Heat Transfer to a Subliming Solid-Vapor Mixture of Hydrogen below Its Triple Point

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Heat transfer coefficients have been measured over a range of Reynolds numbers for a solid-vapor mixture of parahydrogen discharging through a heated brass tube below the triple point pressure. A correlation is given which is shown by a formal analysis of a simple model to account for most of the system variables.

This study was prompted by interest in the venting of liquid hydrogen to a low pressure ($\sim 10^{-6}$ mm. Hg) space environment. It is hoped, however, that the investigation of the heat transfer mechanism begun here will contribute to the understanding of two-phase heat transfer with vaporization in general, since the solid-vapor system is a simple one uncomplicated by surface tension and wave phenomena.

In these experiments liquid parahydrogen at its atmospheric boiling point was flashed through a small orifice down to a pressure of a few millimeters of mercury. This pressure was sufficiently below the triple point (53 mm. Hg) so that freezing times were little different from zero pressure freezing times (10^{-7} sec.) (*1*) and the jet emerging at the inlet of a short heated brass tube broke up into a suspension of solid particles in vapor. Provided the tube wall was hot enough, the mixture discharged as a fluid and its heat transfer coefficient could be measured routinely. That no liquid was present in the tube was evident from visual observations on a similar unheated glass tube. In all cases liquid did not persist more than 1 mm. past the orifice.

EXPERIMENTAL EQUIPMENT

The experimental system is shown schematically in Figure 1. A large vacuum insulated Dewar (A) was constructed, the inner wall of which could be precooled by passing liquid nitrogen through the panels B_1, B_2, and B_3. A coarse vacuum (not less than 2 mm. Hg) could be maintained inside the Dewar by pumping through the 6-in. line (G) with either one, two, or three reciprocating vacuum pumps C_1, C_2, and C_3, each having a capacity of 650 CFM at 10 mm. Hg. The Dewar was fitted with a 6-in. diameter, double-glass, evacuated window (F) for visual observation.

The test liquid filled the storage vessel (D) of 9 liters capacity, which could be pressurized or run at essentially atmospheric pressure with boil-off passing through wet test meter (E), via heat exchanger (H) consisting of a copper coil in a tub of water.

At the bottom of (D) was situated a ¾-in. diameter neck accommodating at its lower end an orifice drilled in a 0.016-in. thick circular stainless steel plate. Flow rate was varied by interchanging plates with different sized orifices or by varying the pressure in vessel (D). Four orifices were used in these experiments with 0.144-, 0.105-, 0.089-, and 0.059-cm. diameters.

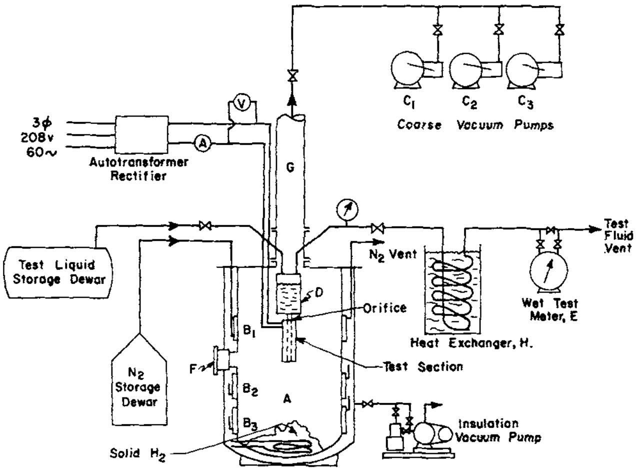

Fig. 1. Schematic arrangement of experimental system.

The brass test section is shown in detail in Figure 2. It was attached at the bottom of the vessel (D) via a thin wall (0.020 in.) stainless steel transition to limit heat conduction to and from the vessel. Calculations showed that under operating conditions this heat conduction was negligible. The four copper-constantan thermocouples were laid in helical grooves, 0.020 in. wide and 0.015 in. deep at 3-in. spacing, machined in the tube wall which, having 1/32-in. wall thickness, left approximately 0.016-in. thickness of brass separating the junctions from the flow stream. Thermal equilibration of the thermocouples with the tube wall was obtained by laying them in the helical grooves for three turns followed by a length along the outer tube wall to the top of the tube. The thermocouple wire, both in the grooves and along the tube, was cemented to the tube with varnish. Finally, in order to enclose the junctions in an isothermal region as nearly as possible, thin strips of brass were soft soldered over the grooves.

