C was applied to both the acetone and nitrogen tetroxide data. Experimental data and results are presented in Tables IX and X,

and in figures 26 and 27.

In the tables, Δemf_{31} is the electromotive force developed across the nickel deposit as measured with the copper leads; t_{32}^* is the temperature calculated from the electromotive force measured between a copper lead and a nickel lead (connected through a cold junction at the ice point to the potentiometer) using the calibration of the nickel leads only (i.e., before correction as described in Appendix E for the different thermoelectric properties of the nickel deposit or electric currents developed); the coolant temperature listed is the average of the measurements with the two coolant thermocouples.

More figures are presented in the tables than the absolute accuracy of the data warrant. Temperatures were measured with the thermocouples to an accuracy of $\pm 0.05^\circ\text{C}$ (sensitivity of 0.01°C). Superheat could be measured (considering the accuracy of the wire resistance calibration and the instrumentation) to an accuracy of ± 7 percent, while fluctuations in its value during some measurements made its uncertainty much higher; consequently, data for high superheats are not very reliable. The electromotive forces Δemf_{31} were measured with the potentiometer to an accuracy of $\pm 0.2\mu\text{V}$ and sensitivity of $0.1\mu\text{V}$. Runs in the tables showing the same vapor superheat refer for the most part to measurements right before and right after a single superheat determination.

The low coolant film heat transfer coefficients apparent from the data were caused by the high viscosity of the coolant at the operating temperatures. This contributed to limiting the range of operation of the equipment, but the main difficulties encountered on operation at lower pressures were fluctuating vapor conditions. The low coolant film heat transfer coefficient actually increases the reliability of the data reduction procedure (which assumed a constant value) since the temperature profile in the condenser would tend to

Table IX.

Acetone Experimental Data Reduction.

Run	Temperature Coolant (°C)	Vapor Vapor (°C)	Vapor superheat (°C)	t_{32}^* (°C)	Δemf_{31} (μV)	Q/A (Watt/cm ²)	C
A01	5.12	19.06	3.12	11.26	29.5	1.467	0.853
A02	4.48	19.02	3.12	10.85	28.5	1.385	0.775
A03	-4.67	20.85	1.20	9.99	55.9	2.808	0.928
A04	-4.41	20.85	1.20	9.99	58.1	2.950	0.968
A05	-4.14	20.98	1.20	10.45	59.3	3.061	1.017
A06	-4.94	21.10	0.00	10.87	60.0	3.033	0.954
A07	-4.94	21.21	0.00	11.05	61.6	3.143	0.987
A08	-3.61	21.30	0.00	11.30	62.0	3.187	1.006
A09	-3.45	21.56	0.00	11.52	61.6	3.155	0.997
A10	-4.35	27.83	1.15	13.26	68.3	3.374	0.883
A11	-3.34	28.12	0.00	12.97	64.9	3.112	0.764
A12	-3.34	28.35	0.00	12.97	64.0	3.074	0.742
A13	-2.55	27.89	0.00	14.25	64.1	3.099	0.813
A14	-0.66	27.37	0.00	14.62	62.9	3.073	0.841
A15	0.76	27.20	0.00	14.85	63.3	3.126	0.871
A16	0.76	27.20	0.00	14.85	63.4	3.132	0.872

Table X.

Nitrogen Tetroxide Experimental Data and Results.

Run	Temperature Coolant (°C)	Vapor Vapor (°C)	Vapor superheat (°C)	t_{32}^* (°C)	Δemf_{31} (μV)	Q/A (Watt/cm ²)	C
N01	1.51	9.83	1.13	6.68	19.8	1.050	1.054
N02	1.59	9.75	1.13	6.71	21.0	1.108	1.151
N03	1.67	9.70	1.13	6.80	20.6	1.073	1.189
N04	1.75	9.72	1.13	6.80	22.0	1.117	1.252
N05	-3.98	11.42	2.73	4.89	30.9	1.611	1.015
N06	-4.25	11.60	2.73	4.80	31.1	1.596	0.967
N07	-4.49	11.74	2.73	4.73	32.1	1.642	0.960
N08	-4.72	11.79	2.73	4.66	32.5	1.657	0.953
N09	-1.41	14.86	1.32	9.27	39.9	2.077	1.204
N10	-1.46	15.42	1.32	9.34	40.6	2.156	1.140
N11	-1.58	15.41	1.32	9.50	43.7	2.246	1.245
N12	-1.70	15.55	1.32	9.32	41.0	2.178	1.126
N13	-1.70	15.66	1.32	9.32	41.0	2.179	1.112
N14	-2.44	17.52	1.32	10.51	48.5	2.543	1.190
N15	-6.40	19.26	0.67	12.38	51.8	2.710	1.202
N16	0.86	19.22	0.67	12.44	45.8	2.430	1.092
N17	4.57	18.12	0.67	13.10	37.7	2.007	0.839
N18	4.75	18.24	0.67	13.31	42.9	2.152	0.844
N19	4.77	18.18	0.67	13.14	37.9	2.018	0.842
N20	-2.71	19.26	0.28	11.52	55.6	2.951	1.131
N21	-3.07	19.27	0.28	11.48	57.6	3.053	1.162
N22	1.27	19.52	0.31	12.82	48.1	2.561	1.111
N23	1.61	19.50	0.31	13.04	46.7	2.485	1.111
N24	4.20	18.38	0.00	13.25	39.7	2.109	1.085
N25	5.57	18.62	0.22	13.87	37.4	1.993	1.123

(Table X, cont.)

Run	Temperature Coolant (°C)	Vapor (°C)	Vapor superheat (°C)	t_{32}^* (°C)	Δemf_{31} (μV)	Q/A (Watt/cm ²)	C
N26	5.73	18.42	0.22	13.96	37.3	1.988	1.132
N27	-0.32	20.84	0.43	13.45	54.9	2.896	1.182
N28	-0.32	20.87	0.43	13.45	54.9	2.901	1.179
N29	3.25	18.14	0.19	12.90	42.9	2.273	1.171
N30	3.25	18.18	0.19	12.90	42.9	2.278	1.166
N31	-7.68	9.88	3.37	2.57	34.4	1.825	1.087
N32	-8.06	9.29	3.37	2.41	34.5	1.803	1.173
N33	-8.06	9.26	3.37	2.41	34.5	1.798	1.180
N34	-2.57	11.54	1.57	6.47	33.6	1.768	1.165
N35	-2.20	11.69	1.57	6.82	33.4	1.732	1.205
N36	-2.20	11.93	1.57	6.82	33.4	1.767	1.150
N37	-0.95	12.81	1.54	7.81	33.7	1.764	1.184
N38	-0.57	12.99	1.54	7.90	32.3	1.717	1.124
N39	-6.05	13.25	2.02	6.49	44.8	2.307	1.227
N40	-5.74	14.10	1.93	7.56	48.2	2.368	1.344
N41	-5.74	14.58	1.93	7.56	48.2	2.519	1.254
N42	-1.97	18.58	0.86	11.74	52.2	2.698	1.235
N43	-1.15	19.12	0.86	12.17	52.9	2.735	1.238
N44	-1.15	19.31	0.86	12.17	52.9	2.754	1.214
N45	1.54	20.34	0.86	13.66	51.5	2.644	1.257
N46	1.54	20.37	0.86	13.66	51.5	2.651	1.253
N47	3.70	19.08	0.19	13.64	44.8	2.361	1.191
N48	3.70	19.23	0.19	13.64	44.8	2.376	1.170
N49	4.81	19.26	0.19	14.16	42.1	2.226	1.182
N50	4.81	19.30	0.19	14.16	42.1	2.231	1.176
N51	5.45	19.64	0.29	14.88	40.6	2.164	1.153
N52	5.45	19.29	0.29	14.88	40.6	2.124	1.208

be determined mainly by heat conduction in the wall (as calculated with the computer program), with fluid dynamics playing a minor role.

As mentioned previously, no problems were encountered in obtaining film condensation, or in the condensation of saturated acetone vapor. It was however difficult to obtain condensation of nitrogen tetroxide vapor of low superheat. The zero superheat listed for run N24 in Table X was actually due to the low bridge current and instrumentation sensitivity in that run, with its superheat being in fact ± 0.2 °C.

Figure 26 presents the results against the Reynolds number, $4(Q/A)L/\mu_L \Delta H_{\text{vap}}^*$. The relatively large scatter of the results is apparent in other condensation experiments; for instance, the data of Kovalev et al. (52) for the condensation of nitrogen tetroxide showed a scatter of ± 15 percent, comparable to the present results. Scatter may be caused by different factors such as noncondensables, fluctuating vapor temperatures or vapor superheat. No trend is apparent in the data with pressure in the condenser, as shown in figure 27.

In spite of the scatter in the figures, it is apparent that (taking acetone as a basis for comparison) nitrogen tetroxide vapor presents a heat transfer coefficient higher by at least 10 to 20 percent than predicted by Nusselt's theory, in approximate agreement with the measurements of Kovalev et al. (52).

The large discrepancy between the acetone and nitrogen tetroxide results can not be explained in terms of uncertainty in physical properties (as done by Kovalev et al.) since the new thermal conductivity data for nitrogen tetroxide (3) were used in the calculations.

Because of the very similar Prandtl numbers of acetone and nitrogen tetroxide (4.0 and 3.6 for the former at 10 °C and 20 °C respectively, 4.6 for nitrogen tetroxide in the

Figure 26.- Experimental results, condensation heat transfer.

Figure 27.- Condensation results as function of the condenser pressure.

same temperature range) and the low Reynolds numbers, calculations based on hydrodynamic factors would not explain the discrepancy. For instance, film turbulence calculations with Dukler's (58) approach account for only 1 percent of the difference. Also, the slightly higher Reynolds numbers of the acetone runs would tend to make its heat transfer coefficient higher when compared with Nusselt's equation than for the nitrogen tetroxide runs.

An explanation based on the mechanism of condensation is advanced below; it may also help understand the difficulties encountered in obtaining saturated nitrogen tetroxide vapor.

Examples of the data reduction results and temperature profile measurements are shown in figures 28 and 29.

Figure 28 shows the calculated film thickness, wall temperature and local heat flux for run N44. It should be noted that the wall temperature was assumed constant for the top 0.125 inches as explained in Appendix E. Also, the heat flux at the leading edge of the condenser is finite (although very high in the example, 1.3×10^6 Watt/cm²) because interfacial effects were at least approximately accounted for; Nusselt's derivation results in an infinite value for it. The arrow in the figure shows the location of the vapor temperature probe.

Figure 29 shows calculated and experimental temperature profiles in the vapor for run N44. In this particular run, the bridge unbalance between the wire closest to the condenser and the fixed resistors was recorded, and the figure corresponds directly to the temperature profile. The arrows in figure 29b show the direction in which the measurements were taken. The small steps in the lines are due to the relatively slow response of the microvoltmeter. The left hand side boundary corresponds to the liquid surface, i.e., when the probe wire closest to the condenser was in contact with the liquid as determined visually. On retreating from the liquid

Figure 28.- Sample results of the data reduction calculations.
Run N44.

Figure 29.- Temperature profile in the vapor, run N44.
 a) Calculated, $\zeta_2 = 1$.
 b) Experimental.

surface, the liquid was pulled along by the wire by capillary action until at point S all contact was suddenly lost. The difference in approaching and retreating measurements for a short distance thereafter is probably due to drying of the wire.

The curve marked '+' in figure 29b corresponds directly to the temperature profile, i.e., increasing temperature in the vertical direction. The curve marked '-' was taken after reversing the current to the bridge and corresponds to temperature increasing in the downward direction. The fair symmetry of the curves gives an indication of the successful probe alignment and the absence of thermoelectric effects.

Point S in the figure is important from another point of view. Extensive testing indicated that the temperature of the wire at that point, right before break-off from the liquid, corresponded very closely to the saturation temperature of the vapor. These tests involved comparison with the liquid kept in the tray (at the saturation temperature of the vapor due to the small mass transfer rates from it), and tests in which either drops of liquid were picked up from the tray and held on the wires by capillary action until they evaporated, or similarly, the complete evaporation of liquid films stretching by capillary action between the wires (no effect of curvature on vapor pressure was detected in these tests). It may be mentioned also that apparently there was good wetting of the wires by nitrogen tetroxide, although in a few cases small spherical drops of liquid could be observed on the wires right after films stretching between them broke due to evaporation.

In figure 29a the theoretical predictions are presented for the cases when both nitrogen tetroxide and nitrogen dioxide condense at the maximum rate, and when only nitrogen tetroxide condenses. The similarity in shape with the experimentally determined temperature profiles is remarkable con-

sidering the approximations and assumptions made in the calculations. More important from the point of view of the condensation mechanism is the fact that the calculated temperature profile in the vapor, when extrapolated to the liquid surface yields a value very close to the saturation temperature when both monomer and dimer condense at the maximum rate (as seen for instance in figure 11), while if monomer does not condense the temperature profile extrapolates to a substantially higher value (e.g., figure 12). From the relative positions of the point S in figure 29b and the value obtained as temperature of the vapor at the vapor-liquid interface, it should be concluded that monomer (NO_2) does condense along with nitrogen tetroxide (N_2O_4). In fact, the temperature profile appears to extrapolate to a value slightly lower than the saturation temperature of the vapor.

Figure 30 shows similar effects for run N51, using the same notation, for both positive and reverse current. In it however, the temperature difference between the wires closest and farthest from the condenser was measured, and the calculated curves were corrected accordingly (as symbolized by the ordinate ΔT).

Figure 31 shows the measurements corresponding to run N48, in which a practically flat temperature profile is predicted for the case when NO_2 does not condense while N_2O_4 condenses at the maximum rate, in opposition to the experimentally determined variable temperature profile in the vapor.

To confirm these findings, a large number of careful tests were carried out specifically to see whether the temperature profile in the vapor extrapolated to a value higher than the saturation temperature at the vapor-liquid interface; in no case an increase in temperature at the interface could be detected. In the tests, a minimum of equipment was used to prevent electrical interference with the measurements,

Figure 30.- Temperature profile in the vapor, run N51.

a) Calculated, $\sigma_2 = 1$.

b) Experimental.

Measured with one wire against the other.

Figure 31.- Temperature profile in the vapor, run N48.
Measured with one wire against the other.

a) Calculated, $\sigma_2 = 1$.

b) Experimental.

and no condensation heat transfer data (other than vapor temperature and condensation heat flux) were taken.

Results of one such test are shown in figure 32, where the relationship between the saturation temperature (point S) and the temperature profile is clearer.

