Mass and Heat Transfer Relations in Evaporation through Porous Membranes

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This study concerns rates of evaporation and mass transfer of water vapor from a heated salt solution through a water repellent porous membrane to a cooled water condensate. This transfer is a result of temperature differences and corresponding vapor pressure differences across the membrane. Three groups of experiments were carried out which indicate that the major factor influencing the rates of transfer is diffusion through a stagnant gas in the membrane pores. However, an equation considering film heat transfer coefficients, membrane thermal conductivity, and an empiricial correction based on temperature driving force appears to be necessary for representing all the data. The empirical correction appears to be related to internal condensation and possibly diffusion along surfaces.

CHARACTERISTICS OF EVAPORATION THROUGH MEMBRANES

A method of evaporation which has potential advantages in approaching thermodynamic reversibility has been described in a previous paper (3). This method involves evaporation through a nonwettable porous membrane from a hot evaporating liquor surface into the membrane pores, through which the vapor transfers to a coolant stream on the opposite side of the membrane. The vapor condenses on the coolant surface and combines with this stream. If carried out with countercurrent flow of hot liquor and coolant the evaporation may be considered to be an essentially infinite-stage flash evaporation similar to the vapor-reheat flash evaporation method (8), with each pore acting as a separate stage under its own conditions of temperature and vapor pressure. Flash evaporation is used here to signify evaporation resulting from the solution's sensible heat. This method requires the same heat addition and removal for evaporation and condensation as conventional evaporation plus the amount of heat conducted through the membrane. This method provides an almost infinite number of stages with a constant liquid pressure apparatus and a close approach to the minimum difference in liquor and coolant temperatures, the boiling point elevation. The coolant may recover the heat of evaporation at nearly the same temperature as the evaporation in the same manner as a countercurrent heat exchanger. A sketch of one method of utilizing this method is shown in Figure 1.

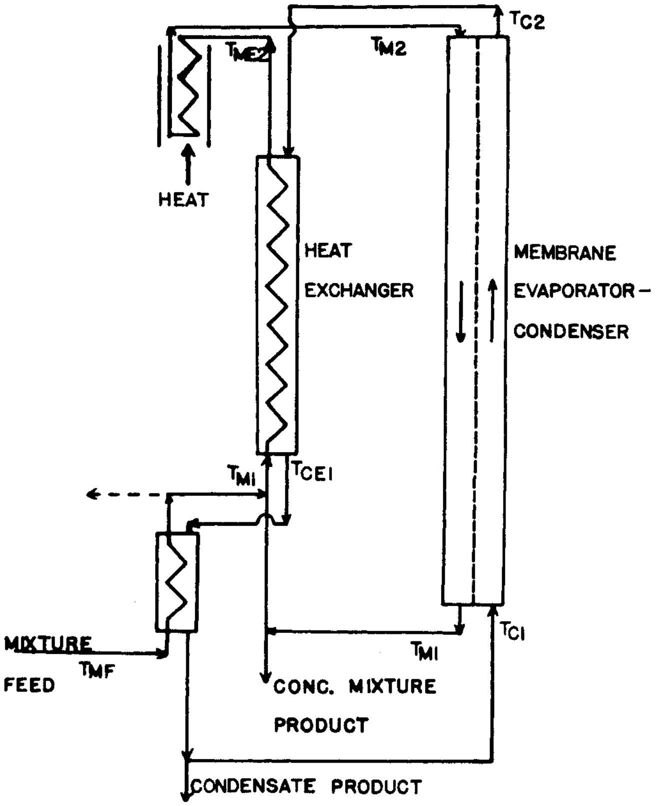

Fig. 1. Infinite-stage flash evaporation through porous membranes.

Previous studies have demonstrated the possibility of this method, and this study has as its purpose the determination of some of the characteristics and mass transfer coefficients which can be obtained with glass fiber and teflon membranes.

This process should be possible with porous membranes having a nonwettable surface and pore sizes sufficiently small so that surface tension forces would withhold liquids from the pores, and prevent contact of the two liquids.

Theoretical considerations suggested that diffusion through a stagnant gas, air, would occur in the membrane at temperatures below the boiling point if air was not removed from the system. Theoretically it appeared to be feasible to remove air from the pores by steaming or boiling which would allow vapors to flow through the pores at a lower pressure than the liquids on either side of the membrane, which should result in higher rates of mass transfer than diffusion. Under these conditions, vapor in each pore would be essentially at the saturated vapor pressure while liquids on both sides of the membrane would be at pressures equal to or higher than their saturated vapor pressures, and surface tension would prevent liquids flowing into the lower pressure pores. The method involving elimination of air appears to be somewhat more difficult to achieve and as yet has not been satisfactorily demonstrated, although several attempts have been made. The reason is apparently that the membranes studied thus far allow liquid water penetration with a pressure difference of about 5 in. Hg.