The application of heat through the brass tube wall was required to be done in such a way that no temperature gradients were induced in the thermocouple wires. This was done by covering the tube and thermocouple leads with a layer of Fiberglas paper which, when attached, was soaked in varnish.

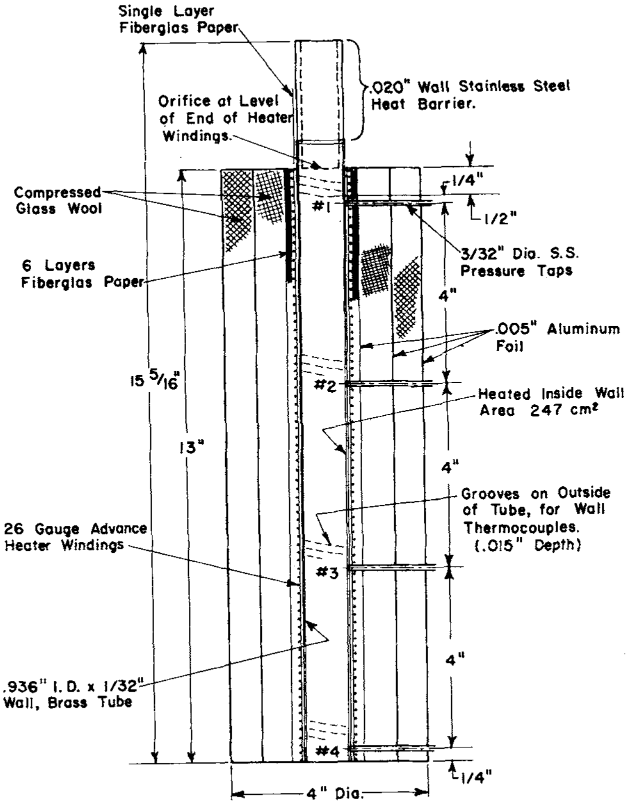

Fig. 2. Heated brass test section.

The heater was wound noninductively, uniformly, and closely over this from 26-gauge, double-glass-covered Advance wire and again soaked in varnish.

It would have been desirable then to enclose the whole tube in a vacuum insulation with a radiation shield. However, the exploratory nature of the experiments led us to prefer a simpler approach where the insulation was obtained by six further layers of Fiberglas paper soaked on with varnish followed by alternate layers of aluminum foil and compressed glass wool, giving a total insulation thickness of about 1½ in.

INSTRUMENTATION

Power from a three-phase, 208-v. source was fed through a three-phase auto transformer and fullwave bridge rectifier circuit to the tube heater and measured by a moving coil ammeter and voltmeter. Accuracy of this measurement is considered to be within 5%.

Thermocouple emf's were referenced to the liquid in the vessel (*D*) and measured potentiometrically; emf's could be measured to within 2 μv., although fluctuations made this accuracy somewhat superfluous. The temperature of the liquid in the storage vessel (*D*) was measured by a platinum resistance thermometer. Both potential drop and current were measured potentiometrically and the measured liquid temperature was accurate to 0.05°K. at liquid hydrogen temperature.

Pressures along the test section and in the Dewar were measured in turn with a McLeod gauge. The readings obtained were reproducible to 0.5 mm. Hg. In the calculation of heat transfer coefficients, the bulk stream temperatures were assumed to be the saturation temperatures corresponding to these pressures, since no simple method could be devised for a direct temperature measurement. Hence, within the limitations of this assumption, the 0.5 mm. Hg corresponded to a worst uncertainty of about 0.1°K. for hydrogen (5 mm. Hg, 10.9°K.).

