Finally, the field is sufficiently old to have generated some quite good secondary sources on reliability. The finest text for engineers currently is Shooman (1968). A few known errors in the first printing have been summarized by the author so that the only substantial error is in the *maximum* likelihood estimates of the parameters of the Weibull distribution on page 475 and following. A monograph by Barlow and Proschan (1965) uses the classic approach and is intended for an audience quite sophisticated in statistical techniques. Ireson (1966) is a handbook for the reliability engineer in the aerospace and defense fields which contains much useful information.

ACKNOWLEDGMENT

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A Theoretical and Experimental Study of the Centrifugal Molecular Still

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A mathematical model of the centrifugal molecular still has been derived based on a fully developed profile, but negligible normal and tangential velocity components. Thermal gradients, film thicknesses, and evaporation rates calculated from this mathematical expression correlate well with reported literature values as well as with the present data.

Mean distillation rates were measured for five pure liquids on a centrifugal still with an effective evaporating surface area of 100 sq. cm. These experimentally obtained rates for liquids exhibiting ideal behavior agreed quite well with theoretical values predicted on the basis of simple kinetic theory. In the case of an associated liquid, however, rate measurements were found to be only 35 to 90% of the theoretical value. Although these low values tend to support the concept of an evaporation coefficient as a true molecular property, there was evidence that surface irregularities could have accounted for all or at least part of the discrepancy noted.

Molecular distillation may be defined as distillation which occurs from the surface of a film of liquid under an operating pressure such that residual gas in a vapor space above the liquid may be considered to have a negligible effect on the process. When a low pressure environment and a nearby condensing surface are provided, escaping molecules have a relatively unobstructed path of travel between the evaporating and condensing surfaces. Since the distance separating these surfaces is of the order of magnitude of the mean-free-path of the vaporizing molecules in the residual gas, molecular distillation has been termed "short-path" or "unobstructed-path" distillation.

As described by Burrows (8) this process can be further categorized by comparison with the two more conventional types of distillation:

Distillation by Boiling. Vapor is generated throughout the liquid at the rate which is proportional to the heat flux; the total pressure acting on the system is the thermodynamic vapor pressure of the liquid phase.

Evaporative distillation. Evaporation which occurs from a liquid below its boiling point at a rate which is a function of the surface temperature and of the vapor conditions above the surface such as occurs in air drying of solids, humidification, and similar processes.

Molecular distillation. A form of evaporative distillation in which the rate is governed solely by the absolute rate of molecular escape from the liquid surface: that is, unlike the first two, there is essentially no return of molecules from the gas to the liquid, and the temperature and corresponding escaping rates attained by the liquid are determined by the heat input, and are unaffected by the vapor space conditions. It can also occur at temperatures higher than the boiling point corresponding to the vapor space pressure. Therefore, molecular distillation occurs at the maximum possible rate of vaporization since the vapor molecules reach the condenser unhindered. It differs from ebullient evaporation because neither boiling point nor bubble formation is a factor, and from evaporative distillation by the fact that it occurs when a temperature difference exists between the evaporating and condensing surfaces, and is independent of the vapor phase conditions except that the pressure must be very low.

Thus molecular distillation, because it represents a means of vaporization at low pressures and correspondingly low temperatures, finds utility in the separation and purification of high molecular weight and thermally sensitive materials, the volatilities of which are too low for distillation to occur at practical rates in conventional equipment.

The theory and methods of applying molecular distillation to the separation and purification of various materials have been investigated and reported by many researchers over the past several decades. From the earliest efforts of Langmuir (*19*) who predicted the evaporation rates from metal surfaces under high vacuum, molecular distillation advanced through laboratory studies in which Bronsted and Hevesy (*4*) purified mercury and Burch (*7*) obtained liquid fractions from previously undistillable petroleum residues (now known as the Apiezon oils). Commercial applications of molecular distillation first appeared in the early 1930's when Hickman (*13*) utilized a falling film type still for the production of vitamins from fish liver oils. From this early work two distinct commercial still designs were established by the late 1940's. First was the wiped-film still which uses rotating wiper blades to spread a falling distilland into a thin film. The second design, based on centrifugal force, utilized a rapidly rotating cone across which the distilland flows in an ever increasing surface area under the action of the induced high gravitational force. At the present time both still types are available in sizes ranging from throughputs of less than 1 liter/hr. to large scale units which can handle several hundred or more gal./hr.

Despite the number of theoretical and experimental research papers published over the years and despite the compendiums available (*8, 28*) little effort has been directed to date toward evaluating quantitatively the variables which describe high vacuum, molecular distillation. Therefore, it was the purpose of this research to supplement existing knowledge in the field by providing a mathematical and experimental study of the centrifugal molecular still. The centrifugal still was chosen for this work because there are relatively little published data of a quantitative nature either experimental or mathematical on this design, and because it involves new and unique applications of basic theory.