The conduction of heat through the membrane is important for three reasons. First, heat conducted through the membrane is not effective in producing evaporation, and even though recovered, this increases the requirements for heat exchange. Also excessive heat conducted from the membrane interior to the coolant could produce internal condensation which would probably further increase membrane heat conductivity and decrease the diffusion or flow of vapors. Eventually internal condensation might cause a continuous liquid channel through the membrane and permit leaking and diffusion of nonvolatile solutes. A third reason why heat conduction should be minimized is that such heat must also be transferred through the two liquids films and increases the temperature drop across these films. Since mass transfer depends upon temperatures and vapor pressures at the surface of the membranes, any temperature drop through the liquid films reduces the available driving force for mass transfer. There should be a minimum membrane thickness for a given overall or total temperature drop corresponding to the thickness at which the heat conducted through the membrane is sufficient to reduce the membrane temperature drop to the boiling point elevation. Thus thickness of membrane is also a significant factor and there should exist some optimum thickness. Heat transfer coefficients for the liquid films are also important for the same reasons.

This study includes experimental work on the relationship of the rate of evaporation with driving forces, partial pressure of air, membrane thickness, and heat conduction through the membranes.

EXPERIMENTAL APPARATUS AND PROCEDURE

The apparatus used consisted of two chambers 2 to 3 in. in diameter sealed by two rubber gaskets with a membrane between them. The arrangement is shown in Figure 2 as used for most of the runs. For the third group of runs the heater was inside the salt water section, and a second heater was used inside the fresh water section. Various materials were used for the plate B′ including brass, plastic, and glass partially to vary the temperature drop across the membrane. As shown, the chambers were sufficiently thick to insert tubing inlets and outlets and thermometers or thermocouples on each side. The salt water side was insulated, but except for the third group of runs, not sufficiently to allow accurate calculation of heat flow through the membrane. A wattmeter and variac were used to set power input to the heater.

The procedure was to fill the salt water side with 7% by weight sodium chloride solution then dip the end of tubing D into a reservoir of distilled water. This permitted any water transfer out of the salt water side to be made up by pure water, thus maintaining the concentration constant. The fresh water side was filled initially with distilled water to a level in the vent about ¼ in. higher than the salt water level so that any leakage would be in the opposite direction to the expected transfer and any water transferred would be definitely due to evaporation from the hot salt water. The bottom outlet was arranged to provide outflow at this level into a graduated cylinder. Heating was started, and after eliminating air from the chamber but not from the membrane, and reaching a steady state condition as determined by temperatures, measurements were started on outflow rate, temperatures, and power. Each run consisted of several increments of time during which all measurements were reasonably constant. At the end of each run, the fresh water was checked with silver nitrate to determine whether or not appreciable chloride ions were present and if so the run was discarded.

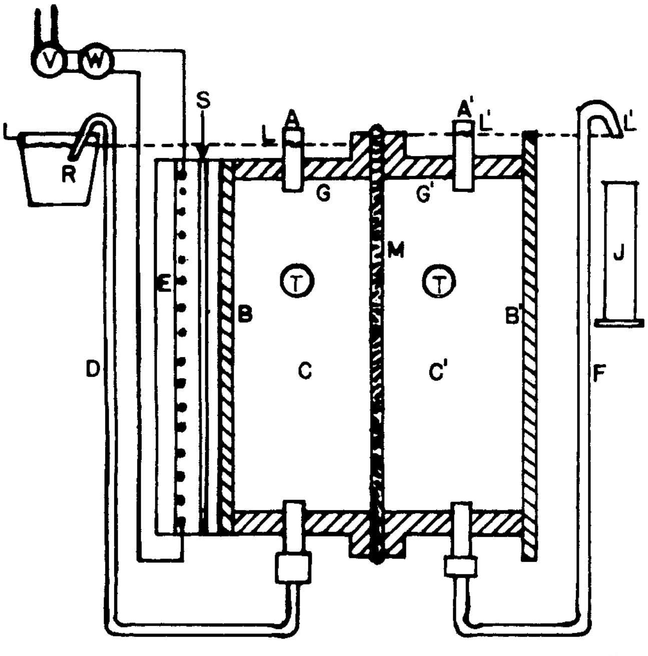

Fig. 2. Experimental nonflow apparatus. A,A′ = vents and filling tubes; B,B′ = brass plates; C,C′ = salt and fresh water chambers; D = make-up line; E = heater; F = fresh water outlet; G,G′ = rubber gaskets; J = graduated cylinder; L,L′ = liquid levels; M = membrane; R = reservoir; S = mica; T = thermometers; V = variable transformer; W = wattmeter.