Figure 33 shows one of the recorded tests in which vapor superheat was low (about 0.04°C) and for which an increasing temperature near the interface was predicted for the case when monomer does not condense. Other calculated possibilities are also shown in the figure, and the conclusions reached can be illustrated with it. The possibility that NO_2 does not condense (curve B) must be discarded in view of the experimental data, and it may also be stated that (relative to $\sigma_{\text{N}_2\text{O}_4} = 1$) the condensation coefficient of monomer is higher than 0.01 (curve D). Moreover, by consideration of curve C ($\sigma_1 = 0.1$, $\sigma_2 = 1.0$) which extrapolates to an interfacial temperature higher than the saturation temperature, the condensation coefficient of NO_2 appears higher than 0.1 relative to that of N_2O_4 .

In fact, the condensation coefficient of N_2O_4 appears to be smaller than that of NO_2 in view of the interfacial temperatures lower than the saturation temperature (e.g., figure 32). The difference should be slight because the observed effects were small (e.g., compared with curve E in figure 33). This is probably the case also in view of the difficulties experienced in obtaining saturated vapor in the condenser, since a much higher superheat would then be obtained on evaporation than in the case $\sigma_1 = \sigma_2 = 1$ shown in Table VII.

It should be noted that determination of the absolute condensation coefficients of nitrogen tetroxide and nitrogen dioxide does not appear possible because the unknown energy accommodation coefficients may compensate for the effects of low values in the temperature profiles. From the condensation heat transfer results however, high values (i.e., close to

Figure 32.- Sample temperature profile in the vapor.
 Measured with one wire against the other.
 Vapor temperature = 17°C
 Condensation mass flux = $4.3 \times 10^{-3} \text{ gr/cm}^2 \text{ sec}$
 a) Calculated, $\sigma_2 = 1$.
 b) Experimental.

Figure 33.- Sample temperature profile in the vapor.
 Measured with one wire against the other.
 Vapor temperature = $16 ^\circ\text{C}$
 Condensation mass flux = $4.2 \times 10^{-3} \text{ gr/cm}^2 \text{ sec}$
 a) Calculated.
 b) Experimental.

unity) are probable.

From the experimental temperature profiles it can be concluded that NO_2 and N_2O_4 condense at comparable rates, with the condensation coefficient of monomer being higher (by a factor estimated as between 2 and 5) than that of dimer.

This conclusion poses though a question in view of the large difference in composition between vapor and liquid nitrogen tetroxide: If the nitrogen dioxide content of the liquid were much higher than the equilibrium composition (only about 0.1 mole percent) the vapor pressure of NO_2 would increase enormously, preventing in fact its condensation. To reconcile this apparent inconsistency, an approximate calculation of the liquid compositions to be expected was performed as follows:

Since at the position of the vapor temperature probe gradients in the vertical direction are small, a one-dimensional solution of diffusion equations for the liquid should be appropriate. In this case, neglecting bulk transport of monomer compared with that due to concentration gradients, and assuming constant properties, equations 35 reduce approximately to:

$$N_1 = -cD_L \frac{dx_1}{dx} \quad (64a)$$

$$\frac{dN_2}{dx} = \frac{c}{\tau} (x_2 - x_{2\text{equil}}) \quad (64b)$$

where the reaction rate (R_2) in the liquid has been written in terms of the relaxation time τ , x_1 and x_2 denote mole fractions of monomer and dimer respectively in the liquid, c is the molar concentration, D_L the binary diffusion coefficient for the liquid phase, and the subscript 'equil' the equilibrium values.

Solution of equations 64 yields the composition profile in the liquid as in equation 65a, and the molar flux of

monomer as in equation 65b.

$$x_1 - x_{1,\text{equil}} = [x_1(x=0) - x_{1,\text{equil}}] e^{\sqrt{\frac{2}{\tau D_L}} x} \quad (65a)$$

$$N_1(x=0) = - \sqrt{\frac{2D_L}{\tau}} [x_1(x=0) - x_{1,\text{equil}}] \quad (65b)$$

In the extreme case when only monomer condenses, the difference between liquid composition at the surface and the equilibrium composition (as given by equations 65) reduces approximately to:

$$x_1(x=0) - x_{1,\text{equil}} = \frac{W}{\rho_L} \sqrt{\frac{\tau}{2D_L}} \quad (66)$$

Diffusion coefficients in the liquid are not available, and they were estimated with the equation of Scheibel as recommended by Reid and Sherwood (59) from viscosity data; values of about $6 \times 10^{-5} \text{ cm}^2/\text{sec}$ were obtained. Using a high value of the condensation mass flux ($10^{-2} \text{ gr/cm}^2 \text{ sec}$) and the value of 0.2×10^{-8} seconds for the relaxation time of the liquid phase reaction given by Chardon and Theobald (43), the difference in monomer content of the liquid surface and the equilibrium value can be calculated from equation 66 as 6×10^{-3} mole percent, which in fact would not cause a large increase in the vapor pressure of monomer (only about 6 percent). Thus, it is possible for both monomer and dimer to condense.

The mechanism in which both monomer and dimer condense at comparable rates may also account for the higher condensation heat transfer coefficients found experimentally. Even though thermodynamic data on the properties of the species in the liquid phase are not available, they can be estimated assuming ideal behavior and using the equilibrium constants

presented in Appendix A for the liquid and gas phase reactions, along with the equilibrium heats of vaporization listed in Table I. This calculation showed that the equilibrium heat of vaporization (which was used in the data reduction) is actually 46 percent higher at the boiling point and 30 percent higher at 0 °C than the heat of vaporization of liquid of composition equal to that of the equilibrium vapor. This shows then that if monomer and dimer condense at comparable rates, considerable less heat dissipation would be required at the vapor-liquid interface, and a correspondingly lower temperature gradient in the liquid.

Higher condensation heat transfer coefficients would result since a substantial portion of the total heat transferred would be released by reaction inside the liquid film instead of at the surface. Equations 65 do not predict a large increase in condensation heat transfer coefficient due to this effect because the additional heat would be generated very close to the liquid surface (due to the low value of D_L). It should be noted though that such calculations include only physical diffusion of individual NO_2 molecules (as in the estimation method) and other phenomena may take place to increase the apparent diffusivity of the molecules.

A possibility would be displacement reactions in which nitrogen dioxide molecules react with nitrogen tetroxide yielding NO_2 molecules deeper into the liquid. This may also help explain the high relative rate of condensation of NO_2 compared with N_2O_4 . The unpaired electron in the NO_2 molecule gives it a free radical character and it is possible that its condensation is more chemical than physical in nature. On striking the liquid with the proper orientation NO_2 molecules may react with dimer, possibly displacing an activated monomer that would propagate further into the liquid. The lower condensation coefficient of N_2O_4 may be explained by its higher complexity, which makes more unlikely its collision with the liquid surface with the proper orientation for condensation.

VI. Summary and Conclusions.

More accurate theoretical calculations were performed to describe the interphase transport between monoatomic and reacting vapors and their liquids for simple situations (mainly, condensation, evaporation and heat transfer between the vapor and the liquid). The treatment was based on the generally accepted concepts of condensation and energy accommodation coefficients of the vapor molecules, and its main feature is that enough equations were developed to solve for all unknowns in the processes studied, in terms of only physical parameters.

The calculations, although approximate, close a gap in our ability to predict the behavior of physical systems during phase transformation. Thus, prediction of apparently unreported effects (e.g., that when there is heat transfer from a vapor to its liquid the pressure of the vapor is higher than the equilibrium vapor pressure at the liquid surface temperature, section III.6) and the explanation of some observed phenomena (e.g., fogging in the condensation with noncondensables, Appendix D) are possible.

By application of the analysis to the condensation of liquid metal vapors it was concluded that their low condensation heat transfer coefficients can be explained in terms of the dimer content of their vapors, and results obtained with some likely mechanisms are presented.

When applied to the interphase transport between nitrogen tetroxide vapor and liquid (a convenient material in view of its physical properties), the analysis underscored the experimental difficulties of the determination of mechanisms of condensation.

Based on the theoretical predictions a sensitive condensation experiment was designed and an apparatus built and operated successfully for the determination of the condensation mechanism of nitrogen tetroxide. Temperature profiles in the vapor near the vapor-liquid interface were measured and it was concluded that monomer (NO_2) and dimer (N_2O_4) condense at comparable rates. This rather surprising result in view of the liquid composition (practically pure N_2O_4) is however consistent with all observed effects.

This appears to be the first determination of the condensation mechanism of a reacting mixture at moderate pressures, where traditional methods do not apply.

Condensation heat transfer data obtained simultaneously with the temperature profile measurements indicated that the condensation heat transfer coefficient of nitrogen tetroxide is higher than predicted by Nusselt's equation, in approximate agreement with previous determinations. This can be explained in terms of the condensation mechanism found, but actual calculation does not appear possible at present.

Nomenclature.

Notes: -Throughout the present report and this nomenclature, the expression "bulk vapor conditions", to which the subscript 'v' is ascribed, is used to denote the vapor far from the liquid surface.

-Symbols of limited utilization are defined in the text; any consistent set of units may be employed.

English:

- a Heat transfer parameter defined by equations 58 and 59.
- $A = \left(\frac{\partial R_2}{\partial Z} \right)_{T,P}$ Constant in a linearized rate of formation of dimer.
- b Reaction parameter defined by equations 58 and 59.
- B Reaction parameter defined by equations 36 and 37.
- $c = \bar{v} + \alpha - \bar{v}\alpha$ Kinetic parameter.
- C Coefficient describing degree of agreement with Nusselt's equation.
- $c_i = \bar{v}_i + \alpha_i - \bar{v}_i\alpha_i$ Kinetic parameter for species i .
- $c_{p, \text{equil}}$ Equilibrium heat capacity of a reacting vapor.
- C_{pi} Molar heat capacity at constant pressure of species i in the vapor.
- $c_{p,v}$ Heat capacity of the vapor at constant pressure.
- C_{vi} Molar heat capacity at constant volume of species i in the vapor.
- $c_{v,v}$ Heat capacity of the vapor at constant volume.
- d Knudsen zone size as used in equation 5.
- D Diffusion coefficient.

- $f = f(x,y,z,u,v,w)$ Mass velocity distribution function, defined so that $f \, dx \, dy \, dz \, du \, dv \, dw$ is the mass of the molecules in a volume element $dx \, dy \, dz$ around the point x,y,z with velocities between u,v,w and $u+du, v+dv, w+dw$.
- F Function defined by equation 44.
- $f_s = \frac{\rho_s}{(2\pi R'T_s)^{3/2}} e^{-\frac{u^2+v^2+w^2}{2R'T_s}}$ Mass velocity distribution function of the vapor molecules in equilibrium with the liquid at the temperature T_s .
- g Gravitational acceleration ($980.245 \, \text{cm sec}^{-2}$ in this investigation).
- $G = \rho_v u_v$ Net mass flux in the x-direction.
- k Thermal conductivity.
- k_{eff} Effective thermal conductivity of a reacting vapor, as determined from energy flux and temperature gradient far from any disturbance.
- k_{equil} Equilibrium thermal conductivity of a reacting vapor; calculated assuming infinitely fast reaction rates.
- k_i Thermal conductivity of pure species i in the vapor.
- k_L Thermal conductivity of the liquid.
- k_v Thermal conductivity of the vapor. The frozen thermal conductivity of a reacting vapor.
- L Height of the condenser (2.375 inches for the values reported in Tables IX and X).
- M Molecular weight of the vapor.
- M_i Molecular weight of species i .
- $N = N_1 + 2N_2$ Net molar flux of the vapor, referred to monomer.
- N_i Molar flux of species i in the x-direction.

- N_{iv} Molar flux of species i far from the liquid surface.
- N_{io} Molar flux of species i at the vapor-liquid interface.
- (NC_p) Average value of $N_1 C_{p1} + N_2 C_{p2}$
- p Component of the stress tensor (reference 38).
- $p_o = p(x=0)$ Value of p at the vapor-liquid interface.
- P Absolute pressure.
- P_{is} Partial pressure of species i in equilibrium with liquid at the temperature T_s [in the general case, of the composition of the liquid surface].
- $Pr = c_{p,v}/\mu_v/k_v$ Prandtl number of the vapor.
- P_s Vapor pressure of the liquid at the temperature T_s . As pointed out by Schrage (16) it would not correspond exactly to the thermodynamic equilibrium vapor pressure (P_s^*) at the temperature T_s , but to the vapor pressure corrected for Poynting effect to account for the higher pressure over the liquid surface during condensation. The effect is minor, and in the calculations in Chapter III and for figure 1 the following was used:

$$R'T_s \ln (P_s/P_s^*) = v_L [P_v + \rho_v u_v^2 (1 - \rho_v/\rho_L) - P_s^*]$$
which considers both the higher pressure P_v over the liquid and the additional momentum of the condensing molecules as given by Bernoulli's equation. This possible effect was neglected in the calculations with multicomponent vapors.
- $P_v = \rho_v R' T_v$ Thermodynamic pressure in the bulk of the vapor.
- P_o Pressure of the vapor at the vapor-liquid interface.
- q Heat flux in the x -direction.
- Q/A Average condensing heat flux.
- R Universal gas constant.
- $R' = R/M$ Gas constant per unit mass of vapor.

$R_i' = R/M_i$	Gas constant of species i, unit mass basis.
R_2	Molar rate of formation of dimer.
S	Energy flux parameter (reference 38).
$S_0 = S(x=0)$	Value of S at the vapor-liquid interface.
S_i	Term expressing the effect of heat flow on the velocity distribution function of species i in the vapor (equation 50).
$S_{i0} = S_i(x=0)$	Value of S_i at the vapor-liquid interface.
T	Absolute temperature.
T_s	Absolute temperature of the liquid surface.
T_{sat}	Saturation temperature of the vapor.
T_v	Absolute temperature of the bulk of the vapor.
T_w	Temperature of the wall of the condenser.
T_0	Absolute temperature of the vapor at the vapor-liquid interface.
t_{32}^*	Measured condenser temperature (Appendix E).
u	Velocity in the x-direction.
$\bar{u}$	Mean velocity of the vapor in the x-direction.
$\bar{u}_i$	Mean velocity of species i in the vapor in the x-direction.
$\bar{u}_{i0} = \bar{u}_i(x=0)$	Value of $\bar{u}_i$ at the vapor-liquid interface.
u_v	Mean linear velocity of the bulk of the vapor in the x-direction.
$\bar{u}_0 = \bar{u}(x=0)$	Mean velocity of the vapor at the vapor-liquid interface.
v	Velocity in the y-direction.
V	Variable defined by equation 38c.
$v_L = \rho_L^{-1}$	Specific volume of the liquid.
$v_v = \rho_v^{-1}$	Specific volume of the bulk vapor.