THEORETICAL RATE OF VAPORIZATION

If a region of liquid surface could be examined on a microscale such that the interfacial dynamics were observable, theory suggests that the evaporation process would be found to take place by way of the following interrelated phenomena:

1. The random movement of liquid phase molecules toward and away from the interface provides constantly changing patterns of molecular orientation at the surface.
2. The emergence of energetic molecules from the liquid surface into the vapor space; they would leave the surface at all possible angles of escape, that is, in any direction within the enclosing hemisphere.
3. Collisions among the vapor space molecules that cause many trajectory reversals and momentum exchanges.
4. Bombardment of the liquid surface by returning molecules; some of those striking the surface remain (that is, they condense), while others rebound back into the vapor.

Although this is an oversimplified picture of the vaporization process, it provides qualitative insight into the relative influence of the individual phases. For example, the rate of vaporization would be maximum if the vapor space were continually swept free of molecules as fast as they appeared. The "rate of vaporization" has been defined (*8*) as the absolute rate at which molecules escape from the liquid. Points 1 and 2 indicate that this rate is solely a function of the molecular species and of the energy distribution of the surface.

This theoretical rate of vaporization has been calculated rigorously from kinetic theory considerations (*18, 20*) based on the assumption that at equilibrium the number of molecules entering and leaving the liquid phase per unit time are equal, and interactions among these molecules are nonexistent. Such an approach was employed by Langmuir (*19*) in his vapor pressure studies of tungsten filaments who derived Equation (1).

$$w = P(M/2\pi RT)^{1/2} \qquad (1)$$

It is interesting to note that Equation (1), which expresses the theoretical rate of vaporization, indicates that molecular distillation is a function of the molecular species and the surface temperature and hence is a surface phenomena as has been previously postulated.

If the conditions in the vapor space above an evaporating surface are such that an appreciable number of molecular collisions occur, the probability is that some of the vaporized molecules will be returned to the liquid; thus the *net* rate of vaporization will be somewhat less than the value obtained from Equation (1). Furthermore, of those molecules that succeed in escaping from the evaporating surface some will undoubtedly be carried out with the vacuum system so that an even lesser number will actually reach the condensing surface. It is also reasonable to expect that in the process of condensation some re-evaporation will occur so that the *net* rate of distillation is the actual rate of distillate collection.

It is apparent therefore that the Langmuir equation provides a limiting value for the rate of molecular distillation, but that it must be corrected to account for the losses described previously. Under optimum design and operating conditions the net rate of distillation is essentially equal to the net rate of evaporation and an efficiency coefficient may be defined as:

$$\alpha = \frac{\text{net rate of evaporation}}{\text{theoretical rate of vaporization}} \qquad (2)$$

Thus, the quantity α has been termed the evaporation coefficient, and when inserted into the Langmuir equation the following modification results:

$$w = \alpha P(M/2\pi RT)^{1/2} \qquad (3)$$

The physical significance of the evaporation coefficient has been the subject of many theoretical and experimental studies over the past years. In the bulk of this research numerous attempts have been made to evaluate the quantity as a real molecular property. Although there is some experimental evidence that this may be true, only moderate theoretical progress has been made thus far. Of interest in this direction, however, are the statistical mechanical theories of Polanyi and Wigner (*24*) and Neumann (*22*), the absolute rate theory of Penner (*23*), and the free-angle-ratio postulated by Wyllie (*29*). Table 1 provides a compilation of experimental and theoretically calculated evaporation coefficients for a number of common compounds.

EXPERIMENTAL APPARATUS

The centrifugal molecular still used in this research was a modified commercial version of the design by Biehler and Hickman (2). This still is a laboratory size self contained, semicontinuous unit with a charge capacity of roughly 1,500 cc. It consists of a cone-shaped evaporating surface rotating in the vertical plane, associated feed, distillate, and distilland receivers, and auxiliary vacuum and heating equipment and their controls. The main portion of the apparatus is enclosed in a glass bell jar which provides a condensing surface which faces the conical rotor, and a reservoir for the feed liquid charge. The rotor has an outside diameter of approximately 4½ in. and the effective distilling area is approximately 100 sq.cm. The rotor has a rotational speed of 1650 to 1750 rev./min. The heat input is continuously variable up to 500 w. For this still the through-put rate varies from 10 to 35 cc./min. The apparatus is shown in the sketch of Figure 1.

In order to adapt the original equipment for the experimental rate studies in this research several design changes were made. A calibrated distillate receiver was attached to the bell jar, the vacuum pumping capacity of the system was increased by adding a second, two-stage diffusion pump (these pumps were installed in parallel in the vapor line between the mechanical fore-pump and the still). In order to eliminate contamination of the pump fluid, cold traps were added to the vacuum manifold, one upstream of the diffusion pumps and the other between diffusion pumps and the fore-pump. A feed preheater was added to the bell jar reservoir, and finally, thermocouples were installed in the feed line to the rotor and in the distilland collecting gutter. In order to obtain a measure of evaporator vapor space pressure, two vacuum gages were installed in the glass envelope, one on each side of the evaporating area. Since these two pressure sensors bracketed the evaporation area an arithmetic average of the two was used to represent an estimate of the working space pressure. With this arrangement pressures across the working space generally averaged between 0.5 and 3.0 microns of mercury during a distillation run. A complete description of the experimental apparatus and the testing procedures is given in (*11*).