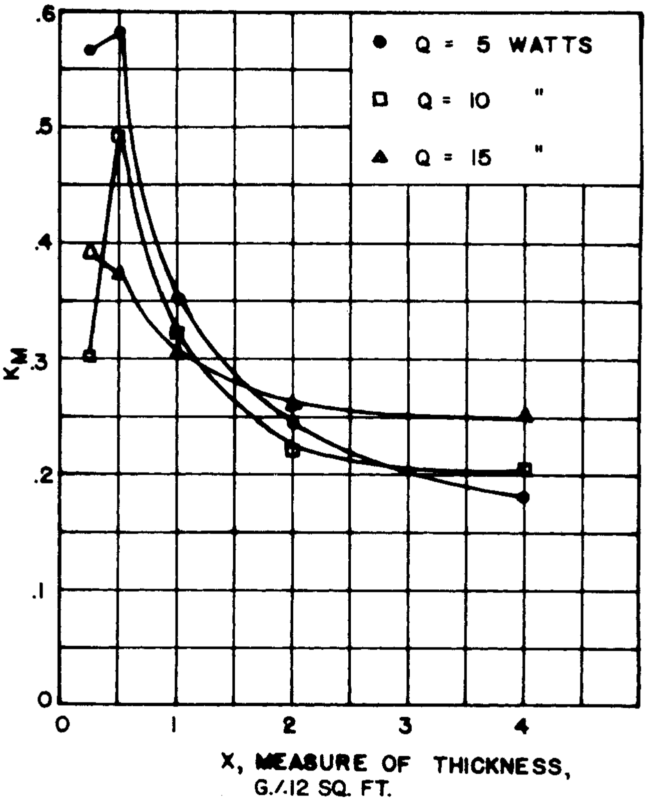

Fig. 3. The effect of membrane weight per unit area, X, or thickness, on the overall mass transfer coefficient, K_m. Group II experiments.

MEMBRANE PREPARATION

Membranes were prepared based on a standard 1 g. membrane containing 1 g. of glass fiber for a membrane 0.12 sq.ft. or 111 sq.cm. in area. Such a membrane was prepared from a slurry containing 5 drops glacial acetic acid, 1 g. of Owens-Corning fiberglass AA, 1μ in diameter, 0.5 ml. of duPont Teflon 30B aqueous dispersion containing 60% solids at a specific gravity of 1.5, and aluminum sulfate added in the above order to about 500 ml. of old filtrate or water. Actual membrane weights were about 1.4 g./g. glass fiber. The first group of experiments contained about 0.1 g. of aluminum sulfate for the above proportions, while the second and third contained about 0.2 g. The above amounts were adjusted proportionally depending on the area and relative thickness desired. The slurry was filtered onto a Buchner funnel, and in the first group the filtrate was saved for making up the next membrane. A vacuum was applied to partially dry and compress the mat. The membrane was further dried by pressing between paper towels. The membranes were dried on a hot plate with occasional pressing or were air dried. They were then heated to approximately 600°F. in an oven for ½ hr., after which they were ready for use. The purpose of the Teflon was to provide a nonwettable surface and the aluminum sulfate was to improve Teflon retention. The acetic acid was to aid dispersion of glass fiber. The heat treatment appeared to improve strength and probably aided in distributing the Teflon. The membrane density in the first group of experiments was about 0.14 g./cc. while in the second and third groups the densities were 0.27 g./cc. and 0.23 g./cc.

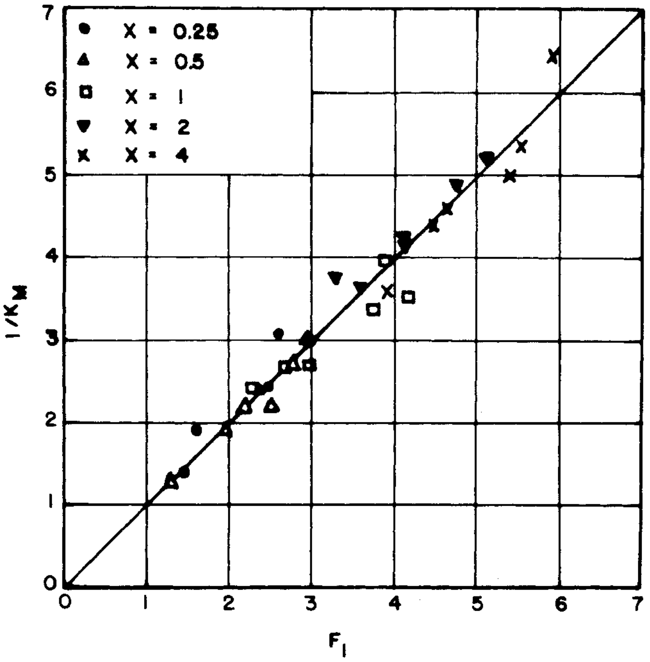

Fig. 4. Overall mass transfer resistance, $1/K_m$, correlation with a function of X, or thickness, temperature difference, partial of vapor pressure with temperature, and latent heat of vaporization, $F_1 = 0.0126X\ (\Delta T\text{-}E) + 0.354\ (\Delta T\text{-}E) + 0.00134\ \lambda\ \partial P/\partial T$. Group II experiments [see Equation (13)].