- w Velocity in the z-direction.
 $W = \left| \rho_v u_v \right|$ Net condensing or evaporating mass flux.
 x Distance from the liquid surface. Also, a direction perpendicular to the surface.
 y Direction parallel to the liquid surface.
 y_i Mole fraction of species i in the vapor.
 y_{is} Mole fraction of species i in saturated vapor at the liquid surface temperature.
 y_{iv} Mole fraction of species i in the bulk of the vapor.
 y_{io} Mole fraction of species i in the vapor at the vapor-liquid interface.
 z Direction perpendicular to x and y. In Appendix C, direction of travel of the incident sound wave.
 $Z = (1+y_2)^{-1}$ Variable used to express composition in linearized diffusion equations.
 $Z_v = (1+y_{2v})^{-1}$ Composition of the bulk vapor.
 $Z_o = (1+y_{2o})^{-1}$ Composition of the vapor at the vapor-liquid interface.

Greek:

- α Energy accommodation coefficient.
 α_i Energy accommodation coefficient of species i.
 $\beta = 2 \epsilon_v^2$ Flow parameter.
 $\gamma = c_{p,v}/c_{v,v}$ Specific heat ratio of the vapor.
 Δemf_{31} Output voltage of the composite thermocouple (Appendix E)
 ΔH_{vap} Heat of vaporization of the liquid.

ΔH_{vap}^*	Heat of vaporization corrected for liquid subcooling (Appendix E).
$\xi_{i0} = \bar{u}_{i0} (2R_i' T_0)^{-1/2}$	Dimensionless velocity of species i at the vapor-liquid interface.
$\xi_{is} = \bar{u}_{i0} (2R_i' T_s)^{-1/2}$	Dimensionless velocity of species i referred to the temperature of the liquid surface.
$\xi_v = u_v (2R' T_v)^{-1/2}$	Dimensionless bulk vapor velocity, positive for net evaporation, negative for net condensation.
$\xi_s = \bar{u}_0 (2R' T_s)^{-1/2}$	Dimensionless velocity at the interface, referred to the liquid surface temperature.
$\xi_0 = \bar{u}_0 (2R' T_0)^{-1/2}$	Dimensionless velocity of the vapor at the vapor-liquid interface.
$\theta = z - z_v$	Composition referred to that of the bulk vapor.
$\lambda = 3 \frac{\mu_v}{\rho_v} \sqrt{\frac{\pi}{8R' T_v}}$	Mean free path at the bulk vapor conditions. It is evaluated at the interfacial conditions in section III.6.
$\lambda^* = 19.20 \frac{\mu_v}{\rho_v} \sqrt{\frac{\pi}{8R' T_v}}$	Mean free path as used in equation 5.
μ_L	Viscosity of the liquid.
μ_v	Viscosity of the vapor.
ρ_L	Density of the liquid.
ρ_s	Density of saturated vapor at the temperature T_s .
ρ_v	Density of the bulk of the vapor.
ρ_0	Density of the vapor at the vapor-liquid interface.
$\zeta [-\zeta_e = \zeta_c]$	Condensation coefficient.
ζ_c	Condensation coefficient (general case).
ζ_e	Evaporation coefficient (general case).
ζ_i	Condensation coefficient of species i .

$\tau = T - T_v$ Temperature referred to that of the bulk vapor.

φ Function defined by equation 43.

$\Phi(x) = \frac{2}{\sqrt{\pi}} \int_0^x e^{-x^2} dx$ Error function.

Subscript:

i , j A species in the vapor (1 or 2).

L Properties of the liquid.

s Properties of saturated vapor at the liquid surface temperature.

v Properties or conditions in the bulk of the vapor, far from the liquid surface.

o Properties or conditions of the vapor at the vapor-liquid interface.

1 Monomer (NO_2 in the experimental section).

2 Dimer (N_2O_4 in the experimental section).

References.

- 1.- B. Misra and C.F. Bonilla, Chem.Eng. Progress, Symposium Series 18 (52), 7-21 (1956).
- 2.- C.F. Bonilla and J.C. Engelbrecht in Proceedings of the First Annual AEC Meeting on High Temperature Liquid Metal Heat Transfer Technology (Argonne National Laboratory, June 14-15, 1961). Also, C.F. Bonilla in ANL report 6507 (1962).
- 3.- L.J. Navarro, J. Larrain and C.F. Bonilla in Proceedings of the Fifth Symposium on Thermophysical Properties, American Society of Mechanical Engineers (Boston, Sept. 30-Oct. 2, 1970).
- 4.- R.B. Bird, W.E. Stewart and E.N. Lightfoot, "Transport Phenomena", John Wiley & Sons, Inc., New York, 1960.
- 5.- M. Jakob, "Heat Transfer", John Wiley & Sons, Inc., New York, 1949.
- 6.- W. McAdams, "Heat Transmission", third edition, McGraw-Hill Book Company, Inc., New York, 1954.
- 7.- J. Lee, A.I.Ch.E. J. 10 (4), 540-4 (1964).
- 8.- J. Lee, Chem.Eng. Progress, Symposium Series 61 (59), 200-9 (1965).
- 9.- D.A. Labuntsov and S.I. Smirnov in Proceedings of the Third International Heat Transfer Conference (Chicago, Aug. 7-12, 1966).
- 10.- S.P. Sukhatme and W.M. Rohsenow, "Heat Transfer During Film Condensation of a Liquid Metal Vapor", MIT-TR-9167-27 (1964).
- 11.- C.F. Bonilla in Proceedings of the (First) International Conference on Peaceful Uses of Atomic Energy (United Nations, Geneva, 1955).
- 12.- D.J. Wilhelm, "Condensation of Metal Vapors: Mercury and the Kinetic Theory of Condensation", ANL-6948 (1964).
- 13.- J.H. Perry, ed., "Chemical Engineer's Handbook", fourth edition, McGraw-Hill Book Company, Inc., New York, 1963.
- 14.- V.I. Subbotin, M.N. Ivanovskii, V.P. Sorokin and B.A. Chulkov, Teplofizika Vysokikh Temperatur 2 (4), 616-22 (1964).
- 15.- N.V. Bakulin, M.N. Ivanovskii, V.P. Sorokin, V.I. Subbotin and B.A. Chulkov in "Zhidkiye Metalli-Sbornik Statye" (Liquid Metals - A Collection of Papers), P.L. Kirillov, V.I. Subbotin and P.A. Ushakova, editors, Atomizdat, Moscow, 1967.

- 16.- R.W. Schrage, "A Theoretical Study of Interphase Mass Transfer", Columbia University Press, New York, 1953.
- 17.- W.J. Minkowycz and E.M. Sparrow, Int.J. Heat and Mass Transfer 9 (10), 1125-44 (1966).
- 18.- E.M. Sparrow, J.W. Minkowycz and M. Saddy, Int.J. Heat and Mass Transfer 10 (12), 1829-45 (1967).
- 19.- M.N. Ivanovskii, Yu.V. Milovanov and V.I. Subbotin, Atomnaya Energiya 24 (2), 146-51 (1968).
- 20.- I.T. Aladyev, N.S. Kondratyev, V.A. Mukhin, M.E. Kipshidze, I. Parfentyeva and V.V. Kisselev in Proceedings of the Third International Heat Transfer Conference (Chicago, Aug. 7-12, 1966).
- 21.- D.G. Kroger, "Heat Transfer During Film Condensation of Potassium Vapor", DSR Report No. 75239-42 (1966).
- 22.- P.M. Meyrial, M.L. Morin and W.M. Rohsenow, "Heat Transfer During Film Condensation of Potassium Vapor on a Horizontal Plate", DSR Report No. 70008-52 (1968).
- 23.- S.G. Sawochka, "Thermal and Hydraulic Performance of Potassium During Condensation Inside Single Tubes", NASA CR-851 (1967).
- 24.- S.J. Wilcox and W.M. Rohsenow, "Film Condensation of Liquid Metals - Precision of Measurement", DSR Report No. 71475-62 (1969).
- 25.- R.E. Balzhiser, project director, "Investigation of Liquid Metal Boiling Heat Transfer", AFAPL-TR-66-85 (1967).
- 26.- J.A. Roth in Proceedings of the 1962 High Temperature Liquid Metal Heat Transfer Technology Meeting (Brookhaven National Laboratory, BNL 756, C-35).
- 27.- B. Paul, ARS J. 32 (9), 1321-8 (1962).
- 28.- R.F. Strickland-Constable, "Kinetics and Mechanism of Crystallization from the Fluid Phase and of the Condensation and Evaporation of Liquids", Academic Press, London, 1968.
- 29.- A.J. Sartor, R.E. Balzhiser and R.E. Barry at the Eleventh National Heat Transfer Conference (A.I.Ch.E. - A.S.M.E., Minneapolis, Minnesota, Aug. 3-6, 1969).
- 30.- E.D. Fedorovich and W.M. Rohsenow, "The Effect of Vapor Subcooling on Film Condensation of Metals", DSR Report No. 70586-53 (1968).
- 31.- V.I. Subbotin, M.N. Ivanovskii and Yu.V. Milovanov, Teplofizika Vysokikh Temperatur 4 (1), 143-4 (1966).

- 32.- V.I. Subbotin, M.N. Ivanovskii and Yu.V. Milovanov, *Atomnaya Energiya* 21 (1), 17-22 (1966).
- 33.- E.H. Kennard, "Kinetic Theory of Gases", McGraw-Hill Book Company, Inc., New York, 1938.
- 34.- J.L. Margrave, ed., "The Characterization of High-Temperature Vapors", John Wiley & Sons, Inc., New York, 1967.
- 35.- W.J. Bornhorst and G.N. Hatsopoulos, *Trans. ASME, J.App. Mechanics, Series E* 34 (4), 840-6 (1967).
- 36.- T.M. Muratova and D.A. Labuntsov, *Teplofizika Vysokikh Temperatur* 7 (5), 959-67 (1969).
- 37.- L.B. Loeb, "The Kinetic Theory of Gases", third edition, Dover Publications, Inc., New York, 1961.
- 38.- H. Grad, *Comm. Pure Appl.Math.* 2 (4), 331-407 (1949).
- 39.- J.O. Hirschfelder, C.F. Curtiss and R.B. Bird, "Molecular Theory of Gases and Liquids", John Wiley & Sons, Inc., New York, 1954.
- 40.- W.J. Bornhorst and G.N. Hatsopoulos, *Trans. ASME, J.App. Mechanics, Series E* 34 (4), 847-53 (1967).
- 41.- W.E. Meador, NASA TN D-5909 (1970).
- 42.- J.P. Hirth and J.M. Pound, "Progress in Material Science", Volume II, Bruce Chalmers, editor, Pergamon Press, Oxford, 1963.
- 43.- J.C. Chardon and J.G. Theobald, *C.R.Acad.Sc. Paris, Ser. A, B* 264B (23), 1577-9 (1967).
- 44.- H. Blend, "An Ultrasonic Investigation of the Dissociation Kinetics of Nitrogen Tetroxide", U.S.Dept.Comm., Office Tech.Serv., AD 283,964 (1962).
- 45.- P. Gray, "The Chemistry of Dinitrogen Tetroxide", The Royal Institute of Chemistry; Lectures, Monographs and Reports, No. 4, 1958.
- 46.- R.A. Svehla and R.S. Brokaw, "Thermodynamic and Transport Properties for the $\text{N}_2\text{O}_4 \rightleftharpoons 2 \text{NO}_2 \rightleftharpoons 2 \text{NO} + \text{O}_2$ System", NASA TN D-3327 (1966).
- 47.- R.S. Brokaw, *J.Chem.Phys.* 35 (5), 1569-80 (1961).
- 48.- A.A. Frost and R.G. Pearson, "Kinetics and Mechanism", second edition, John Wiley & Sons, Inc., New York, 1961.
- 49.- C.T. Ewing, J.P. Stone, J.P. Spann, E.W. Steinkuller, D.D. Williams and R.R. Miller, "High Temperature Properties of Potassium", NRL-6233 (1965).

- 50.- D. Lee, "Thermodynamic and Transport Properties of the Alkali Metal Vapors", D.Eng.Sc. Dissertation, Columbia University, 1967.
- 51.- G.H. Golden and J.V. Tokar, "Thermophysical Properties of Sodium", ANL-7323 (1967).
- 52.- S.A. Kovalev, A.S. Komendantov and B.S. Petukhov, Teplofizika Vysokikh Temperatur 7 (6), 1151-4 (1969).
- 53.- N. Hall, editor, "Metal Finishing", Guidebook Directory for 1970, Metals and Plastics Publications, Inc., Westwood, New Jersey.
- 54.- S. Wernick and R. Pinner, "The Surface Treatment of Aluminum and its Alloys", third edition, Robert Draper Ltd., Teddington, 1964.
- 55.- R.J. Moffat, "Temperature, its Measurement and Control in Science and Industry", Volume 3, C.M. Herzfeld, ed., Reinhold Publishing Corporation, New York, 1962.
- 56.- J.W. Mellor, Supplement to "Inorganic and Theoretical Chemistry", Longmas, Green and Company Ltd., London, 1928.
- 57.- J.F. Swindells, editor, "Precision Measurement and Calibration", Volume 2, NBS Special Publication 300, U.S. Dept. of Commerce, 1968.
- 58.- A.E. Dukler, Chem.Engr.Prog. 55 (10), 62-7 (1959).
- 59.- R.C. Reid and T.K. Sherwood, "The Properties of Gases and Liquids", second edition, McGraw-Hill Book Co., New York, 1966.
- 60.- W.F. Giauque and J.D. Kemp, J.Chem.Phys. 6, 40-52 (1938).
- 61.- G.N. Richter, H.H. Reamer and B.H. Sage, Ind.Eng.Chem. 45, 2117-9 (1953).
- 62.- W.G. Schlinger and B.H. Sage, Ind.Eng.Chem. 42, 2158-63 (1950).
- 63.- H.H. Reamer and B.H. Sage, Ind.Eng.Chem. 44, 185-7 (1952).
- 64.- A.Mittasch, E. Kuss and H. Schlueter, Z.Anorg.Allgem. Chem. 159, 1-36 (1927).
- 65.- T.E. Thorpe and J.W. Rodger, Phil.Trans. 185A, 397-710 (1894).
- 66.- P. Gray and P. Rathbone, J.Chem.Soc., 1958, 3550-7.
- 67.- J.C. Chardon and J.G. Theobald, Ann.Sci.Univ. Besançon. Phys. (3), No. 5, 6-8 (1966).