THE MATHEMATICAL MODEL

Using the approach suggested by Emslie et al. (*10*) which was based on a consideration of the flow of a viscous liquid across the surface of a rapidly rotating truncated cone, a fluid dynamical analysis yields

$$-g \sin\varphi + (2\pi\omega)^2\xi \sin\varphi + \nu \frac{\partial^2 u}{\partial y^2} = 0 \qquad (4)$$

subject to the boundary conditions

$$u = 0, \quad y = 0 \quad \text{(at the wall)}$$

$$\frac{\partial u}{\partial y} = 0, \quad y = \delta \quad \text{(at the free surface)}$$

A sketch of the coordinate system is shown in Figure 2. Equation (4) is based on the following assumptions:

1. The film thickness is small compared to the cone radius.
2. The liquid film is in viscous motion.
3. Rotational symmetry is assumed.
4. The tangential and surface normal velocity components are negligible compared to the radial component.
5. And finally the radial velocity change across the rotor is small with respect to its change across the film.
6. Constant static pressure is assumed.

From Equation (4), by integration, the mean velocity becomes

TABLE 1. EXPERIMENTAL AND ESTIMATED EVAPORATION COEFFICIENTS

Compound	Evaporation coefficient Exp'l.	Evaporation coefficient Theor.*	Free angle ratio**	Temperature, °C.
Benzene (*29*)	0.90	0.078	0.85	6
Carbon Tetrachloride (*1, 29*)	1.0	0.79	1.0	0
Chloroform (*29*)	0.16	0.086	0.54	2
Dibutyl Phthalate (*3*)	1.0	0.052	$\sim 7 \times 10^{-4}$	20
Diethyl Adipate (*26*)	0.177	0.54	0.05	0
Di (2-Ethylhexyl) Phthalate (*15*)	1.0	0.042	$\sim 6 \times 10^{-5}$	100
Di (2-Ethylhexyl) Sebacate (*15*)	1.0	0.040	$\sim 5 \times 10^{-7}$	136
Ethanol (*6*)	0.024	0.20	0.018	12-15
Glycerol (*12*)	0.05	0.06	0.046	19
Glycerol (*27*)	1.0	0.06	0.046	18-70
Methanol (*29*)	0.045	0.30	0.048	0
Water (*21*)	0.35-1	0.033	0.04	7-50

* Polanyi and Wigner (*24*).
** Wyllie and Wills (*29*).

$$\overline{u} = \left[\frac{(2\pi\omega)^2}{3\nu} \sin \varphi \right] \xi\delta^2 \tag{5}$$

where for large values of the centrifugal force it has been assumed that

$$\frac{g}{\nu} \sin \varphi << \frac{(2\pi\omega)^2}{\nu} \xi \sin \varphi$$

The continuity equation provides the mass flow-evaporation relationship

$$d(\xi\,\Gamma) + \left(\frac{w}{\sin \varphi} \right) \xi d\xi = 0 \tag{6}$$

where $\Gamma = \delta\rho\overline{u}$ the flow rate per unit perimeter and the geometrical relationship $\xi = \xi_0 + x \sin \varphi$ have been substituted.

Recalling that for molecular distillation evaporation is a surface phenomenon, an approximate solution to Equation (6) can be obtained by assuming a mean film surface temperature and hence a mean evaporation rate $\overline{w}$.

$$\xi\,\Gamma - \xi_0 F_0 + \frac{\overline{w}}{2 \sin \varphi} (\xi^2 - \xi_0^2) = 0 \tag{7}$$

After introducing the normalizing parameters $\delta^* = \delta/\delta_0$ and $\xi^* = \xi/\xi_0$ substituting for Γ and $\overline{u}$ one obtains

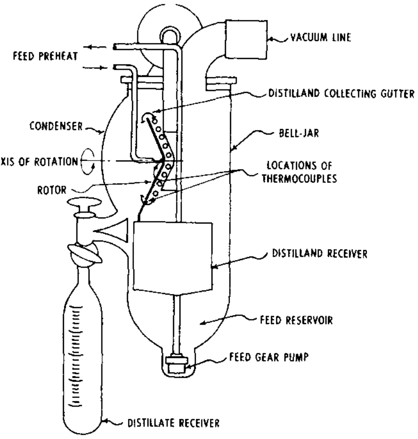

Fig. 1. The CMS-5 molecular still, a profile view.