The rate of flow of liquid through the orifice was determined by a continuous record on an oscillograph chart of liquid level in the storage vessel. The signal for this was derived from a capacitance liquid-level gauge balanced across an a.c. bridge circuit against a standard capacitor. The capacitance gauge itself consisted of two concentric tubes (¾-in. O.D. and ⅞-in. O.D. × 11¾ in.) standing in the storage vessel and fitted with drainage holes. Thus the capacitance, depending on the depth of liquid in the vessel and the difference in the dielectric constants of the liquid and vapor, was linear with liquid depth. The storage vessel capacity had been calibrated against depth and was also found to be linear.

To correct flow rates obtained from the rates of fall of liquid level for boil-off from the storage vessel, the boil-off gas was passed through the heat exchanger (*H*) and then through the wet test meter (*E*).

EXPERIMENTAL PROCEDURE

The inner wall of the Dewar was first precooled with liquid nitrogen and the Dewar evacuated with one of the pumps (*C*). The storage vessel (*D*) was then filled with the test liquid and extra pumps were cut in as necessary to maintain the vacuum between 4 and 5 mm. Hg. In some cases, however, where high power was applied to the test section, Dewar pressure ran as high as 17.5 mm. Hg. Liquid from (*D*) discharged into the Dewar and formed a solid, which collected in the bottom of the Dewar, and vapor, which was pumped off. The storage vessel was allowed to empty completely once before any measurements were taken in order to achieve cool-down of the inner wall of the Dewar and all supports leading to the vessel itself.

The system was then ready for a heat transfer measurement. Power was applied to the test section until the thermocouple emf's indicated the required temperature. It was then adjusted until a power level was found at which temperatures stabilized and, after several minutes of such steady operation, the emf's were recorded in turn, together with the potential drop across the platinum resistance thermometer. At this time also the McLeod gauge was read at each station. Normally, the highest power level to be run was applied first and successively lower levels applied until either a solid flow restriction was formed in the tube or the power was considered to be at the lower limit for accurate measurement.

With the larger orifices and, consequently, higher discharge rates, solid tended to pile up in the bottom of the Dewar to such a height that free discharge from the tube was impeded. In these cases, it was found possible to maintain unimpeded operation by operating a wiper arm, which reached down into the Dewar and with which the solid could be pushed clear. This circumstance set an upper limit to orifice size used. A lower limit was set by two factors. First, since boil-off was independent of orifice size, the boil-off correction to flow rate became proportionately larger for the small orifices. Second, the discharge through a small orifice was found to be quite variable and steadily decreased during the course of a day's run. It seems likely that solid impurities may have built up in the small orifices or that cavitation at the orifice may have been the cause.

CALIBRATIONS

The wall thermocouples were calibrated by a single temperature check in which the brass test section was made into an ice bath by plugging the lower end, and the cold junction was immersed in liquid nitrogen. A single factor for each thermocouple was then applied to the standard copper-constantan tables of Powell, Bunch, and Corruccini (2) to give the correct value of emf at this point.

A second calibration required was for the heat loss through the insulation of the brass test section. This was done at room temperature by inserting glass wool into the tube to eliminate convection and by plugging both ends of the tube. In this way all heat applied had to leave through the insulation at steady state. The wall temperatures for a single low power input were recorded at steady state and it was assumed that the heat loss was radial through the insulation and was proportional to the difference between the wall temperatures and the outside temperature of the insulation. Since it was recognized that the thermal conductivity of the insulation would decrease with temperature, the determination was performed again with the test section cooled to liquid nitrogen temperature. The constant of proportionality was approximately halved

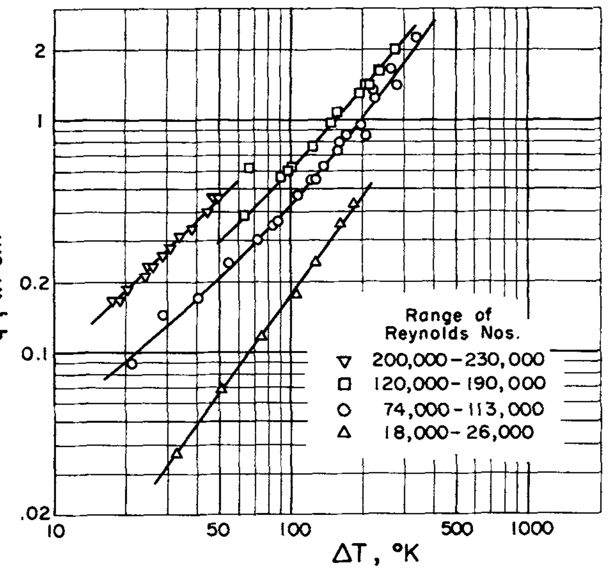

Fig. 3. Heat flux vs. temperature difference at station 4.