In all experiments, X was used as a measure of thickness, where

$X =$ wt. of glass fiber in g./111 sq.cm. of membrane or $X = 0.12\ Wg$

where

$Wg =$ wt. of glass fiber in g./sq.ft. of membrane. Considering 1.4 as the total weight per unit wt. of glass fiber and a density of 0.27 g./cc., the thicknesses corresponding to

$X = 0.25$, 0.5, 1, 2, and 4 were 0.0045, 0.0091, 0.018, 0.036, and 0.072 in. respectively. Corresponding total weights were 0.064, 0.028, 0.0257, 0.051, and 0.103 lb./sq.ft. Group I membranes corresponded to $X = 1$.

METHODS OF CALCULATION

The basis of all calculations was the assumed and verified dependence of mass transfer upon vapor pressure differences across the membrane. For this reason an overall mass transfer coefficient was defined as follows:

$$K_m = \frac{M}{A(P_s - P_w)}$$

P_s was taken to be 0.96 times the vapor pressure of water at T_s, based on the boiling point elevation of 7% salt water. The data were thus expressed in terms of K_m and the analysis was carried out primarily on K_m values obtained.

DRIVING FORCE

The appropriate driving force for this type of evaporation might be either the difference in mol fraction of water vapor at the two liquid surfaces for the case of diffusion controlling (*1*), vapor pressure difference at the two surfaces in the case of vapor flow controlling or Knudsen diffusion through the membrane controlling (*5*). For the case of interfacial resistance to evaporation and, or, condensation controlling, the vapor pressure differences would also be approximately the appropriate driving force (*6*). In any case except film heat transfer controlling, the driving force should be related to a large degree with vapor pressure differences. Microscopic examination indicated most pores to be parallel with membrane surfaces and about 1 μ or greater in diameter, and Knudsen diffusion within these should be unimportant. However, in the perpendicular direction of mass transfer the openings would likely be much more random and in the smaller openings Knudsen diffusion might be important, especially if larger openings were blocked by condensation.

GROUP I EXPERIMENTS

In order to determine the effect of vapor pressure difference on evaporation rates, several membranes were tested at various levels of heat input. The evaporation rates were plotted vs. the vapor pressure difference from the salt water side to the cold fresh water side. These results are shown in Figure 3 and 4 and indicate a linear relationship with a zero intercept. Runs 5 and 6 were the only two runs on the same membrane. This confirms the relationship

$$N_a = K_m\ (P_s - P_w) \qquad (1)$$

over a reasonable range of conditions.

If diffusion through a stagnant gas, air, is the controlling factor in the transfer, an appropriate equation for the rate of evaporation (*1*) would be

$$N_a = \frac{K_{m1}(P_s - P_w)}{P_{Blm}} \qquad (2)$$

If Equation (2) is correct then K_m as determined from Equation (1) should be a function of the log mean partial pressure of air and the relationship should be

$$K_m = K_{m1}/P_{Blm} \qquad (3)$$

A plot was made of K_m values calculated from Equation (1) vs. $1/P_{Blm}$. The first group results obviously did not fit into the form of Equation (3), because the intercept was not zero and the slope was in the wrong direction. This indicates either that the stagnant gas is unimportant or that Equation (3) is oversimplified and other factors are involved which hide this effect. Later results indicate that the stagnant gas is an important factor but that Equations (1) and (3) must be corrected for heat transfer effects.

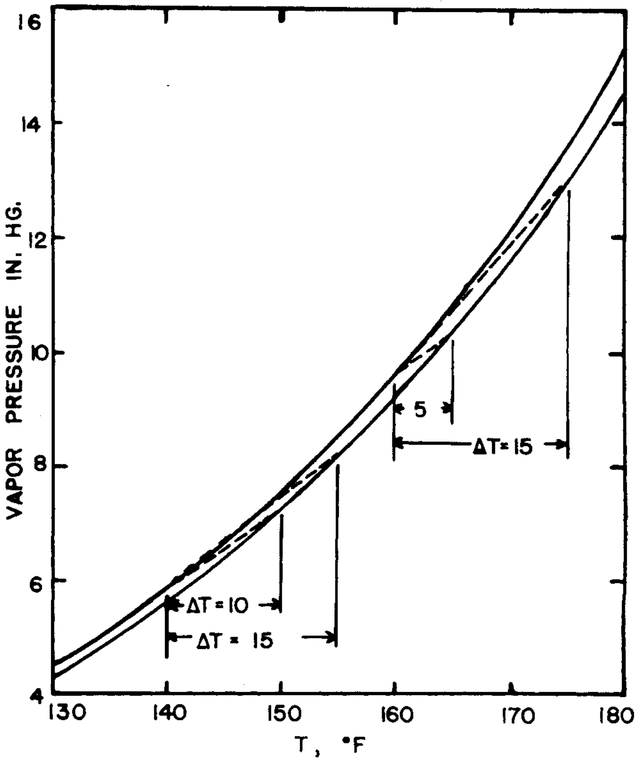

Fig. 5. Vapor pressure curves for 7% salt water and pure water showing approximate variation of partial pressure of water vapor with temperature through a porous membrane.