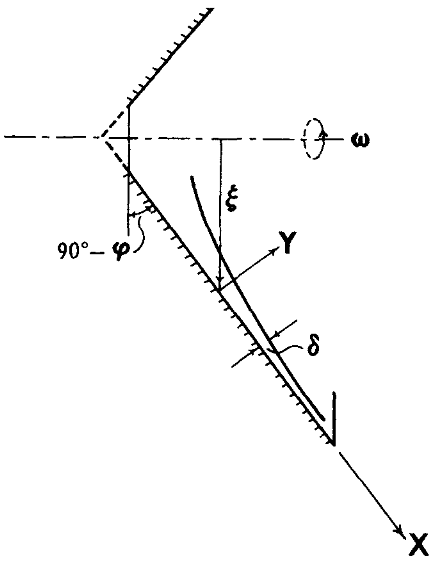

Fig. 2. Sketch of coordinate system.

$$u^* = \left(\frac{1}{\xi^*} \right)^{1/3} [1 - \beta\overline{w} (\xi^{*2} - 1)]^{2/3} \tag{8}$$

where

$$\beta = 3\nu/(4\pi^2\omega^2\delta_0{}^3\rho \sin^2 \varphi), \text{ and } u^* = \overline{u}/u_0$$

In evaluating the heat transfer, if it is stipulated that the feed and mean distilland residue temperatures are equal, then it is reasonable to assume that heat transport occurs through the film from the cone wall by conduction, the flux being exactly that required to supply latent heat for evaporation from the surface film. Therefore, if radiation loses and convective effects are neglected, (a reasonable assumption for the relatively low temperature distillations encountered here (9, 28), especially since the evaporating and condensing surface temperature differential was maintained small), the evaporation may be written as

$$dG = \left(\frac{1}{\lambda} \right) dq = \left(\frac{k}{\lambda\delta} \right) 2\pi\xi\Delta T dx \tag{9a}$$

$$dG = 2\pi\xi w dx \tag{9b}$$

Here, the rate of mass flow across the cone is defined by

$$G = 2\pi\xi\rho\overline{u}\,\delta = (8\pi^3\omega^2\rho \sin \varphi/3\nu)\xi^2\delta^3 \tag{10}$$

where $\overline{u}$ has been eliminated with Equation (5).

From Equation (10) the evaporation is also obtained as the differential change in the mass flow G across the rotor. Thus, differentiating Equation (10) and equating the result to Equation (9) one obtains after some rearrangement

$$\frac{d\tau}{d\xi} + \frac{5}{3}\left(\frac{\tau}{\xi} \right) = -\frac{\nu k \Delta T}{(\pi\omega)^2 \lambda\rho \sin^2\varphi} \tag{11}$$

Here, considerable simplification has been achieved by means of the transformation $\tau = \xi\delta^4$.

Equation (11) is integrable providing that ΔT can be expressed as a function of ξ (or δ). Since Equation (9) indicates that $\Delta T/\delta$ is proportional to the flux q if the heat flux through the film is assumed constant or if it varies only moderately across the rotor surface, then we may write

$$\frac{\Delta T}{\Delta T_0} \cong \frac{\delta}{\delta_0} = f(\xi^*)$$

or

$$\Delta T^* \cong \delta^* = f(\xi^*) \tag{12}$$

where $f(\xi^*)$ is a functional relationship which depends on the evaporation to be determined. If Equation (12) is substituted into Equation (11) and the result rearranged in integral form

$$\int d(\tau^* \xi^{*5/3}) =$$

$$-\frac{\xi_0}{\tau_0} \left[\frac{\rho\lambda\nu k\Delta T_0}{(\pi\omega\lambda\,\rho \sin \varphi)^2} \right] \int \xi^{*5/3} f(\xi^*) d\xi^* + C \tag{13}$$

for which the boundary condition is $\xi^* = \tau^* = 1$.

From the previous restriction of a moderate change in the heat flux across the rotor, and the approximate solution of the continuity equation for the constant evaporation rate case we obtain

$$f(\xi^*) = \delta^* = \left(\frac{1}{\xi^*} \right)^{2/3} [1 - \beta\overline{w} (\xi^{*2} - 1)]^{1/3} \tag{14}$$

and defining the evaporation coefficient α in terms of the rates of the experimentally determined mean evaporation rate to the calculated mean value

$$\alpha = w_e / \overline{w} \tag{15}$$

Thus, introducing Equations (9), (14), and (15) into (13), integrating and rearranging the result, the final equation becomes

$$\delta^* = \left(\frac{1}{\xi^*}\right)^{2/3} \left[1 - \left(\frac{\alpha w}{w_e}\right) \{1 - [1 - \beta \overline{w} (\xi^{*2} - 1)]^{4/3}\} \right]^{1/4} \tag{16}$$

Equation (16) is an expression relating the film thickness of the fluid and the evaporation rate as a function of position on the rotor surface. This equation along with Equations (3) and (9), which respectively relate surface temperature to evaporation and film thickness with temperature, represents a system of equations which provide an approximate analysis of the coupled phenomena of fluid dynamics, heat transfer, and surface evaporation for the centrifugal molecular still.