- 68.- B.J. McBride, S. Heilmel, J.G. Ehlers and S. Gordon, "Thermodynamic Properties to 6000 °K for 210 Substances Involving the First 18 Elements", NASA SP-3001 (1963).
- 69.- M. Bodenstein, Z.Physik.Chem. 100, 68-123 (1922).
- 70.- D.R. Stull, project director, "JANAF Thermochemical Tables", Dow Chemical Co., Midland, Michigan, 1961.
- 71.- I.C. Hisatsune, J.Phys.Chem. 65, 2249-53 (1961).
- 72.- F.H. Verhoek and F. Daniels, J.Am.Chem.Soc. 53, 1250-63 (1931).
- 73.- R.A. Svehla, "Thermodynamic and Transport Properties of the Hydrogen-Oxygen System", NASA SP-3011 (1964).
- 74.- R. Hultgren, R.L. Orr, P.D. Anderson and K.K. Kelley, "Selected Values of Thermodynamic Properties of Metals and Alloys", John Wiley & Sons, Inc., New York, 1963.
- 75.- S. Heilmel, "Thermodynamic Properties of Potassium to 2100 °K", NASA TN D-4165 (1967).
- 76.- C.J. Meisl and A. Shapiro, "Thermodynamic Properties of Alkali Metal Vapors and Mercury", General Electric Co., Report No. R60FPD358-A, Second Revision (1960).
- 77.- R.N. Lyon, editor, "Liquid Metals Handbook", AEC - Dept. of Navy (1952).
- 78.- D. Bierens de Haan, "Nouvelles Tables D'Integrales Definies" - Edition of 1867, Corrected, G.E. Stechert & Co., New York, 1939.
- 79.- M.N. Ivanovskii, Yu.V. Milovanov, V.P. Sorokin, V.I. Subbotin and B.A. Chulkov, preprint of 'Heat Transfer through Film and Dropwise Condensation of Metals', Moscow (1966).
- 80.- T.C. Harman and J.M. Honig, "Thermoelectric and Thermomagnetic Effects and Applications", McGraw-Hill Book Company, New York, 1967.
- 81.- P. Pascal, director, "Nouveau Traité de Chimie Minérale", Masson et Cte., editors, Paris, 1956.
- 82.- A.P. Colburn in "General Discussion on Heat Transfer", pp. 1-11, Inst. Mech. Eng. (ASME), Sept. 11-13, 1951.
- 83.- M.G. Salvadori and M.L. Baron, "Numerical Methods in Engineering", second edition, Prentice-Hall, Inc., Englewood Cliffs, New Jersey, 1961.
- 84.- "International Critical Tables", McGraw-Hill Book Company, Inc., New York, 1933.
- 85.- C.D. Hodgman, editor in chief, "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, 1959.

Appendix.

A. Physical Properties of Nitrogen Tetroxide.

Knowledge of the properties of the fluids involved is necessary for the calculations described in this report. In the correlations presented T is assumed to be the absolute temperature in degrees Kelvin.

The vapor pressure equation of Giauque and Kemp (60), shown in figure A.1 along with available experimental data, was adopted. For the vapor pressure P in atmospheres:

$$\log_{10} P = -1753.000/T + 6.12355 - 1.18078 \times 10^{-3} T + 2.0954 \times 10^{-6} T^2 \quad (\text{A-1})$$

A small correction was applied in the calculations since Giauque and Kemp used 273.10°K as equal to 0°C , while throughout this investigation 0°C was taken as 273.15°K in accordance with more recent determinations.

The following fit to mainly the data of Mittasch et al. (64) was adopted for the liquid density ρ_L in gr/cm^3 :

$$\rho_L = 2.12231 - 0.0023077 T \quad (\text{A-2})$$

This equation and available data are shown in figure A.2.

The following equation, derived to fit the three experimental points of Giauque and Kemp (60) was adopted for the heat capacity of liquid nitrogen tetroxide in $\text{cal/gr.}^\circ\text{K}$:

$$c_{p,L} = 0.58304 - 2.010955 \times 10^{-3} T + 4.3471 \times 10^{-6} T^2 \quad (\text{A-3})$$

Figure A.1.- Vapor pressure of nitrogen tetroxide.

Figure A.2.- Density of liquid nitrogen tetroxide.

The equation of Thorpe and Rodger (65) was adopted for the viscosity of liquid nitrogen tetroxide:

$$\mu_L = 28.155 [T-132.26]^{-1.7349} \text{ poise} \quad (\text{A-4})$$

Due to the scarcity of experimental data, the thermal conductivity of liquid nitrogen tetroxide was measured in this investigation as reported elsewhere (3), and the following correlation obtained:

$$k_L = [0.00146524 - 3.857 \times 10^{-6} T] \text{ cal/cm. sec. } ^\circ\text{K} \quad (\text{A-5})$$

A least squares fit to the reported measurements of Gray and Rathbone (66) for the equilibrium constant of the dissociation reaction in the liquid phase yielded:

$$\log_{10} \frac{C_{\text{NO}_2}^2}{C_{\text{N}_2\text{O}_4}} = 12.2715 - 4027.22/T - 1.03553 \log_{10} T \quad (\text{A-6})$$

where C represents concentration in g-mole liter⁻¹. This relationship presented a 0.5 percent standard deviation from the data and was used with the liquid density expression (equation A-2) to calculate liquid compositions. The calculated compositions are also in satisfactory agreement with the determinations of Chardon and Theobald (67).

The procedures used by Svehla and Brokaw (46) in their extensive correlation of the properties of nitrogen tetroxide vapor were adopted in the present investigation. Even though in the experimental temperature and pressure ranges species other than nitrogen tetroxide and dioxide can be neglected, four species were included in the calculation of thermodynamic properties: N_2O_4 , NO_2 , NO and O_2 .

The vapor composition was calculated from thermodynamic data for the pure components (assumed to behave ideally in the gas phase) taken from the compilation of McBride et al. (68), who published the coefficients of polynomial fits shown in Table A-I. A comparison of available data on the dissociation of nitrogen tetroxide is shown in figure A.3.

The transport properties of the vapor were calculated with the methods of references 39 and 73 from the Lennard-Jones (6-12) constants fitted by Svehla and Brokaw (46) to experimental transport properties, and listed in Table A-II.

The equation derived by Blend (44) from his experimentally determined reaction rates was adopted since Blend's experimental range was close to the conditions of the present tests:

$$k'_{12} = 10^{14.4} e^{-\frac{10240}{RT} \frac{\text{cal}}{\text{g-mole}}} \frac{\text{liter}}{\text{g-mole sec}} \quad (\text{A-7})$$

where k'_{12} is the specific first order rate constant of dissociation of nitrogen tetroxide into nitrogen dioxide. The net rate of formation of dimer per unit volume and unit time (R_2) at a total pressure P and absolute temperature T is given by:

$$R_2 = \left[\frac{P}{RT} \right]^2 k'_{12} \left[-y_2 + \frac{y_{2,\text{equil}}}{y_{1,\text{equil}}} y_1^2 \right] \quad (\text{A-8})$$

where y_1 denotes the mole fraction of nitrogen dioxide and y_2 the mole fraction of nitrogen tetroxide, and the subscript 'equil' denotes the equilibrium values at constant temperature and total pressure.

A linearization of the reaction rate around an equilibrium point yields the following expression for the rate parameter needed in the description of interphase processes

Table A-I.

Thermodynamic data for the N_2O_4 - NO_2 - NO - O_2 system
according to McBride et al. (68).

$$\frac{C_P^0}{R} = a_1 + a_2T + a_3T^2 + a_4T^3 + a_5T^4$$

$$\frac{H_T^0}{R T} = a_1 + a_2T/2 + a_3T^2/3 + a_4T^3/4 + a_5T^4/5 + a_6/T$$

$$\frac{S_T^0}{R} = a_1 \ln T + a_2T + a_3T^2/2 + a_4T^3/3 + a_5T^4/4 + a_7$$

The temperature coefficients are listed below.
 Absolute temperature T in degrees Kelvin.

Species	a_1	a_2	a_3	a_4	a_5	a_6	a_7
N_2O_4 (g)	3.1652553	2.7191496×10^{-2}	$-2.5350636 \times 10^{-5}$	1.0992581×10^{-8}	$-1.6603821 \times 10^{-12}$	-767.31966	11.477609
NO_2 (g)	3.4344563	2.2234297×10^{-2}	6.7148975×10^{-6}	$-9.7427719 \times 10^{-9}$	$3.7212523 \times 10^{-12}$	2864.7685	8.4084647
NO (g)	4.1469476	$-4.1197237 \times 10^{-3}$	9.6922467×10^{-6}	$-7.8633639 \times 10^{-9}$	$2.2309512 \times 10^{-12}$	9744.7894	2.5694290
O_2 (g)	3.7189946	$-2.5167288 \times 10^{-3}$	8.5837353×10^{-6}	$-8.2998716 \times 10^{-9}$	$2.7082180 \times 10^{-12}$	-1057.6706	3.9080704

Figure A.3.- Equilibrium constant for the reaction

$$\text{N}_2\text{O}_4 = 2 \text{NO}_2$$

Table A-II.

Lennard-Jones (6-12) potential force
constants for the N_2O_4 - NO_2 - NO - O_2 system,
according to Svehla and Brokaw (46).

<u>Interaction</u>	<u>σ, Å</u>	<u>ϵ/k, °K</u>
N_2O_4 - N_2O_4	4.621	347
NO_2 - NO_2	3.765	210
NO - NO	3.492	116.7
O_2 - O_2	3.467	106.7
N_2O_4 - NO_2	4.193	270
N_2O_4 - NO	4.0565	201.2
N_2O_4 - O_2	4.044	192.4
NO_2 - NO	3.6285	156.5
NO_2 - O_2	3.616	149.7
NO - O_2	3.4795	111.6

involving nitrogen tetroxide vapor:

$$A = \left[\frac{\partial R_2}{\partial Z} \right]_{T,P} = \left[\frac{P}{T} \right]^2 Z^{-3} y_1^{-1} e^{31,250-5152.8/T} \frac{\text{g-mole}}{\text{cm}^3 \text{sec}} \quad (\text{A-9})$$

where $Z = (1+y_2)^{-1}$, the total pressure P is in atmospheres and T in degrees Kelvin.

These reaction rates are (at the experimental conditions) almost twice those selected by Svehla and Brokaw (46). Since lower reaction rates increase the calculated diffusional and thermal effects at the interface, the use of the values of Svehla and Brokaw would only reinforce the conclusion reached in Chapter V.

The latent heat of vaporization of nitrogen tetroxide was calculated from the selected vapor pressure expression and the liquid and vapor densities, using the Clapeyron equation. Good internal consistency was obtained with the selected heat capacity of the liquid and the thermodynamic properties of the vapor.

B. Physical Properties of Liquid Metals.

The properties of liquid metals used in the calculations reported are presented below:

Correlations of the following form were used for the vapor pressures:

$$\log_{10} P = A + B/T + C \log_{10} T$$

where the vapor pressure P is in absolute atmospheres and T is the absolute temperature in degrees Kelvin. The constants A , B and C are listed in the table below:

<u>Metal</u>	<u>A</u>	<u>B</u>	<u>C</u>	<u>Comments</u>
Mercury	7.2188	-3295.2	-0.7095	Fit to three of the selected values (at 0.01, 0.1 and 1.0 atm) of Hultgren et al. (74).
Potassium	6.5982	-4625.3	-0.7006	Heimel's equation (75).
Sodium	6.3542	-5567.0	-0.50	Equation of Ditchburn and Gilmour, recommended by Golden and Tokar (51).

Even though the latent heat of vaporization can be calculated with the Clapeyron equation from vapor pressure and density information, independent correlations were preferred. The correlations took the form:

$$\Delta H_{\text{vap}} = A + B/T$$

where ΔH_{vap} is the equilibrium heat of vaporization in calories per g-atom and T the absolute temperature in

degrees Kelvin. The constants are listed below:

<u>Metal</u>	<u>A</u>	<u>B</u>	<u>Comments</u>
Mercury	14581.1	-0.90174	Equation of Meisl and Shapiro (76).
Potassium	21778.0	-4.2222	Fit to the experimental data in reference 75.
Sodium	23106.0	0.0	Liquid Metals Handbook (77).

The compositions of the vapors at the relatively low pressures of interest in this investigation were obtained from the ideal gas law and equilibrium constants for the dimerization reactions:

where the subscript '1' denotes monomer (the atoms) and '2' the diatomic molecules.

Heavier species (if present) were neglected. The equilibrium constants in terms of partial pressures have been correlated assuming a constant heat of reaction as:

$$\log_{10} K_p = \log_{10} \frac{P_2}{P_1^2} = A + B/T$$

With the partial pressures P_1 and P_2 in atmospheres and the absolute temperature T in degrees Kelvin, the table below lists the constants used:

<u>Metal</u>	<u>A</u>	<u>B</u>	<u>Comments</u>
Mercury	-1.6136	328.62	Estimated by Wilhelm (12).
Potassium	-3.8611	2951.39	Reference 49.
Sodium	-4.3249	4002.33	Reference 51.

The transport properties of the liquid metal vapors were obtained from the Lennard-Jones (6-12) parameters for monomer and dimer molecules listed in the table below:

<u>Parameter</u>		<u>Mercury</u>	<u>Potassium</u>	<u>Sodium</u>
σ_1	(Å)	2.969	4.54	3.66
ϵ_1/k	(°K)	750	1200	1340
σ_2	(Å)	4.2	6.42	5.17
ϵ_2/k	(°K)	1062	1700	1900
σ_{12}	(Å)	3.58	5.48	4.415
ϵ_{12}/k	(°K)	891	1430	1600

The parameters for monoatomic mercury were taken from reference 59. The parameters for monoatomic potassium and sodium were estimated from the boiling point and molar volume or the liquid as recommended by Bird et al. (4):

$$\sigma_1 = 1.166 v_b^{1/3} \quad , \quad \epsilon_1/k = 1.15 T_b$$

The parameters for dimer were estimated as the square root of 2 times those of monomer. σ_{12} and ϵ_{12} were then estimated from the combination rules (4):

$$\sigma_{12} = \frac{1}{2} [\sigma_1 + \sigma_2] \quad , \quad \epsilon_{12} = [\epsilon_1 \epsilon_2]^{1/2}$$

These estimates are consistent with available transport property data for the vapors involved. Inaccuracies in the parameters are reflected mainly as unknown proportionality constants in the reaction rate estimates, in which the Lennard-Jones diameters were used as collision diameters.

The rates of the dimerization reactions were estimated as those calculated with Tolman's technique (48) according to

the expression given by Frost and Pearson (48) for the collision number for collisions between molecules A, B and C such that A and C are within a distance δ of B, which reduces, for triple collisions between monomer molecules to:

$$z'_{111} = 32 \pi^{3/2} \sigma_1^4 \delta \sqrt{\frac{kT}{m_1}} n_1^3$$

where n_1 is the number density of monomer molecules, σ_1 the collision diameter of the monomer molecules, k is Boltzmann's constant, m_1 the mass of a monomer molecule and T the absolute temperature.