in this case. The lower value was used for all corrections to power, since it represented a safe upper limit; the outside of the test section was always colder than liquid nitrogen during an experiment, being swept by hydrogen vapor subliming from the solid in the bottom of the Dewar.

RESULTS

In order to analyze the results it was necessary to calculate the quality of the mixture at each station. By having calculated that the kinetic energy of the stream was negligible, an energy balance could be applied as follows:

$$MH_l = Mx_nH_v + M(1 - x_n)\, H_s - qA_n$$

Enthalpies below the triple point for parahydrogen were obtained from Mullins, Ziegler, and Kirk (*3*) and liquid enthalpies were obtained from Roder and Goodwin (*4*). With quality thus determined at each station, a mean density and mean fluid velocity could be calculated.

In the calculation of such quantities as Reynolds number (GD/μ_{vb}), Prandtl number ($(\mu_v C_p/k_v)_b$), and Nusselt number ($h_{\exp}D/k_{vb}$), the transport properties of the vapors were required. Viscosities at these low temperatures were obtained by extrapolation of the low pressure viscosities given by Johnson (*5*) by using the Chapman-Enskog (*6*) formula for monatomic gases. Thermal conductivities were computed from the Eucken (*6*) equation by using these viscosities and the specific heat derived from the enthalpies mentioned above.

The heat flux q to the solid-vapor stream was calculated at each station from the power input and the heat leak, assumed to be radial, through the insulation. The temperature difference ΔT between the inside wall and the bulk stream was calculated from the measured outside wall temperature, corrected for temperature drop through the wall, and the solid-vapor saturation temperature corresponding to the pressures measured at each station. The experimental heat transfer coefficient $h_{\exp}$ is then $q/\Delta T$ for each station.

The uncertainty in heat flux measurement was about 5%. The percentage correction due to heat leak through the insulation was quite variable, but most corrections were less than 5% with a few points as high as 16%. Combined uncertainties in the measurement of temperature difference led to a worst uncertainty of 0.6°K.

Each orifice gave a more or less constant Reynolds number so that an experimental run can be defined by a range of Reynolds numbers. The results for station 4 are shown in Figure 3 as a plot of q vs. ΔT for all the Reynolds number ranges measured. In Figure 4 the influence of position along the tube is illustrated by plotting q vs. ΔT at each station for the Reynolds number range 74,000 to 113,000.

DISCUSSION OF RESULTS

In general, the nature of two-phase flow and heat transfer is such that no simple correlation can be expected to represent experimental data except in a limited range or where many of the significant variables are held virtually constant. This is illustrated in Figure 5 where the Nusselt number is plotted against Reynolds number for station 4. It is a conventional way of representing heat transfer data in a single-phase system and indeed the data show typical single-phase behavior in spite of scatter. Dimensional analysis of the governing differential equations can often be used to identify the groups which from similarity theory can be expected to represent data for different fluids and geometries. This is most useful when applied to a situation without specifying a particular model, but in two-phase flow the result usually involves many unknown or unmeasurable factors such as interface curvatures and droplet or particle size distribution. In what follows, some important dimensionless groups are identified for heat transfer to a freely flowing solid-vapor mixture in a tube by a formal analysis of a simple model.