EXPERIMENTAL RESULTS

A total of 102 isothermal runs were made with five different prepurified materials. Three different feed rates were used in each series of runs. Changes in this rate were achieved by replacing the spur gear in the rotary feed pump, a device whose volumetric efficiency was viscosity dependent. Thus, feed rates for each gear varied by about 10% over the temperature span of interest.

Figures 3, 4, and 5 represent the experimental data which are plotted as mean evaporation versus mean temperature for each compound. Also, on these graphs, for purposes of comparison, are reported the theoretical rates of evaporation. These curves have been calculated from Equation (3) in which an evaporation coefficient of unity has been assigned.

Profiles for film thickness, mass flow rate, velocity, and surface temperature have been evaluated from the mathematical model, Equations (3), (9), and (16). The relatively straight-forward computational scheme commenced with the partitioning of the evaporating surface into constant temperature, equi-area segments. From appropriate initial assumptions for α and $\overline{w}$ and an estimate of the surface temperature, local values for the evaporation rate, film temperature drop and thickness were calculated from

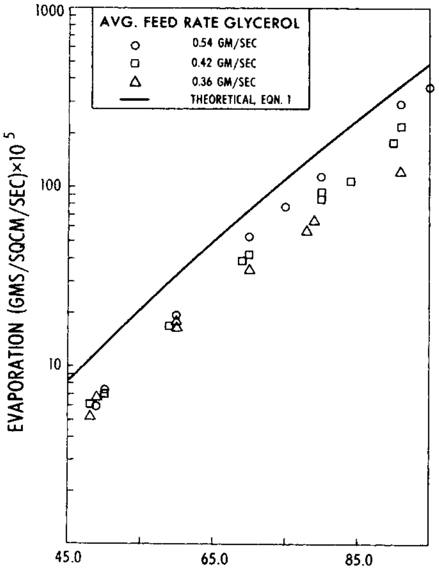

Fig. 3. Comparison of experimental and theoretical rates of distillation for glycerol.

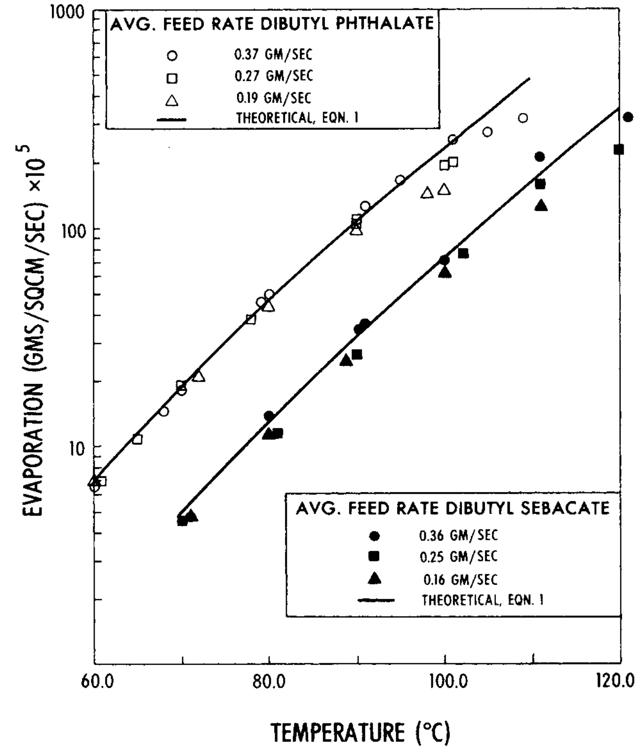

Fig. 4. Comparison of experimental and theoretical rates of distillation for di-*n*-butyl phthalate and di-*n*-butyl sebacate.

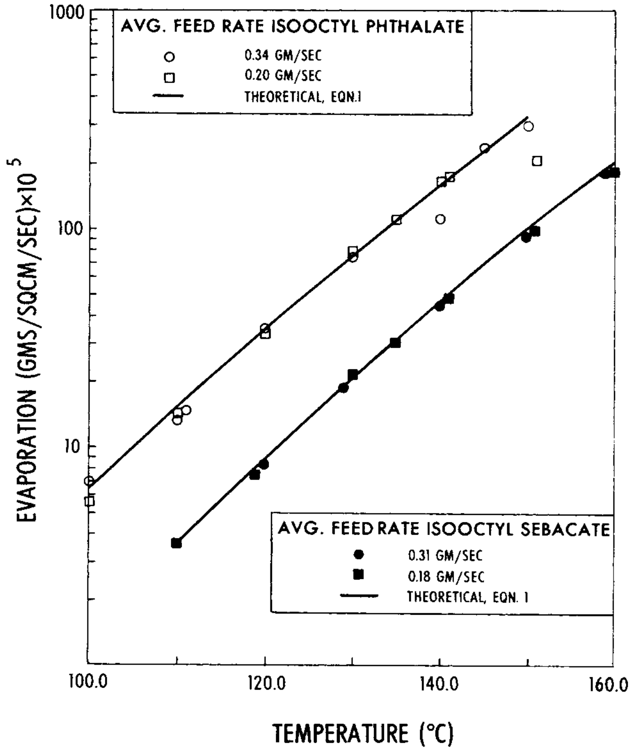

Fig. 5. Comparison of experimental and theoretical rates of distillation for di-(2-ethylhexyl) phthalate and di-(2-ethylhexyl) sebacate.