GROUP II EXPERIMENTS

A second group of experiments was run to investigate the effect of membrane thickness on mass transfer. Some changes in membrane preparation were also initiated primarily in order to provide more reliable water repellancy. The major differences were a more thorough pressing, which approximately doubled the density, and increased aluminum sulfate to improve Teflon retention. The results of these experiments are shown in Figure 5. The most significant aspect appears to be a peak in the mass transfer coefficient at a weight of 0.5 g./0.12 sq.ft., or $X = 0.5$, in 2 out of 3 sets of data at a given heat input level.

As previously discussed, it is logical to expect some maximum in overall mass transfer coefficient as thickness is varied. This reasoning can be expressed by assuming Equation (1) may be written approximately as

$$N_a = K_m (T_s - T_w - E) \frac{\partial P}{\partial T} \tag{4}$$

or

$$\text{overall resistance} = \frac{1}{K_m} = \frac{(T_s - T_w - E) \frac{\partial P}{\partial T}}{N_a} \tag{5}$$

If the mass transfer coefficient of the membrane alone is k_x/X where X is proportional to thickness, and k_x is a sort of vapor conductivity

$$N_a = \frac{k_x}{X} (P_1 - P_2) = \frac{k_x}{X} (T_1 - T_2 - E) \frac{\partial P}{\partial T} \tag{6}$$

then

$$(T_1 - T_2 - E) = \frac{N_a X}{k_x \frac{\partial P}{\partial T}} \tag{7}$$

also

$$T_s - T_1 = \frac{q_T}{h_{sf}} = \frac{q_v + q_c}{h_{sf}} = T_2 - T_w \tag{8}$$

This assumes equal film resistances on both sides of the membrane. Membrane heat conduction may be written as $q_c = k/X\ (T_1 - T_2)$ with k = membrane thermal conductivity, based on units of X. Then approximately,

$$T_s - T_1 = T_2 - T_w = \left[N_a \lambda + \frac{k}{X} (T_1 - T_2) \right] \left(\frac{1}{h_{sf}} \right) \tag{9}$$

$$T_s - T_1 + T_2 - T_w = 2 \frac{N_a \lambda}{h_{sf}} \left[1 + \frac{k(T_1 - T_2)}{X\ N_a \lambda} \right] \tag{10}$$

Substituting Equation (7) inside brackets for N_a

$$T_s - T_1 + T_2 - T_w = \frac{2 N_a \lambda}{h_{sf}} \left[1 + \frac{k\ (T_1 - T_2)}{X \frac{k_x}{X} \frac{\partial P}{\partial T} \lambda (T_1 - T_2 - E)} \right] \tag{11}$$

This is the loss of temperature driving force due to liquid films on both sides. Combining (11) and (7),

$$T_s - T_w - E = T_s - T_1 + T_2 - T_w + T_1 - T_2 - E$$

$$= \frac{2 N_a \lambda}{h_{sf}} \left[1 + \frac{k\ (T_1 - T_2)}{k_x \frac{\partial P}{\partial T} \lambda\ (T_1 - T_2 - E)} \right] + \frac{N_a\ X}{k_x \frac{\partial P}{\partial T}}$$

$$T_s - T_w - E = \frac{2\ N_a \lambda}{h_{sf}} \left[1 + \frac{k}{k_x \frac{\partial P}{\partial T} \lambda} \left(1 + \frac{E}{T_1 - T_2 - E} \right) \right] + \frac{N_a X}{k_x \frac{\partial P}{\partial T}}$$

substituting for $T_1 - T_2 - E$

$$T_s - T_w - E = \frac{2 N_a \lambda}{h_{sf}} \left[1 + \frac{k}{k_x \frac{\partial P}{\partial T} \lambda} \left(\frac{1 + \frac{E}{N_a X}}{k_x \frac{\partial P}{\partial T}} \right) \right] + \frac{N_a X}{k_x \frac{\partial P}{\partial T}}$$

Putting the above expression into Equation (5),

$$\frac{1}{K_m} = \frac{X}{k_x} + \frac{2 \frac{\partial P}{\partial T} \lambda}{h_{sf}} + \frac{2}{h_{sf}} \frac{k}{k_x} + \frac{2k \frac{\partial P}{\partial T} E}{h_{sf}\ N_a X} \tag{12}$$

The first term would be the resistance with no heat effects, and the second the effect of the films due to latent heat transfer. The third term is the film effect on mass transfer due to parallel heat conduction if driving forces were the same in terms of temperature. The last term corrects the third term for the fact that boiling point elevation reduces the mass transfer driving force. As X increases the first term contributes to overall mass transfer resistance, while as X approaches 0, the last term would increase rapidly.