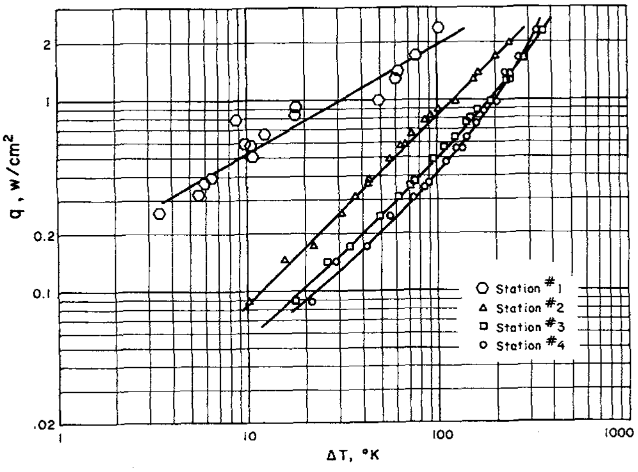

Fig. 4. Heat flux vs. temperature difference. Range of Reynolds numbers, 74,000 to 113,000.

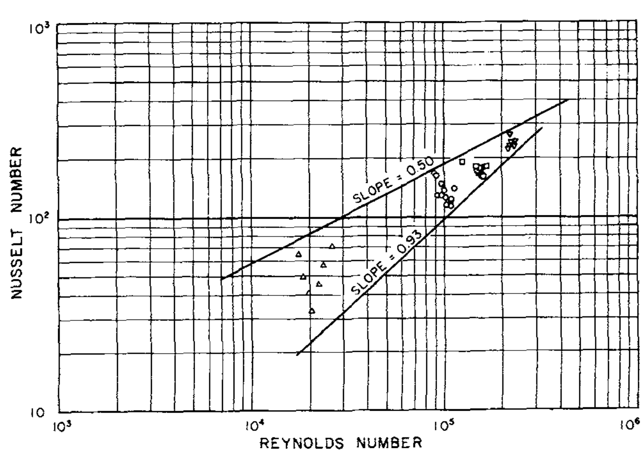

Fig. 5. Nusselt number vs. Reynolds number for station 4; $Z/R = 26.8$.

Since the measured heat transfer coefficients are of the same order of magnitude as for pure vapor traveling at the same mean velocity as the mixture, and since the solid does not apparently contact the tube wall in a freely flowing mixture, it is suggested that vaporization of solid gives rise to an annulus of vapor in contact with the tube wall as in film boiling. In this connection it is noted that most of the data are at a ΔT greater than 10°K. which in the liquid-vapor case would indeed correspond to film boiling. The following further assumptions are made:

1. The core consists of a suspension of solid in vapor and is a region of zero velocity and temperature gradient. In the absence of metastability the core temperature would be the local saturation temperature.
2. There is zero relative velocity between solid and vapor in the core.
3. Vaporization takes place at the boundary of the core enlarging the annulus at the expense of the core.
4. There is no significant diffusion of solid particles toward the wall.
5. The velocity profile in the annulus is always fully developed, be it laminar or turbulent, and vapor properties are constant across the annulus.

The model is thus a separated flow model in which the solid-vapor core is treated as one of the phases. It is therefore necessary to make one further assumption to render the velocity in the annulus determinate. Two simple possibilities are available: (1) the core velocity U is constant along the axis of the tube, or (2) the total density of the core remains constant, that is, particle concentration does not change along the core axis. For simplicity of illustration, assumption (1) will be followed, although (2) is perhaps the more realistic of the two in that it allows for an acceleration of the core as vaporization proceeds.

In principle since both momentum and energy transport are confined by the model to the vapor annulus, the momentum and heat transport problem can be solved and this is actively being pursued at this laboratory. The result given by Frederking (7) for the simple case of forced convection, laminar film boiling on a flat plate could be used here, where curvature effects could be ignored:

$$N_{Nu,z} \equiv \frac{hz}{k} = \left(N_{Re,z} \cdot N_{Pr} \cdot \frac{\lambda}{C_p \Delta T}\right)^{1/2}$$

However, in the present case we have to do with turbulent transport and no such simple expression may be expected. In the present treatment the procedure one would follow will only be indicated formally to identify the groups which must be related by the solutions.