Equations (3), (9a), and (16) respectively. As suggested by Bruin (5), a linear temperature profile across the film was assumed. These iterative computations proceeded in stepwise fashion from the feed position outward to the rotor edge at which point a new $\bar{w}$ was ascertained. The iterations continued in this manner until succeeding values of surface temperature profiles across the rotor and evaporation rates agreed. These computations were performed for each run on the IBM 1620. Typical results from these calculations are presented in Table 2 for glycerol.

DISCUSSION OF RESULTS

Calculated values of temperature differences through the film vary from a maximum at the vertex to a minimum at the rotor periphery. The maximum gradient is approximately twice the minimum in the runs reported here, thus reflecting the effects of a decreasing film thickness and small increase in the rate of thermal energy transport through the film.

Representative mean thermal gradient data calculated for several glycerol and dibutyl phthalate runs are presented in Table 3. Although a wide variation in the thermal gradient is observed over the operating range for glycerol, the data appear remarkably consistent at any given temperature. This is demonstrated for both glycerol and dibutyl phthalate at 70°C. over a range of mass flow rates for which the thermal gradients are relatively unchanging. Thermal gradients of the same order of magnitude are reported by Prüger (*25*) who probed the evaporating surface of carbon tetrachloride with a fine thermocouple whose junction had been flattened to a thickness of 0.04 mm. In his research, Prüger measured a temperature drop of about 3°C. within a surface layer of approximately 0.3 mm. thus obtaining a gradient of roughly 100°C./cm.

TABLE 2. CALCULATED RESULTS: RUN NO. 4, GLYCEROL
$\alpha = 0.88$, $T = 91.0$°C., $\bar{w} = 3.32 \times 10^{-3}$ g./sq.cm./sec.

Radial position, cm.	Film thickness, $10^2 \times$ cm.	Mass flow rate, g./sec.	Linear velocity, cm./sec.	Surface temperature, °C.	
1.11	1.00	0.54	6.39	91.0	feed position
2.08	0.65	0.51	5.00	87.9	
2.72	0.53	0.48	4.39	88.3	
3.23	0.46	0.45	3.95	88.6	
3.68	0.41	0.42	3.60	88.8	
4.08	0.38	0.39	3.29	88.9	
4.44	0.34	0.35	3.01	89.1	
4.77	0.32	0.32	2.75	89.2	
5.08	0.29	0.28	2.49	89.3	
5.38	0.27	0.25	2.24	89.4	
5.66	0.25	0.21	1.98	89.5	

TABLE 3. MID-ROTOR FLOW AND THERMAL CONDITIONS

Run no.	Mean film temperature, °C.	Thermal gradient, °C./cm.	Mass rate of flow, g./sec.	Film thickness, cm.	Compound
9	50	43	0.523	0.00786	Glycerol
14	91	1114	0.251	0.00033	Glycerol
11	70	238	0.447	0.00530	Glycerol
16	69	219	0.452	0.00538	Glycerol
21	70	239	0.350	0.00489	Glycerol
33	70	45	0.375	0.00245	DBP
47	70	46	0.260	0.00216	DBP
51	72	55	0.183	0.00190	DBP

ANALYSIS OF THE PHTHALATE AND SEBACATE RUNS

Phthalates and sebacates (especially the isooctyl esters EHP and EHS) have been the subject of numerous molecular distillation studies over the past years and so provide a basis for comparing the research reported in this study.

Perhaps the most definitive studies on still dynamics have been published by Hickman (*14*) and Coli (*9*). In his work, Hickman obtained film thickness estimates by means of optical density measurements of dyes introduced on the spinning rotor. For a rotational speed of about 1,650 rev./min., corresponding to the angular velocities in this study, he reported film thicknesses ranging from approximately 0.06 to 0.01 mm. over the rotor from center to edge. Coli, on the other hand, obtained average thicknesses for his runs by dividing the volume feed by the surface of revolution generated by a radial element of the rotor, over equal time intervals. His reported mean values, at roughly the some rotational speed, were about a hundredth of those of Hickman. As Watt (*28*) points out, however, this indirect calculation by Coli does not include the effect of variables such as viscosity, density, and surface tension, etc., and therefore is somewhat questionable. Film thicknesses evaluated here from the mathematical model, for the phthalates and sebacates, agree quite well with Hickman's data. Several typical mean values are included in Table 3 for purposes of comparison.