The values of k_x, h_{sf}, and k were assumed constants to be evaluated. A linear least squares program was used to determine the appropriate constants in Equation (12) and similar equations, and the fits were evaluated by the residual variance. The best estimate equation on the basis of least variance for $1/K_m$ was an equation, where the 1st and 3rd terms of Equation (12) were empirically modified by a $\Delta T - E$ factor, as follows:

$$\frac{1}{K_m} = 0.0126\ (\Delta T - E) X + 0.00134 \frac{\partial P}{\partial T} \lambda + 0.354\ (\Delta T - E) \tag{13}$$

where X is membrane weight in g./0.12 sq.ft., assumed proportional to thickness and $\Delta T = T_s - T_w$. Essentially equivalent was the equation,

$$\frac{1}{K_m} = 0.123\ X + 0.0011 \frac{\partial P}{\partial T} \lambda + 0.364\ (\Delta T - E) \tag{14}$$

Equation (13) is shown in Figure 4. Both of these equations show the necessity of modifying Equation (12) with a ΔT term. It seems probable that increasing $(\Delta T - E)$ values would not increase, but decrease the overall resistance if this effect was primarily on the film coefficients h_{sf} and h_{wf} or on N_a in Equation (12). Therefore, it appears that either k or k_x are probably related to $\Delta T - E$. As will be discussed later, the greater is the value of $\Delta T - E$, the greater are the possibilities for internal condensation within the membrane. Internal condensation would appear to contribute toward a greater resistance by increasing k and decreasing k_x in Equation (12). In both Equations (13) and (14), the $\Delta T - E$ term is an important part of the resistance, but is empirical and not capable of being extrapolated satisfactorily to the other groups of experiments.

GROUP III EXPERIMENTS

In the first two groups of experiments, the driving forces were never completely independent of other experimental conditions. In fact, the driving forces resulted from setting the heat input for the given apparatus and membrane, and as the ΔT increased, so did the temperature level and water vapor pressure, and air partial pressure decreased. Thus there was not adequate data to differentiate the effects of these variables. In group III experiments, temperatures on each side could be independently established by means of a second heater on the fresh water side. Membrane properties were somewhat different, but similar to the second group membranes.

For correlating these results a theoretical equation based on a diffusion mechanism was derived by assuming that the equation for diffusion through a stagnant gas in a membrane is a modification of a gaseous diffusion equation (1), thus,

$$N_a' = \frac{\pi \; D_E \; (P_1 - P_2)}{RTX' \; P_{Blm}} \tag{15}$$

In this equation, D_E should be proportional to D_{AB}, the gas diffusivity of water vapor and air, which may be estimated from the equation of Fuller, Schettler, and Giddings (*4*),

$$D_{AB} = \frac{d \; T^{1.75} \left(\frac{1}{Ma} + \frac{1}{Mb} \right)^{1/2}}{\pi (V_A{}^{1/3} + V_B{}^{1/3})} \tag{16}$$

All terms in the above equation except T and π are constant for air-water systems so we may write

$$D_E = \frac{k_1 \; T^{1.75}}{\pi} \tag{17}$$

Substituting this in Equation (15),

$$N_a = \frac{k_2 (\overline{T})^{3/4}}{X} \; \frac{(P_1 - P_2)}{P_{Blm}} \tag{18}$$

Where N_a is in lb./hr. sq.ft., $\overline{T}$, the average of T_s and T_w in °R., is assumed to be the appropriate temperature and $k_2 = k_1(\text{mol. wt})/R(0.00188 \text{ ft./unit } X)$. A 1 g. membrane had a thickness of 0.00188 ft. in these experiments.

Comparing Equation (18) with Equation (6), it is evident that

$$k_x = \frac{k_2 (\overline{T})^{3/4}}{P_{Blm}} \tag{19}$$

Since P_{B2} and P_{B1} were not greatly different in these experiments P_{Blm} is approximately $P_{Bavg.} = \pi - \frac{P_s + P_w}{2}$, and Equation (12) then becomes

$$\frac{1}{K_m} = \frac{XP_{Bavg}}{k_2 (\overline{T})^{3/4}} + \frac{2(\partial P/\partial T)\lambda}{h_{sf}} + \frac{2\,k\,P_{Bavg.}}{h_{sf} k_2 (\overline{T})^{3/4}} + \frac{2\,k\,(\partial P/\partial T)\,E}{h_{sf} N_a \, X} \tag{20}$$

The last term is theoretically small and turned out to be statistically insignificant. Omitting the last term, the coefficients were evaluated for the third group of experiments to give the following equation:

$$\frac{1}{K_m} = \frac{7.406 \; X \; P_{Bavg.}}{(\overline{T})^{3/4}} + 0.00646 \; (\partial P/\partial T)\lambda + \frac{3.76 \; P_{Bavg.}}{(\overline{T})^{3/4}} \tag{21}$$

The first coefficient of Equation (21) indicates that $1/k_2 = 7.406$, or converting to effective diffusivity at 0°C., $D_E = 0.140$ sq.cm./sec. This value, if multiplied by $\sqrt{2}$ to eliminate the effect of tortuosity (*2*), and if divided by the void fraction to eliminate the effect of cross-sectional area, gives a gaseous diffusion coefficient, D_{AB}, of 0.217 sq.cm./sec. The value of D_{AB} given by Perry's Handbook (*10*) is 0.220 sq.cm./sec. at 0°C.