In the calculations, δ was taken as 1 Angstrom as suggested by Frost and Pearson (48), a 100 percent efficiency was assumed for the production of dimer, and the Lennard-Jones parameters σ_1 of the atoms were used as their collision diameters. Uncertainties in the assumed quantities are reflected as unknown proportionality constants in the expression, equivalent to unknown efficiency factors.

C. Reflection of Sound Waves by a Liquid Surface.

This study was prompted by suggestions in the literature that the reflection of sound waves by a liquid surface in contact with its vapor could be used to obtain the condensation coefficient. The argument generally used is that if the condensation coefficient were unity there would be a difference in phase between the incident and reflected waves caused by the tendency of the liquid to maintain a constant pressure at the interface. The present results confirm the existence of this phase difference, which seems however to be too small for the accurate determination of the condensation coefficient. This result was obtained because of the inclusion in the analysis of the behavior of the liquid, considering the latent heat of the condensing and evaporating molecules. According to the calculations, the temperature of the liquid surface does not stay constant, but actually oscillates with the frequency of the sound waves, causing the relatively small sensitivity to the condensation coefficient.

Only pure vapor behaving as an ideal gas was considered, and in the analysis the following three independent results were combined:

1) A plane sound wave of low amplitude and frequency travelling in the +z direction in an ideal gas at mean pressure P_v and mean temperature T_v is described adequately (4) by:

$$\text{Pressure: } P = P_v + (\Delta P) \sin[\omega(t-z/c_s)+\beta] \quad (C-1)$$

$$\text{Temperature: } T = T_v + \frac{T_v (\gamma - 1)}{\gamma P_v} (P - P_v) \quad (C-2)$$

$$\text{Velocity: } v_z = \frac{P - P_v}{c_s \rho_v} \quad (C-3)$$

where t denotes time, (ΔP) and β are constants, γ the specific

heat ratio of the gas, $c_g = [\gamma R' T_v]^{1/2}$ is the speed of sound in the gas and ω the circular frequency of the sound. Heat transfer and viscous and second order effects were neglected. Also, in the case of a saturated vapor it is assumed that no condensation or fog formation occurs due to the pressure and temperature variations.

ii) Consider a semi-infinite liquid (or solid) extending from $x = -\infty$ to $x = 0$, with the surface located at $x = 0$, and let y be an axis parallel to the surface. Assume that the temperature of the liquid surface varies according to a travelling wave of the form:

$$T(x=0) = T_L + (\Delta T)_L \sin[\omega t + \Omega y + \beta] \quad (C-4)$$

where ω , Ω , β , T_L and $(\Delta T)_L$ are constants. It may be proven that in the stationary state the temperature profile in the liquid takes the form:

$$T(x,y,t) = T_L + (\Delta T)_L e^{bx} \sin[\omega t + \Omega y + ax + \beta] \quad (C-5)$$

where a and b are the positive roots of: $\omega = 2ab\alpha_L$
 $b^2 = a^2 + \Omega^2$

and $\alpha_L = k_L / (\rho_L c_{p,L})$ is the thermal diffusivity of the liquid.

In the application of this result to the reflection of sound waves it was assumed that the vapor-liquid interface remains at $x = 0$, neglecting the variations in position caused by condensation and evaporation. These variations might generate harmonics in the reflected wave, but otherwise their effect is probably small because of the large density of the liquid compared with the vapor. In practice also, the liquid layer would not be infinite; however, as discussed by Jakob (5) the constant b is usually large, with the effects of temperature oscillations at the surface dying out at relatively short depths into the material, with equation C-5 applying in most instances.

iii) As boundary condition at the interface a first order approximation to the mass balance (equation 18), valid for small temperature differences and fluxes was used:

$$\sqrt{\pi} \xi_0 = \frac{\sigma}{2 - \sigma} \left[\frac{P_s - P_o}{P_v} - \frac{T_s - T_o}{2 T_v} \right] \quad (C-6)$$

where $\xi_0 = v_{x,x=0} / [2 R' T_v]^{1/2}$ and the subscripts 's' and 'o' denote the conditions of the liquid surface and of the vapor at the interface respectively.

This boundary condition is equivalent to Schrage's equation since heat transfer was neglected as in (i). If both mass and heat transfer equations (equations 18 and 19) are considered, it can be proven that the average temperatures of the vapor (T_v) and of the liquid (T_L) are equal, and that the average pressure of the vapor (P_v) is equal to the vapor pressure of the liquid at the average liquid temperature.

Also, an approximate heat balance at the liquid side of the interface was used to relate the temperature gradient in the liquid (obtained from equation C-5) and the mass evaporation rate:

$$- k_L \left. \frac{\partial T}{\partial x} \right|_{x=0} = \rho_v \Delta H_{\text{vap}} v_{x,x=0} \quad (C-7)$$

These equations were applied to the reflection of a train of plane sound waves impinging on the liquid surface with an angle of incidence α as shown in figure C.

The vapor conditions are given by the superposition of incident and reflected waves, given each by equations such as C-1, C-2 and C-3. The liquid temperature is given by the superposition of equations similar to C-5 for each sound wave. Equations C-6 and C-7 permit then the calculation of the parameters of the reflected waves and the temperature of the liquid in terms of the parameters of the incident wave.

It was found that there is only one reflected wave (i.e.,

Figure C.- Schematic diagram of the reflection of a train of plane sound waves by a liquid surface.

that no harmonics are generated) having the same frequency as the incident wave, with the angle of reflection being equal to the angle of incidence (α) as shown in figure C. The results are summarized in the following equations:

Incident wave: $P = P_v + (\Delta P)_i \sin[\omega t + \omega(y \sin \alpha - x \cos \alpha)/c_s + \beta_i]$

Reflected wave: $P = P_v + (\Delta P)_r \sin[\omega t + \omega(y \sin \alpha + x \cos \alpha)/c_s + \beta_r]$

Liquid surface: $T_s = T_v + (\Delta T)_s \sin[\omega(t - y \sin \alpha/c_s) + \beta_i - \varphi + \epsilon]$

with:

$$\frac{(\Delta P)_r}{(\Delta P)_i} = \left[\frac{C_1^2 + C_3^2}{C_2^2 + C_3^2} \right]^{1/2}$$

$$\frac{(\Delta T)_s}{(\Delta P)_i} = \frac{(\gamma + 1) \Delta H_{\text{vap}} \cos \alpha (\alpha_L/\omega)^{1/2}}{\gamma c_s k_L (1 + C_5^2)^{1/4} (C_2^2 + C_3^2)^{1/2}}$$

$$\tan(\beta_i - \beta_r) = \frac{\gamma + 1}{\gamma (C_3 + C_1 C_2 / C_3)} \quad [0 \leq \beta_i - \beta_r \leq \pi]$$

$$\tan \varphi = [1 + C_5^2]^{1/2} - C_5 \quad [0 \leq \varphi \leq \pi/4]$$

$$\tan \epsilon = C_3 / C_2 \quad [0 \leq \epsilon \leq \pi/2]$$

$$C_1 = \left[\frac{2 - \gamma}{\gamma} \right] \left[\frac{\pi}{2\gamma} \right]^{1/2} \cos \alpha + C_4 \cos \varphi - \frac{\gamma + 1}{2\gamma}$$

$$C_2 = \left[\frac{2 - \gamma}{\gamma} \right] \left[\frac{\pi}{2\gamma} \right]^{1/2} \cos \alpha + C_4 \cos \varphi + \frac{\gamma + 1}{2\gamma}$$

$$C_3 = C_4 \sin \varphi$$

$$C_4 = \left[\frac{d \ln P_s}{d \ln T_s} - \frac{1}{2} \right] \frac{P_v \Delta H_{\text{vap}}}{T_v c_s k_L} \left[\frac{\alpha_L}{\omega} \right]^{1/2} \frac{\cos \alpha}{(1 + C_5^2)^{1/4}}$$

$$C_5 = \omega \alpha_L [\sin \alpha / c_s]^2$$

When the condensation coefficient is zero, these results reduce to $(\Delta P)_r = (\Delta P)_i$ and $\beta_r = \beta_i$, and the wave is reflected specularly.

When the condensation coefficient is different from zero, the amplitude of the reflected wave is less than that of the incident wave $[(\Delta P)_r < (\Delta P)_i]$. This implies a loss of energy on reflection and is probably not very significant because it arises in part from the overly simplified energy balance used at the interface (equation C-7).

Incident and reflected waves show a difference in phase, which may be expressed as: the phase of the reflected wave is as if the incident wave were reflected specularly by a plane located inside the liquid at a depth $d = \lambda_s(\beta_i - \beta_r)/(4\pi \cos \alpha)$ measured from the liquid surface, where $\lambda_s = 2\pi c_s/\omega$ is the wavelength of the sound.

Table C shows a sample calculation for steam and mercury vapor assuming condensation coefficients of unity, for waves travelling perpendicular and at 45 degrees to the liquid surface. This table gives an estimate of the applicability of the method to the measurement of condensation coefficients (noting that when $\bar{C} = 0$ the waves are reflected specularly).

As mentioned above, the calculated attenuation of the wave on reflection may not be significant due to the approximations in the derivation, and the following discussion concentrates on the phase lag of the reflected wave.

The effect of the latent heat of the condensing and evaporating molecules is apparent from the table, since if it were neglected a 180° phase lag might be justified by assuming a constant pressure at the interface. Also, the effect is shown by the different variation of the phase difference with pressure for water and mercury, which is caused mainly by the properties of the liquid phases.

As a general rule, high angles of incidence show a higher phase difference. Usually also, the phase difference

Table C.

Calculated Reflection by the Liquid Surface of Sound Waves in
Steam and Mercury Vapor, Condensation Coefficients of Unity.

Sound frequency = 10,000 Hertz.

Figures in parenthesis () refer to a frequency of 10^6 Hz.

d = depth into the liquid at which a perfectly
reflecting surface would give a reflected wave
with the same phase relationship as calculated.

	Vapor Conditions (Saturation)	$\frac{(\Delta P)_r}{(\Delta P)_i}$		$\beta_1 - \beta_r$ (degrees)		d (cm)	
		$\alpha = 0$	$\alpha = 45^\circ$	$\alpha = 0$	$\alpha = 45^\circ$	$\alpha = 0$	$\alpha = 45^\circ$
Steam	4.0 °C	0.387	0.251	23	41	0.136	0.430
	8.03×10^{-3} atm	(0.317)	(0.047)	(11)	(146)	(0.001)	(0.015)
	100.0 °C	0.968	0.955	2	3	0.012	0.038
	1.00 atm	(0.738)	(0.652)	(13)	(18)	(0.001)	(0.002)
Mercury Vapor	176.0 °C	0.117	0.060	9	162	0.022	0.559
	1.00×10^{-2} atm	(0.098)	(0.075)	(1)	(178)	(0.000)	(0.006)
	356.6 °C	0.617	0.507	18	34	0.051	0.138
	1.00 atm	(0.143)	(0.065)	(30)	(92)	(0.001)	(0.004)

increases when the frequency is increased, with exceptions (some appearing in the table) being due to the quadratic nature of terms in $\tan(\beta_i - \beta_r)$. In any case, the upper limit of the phase difference is reached when the frequency of the sound increases indefinitely.

The possibly large effect of the heat transfer terms neglected in equations C-6 and C-7 (boundary conditions at the interface) and the sensitivity of the solution to them is illustrated by the phase lags larger than 90 degrees shown in the table. These are obtained when $C_3 + C_1 C_2 / C_3$ is less than zero, i.e., only if C_1 may become negative. The terms in C_1 are directly related to the boundary conditions used at interface, with possible small corrections to these equations directly affecting its sign. The present approximate solution predicts for instance that for an ideal monoatomic gas (as mercury was assumed in Table C) the phase difference between incident and reflected waves varies between 0 and 90 degrees when the angle of incidence is less than 34.5 degrees, and between 0 and 180 degrees otherwise. Such discontinuous behavior is unlikely.

The depth into the liquid over which the temperature fluctuations decrease to 5 percent of their value at the surface ($3/b$ in equation C-5) was calculated as less than 7×10^{-4} cm. for water and 5×10^{-3} cm. for mercury at the lower frequency considered in the table (10^4 Hertz). This shows that in practice shallow layers of liquid can be considered as infinite.

Instead of the phase difference, a probably better criterion for applicability of this method to the measurement of the condensation coefficient is d , the distance from the surface at which a perfectly reflecting plane would give a wave with the same phase relationship as the wave reflected by the liquid surface. As shown in the table, low frequencies are more favorable then, although d is small in general.

The difficulty of calibrating an apparatus using this

method may be estimated with the distance d . Obtaining a perfectly reflecting surface for such calibration may also prove difficult with the saturated vapors involved; perhaps the addition of contaminants to the liquid surface (making the condensation coefficient equal to zero) might be useful.

The results may be applied to the reflection of sound waves of shape other than sinusoidal. A Fourier analysis of the incident wave would yield its sinusoidal components, and the sinusoidal components of the reflected wave could be calculated with the present results.

D. Condensation in the Presence of a Noncondensable Gas.

Small amounts of noncondensables are known to cause large decreases in condensation heat transfer coefficients because they tend to accumulate adjacent to the condensate surface, lowering the partial pressure of the condensing vapor. Under ideal conditions, temperature and composition profiles for this situation are satisfactorily given by (c.f., 4, 24):

$$T - T_v = (T_o - T_v) e^{[N_1 C_{p1}/k_v] x} \quad (D-1)$$

$$P_{NC} = P_{NC0} e^{[RN_1 T/PD] x} \quad (D-2)$$

$$P_1 + P_{NC} = P_v \quad (D-3)$$

where the subscript '1' denotes the condensing vapor and 'NC' the noncondensable gas, with the quantities in brackets [] taken as constant. N_1 is the molar flux of the condensing vapor (a negative constant), T_v the temperature of the vapor far from the liquid surface and P_v the total pressure of the vapor. It is assumed that the total amount of noncondensable is fixed and that it behaves as a stagnant layer of gas adjacent to the liquid surface, with the vapor far from the condenser being essentially pure 1.

With these assumptions the total number of moles of noncondensable per unit area of liquid surface is given by direct integration (78) as:

$$\int_0^\infty \frac{P_{NC}}{RT} dx = - \frac{P_{NC0}}{RT_v} \sum_{n=0}^\infty \frac{\left[\frac{T_v - T_o}{T_v} \right]^n}{[RN_1 T/PD] + n[N_1 C_{p1}/k_v]} \quad (D-4)$$

As T_o is usually close to T_v this series converges rapidly and a few terms suffice in most instances.