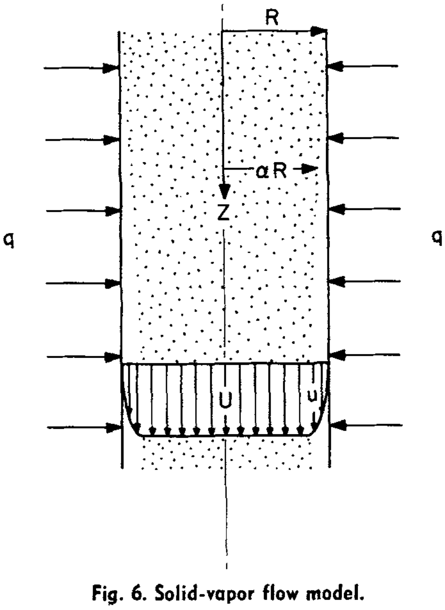

Fig. 6. Solid-vapor flow model.

Referring to Figure 6, let the radius of the core at a distance z along the heated tube be αR. The momentum equation for the vapor annulus subject to the boundary conditions

$$\left.\begin{array}{l} u = O \text{ at } r = R \\ u = U \text{ at } r = \alpha R \end{array}\right\} \tag{1}$$

leads to the following dimensionless groups

$$\left[f, N_{Re}, \alpha, \frac{\bar{u}}{U}, \frac{z}{R}\right]$$

in which N_{Re} may be defined as $(R\rho_v U/\mu_v)$ and the friction factor f as $(R/\rho_v U^2)$ $(\Delta P/\Delta L)$. There is thus a functional relationship between these groups for either laminar or turbulent flow which may be written as

$$\frac{\bar{u}}{U} = \phi_1\left(f, N_{Re}, \alpha, \frac{z}{R}\right) \tag{2}$$

An integral constraint on volume flow rate can now be applied across the whole tube at any axial distance z:

$$\frac{d}{dz}\int_0^R 2\pi r u\,dr = \frac{q}{\rho_v\lambda}2\pi R \tag{3}$$

Here λ is rigorously a corrected latent heat of sublimation to allow for superheating in the vapor film, but as an approximation the actual latent heat will be used. Since the annular film thickness is zero at $z = 0$, integration with respect to z gives, noting assumption (2)

$$2\pi U \int_0^{\alpha R} r\,dr + 2\pi \int_{\alpha R}^{R} r\,u\,dr = \frac{q}{\rho_v\lambda}2\pi R z + \pi R^2 U \tag{4}$$

By denoting the second integral by Q (which may be evaluated from the solution of the momentum equation), this may be rearranged to give

$$\frac{Q}{\pi R^2 U} = \frac{2q}{\rho_v U\lambda}\cdot\frac{z}{R} + (1-\alpha^2) \tag{5}$$

The group $q/\rho_v U\lambda$ has been called the boiling number by some authors in the forced convection boiling literature. However, it has been suggested (8) that in recognition of the early work of Sterman (9) the name Sterman parameter be used. In the present case of solid vaporization this certainly seems more appropriate and therefore the abbreviation N_{St} will be used. Equation (5) may be written formally

$$\frac{Q}{\pi R^2 U} = \phi_2\left(N_{St}, \frac{z}{R}, \alpha\right) \tag{6}$$

Now $\bar{u} = Q/\pi R^2(1-\alpha^2)$; therefore an equivalent relationship to Equation (6) would be

$$\frac{\bar{u}}{U} = \phi_3\left(N_{St}, \frac{z}{R}, \alpha\right) \tag{7}$$

By combining Equations (2) and (7), one obtains

$$\alpha = \phi_4\left(N_{St}, \frac{z}{R}, f, N_{Re}\right) \tag{8}$$

In the absence of viscous dissipation and volume work the energy equation applied to the vapor annulus would lead to the following:

$$\frac{hD}{k_v} = \phi_5\,(N_{Re}, N_{Pr}, \alpha) \tag{9}$$

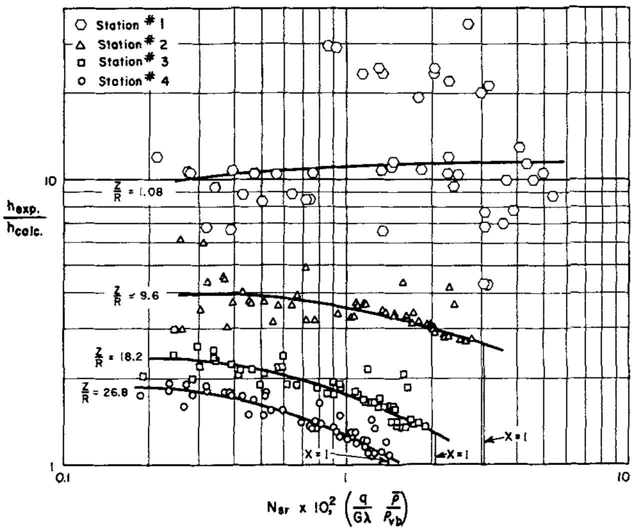

Fig. 7. Heat transfer coefficient ratio vs. Sterman parameter at stations 1, 2, 3, and 4. Reynolds number range, 18,000 to 230,000.

Therefore, finally from Equations (8) and (9) we may eliminate α and write

$$N_{Nu} = \phi_6\left(N_{Re}, N_{Pr}, N_{Sr}, \frac{z}{R}, f\right) \qquad (10)$$

According to Equation (10), without experimental data for the friction factor or at least a means of predicting it, one cannot theoretically expect to account for the observed heat transfer coefficient from this simple model, but in the absence of both, its influence will have to be neglected for this study. Furthermore, as the core radius shrinks we know that in the limit the heat transfer coefficient at large z/R must approach the single-phase value which may be represented by the Sieder and Tate correlation:

$$\frac{hD}{k_v} = 0.026\,(N_{Re})^{0.8}\,(N_{Pr})^{0.33}\left(\frac{\mu_{vb}}{\mu_{v^\circ}}\right)^{0.14} \qquad (11)$$

Assuming, then, that dependence of hD/k_v on N_{Re} and N_{Pr} is separable from its dependence on N_{Sr} and z/R and that the term $(\mu_{vb}/\mu_{v^\circ})^{0.14}$ accounts for the variation of viscosity across the annulus, one would have

$$\frac{hD}{k_v} = 0.026\,(N_{Re})^{0.8}\,(N_{Pr})^{0.33}\left(\frac{\mu_{vb}}{\mu_{v^\circ}}\right)^{0.14}\cdot\phi_7\left(N_{Sr}, \frac{z}{R}\right) \qquad (12)$$

or

$$\frac{h_{\text{exp}}}{h_{\text{calc}}} = \phi_7\left(N_{Sr}, \frac{z}{R}\right) \qquad (13)$$

where h_{calc} is the heat transfer coefficient calculated from Equation (11). In Figure 7 the heat transfer coefficient ratio of Equation (13) is plotted against the Sterman parameter with z/R as a parameter for all the data.

The apparent improvement in the correlation of the data over what was obtained in Figure 5 may itself not be taken to indicate that the physical picture is nearer the truth than the simple single-phase picture implied in Figure 5; the scatter of the experimental data has been suppressed by incorporating one of the prime measured quantities q into both ordinate and abscissa. However, it is to be noted that a definite trend is indicated: for station 4 at low values of the Sterman parameter the heat transfer coefficient ratio approaches the value 2. For high values where, as indicated, a mean quality of 1.0 is approached, the ratio tends toward 1.0. This trend demonstrates that the Sterman parameter is of significance in this process.

It may be concluded that the simple analysis presented has led to an insight into the mechanism involved in heat transfer to a subliming solid-vapor mixture and the data presented have confirmed the significance of the Sterman parameter in this process.