In his study to assess the thermal hazard of this still, Hickman estimated the time the liquids flowing across the rotor were exposed to the high evaporation temperatures. These residence time measurements were made by photographing dye marks introduced with the feed at various rotor positions for known time intervals. Based on Hickman's results, average exposure times vary from 0.05 to 0.20 sec. over the useful range of operation of the CMS-5 molecular still. Mean radial velocities for the phthalates and sebacates, computed from the mathematical model, varied from about 4 to 8 cm./sec. for the conditions used in this study. If the radial distance from center to edge is approximately 5 cm., the residence time for a typical fluid particle traversing the rotor varies roughly from 0.6 to 0.8 sec. These results, therefore, are about 4 to 10 times greater than the previously reported values. There is no satisfactory explanation for this apparent anomaly since Hickman's original data are not available. The possibility exists, however, that Hickman's measurements were made at greater throughput rates which would easily account for the higher velocities encountered in his case.

The evaporation coefficients that have been obtained for the sebacates and phthalates in this study agree remarkably well with the values previously reported by other investigators. The values of the evaporation coefficient for these substances in all runs for which the calculation was made, ranged from 0.91 to approximately unity. It has been postulated by Hickman and Trevoy (*15*) that these pure substances exhibit ideal liquid phase behavior and should attain evaporation coefficients of unity. Similar conclusions have been reached by other researchers. The fact that values obtained here are low in some cases by as much as 6 to 9% might be attributed to experimental errors in film temperature measurement. As can be shown a probable error of 1° in the residue thermocouple reading would cause a corresponding 9% error in the evaporation rate calculated from the Langmuir Equation (3).

ANALYSIS OF THE GLYCEROL RUNS

Because of its unique physical and chemical properties, glycerol has produced most interesting results. Comparison with the phthalate and sebacate runs shows that film thicknesses for glycerol were about twice as large under comparable still operating conditions. Although a higher range of feed rates was attained using glycerol (because the feed pump operated at a higher volumetric efficiency with the viscous liquid) radial velocities tended to be less than half of those calculated for the previous materials; therefore, residence time estimates for glycerol were determined to be roughly twice as great (on the order of one second exposure across the rotor). All of these differences are attributed to the viscous nature and the corresponding fluid dynamical behavior exhibited by glycerol during molecular distillation.

The evaporation coefficient determinations for glycerol provided the severest test of the mathematical model. In the past glycerol has been the subject of several studies in this area; however, published values of evaporation coefficient measurements vary over a twenty-fold range, from about .05 as reported by Heideger and Boudart (*12*) to unity by Hickman and Trevoy (*15*). Much of the previous experimental work on evaporation coefficient determinations has been the subject of criticism for one or more of the following reasons:

1. Questionable purity of material
2. Possibility of surface contamination
3. Geometrical interference problems
4. Inaccurate evaluation of surface temperature

Of the possible sources of error listed above, the most difficult to overcome from an experimental standpoint has been the evaluation of the surface temperature. Because evaporation is a surface phenomenon involving the most energetic molecules, steep thermal gradients can arise in the surface layers of an evaporating liquid (*25*). Therefore unless the surface temperature is accurately known, the experimental rate of evaporation will always be less than the theoretical value by an amount proportional to the degree of surface cooling. This can involve as much as 8 to 10% of the total evaporation per temperature degree as was shown earlier. Undoubtedly, this has been a contributing factor in many of the low evaporation rates reported in the literature, and hence evaporation coefficients as well.

When the mathematical model developed in this work was applied to glycerol, it was found that calculated values of the evaporation coefficient varied from 0.88 to a low of 0.36, despite the fact that temperature gradients across the film as high as 1,114°C./cm. were calculated.

In view of the fact that values less than unity have been obtained here, whereas there have been unity values reported in the literature for glycerol, it is important to examine this research for reasons why there is an apparent lack of agreement between theory and experiment.

Purity. While the actual purity cannot be assessed quantitatively, the starting material was reagent grade and the preprocessing technique of redistilling a heart-cut was carefully executed.

Vapor pressure. There has been some conflict in literature values reported for the vapor pressure of glycerol. The data chosen for this work (*19*), however, were thermodynamically sound and checked well with most of the latest published values.

Distilland temperature. As was previously indicated, a thermocouple reading registering 1°C. higher than the actual fluid temperature would cause the actual evaporation rate to be lower by roughly 9% than anticipated.

Hydrodynamical effects on the rotor. As Figure 1 indicates, the feed tube, which is directed to the cone center, discharges the feed liquid in a normal rather than tangential direction with respect to the rotational plane. The effect of such a feed geometry is to superimpose an additional radial component upon the centrifically generated radial velocity. The resulting fluid motion away from the cone center tends to produce an uneven fluid surface. This condition is further amplified by feed pump irregularities and surface tension effects at the feed discharge nozzle which generate surges in the feed liquid. This effect has been observed during the course of still operation. As a consequence of such behavior larger temperature differences will be set up at the points of greatest film thickness thus creating correspondingly cooler surface temperatures. The net result will be a lower experimental rate of evaporation that reflects an actual average surface temperature less than theory predicts.