The description of the condensation process is completed by applying the mass balance (equation 51) to the condensing vapor and the energy balance (equation 52) at the interface.

Because $\bar{u}_{NC} = 0$, the dimensionless velocity to use with equations 51 and 52 for the condensing vapor reduces to:

$$\zeta_{10} = \frac{N_1}{P_{10}} [RT_o M_1 / 2]^{1/2} \quad (D-5)$$

and the energy balance (equation 52) becomes:

$$\frac{C_{v1}}{\sqrt{M_1}} E_1 + \frac{C_{vNC}}{\sqrt{M_{NC}}} \left[P_{NC0} \alpha_{NC} \frac{(T_o - T_s)}{\sqrt{T_o}} + \frac{S_{NC0}}{4} \sqrt{\frac{\pi M_{NC}}{2R}} (2 - \alpha_{NC}) \right] \quad (D-6)$$

Figure D.1 presents results obtained for the condensation of potassium vapor (assumed saturated away from the condenser, and monoatomic with a condensation coefficient of unity) in the presence of a constant amount of argon (noncondensable) for two total pressures (1 atm and 0.01 atm). The total argon content was taken as 7.377×10^{-9} g-mole/cm² of condensing surface, which corresponds to the amount in a 0.5 ft³ system with a 4x4 inch condensing plate at a partial pressure of 1 μ Hg at 25 °C. Also, results for 100 times that amount of argon are shown along with the predictions for pure potassium (assumed monoatomic as in Chapter III). The properties of the potassium-argon mixture were evaluated at the interfacial conditions using the parameters given by Wilcox and Rohsenow (24).

In the figure, the condensation heat flux is plotted as a function of the difference between the temperature of the bulk of the vapor (T_v) and that of the liquid surface (T_s). The large effect of minute amounts of noncondensables on heat transfer is evident. The energy accommodation coefficient of

Figure D.1.- Condensation of saturated potassium vapor assumed monoatomic with $\sigma = 1$.

- a) $P_v = 1.0$ atm
 b) $P_v = 0.010$ atm

A - pure potassium
 B - $7.377 \cdot 10^{-9}$ g-mole argon/cm²
 C - $7.377 \cdot 10^{-7}$ g-mole argon/cm²

argon has a negligible effect on the calculated heat flux, with the extreme values (for $\alpha_{Ar} = 0$ and $\alpha_{Ar} = 1$) being practically identical. It might be added that the energy accommodation coefficient of noncondensables is likely to be close to unity, as shown by the decreasing temperatures near the interface measured by Ivanovskii et al. (79).

The calculations for a potassium condensing system with 7.377×10^{-9} g-mole of argon/cm² of condensing surface are re-plotted in figure D.2. This figure shows the condensation coefficient that would have been calculated with Schrage's equation (equation 2) if the presence of noncondensables were not considered, as a function of the saturation pressure at the liquid surface temperature (P_s). The results are practically independent of both energy accommodation coefficient of argon and condensation rate. The plot is in very good agreement with the deduction by Wilcox and Rohsenov (24) that a fixed amount of noncondensables in a system would imply a constant (less than unity) calculated condensation coefficient throughout the pressure range. Because the condensation coefficients calculated from their data show significant variations (figure 1) Wilcox and Rohsenov pointed out that the presence of noncondensables in their sealed system would not explain their low values.

It is worth mentioning that in some cases (i.e., large amounts of noncondensables, high heat fluxes, high energy accommodation coefficient of the noncondensables, and depending on physical properties) the vapor at the interface and for some distance from it was calculated as being supersaturated (i.e., partial pressure higher than the vapor pressure of the liquid at the local temperature). If nucleation were assumed to take place, the analysis would explain the experimental observation of fog formation under such conditions reported by McAdams (6).

Figure D.2.- Condensation coefficients calculated with Schrage's equation for saturated potassium (monoatomic, $\sigma = 1$) condensing in the presence of 7.377×10^{-9} g-mole of argon/cm² of condensing surface.

E. Data Reduction.

The most important information sought from the measurements with the composite condenser was the condensing mass flux at the position of the temperature probe in the vapor. For this reason, the leads to the composite condenser were located around that position, but not too close to interfere with each other or distort the heat flux field significantly (figure 23). The condenser also provided information on how well Nusselt's equation describes the condensation of nitrogen tetroxide vapor.

The following equations describe the thermoelectric phenomena taking place in the condenser (80):

The electric current density vector ($\vec{J}$) in a homogeneous, isotropic conductor is:

$$\vec{J} = -s (\nabla V + \alpha \nabla T) \quad (\text{E-1})$$

where s is the electrical conductivity and α the Seebeck coefficient of the material, V the electric potential and T the absolute temperature.

If k is the thermal conductivity of the material, the total energy flux vector ($\vec{J}_E$) is given by:

$$\vec{J}_E = -k \nabla T + (V + \alpha T) \vec{J} \quad (\text{E-2})$$

and the laws of conservation of electric charge and energy can be written for the steady state as:

$$\nabla \cdot \vec{J} = 0 \quad (\text{E-3a})$$

$$\nabla \cdot \vec{J}_E = 0 \quad (\text{E-3b})$$

The energy transport equation E-3b can be expressed more conveniently as:

$$\nabla \cdot \vec{J}_E = -\nabla \cdot [k \nabla T] + \tau \vec{J} \cdot \nabla T - \frac{J^2}{\sigma} \quad (E-3c)$$

which is seen to include heat conduction, Joule heating and thermoelectric cooling (through the Thompson coefficient $\tau = T \frac{d\alpha}{dT}$).

As boundary conditions, the following apply: Across the interface between two materials A and B the electric potential (V) and the normal components of the electric current density (J_n) and total energy flux (J_{En}) are conserved:

$$V_A = V_B \quad (E-4a)$$

$$[J_n]_A = [J_n]_B \quad (E-4b)$$

$$[J_{En}]_A = [J_{En}]_B \quad (E-4c)$$

These equations were solved numerically in two dimensions for the geometry of the condenser, shown schematically in figure E.1 with the following boundary conditions and approximations:

At the surface S_1 (nickel protective layer in contact with the coolant) a constant heat transfer coefficient (h) between S_1 and the coolant was assumed:

$$h [T_1 - T_c] = k_{Ni} \frac{\partial T}{\partial x} \quad (E-5)$$

where T_1 is the temperature of the surface of the nickel layer and T_c the coolant temperature. Due to the high flow rates used the coolant temperature increased by less than 0.5°C when passing through the condenser, and a constant T_c , equal to the arithmetic average of the temperatures measured

Figure E.1.- Schematic diagram of the condenser.
Not to scale.

by the coolant thermocouples, was used in the calculations. Furthermore, shortcircuiting of the surface S_1 to the aluminum sides of the coolant cavity by the coolant was neglected because the relatively high electrical resistivity of the coolant makes such leakage currents very small compared with the ones developed within the metallic layers:

$$J_n \approx 0 \quad \text{on } S_1 \quad (\text{E-6})$$

The top and bottom surfaces of the layers (planes S_2 and S_3) were assumed to be perfectly insulated thermally and electrically:

$$J_y = \frac{\partial T}{\partial y} = 0 \quad \text{on } S_2 \text{ and } S_3 \quad (\text{E-7})$$

The same was assumed for the corresponding surfaces S_4 and S_5 within the aluminum base metal.

The top and bottom sections of the condensing surface (planes S_6 and S_7) were assumed to have a constant temperature.

This and the other assumptions were made because of the practical impossibility of accounting accurately for end effects in the condenser. However, because the aluminum base form was made fairly thin (0.125 inches nominal) and because of the location of the electrical leads to the condenser, these approximations do not introduce a large uncertainty in the desired measurements. Also, direct calibration of the condenser with another fluid (acetone) under similar conditions as during the nitrogen tetroxide tests minimizes these effects.

It may be noted that the largest uncertainty in this respect would derive from the assumption of a constant temperature at the surface S_6 (at the leading edge of the condensing surface) because of the higher heat fluxes expected there. This area is small, and the aluminum has a higher

thermal conductivity than that of the electrodeposits, allowing for more heat withdrawal at the sides of the coolant cavity to account for that and other possible thermal effects. For the same reason, coolant was introduced at the top of the condenser.

Because nitrogen tetroxide and acetone are non-conducting fluids (81) no electrical current flows through the condensing surface:

$$J_x = 0 \quad \text{on } S_8 \quad (\text{E-8})$$

The energy flux at this surface can not be obtained directly from the measurements (which in essence consisted of only two voltage differences), and an indirect method was used, which includes a Nusselt's-type correlation as to its variation:

Letting T_w be the temperature of the condensing surface (plane S_8) and T_{sat} the saturation temperature of the vapor, the film thickness δ at a distance y from the leading edge of the condenser is given by the modified Nusselt-type equation:

$$\delta^4 \left[1 + \frac{4k_L}{3\beta\delta\Delta H_{\text{vap}}} \right] = \frac{4k_L\mu_L}{C^4 \rho_L^2 g\Delta H_{\text{vap}}} \int_0^y [T_{\text{sat}} - T_w - \tau] dy \quad (\text{E-9})$$

where inertia and energy convection terms were neglected as in reference 17.

The coefficient C accounts for departures from Nusselt's equation and was assumed constant. C can be interpreted as the ratio between the actual condensation heat flux and that predicted by Nusselt's theory when only hydrodynamic effects are considered.

The condensing mass flux of the vapor is given by:

$$W = \frac{C_L^4 \rho_L^2 g \delta^2}{\mu_L} \frac{d\delta}{dy} = \frac{k_L}{\delta \Delta H_{\text{vap}}^*} \frac{[T_{\text{sat}} - T_w - \gamma]}{[1 + k_L / \beta \delta \Delta H_{\text{vap}}^*]} \quad (\text{E-10})$$

β and γ account for irreversible effects at the vapor-liquid interface, and were defined through the equation:

$$W = \beta [T_{\text{sat}} - T_s - \gamma] \quad (\text{E-11})$$

where T_s is the liquid surface temperature.

β and γ may be obtained by a linearization of the equations presented in Chapters III and IV. Schrage's equation (equation 2) yields for small temperature differences and fluxes:

$$\beta = \sqrt{\frac{2}{\pi R^* T_{\text{sat}}}} \frac{\sigma}{2 - \sigma} \left[\frac{dP}{dT} + \frac{P_v}{2T_{\text{sat}}} \right] \quad (\text{E-12a})$$

$$\gamma = \frac{T_v - T_{\text{sat}}}{2T_{\text{sat}} \frac{dP}{dT} - 1} \quad (\text{E-12b})$$

where σ is the condensation coefficient and $\frac{dP}{dT}$ denotes the derivative of the vapor pressure of the liquid with respect to temperature.

Expressions E-12 were used in the data reduction because of the very minor effect interfacial phenomena would have on the condensation heat transfer of acetone and nitrogen tetroxide. Condensation coefficients of unity, with the average molecular weight of the vapor for nitrogen tetroxide, were considered adequate.

The liquid surface temperature is given by:

$$T_s = T_{sat} - \frac{\gamma + (T_{sat} - T_w) \frac{k_L}{\beta \Delta H_{vap}^*}}{1 + k_L / \beta \Delta H_{vap}^*} \quad (E-13)$$

The liquid properties were evaluated at a temperature $T_w + 0.25 (T_s - T_w)$ as recommended by Drew (as quoted in reference 82). ΔH_{vap}^* is the difference in enthalpy per unit mass between the vapor and the liquid at a temperature $T_w + 0.625 (T_s - T_w)$, which is the mixing-cup average temperature of the condensate when a semi-parabolic velocity profile and a linear temperature distribution are assumed, thus accounting approximately for liquid subcooling.

Finally, the boundary condition at the aluminum condensing surface is given by the heat flux as:

$$k_{Al} \frac{\partial T}{\partial x} = W \Delta H_{vap}^* \quad \text{on } S_8 \quad (E-14)$$

A digital computer program written to solve to solve these equations numerically used central differences as approximations for the derivatives because of their higher accuracy (83). Seven nodal points in the y-direction and three in the x-direction for each layer were found to provide an adequate compromise between absolute accuracy and computer time requirements. A relaxation method combined with iterations for the different unknowns was followed in the solution.

The computer program is presented in Appendix F, as used in the reduction of the condensation data for acetone to obtain the results in Table IX. It includes the correlations obtained from general references (84, 85) for the properties of acetone and metals, along with thermocouple calibration information. The properties of the deposits were assumed to

be constant, as justified by the small temperature variations calculated for the extended thermocouple, and were evaluated at an average temperature for each deposit.

Basically, two measurements were made with the extended thermocouple: In figure E.1 (where dimensional information additional to that in figure 23 is presented) three leads are shown attached to points A, B and C in the condenser. This particular set of leads was chosen in the data reduction in preference to the other possible one in figure 23 because the uppermost copper lead in it was the closest to the condensing surface, thus yielding information principally in the region where knowledge of heat flux and temperature is most important. Leads 1 and 3 are copper wires and are connected directly to a potentiometer. The third lead (number 2) is nickel and is connected to a potentiometer through a copper wire and a reference junction maintained at a temperature T_{ref} ($0.00^{\circ}\text{C} = 273.15^{\circ}\text{K}$). The voltages measured with the potentiometer (which in general has a copper circuit) between these leads are given by:

$$\Delta \text{emf}_{31} = V_3 - V_1 = \int_{T_A}^{T_C} \alpha_{\text{Cu}} dT + V_C - V_A \quad (\text{E-15})$$

$$V_3 - V_2 = \int_{T_{\text{ref}}}^{T_B} (\alpha_{\text{Cu}} - \alpha_{\text{Ni,L}}) dT + \int_{T_B}^{T_C} \alpha_{\text{Cu}} dT + \\ + V_C - V_B \quad (\text{E-16})$$

where the subscripts A, B and C denote values at the points A, B and C respectively. The subscript L is used to denote the properties of the nickel lead. Because in general copper is electrodeposited quite uniformly and with low stresses (53), it was assumed that the copper deposits and their leads

had the same properties, which were obtained from the literature (84).