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NOTATION

A_n = inside surface area of test section up to n^{th} station, sq. cm.
C_p = constant pressure specific heat of vapor at bulk conditions, joules/(g.) (°K.)
D = inside diameter of test section, cm.
f = friction factor
G_v = mass velocity in test section for vapor alone travelling at mean velocity of mixture V, g./(sq. cm.) (sec.)
H_l = enthalpy of liquid in vessel D, joules/g.
H_s = enthalpy of saturated solid, joules/g.
H_v = enthalpy of saturated vapor, joules/g.
h_{calc} = heat transfer coefficient calculated from Sieder and Tate correlation for vapor traveling at velocity V, w./(sq. cm.) (°K.)
h_{exp} = experimental heat transfer coefficient $q/\Delta T$, w./(sq. cm.) (°K.)
k_b = thermal conductivity of vapor at bulk conditions, w./(cm.) (°K.)
M = mass flow rate, g./sec.
N_{Nu} = Nusselt number, $(h_{\text{exp}}D/k_v)$
N_{Pr} = Prandtl number, $(\mu_v C_p/k_v)$
q = heat flux at test section wall, w./sq. cm.
Q = volume flow rate in annular film, cc./sec.
r = radial coordinate, cm.
R = tube radius, cm.
N_{Re} = Reynolds number, GD/μ_v
N_{Sr} = Sterman parameter, $= q/\rho_v V\lambda = (q/G\lambda)(\bar{\rho}/\rho_v)$
T = temperature, °K.
ΔT = inside wall temperature minus local saturation temperature, °K.
u = velocity in annular film of vapor, cm./sec.
$\bar{u}$ = mean velocity in annular film, cm./sec.
U = velocity of core
V = mean velocity in test section $G/\bar{\rho}$, cm./sec.
x_n = quality (g. vapor/g. mixture) at n^{th} station
z = axial distance along test section measured from top of heated portion, cm.

Greek Letters

α = core radius/tube radius
λ = latent heat of sublimation, joule/g.
μ_v = viscosity of vapor at bulk conditions, g./(sec.) (cm.)
$\bar{\rho}$ = mean density in test section, g./cc.
ρ_v = density of vapor, g./cc.
ρ_s = density of solid, g./cc.
ϕ = functional relationship

Subscripts

b = vapor property at bulk conditions
$^\circ$ = vapor property at wall conditions

Note: Bulk conditions in this report are taken to be local pressure and corresponding saturation temperature

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Interfacial Tensions of Binary and Ternary Two-Phase Liquid Systems

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A theory is developed to enable prediction of interfacial tension in unsymmetrical, regular, binary liquid systems from solubility data. This is also shown to be applicable to nonregular aqueous binary systems by using solubility parameters and molar volumes calculated from mutual solubilities as substitutes for true molar volumes and the solubility parameters obtained from energies of vaporization.

The theory is extended to include unsymmetrical, regular, ternary liquid systems, and is shown to be applicable to systems consisting of perfluoro-*n*-hexane and other nonpolar organic liquids. The theory is not adequate for aqueous ternary systems.

In several previous theoretical studies of interfacial tension in binary liquid systems, the theory of *strictly regular* solutions has been used as a basis (*2, 3, 8*). Strictly regular systems occur when both components possess identical molar volumes and both liquid phases are regular, which results in temperature-solubility curves which are symmetrical about a critical solution composition $x_{1CS} = x_{2CS} = 0.5$. Since real binary systems are in general neither symmetrical nor completely regular, these previous theoretical models cannot be directly applied in the prediction of interfacial tensions in actual systems. In the development which follows the assumption of identical molar volumes is not made and thus the theory may be applied directly to real binary systems and, as will be shown, even to nonregular aqueous systems. It is also extended to real, regular ternary systems of any degree of immiscibility of the nonconsolutes and for all concentrations of the distributed component. This work is then complementary to that of Shain and Prausnitz (*11*), who treated the initial change of interfacial tension with concentration of a polar distributed component for completely insoluble liquid pairs at infinite dilution of the distributed component. The complete details of the present development are available elsewhere (*9*).

BINARY TWO-LIQUID PHASE SYSTEMS

The theoretical development is based upon the following assumptions, which are similar to those used by Kahlweit (*8*):

1. The system consists of two components present in two coexisting liquid phases at equilibrium.
2. The solutions possess a lattice structure of the same configuration in both phases.
3. Both the bulk phases and the interface layer between them can be described by regular solution theory (*6, 7*).

The lattice structure of assumption 2 is inherently incompatible with the desire to remove all restrictions on relative liquid volumes, since presumably only molecules of a limited ratio of molecular size may be accommodated in a single lattice. Hildebrand and Scott (*7*) have further shown that the lattice concept, together with such other frequently used structure theories as the hole theory, is an unlikely model for liquids generally, perhaps especially for solutions which are so random as to be described by the regular solution theory of assumption 3. Nevertheless, the concept of a lattice for a regular solution has recently been used to good advantage in consideration of interfacial tension (*8, 11*). The lattice struc-

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