The second coefficient indicates the value h_{sf} (where both film coefficients are assumed equal) is 310 B.t.u./hr.°F. sq.ft. Other tests made in similar apparatus by glueing fine thermocouples to the membrane surface gave average values of h_{sf} and h_{wf} of 425 B.t.u./hr. sq.ft. °F. This result is probably high since heat losses from the apparatus were not deducted from heat input.

The third coefficient indicates k to be equivalent to 0.148 B.t.u. ft./hr. sq.ft. °F. if the values of h_{sf} and k_2 are correct. If the thermal conductivities of air and glass are weighted according to the volume fraction, a thermal conductivity of about 0.06 is estimated for the composite membrane. Any liquid moisture penetrating or condensing in the membrane would increase the thermal conductivity. All three coefficients indicate that the diffusion mechanism of Equation (12) is probably correct if one takes into account likely variations of thermal and diffusion characteristics in the membrane.

Equation (20) was also applied to the second group of results and gave the following least squares equation:

$$\frac{1}{K_m} = \frac{5.131 \; X \; P_{Bavg.}}{(\overline{T})^{3/4}} + 5.627 \; (10^{-3}) \; \frac{\partial P}{\partial T} \lambda + 4.808 \, \frac{P_{Bavg.}}{(\overline{T})^{3/4}}$$

However, the variance of the error in this equation was significantly greater than the error variance in Equations (13) or (14). This indicates that a term involving the ΔT is still required to obtain the best correlation of all the data.

EFFECT OF ΔT

It can be shown by reasoning similar to Mickley's (*7*) on fogging in humidification towers, that as the ΔT across the membrane increases, the likelihood of internal condensation increases. This is shown by Figure 5, where the two curves represent the vapor pressures of 7% salt water and water as a function of temperature. The dashed lines represent the approximate variation of water vapor partial pressure with temperature through the membrane vapor phase at different ΔT values. It can be seen that the greater the ΔT, the greater the likelihood that the partial pressure within the membrane becomes greater than the saturated water vapor pressure which should result in condensation. It can also be shown that the greater the curvature of the vapor pressure curve, which is approximately proportional to $1/T^3$ the more likely internal condensation becomes. For this reason, the differences and ratios of a theoretical overall resistance based on Equation (21) and the experimental resistance were plotted as a function of $\Delta T - E$ and also as a function of $(\Delta T - E)/\overline{T}^3$. These plots were all similar and for simplification, differences are plotted vs. $\Delta T - E$ in Figure 6. This indicates that there is a relationship between the deviation from theoretical and $\Delta T - E$, which seems most likely due to some effect of internal condensation. The points from runs 5 and 6 of the first group were all obtained on the same membrane, and it is quite possible that the discrepancy of these points was due to a slight leak in the membrane or apparatus which decreased the measured transfer rates and increased

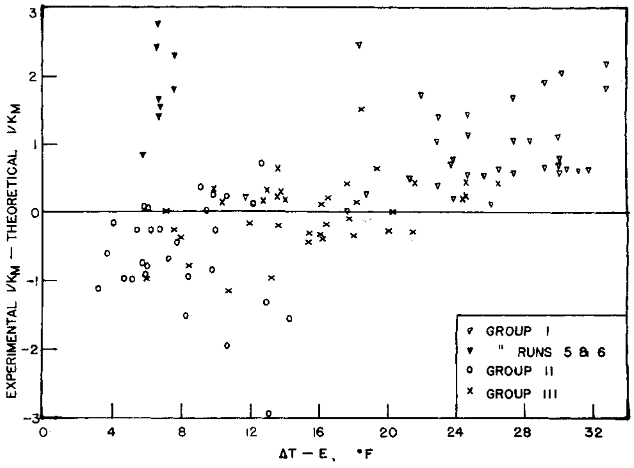

Fig. 6. Difference between experimental resistance and theoretical resistance from Equation (21) as a function of temperature driving force, ΔT-E.