Experimental values of Δemf_{31} are listed in Tables IX and X. The temperatures t_{32}^* in the tables were obtained from the measured voltage differences $V_3 - V_2$ and the nickel lead properties with the relationship:

$$V_3 - V_2 = \int_{T_{ref}}^{t_{32}^*} (\alpha_{Cu} - \alpha_{Ni,L}) dT \quad (E-17)$$

Calibration of the condenser was necessary to determine the properties needed in the data reduction. Simultaneously with the calibration of all the thermocouples, a constant temperature calibration of the condenser was performed by immersing them in a well-stirred bath at a constant temperature T (determined with calibrated thermometers). This provided information only on the nickel leads according to equations E-15 and E-16:

$$V_3 - V_1 = 0 \quad (E-18)$$

which served as a test of the uniformity of the copper leads, and

$$V_3 - V_2 = \int_{T_{ref}}^T (\alpha_{Cu} - \alpha_{Ni,L}) dT \quad (E-19)$$

from which the thermoelectric properties of the nickel leads were obtained and correlated against temperature. The thermocouple calibration was carried out in the range -10 to $+30^\circ\text{C}$, and the measured electromotive forces were correlated by least squares with equations of the form: $\alpha - \alpha_{Cu} = a + bT$, which was considered adequate for the narrow experimental range. The correlations showed uniformly standard deviations

corresponding to uncertainties of less than 0.05 °C in the temperature measurements. Good agreement was found with published values for the materials involved.

To check the properties of the aluminum base form, a strip cut from the same plate was partly sawed from alternate edges so that, on folding, a long piece, about 3/32-inch square cross section, was obtained. The electromotive force of this wire was measured against copper, obtaining good agreement (6 percent discrepancy on the average) with literature values for aluminum (84). Literature values were considered more reliable for the data reduction since the small discrepancy in the values may have been caused by stresses in the sample.

A uniform heat flux calibration of the condenser was attempted by attaching to it an electrolytic copper block of the same cross section, 2-1/8 inches thick, with a nichrome wire heater bolted to the top surface. The heater was supplied with direct current and was fitted with both current and potential leads. A carved styrofoam block provided thermal insulation to the assembly. A precision power resistor and voltage divider arrangement permitted the accurate measurement (better than 0.1 percent) with the potentiometer of the power delivered to the heater. This type of calibration can provide information on the properties of the electro-deposits with the relationships:

$$V_3 - V_1 = \int_{T_{AB}}^{T_{BC}} (\alpha_{Cu} - \alpha_{Ni}) dT \quad (E-20)$$

$$V_3 - V_2 = \int_{T_{ref}}^{T_B} (\alpha_{Cu} - \alpha_{Ni,L}) dT + \int_{T_B}^{T_{BC}} (\alpha_{Cu} - \alpha_{Ni}) dT \quad (E-21)$$

where T_{AB} and T_{BC} denote the temperatures at the interfaces between layers A and B and B and C respectively, and may be obtained from the thermal conductivity of the materials with the one-dimensional heat flux equation. Since thermoelectric properties would be affected most drastically by stresses such as in nickel electrodeposits, literature values for the thermal conductivity of pure nickel were adopted. This assumption introduces only a small uncertainty in the condenser wall temperature because the nickel lead was attached very close to the copper deposit in contact with the aluminum. The identical treatment of the acetone and nitrogen tetroxide data reduce the uncertainty even further.

The results obtained had considerable scatter due to non-uniform contact between the condenser surface and the copper block. This calibration was carried out in the range -4 to 43°C and the results are presented in figure E.2. The points in the figure represent the average values of several measurements with the copper block shifted slightly in position. For comparison purposes, figure E.2 also shows the values corresponding to the thermoelectric properties adopted from the condensation of acetone.

As an additional test, the temperature drop across the aluminum was determined by measuring with a microvoltmeter the electromotive force developed between a copper wire attached to the copper block and copper lead number 3. Within the uncertainty caused by the small electromotive force of the aluminum-copper couple, the values obtained were consistent with those obtained from the heat flux and the thermal conductivity of aluminum.

In view of the failure of this calibration, the properties of the nickel deposit were obtained from the experiments on the condensation of acetone with the following procedure: The computer program described previously was used to find the values of h (coolant film heat transfer coefficient) and

Figure E.2.- Results of attempted constant heat flux condenser calibration.

α_{Ni} (Seebeck coefficient of the nickel deposit) consistent with the measured voltage differences V_3-V_1 and V_3-V_2 , and the measured coolant temperature and vapor conditions. Exact agreement with Nusselt's equation (i.e., $C = 1$) was assumed. In view of the rather large scatter obtained for α_{Ni} (due most probably to the presence of noncondensables) the values for the best runs (where continuous pump-down was effected, which also showed noticeable higher heat fluxes) were averaged, and that value used in the nitrogen tetroxide calculations. A constant value was considered adequate in view of the small experimental range, and also the apparent lack of trend of the points in figure E.2 with temperature. The resulting value of α_{Ni} ($\alpha_{Cu}-\alpha_{Ni} = 74.05 \mu V/^{\circ}C$) was considerably different from that of pure nickel, and may actually be due to differences in both thermal conductivity and thermoelectric properties of the material. The identical data reduction for both acetone and nitrogen tetroxide would tend to minimize its effect as discussed earlier.

For the nitrogen tetroxide runs the values of h and C consistent with the measured voltage differences V_3-V_1 and V_3-V_2 , coolant temperature and vapor conditions were calculated with the computer program using an iterative method. This same (reverse) calculation was applied to the acetone data to obtain the results listed in Table IX. The computer program is presented in Appendix F and contains the properties of acetone and thermoelectric properties used in the calculations.

The results listed in Tables IX and X do not include the lower 0.125-inch of the condenser (surface S_7 in figure E.1) since even though that portion could be calculated with the program (and the assumptions made) it is not part of the area covered by the thermocouple.

The vapor temperature probe used to obtain the temperature profiles and superheat was calibrated in place with the

following procedure: First, all bridge resistors were calibrated using the potentiometer to measure voltage drops in the resistors and in a standard one connected in series with a battery. An average value of 0.29 ohms was obtained for each lead wire. Different experimental determinations of the wire resistances during operation of the apparatus were pooled and used to correlate them against temperature. The correlations took the form $R = R_0(1+\alpha t)$ where t is in $^{\circ}\text{C}$. A regression analysis of the data yielded the values of R_0 for each wire (22.77 ohms for wire 1 and 23.33 ohms for wire 2, wire 2 being the closest to the condenser) and the value of the temperature coefficient of resistance ($\alpha=9.54 \times 10^{-4}/^{\circ}\text{C}$), assumed to be the same for both wires.

Figure E.3 presents a comparison between the calculated and experimental points. As reference, the lines corresponding to $+2^{\circ}\text{C}$ and -2°C uncertainty in temperature between that measured with the thermocouple and that calculated from the wire resistance expressions, are also shown. The scatter apparent in the figure is due to several factors such as fluctuating vapor temperature during the measurements, effect of electrical noise, inclusion in the analysis of measurements at low heat fluxes (where the distortion of the temperature profile in the vapor caused by the colder liquid tray became important), and to ambient temperature variations that affected the day to day operation of the bridge. The uncertainty in the temperature coefficient of resistance is estimated as ± 5 percent, which added to the 2 percent accuracy of the microvoltmeter (as calibrated by the manufacturer) yields a 7 percent uncertainty in the superheat and temperature profile measurements.

With these values, the bridge output $V_B - V_C$ in figure 24 can be calculated by a linearization of the equations describing the behavior of the bridge as, approximately:

Figure E.3 .- Results of the wire resistance calibration.

$$V_B - V_C = B_1 V_1 [\Delta t_2 - 0.9989 \Delta t_1] \quad (E-22)$$

where $V_B - V_C$ is in microvolts, V_1 is the bridge supply voltage (measured with the potentiometer) in millivolts, and Δt_2 and Δt_1 are temperature deviations of wires 2 and 1 respectively in degrees centigrade from the balance point. B_1 is a factor, a slight function of the actual temperature (resistance) level of operation, typically equal to 0.235 .

This approximation shows that in fact $V_B - V_C$ is a very closely linear function of the temperature difference between the wires; the approximate value 0.9989 is due to the slightly different resistance of the two wires.

The effects of lack of straightness of the wires (estimated as less than 0.003 inches for the wire closest to the condenser, slightly higher for the trailing wire) or possible conduction of heat along the leads (which would be small due to the high L/r ratio) were neglected.

F. Digital Computer Program for the Reduction
of the Condensation Heat Transfer Data.

```

DIMENSION F(7,11,6),AK(6),H(6),T(7,11,6),TB*KT(6),T8(6)
DIMENSION A(6),BZ(6),B2P1(6),R52KT(6),T85KT(6),S(6),SH(6)
REAL K,KT(6)
EQUIVALENCE (TPEFC,TN16,TS32)
LAYERS.-
C   1. NICKEL PROTECTIVE LAYER.
C   2. TOP COPPER LAYER.
C   3. NICKEL DEPOSIT.
C   4. LOWER COPPER LAYER.
C   5. ZINC (NOT INCLUDED IN THE ACTUAL CALCULATIONS).
C   6. ALUMINUM CONDENSER WALL.
C NOTATION.-
C   A(1)=SEEBECK COEFF. OF 1, VOLT/K
C   AKL= LIQUID THERMAL CONDUCTIVITY, WATT/CM.C
C   DENSI=LIQUID DENSITY,GR/CC
C   DHVAP=HEAT OF VAPORIZATION CORRECTED FOR SUBCOOLING, JOULE/GR
C   DTSUP=VAPOR SUPERHEAT, C
C   KT(1)=THERMAL CONDUCTIVITY OF 1, WATT/CM.C
C   NITER=NUMBER OF ITERATIONS
C   S(1)=ELECTRICAL CONDUCTIVITY LAYER 1,MHO/CM
C   T8(1)=THOMPSON COEFF. LAYER 1,VOLT/K
C   TCCOLC=AVERAGE COOLANT TEMPERATURE, C
C   TVAPC=VAPOR TEMPERATURE, C
C   VISL=LIQUID VISCOSITY, POISE
DATA M,ML,K,A(2),A(4),A(5),T8(5),S(5),KT(5)/7.6,0.9525,0.0,0.0,
1-0.098E-06,0.0,1.0E 10,1.0E 10/
DATA H/0.00254,0.07620,0.07366,0.14478,3.937E-07,0.15748/
DATA B2/7.11111E-06,0.00540,5.98044E-03,0.023104,1.70844E-13,
1 2.733511E-02/
DATA B2P1/1.000007,1.00640,1.005980,1.023104,1.0,1.027335/
DATA BLANK/' '
500 READ (5,110) RUN,EMFV,EMFC1,EMFC2,EMF32,DEMF31,DTSUP,NITER
C MILLIVOLT,MICROVOLT,C
110 FORMAT (A4,6X,6F10.0,15)
IF (RUN.EQ.BLANK) STOP
TVAPC=0.0
TS32=0.0
TC1=0.0
TC2=0.0
DO 771 I=1,10
TVAPC=EMFV/(3.756844E-02+7.079369E-05*TVAPC)
TS32=EMF32/(1.953015E-02+2.927311E-05*TS32)
TC1=EMFC1/(3.816453E-02+5.831961E-05*TC1)
TC2=EMFC2/(3.827903E-02+4.933597E-05*TC2)

```

```

771  CONTINUE
      TSATC=TVAPC-DTSUP
      TCOOLC=(TCL+TC2)/2.0
      DEMF10=1.0E-06*DEMF31
C     FIRST GUESSES
      COEFF=1.0
      TAV1=TN16
      TAV2=TN16
      TAV3=TN16
      TAV4=TN16
      TAV6=TN16
      TAVW=TN16
      TSATK=273.15+TSATC
      TREF=273.15+TN16
C     ACETONE
      PVAPOR=EXP(11.60157-3827.905/TSATK)
      BETA =675.7043*PVAPOR*(3927.905/TSATK-0.5)/(TSATK*SQRT(TSATK))
      GAMMA=DTSUP/(7655.81/TSATK-1.0)
      TSAT=TSATC-TN16-GAMMA
      TCOOL=TCOOLC-TN16
      DO 60 ITER=1,NITER
      IF (ITER.EQ.1) GO TO 515
      IF (MOD(ITER-1,25).NE.0) GO TO 510
      IF ((ITER.IT.160)GO TO 510
      TAV1=TPFEC+(T(1,1,1)+T(1,7,1)+T(3,1,1)+T(3,7,1))/4.0
      TAV2=TPFEC+(T(1,1,2)+T(1,7,2)+T(3,1,2)+T(3,7,2))/4.0
      TAV3=TPFEC+(T(1,1,3)+T(1,7,3)+T(3,1,3)+T(3,7,3))/4.0
      TAV4=TPFEC+(T(1,1,4)+T(1,7,4)+T(3,1,4)+T(3,7,4))/4.0
      TAV6=TPFEC+(T(1,1,6)+T(1,7,6)+T(3,1,6)+T(3,7,6))/4.0
      TAVJ=TPFEC+(T(3,1,6)+T(3,7,6))/2.0
515  CONTINUE
C     EXPERIMENTAL N1 LEADS
      AN1L=-1.95801E-05-5.854622E-09*TAV3
      KT(1)=0.586+2.95344E-04*TAV1
      KT(2)=3.88-11.2078E-03-9.7E-06*TAV2)*TAV2
      KT(3)=0.586+2.95344E-04*TAV3
      KT(4)=3.88-11.2078E-03-9.7E-06*TAV4)*TAV4
      KT(6)=2.03+0.35525E-03*TAV6
      TB(1)=-15.25E-06-(3.507E-09-7.960E-11*TAV1)*TAV1
      S(1)=0.14430E 06/(1.0+(5.44E-03+6.0E-06*TAV1)*TAV1)
      AI(1)=-19.030E-06-(6.1326E-08-3.930E-11*TAV1)*TAV1
      TB(2)=1.50E-06+0.48E-08*TAV2
      S(2)=0.58685E+06/(1.0+3.8E-03*TAV2)
      S(3)=0.14430E+06/(1.0+(5.44E-03+6.0E-06*TAV3)*TAV3)
      TB(3)=0.0
      AI(3)=-7.4052E-05
      TB(4)=1.50E-06+0.48E-08*TAV4
      S(4)=0.58685E+06/(1.0+3.8E-03*TAV4)
      TB(6)=0.094E-6-(2.305E-09+9.313E-11*TAV6)*TAV6
      S(6)=0.38168E+06/(1.0+(4.46E-03+1.18E-06*TAV6)*TAV6)
      AI(6)=-3.177E-06-(0.5148E-08+4.159E-11*TAV6)*TAV6
      TAVL=(3.0*TAVJ+TSATC)/4.0
C     ACETONE PROPERTIES
C     AT 3/8 FROM WALL,      JOULE PER GRAM