A further consideration of fluid dynamics upon the evaporation coefficient has been postulated by Hirth and Pound (*16, 17*). For polar molecules they have correlated α with surface motion by reasoning that an undisturbed, quiescent liquid promotes an alignment of the surface dipoles which offers a natural barrier inhibiting evaporation. This leads to the observation of low values of α. Conversely, α's approaching unity are achieved when a perturbed surface generates an unpolarized liquid-vapor interface that reduces the evaporation barrier's effectiveness.

Applying this concept to the centrifugal still in the present work, however, appears to be somewhat inconclusive. In this case the hydraulic effects previously cited coupled with the continuous generation of new surface induced by flow across the rotor's conical surface, most probably initiates depolarization of the liquid interface. The extent of such an effect is at present experimentally unknown.

Of equal significance is the possibility that the previously described surface irregularities might promote dry regions on the rotor surface. This would be especially likely near the rotor periphery where the film is thinnest. Although there is no visual proof of such occurrences, an examination of the constant temperature runs in Table 4 suggests that a degenerating condition of this nature might have existed. From the data presented it can be seen that both the evaporation coefficient and the measured evaporation rate decrease as the feed rate decreases. On the other hand, however, the calculated mean evaporation rate remains

TABLE 4. CONSTANT TEMPERATURE RUNS—GLYCEROL

Run no.	Mean film temperature, °C.	Feed rate, g./sec.	$\alpha = w_e/\overline{w}$	Evaporation rate, (g./sq. cm./sec.) $\times 10^5$	
				w_e	$\overline{w}$
4	91	0.544	0.879	291.5	331.8
14	91	0.412	0.642	218.6	340.7
18	90	0.414	0.560	177.4	316.6
23	91	0.330	0.387	124.9	322.5
7	70	0.613	0.747	53.3	71.3
11	70	0.482	0.591	42.4	71.7
16	69	0.485	0.590	39.1	66.2
21	70	0.386	0.498	35.6	71.7

virtually constant. This latter fact indicates that the surface temperature remains substantially constant in these runs. Since the film thicknesses must decrease as the feed rate decreases, theory predicts that the heat transfer and the resultant evaporation rate should increase with a decreasing rate of feed. This latter deduction is therefore in direct conflict with experimental observations as Table 4 indicates. The only reasonable explanation for these seemingly anomalous results at this time is the fact that portions of the rotor surface must become dry, thus reducing the effective evaporation surface.

CONCLUSIONS

Many questions were raised during the course of this work. These reflect the stage of development of the field, and provide points of departure for further researches in the area. The following points are those most worthy of mention:

The results of this work show that the existence of an evaporation coefficient less than unity is primarily dependent upon the liquid used. Evaporation coefficients for ideal liquids such as the phthalate and sebacate esters studied were found to be unity, within the range of experimental error. Similar evaluations with glycerol, however, have yielded evaporation coefficients which ranged from 0.36 to 0.89 approximately. This may be due to its nonideal associated nature, or to its unique physical properties.

Various reasons have been suggested as to why the measured rate of evaporation decreased with decreasing film thicknesses while surface temperatures remained constant. No one of these can be accepted universally. Based on limited evidence, it appears likely that mechanically induced surface irregularities in the flowing fluid may be responsible for this apparent anomaly.

The mathematical model has been used to predict film thickness and thermal gradients across the film which are consistent with values previously reported in the literature. It does not account for tangential acceleration effects and is based on the assumption of a fully developed velocity profile. Both of these factors can lead to errors, especially in the vicinity of the vertex.

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NOTATION

g = gravitational acceleration
g_c = gravitational constant
G = mass rate of flow
k = thermal conductivity
M = molecular weight
P = vapor pressure
q = heat flux per unit area
Q = volume rate of flow
T = temperature
u = point velocity
w = local evaporation rate per unit area
w_e = experimental evaporation rate per unit area
x = radial coordinate
y = normal coordinate
α = evaporation coefficient
β = $3\nu/(4\pi^2\omega^2\delta_0^3 \sin \varphi \, \rho)$
δ = film thickness
Γ = mass flow per unit perimeter
λ = latent heat of vaporization
μ = viscosity
ν = kinematic viscosity
ξ = $\xi_0 + x \sin \varphi$, cone radius
ρ = density
τ = $\xi\delta^4$, a transformation variable
φ = cone vertex half-angle
ω = angular speed of cone
ΔT = $Ts - Tw$, film temperature drop

Subscripts and Superscripts

$-$ = mean value
s = pertains to surface
w = pertains to wall
0 = initial value
$*$ = normalized, dimensionless variable

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