```

```

DHVAP=564.0-0.6*TSATC+10.79425+1.2E-03*TAVL)*(TSATC-TAVH)+
1  DTSUP*L.45185
C  AT TAVL, POISES = WATT/CM C , GR / CC
VISC=572.63/(1207.08+TAVL)**2.2244)
AKL=1.959E-03-3.628E-06*TAVL
DENSEL=0.8125-0.0011*TAVL
C5=2.0*AKL*VISC/(980.245*(DENSEL**2)*DHVAP)
C4=AKL*H(6)/KT(6)
C3=AKL/(BETA*DHVAP)
C2=C3/0.75
C1=C5*K/COEFF
C6=0.635*C5/COEFF
DO 1 L=1,6
IF (L.EQ.5) GO TO 1
RS2KT(L)=0.25*S(L)/KT(L)
TBSKT(L)=TB(L)*RS2KT(L)
SH(L)=S(L)/H(L)
TBSKT(L)=TB(L)*H(L)/KT(L)
1  CONTINUE
IF (ITER.NE.1) GO TO 510
INITIALIZATION
SUMR=H(4)/KT(4)+H(6)/KT(6)
D2=12.065*C1/K
D1=1.333333*AKL/D2
DEL=(0.9*D2*TSAT)**0.25
SUMRC=H(1)/KT(1)+H(2)/KT(2)+H(3)/KT(3)
DO 2 I=1,10
DEL3= TSAT / (DEL/D2+D1*SUMR+C2/D2)
DEL=DEL3**0.333333
2  CONTINUE
QBAR=D1*DEL3
DTCOND=TSAT-QBAR*SUMR
T(1,1,1)=-QBAR*SUMRC
DTCOOL=T(1,1,1)-TCOOL
HFILM=QBAR/DTCOOL
HFHKT=HFILM*H(1)/KT(1)
F(1,1,1)=0.0
DO 6 L=1,6
N=3
DO 5 I=1,N
IF (I.EQ.1) GO TO 3
F(I,1,L)=F(I,1,L)
T(I,1,L)=T(I-1,1,L)+QBAR*H(L)/KT(L)
3  CONTINUE
DO 4 J=2,M
T(I,J,L)=T(I,1,L)
F(I,J,L)=F(I,1,L)
4  CONTINUE
5  CONTINUE
IF (L.EQ.6) GO TO 6
T(1,1,L+1)=T(N,1,L)
F(1,1,L+1)=F(N,1,L)+(A(L)-A(L+1))*T(N,1,L)
6  CONTINUE
510 CONTINUE

```

```

C      LEFT FACE OF 1
      F(1,1,1)=(F(2,1,1)+B2(1)*F(1,2,1))/B2P1(1)
      T(1,1,1)=(T(2,1,1)+B2(1)*T(1,2,1)+TCOOL*HFH(KT))/(B2P1(1)+HFH(KT))
      DO 10 J=2,M1
      F(1,J,1)=(F(2,J,1)+B2(1)*(F(1,J-1,1)+F(1,J+1,1)))/2.0/B2P1(1)
      T(1,J,1)=(T(2,J,1)+TCOOL*HFH(KT)+B2(1)*(RSZKT(1)*(F(1,J+1,1)-
1      F(1,J-1,1))*2)+(T(1,J+1,1)+T(1,J-1,1))/2.0))/
2      (B2P1(1)+HFH(KT))
10     CONTINUE
      F(1,M,1)=(F(2,M,1)+B2(1)*F(1,M1,1))/B2P1(1)
      T(1,M,1)=(T(2,M,1)+B2(1)*T(1,M1,1)+TCOOL*HFH(KT))/(B2P1(1)+HFH(KT))
      DO 40 L=1,6
      IF (L.EQ.5) GO TO 40
      N=3
      N1=2
C      IN BULK OF L
C      FROM TOP DOWN
      I=2
      F(I,1,L)=(F(I-1,1,L)+F(I+1,1,L))/2.0+B2(L)*F(I,2,L)/B2P1(L)
      T(I,1,L)=(TSKY(L)+(F(I+1,1,L)-F(I-1,1,L))*(T(I+1,1,L)-
1      T(I-1,1,L))+RSZKT(L)*(F(I+1,1,L)-F(I-1,1,L))*2)+
2      (T(I+1,1,L)+T(I-1,1,L))/2.0+B2(L)*T(I,2,L)/B2P1(L)
      DO 20 J=2,M1
      F(I,J,L)=(F(I+1,J,L)+F(I-1,J,L)+B2(L)*(F(I,J+1,L)+F(I,J-1,L)))/
1      (2.0+B2P1(L))
      T(I,J,L)=(TSKY(L)+(F(I+1,J,L)-F(I-1,J,L))*(T(I+1,J,L)-
1      T(I-1,J,L))+B2(L)*F(I,J+1,L)-F(I,J-1,L))*(T(I,J+1,L)-
2      T(I,J-1,L))+RSZKT(L)*(F(I+1,J,L)-F(I-1,J,L))*2+B2(L)*
3      (F(I,J+1,L)-F(I,J-1,L))*2)+(T(I+1,J,L)+T(I-1,J,L)+B2(L)*
4      (T(I,J+1,L)+T(I,J-1,L)))/2.0/B2P1(L)
20     CONTINUE
      F(I,M,L)=(F(I-1,M,L)+F(I+1,M,L))/2.0+B2(L)*F(I,M1,L)/B2P1(L)
      T(I,M,L)=(TSKY(L)+(F(I+1,M,L)-F(I-1,M,L))*(T(I+1,M,L)-
1      T(I-1,M,L))+RSZKT(L)*(F(I+1,M,L)-F(I-1,M,L))*2)+
2      (T(I+1,M,L)+T(I-1,M,L))/2.0+B2(L)*T(I,M1,L)/B2P1(L)
21     CONTINUE
C      INTERFACE BETWEEN L AND L+1
      IF (L.EQ.6) GO TO 40
      L1=L+1
      IF (L.EQ.4) L1=6
      F(1,1,L1)=(SH(L)*(B2P1(L)+(A(L)-A(L1))*T(1,1,L))+F(N1,1,L)+
1      B2(L)*F(N,2,L))+SH(L1)*(F(2,1,L1)+B2(L1)*F(1,2,L1)))/
2      (SH(L)*B2P1(L)+SH(L1)*B2P1(L1))
      F(N,1,L)=F(1,1,L1)-(A(L)-A(L1))*T(1,1,L1)
      AJN=SH(L)*(F(N,1,L)+B2P1(L)-F(N1,1,L)-B2(L)*F(N,2,L))
      A4=H(L)*(1.0+AJN*TSKY(L))/KT(L)
      B4=H(L1)*(AJN*TSKY(L1)-L.0)/KT(L1)
      T(1,1,L1)=(AJN*(A(L)-A(L1))*TRFF+(T(N1,1,L1)+RSZKT(L)+
1      (2.0*AJN/SH(L1))*2)+B2(L)*T(N,2,L)/A4-(T(2,1,L1)+RSZKT(L1)*
2      (2.0*AJN/SH(L11))*2)+B2(L1)*T(1,2,L1)/B4)/
3      (B2P1(L)/A4-AJN*(A(L)-A(L1))-B2P1(L1)/B4)
      T(N,1,L)=T(1,1,L1)
      DO 30 J=2,M1
      F(1,J,L1)=(SH(L)*(B2P1(L)*(A(L)-A(L1))*T(1,J,L))+

```



```

1  F(N1,J,L)+D2(L)*(F(N,J+1,L)+F(N,J-1,L))/2.0)+
2  SH(L)*(F(2,J,L)+B2(L)*(F(1,J+1,L)+F(1,J-1,L))/2.0))/
3  (SH(L)+B2P(L)*(1+SH(L)+B2P(L)))
  F(N,J,L)=F(1,J,L)-(A(L)-A(L1))*T(1,J,L)
  AJN=SH(L)*(F(N,J,L)+B2P(L)-F(N1,J,L)-B2(L)*(F(N,J+1,L)+F(N,J-1,L)
1  )/2.0)
  A4=H(L)*(1.0+AJN*TBHKT(L))/KT(L)
  B4=H(L)*(AJN*TBHKT(L)-1.0)/KT(L)
  T(1,J,L)=(AJN*(A(L)-A(L1))*TRFF+(T(N1,J,L)+TBSKT(L)+B2(L)*
1  (F(N,J+1,L)-F(N,J-1,L))*T(N,J+1,L)-T(N,J-1,L))+RS2KT(L)*
2  ((2.0*AJN/SH(L))*2+B2(L)*(F(N,J+1,L)-F(N,J-1,L))*2))/
3  B2(L)*(T(N,J+1,L)+T(N,J-1,L))/2.0)/A4-(T(2,J,L)+B2(L)*
4  (F(1,J+1,L)-F(1,J-1,L))*T(1,J+1,L)-T(1,J-1,L))+TBSKT(L)+
5  RS2KT(L))*((2.0*AJN/SH(L))*2+B2(L)*(F(1,J+1,L)-F(1,J-1,L)
6  )**2))+B2(L)*(T(1,J+1,L)+T(1,J-1,L))/2.0)/B4)/
7  (B2P(L)/A4-AJN*(A(L)-A(L1))-B2P(L)/B4)
  T(N,J,L)=T(1,J,L)
30  CONTINUE
  F(1,M,L)=(SH(L)*(B2P(L)*(A(L)-A(L1))*T(1,M,L)+F(N1,M,L)+
1  B2(L)*F(N,M,L)+SH(L)*(F(2,M,L)+D2(L)*F(1,M,L)))/
2  (SH(L)+B2P(L)+SH(L)+B2P(L)))
  F(N,M,L)=F(1,M,L)-(A(L)-A(L1))*T(1,M,L)
  AJN=SH(L)*(F(N,M,L)+B2P(L)-F(N1,M,L)-B2(L)*F(N,M,L))
  A4=H(L)*(1.0+AJN*TBHKT(L))/KT(L)
  B4=H(L)*(AJN*TBHKT(L)-1.0)/KT(L)
  T(1,M,L)=(AJN*(A(L)-A(L1))*TRFF+(T(N1,M,L)+RS2KT(L)*
1  ((2.0*AJN/SH(L))*2+B2(L)*T(N,M,L))/A4-(T(2,M,L)+
2  RS2KT(L))*((2.0*AJN/SH(L))*2+B2(L)*T(1,M,L))/B4)/
3  (B2P(L)/A4-AJN*(A(L)-A(L1))-B2P(L)/B4)
  T(N,M,L)=T(1,M,L)
40  CONTINUE
C  BOUNDARY CONDITION AT THE CONDENSING PLATE
  F(N,1,6)=(F(N1,1,6)+B2(6)*F(N,2,6))/B2P(6)
C  T IS ASSUMED CONSTANT AT THE TOP
  AINT=C6*(TSAT-T(N,1,6))
  DEL=AINT*0.25
  DO 50 I=1,5
50  DEL=(AINT/(1.0+C7/DEL))*0.25
  T(N,1,6)=(T(N1,1,6)+C4*TSAT/(DEL+C3)+B2(6)*T(N,2,6))/
1  (B2P(6)+C4/(DEL+C3))
  DO 52 J=2,M1
  AINT=AINT+C1*(2.0*TSAT-T(N,J,6)-T(N,J-1,6))
  DO 51 I=1,5
51  DEL=(AINT/(1.0+C2/DEL))*0.25
  F(N,J,6)=(F(N1,J,6)+B2(6)*F(N,J+1,6)+F(N,J-1,6))/2.0/B2P(6)
  T(N,J,6)=(T(N1,J,6)+C4*TSAT/(DEL+C3)+B2(6)*(F(N,J+1,6)-
1  *(T(N,J+1,6)-T(N,J-1,6))*TBSKT(6)+RS2KT(6)*(F(N,J+1,6)-
2  F(N,J-1,6)))+B2(6)*(T(N,J+1,6)+T(N,J-1,6))/2.0)/
3  (B2P(6)+C4/(DEL+C3))
52  CONTINUE
C  T IS ASSUMED CONSTANT AT THE BOTTOM
  AINT=AINT+C1*(2.0*TSAT-T(N,M,6)-T(N,M1,6))
  ON 53 I=1,5
53  DEL=(AINT/(1.0+C2/DEL))*0.25

```

```

F(N,M,6)=(F(N1,M,6)+B2(6)*F(N,M1,6))/B2P1(6)
T(N,M,6)=(T(N1,M,6)+C4*TSAT/(DEL+C3)+B2(6)*T(N,M1,6))/
1 (B2P1(6)+C4/(DEL+C3))
DEL=0.0
IF (MOD(ITER,25).NE.0) GO TO 200
IF (ITER.LT.160) GO TO 200
DTCOND=TSAT-T(3,4,6)
DYCOOL=T(1,4,1)-TCOOL
FF1=0.28070*F(2,3,4)+0.71930*F(3,3,4)
FF2=0.8*F(2,5,2)+0.2*F(3,5,2)
FF3=0.82759*F(2,4,3)+0.17241*F(3,4,3)
D1=DEMF10/(FF2-FF1)
IF (D1.GT.1.1) D1=1.1
IF (D1.LT.0.9) D1=0.9
T3OLD=0.82759*T(2,4,3)+0.17241*T(3,4,3)
T1MT3=T(3,4,6)-T3OLD
T3MT2=T3OLD-T(1,4,1)
DELT=(A13)*T3OLD-FF1+FF3)/ANEL-T3OLD
IF (ABS(DELT).GT.1.0) DELT=SIGN(1.0,DELT)
IF (DELT.LT.0.0.AND.DELT.LT.-DYCOOL/10.0) DELT=-DYCOOL/10.0
IF (DELT.GT.0.0.AND.DELT.GT.DTCOND/10.0) DELT=DTCOND/10.0
DELT1=DELT+T1MT3*(D1-1.0)
DELT2=DELT-T3MT2*(D1-1.0)
COEFF=COEFF*D1*(D1/(1.0-DELT1/DTCOND))**3)
HFILN=HFIL*(D1/(1.0+DELT2/DYCOOL)
HFMKT=HFIL*(D1/(KT**1))
200 CONTINUE
D1=F(1,1,1)
DO 56 I=1,3
DO 56 J=1,7
DO 56 L=1,6
F(1,J,L)=F(1,J,L)+D1
56 T(1,J,L)=T(1,J,L)+DELT
60 CONTINUE
C=COEFF**0.25
QAVG=AKL*K*(DEL**3)/(8.5725*C1)
WRITE (6,104) RUN,TCOOLC,TVAPC,DTSUP,TS32,DEMF31,QAVG,C
104 FORMAT ('D RUN' 1,A4,' COOLANT',F10.2,' C',' VAPOR',F10.2,
1 ' C',' SUPERHEAT',F10.2,' C',' TS32',F10.2,' C'
2 ' DEMF31',F10.1,' UV',' Q/A',F10.3,' WATT/CM**2'
3 ' C',F10.3//)
GO TO 500
END

```