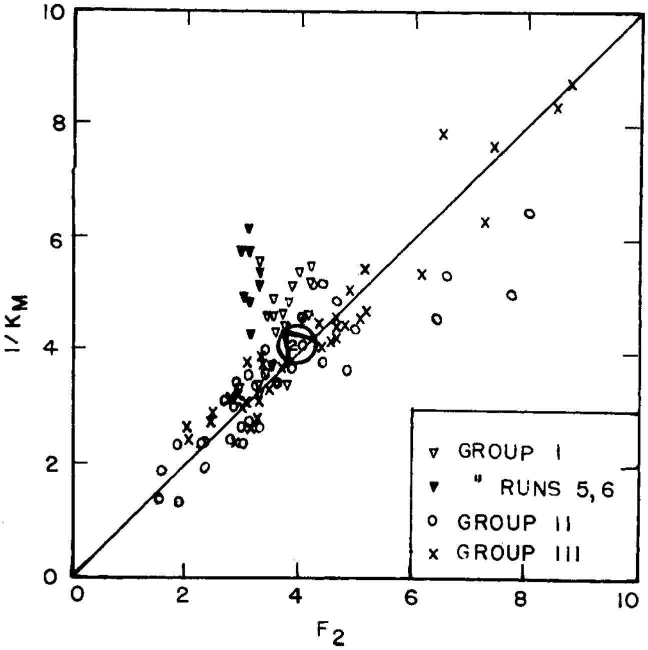

Fig. 7. Mass transfer resistance vs. F_2 where $F_2 = 7.406\ (XP_{Bavg.})/(\overline{T})^{3/4} + 0.00642\ \lambda\ \partial P/\partial T + 3.762\ (P_{Bavg.})/(\overline{T})^{3/4} - 0.643 + 0.043\ (\Delta T\text{-}E)$. See Equation (22).

the apparent resistance. It is uncertain why some of the points particularly in the second group give a lower resistance than that expected on a theoretical diffusion basis. This could be due to diffusion of adsorbed water along the surface of the glass or Teflon which would increase the rate and decrease the apparent resistance. It should be kept in mind in observing this figure that the membranes of each group were made in a different manner and should not be expected to have exactly the same response to ΔT variation.

To attempt to empirically correct overall resistance for the effect of ΔT, a least squares equation was obtained on the data from the third group of experiments only. A constant term and a $\Delta T - E$ term were correlated with the differences to allow both positive and negative corrections for the effect of $\Delta T - E$. The following equation was the result.

$$\frac{1}{K_m} = 7.406\frac{X\,P_{Bavg.}}{(\overline{T})^{3/4}} + 0.00642\frac{\partial P}{\partial T}\lambda + 3.762\frac{P_{Bavg.}}{(\overline{T})^{3/4}} - 0.643 + 0.043\,(\Delta T - E) \qquad (22)$$

The standard deviation of the residual error of this equation for group III was 0.47. The 2 sigma limits of $1/K_m$ would be ± 0.94.

Figure 7 shows the results of all three groups of data plotted vs. the right hand side of Equation (22), which was determined from the third group only. If runs 5 and 6 are ignored and if it is kept in mind that membrane preparation was different for each group, the results appear to verify a diffusion mechanism modified by a ΔT effect, and possibly a surface diffusion effect. Equation (22) is the only equation obtained which appears to fit all 3 groups of data reasonably well. This is probably true because it represents a theoretical diffusion mechanism plus an effect of ΔT.

Since the first three terms of Equation (22) are theoretically based on reasonable coefficients, and since the final two terms are corrections which would not be expected to vary widely, this equation appears likely to be suitable for extrapolation to conditions not yet studied. However, if temperature and ΔT values differ widely from those studied here, the correction terms would become questionable. In some cases complete saturation may occur and completely prevent suitable operation.

It appears that there is not a great deal of variation with membrane density. This is probably true because for a given weight per unit area as the density increases, the thickness decreases and porosity is reduced, and these variables have opposite effects on the diffusion.

If Equation (22) is generalized to more conventional units with a constant tortuosity factor of 1.414 for water-air systems, the resulting equation is

$$\frac{1}{K_m} = \frac{3.58\,(10^3)\,X'\,P_{Bavg.}}{e(\overline{T})^{3/4}} + 6.46(10^{-3})\frac{\partial P}{\partial T}\lambda + \frac{3.42\,P_{Bavg.}}{e(\overline{T})^{3/4}} - 0.643 + 0.043\,(\Delta T - E) \qquad (23)$$

In this equation pressures are in inches Hg., temperatures are in °R., λ is in B.t.u./lb. and e is void fraction. Equation (22) is not suitable for diffusing components other than water due to the empirical correction factor involved. However, generalizing Equation (12) which has been indicated to be approximately correct would give

$$\frac{1}{K_m} = \frac{1.414\,X'\,RT\,P_{Blm}}{\pi\,D_{AB}\,e(\text{mol.wt.})} + \frac{2\frac{\partial P}{\partial T}\lambda}{h_{sf}} + \frac{2.828k\,RT\,P_{Blm}}{h_{sf}\,\pi\,D_{AB}\,e(\text{mol.wt.})} + \frac{2\,k\frac{\partial P}{\partial T}E}{h_{sf}N_aX'} \qquad (24)$$

Where the units of each term on the right must correspond to units of $1/K_m$. The last term of Equation (24) could probably be ignored in many cases. Equations (23) and (24) should not be relied on for conditions unsimilar to those in this investigation, but they should be useful for approximately estimating transfer coefficients where no data is available. Refinement of the correction term and the mechanism behind it is one area which should be studied further for future applications of this method of evaporation.

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NOTATION

A = area of membrane in sq.ft.
a = activity of water in solution, assumed constant at 0.96
D_E = effective diffusivity, sq.ft./hr.
D_{AB} = gas diffusivity of A and B, water and air in this study, sq.ft./hr.
E = boiling point elevation of solution, assumed constant at 1.4°F. for 7% saltwater
e = void fraction
h_{sf} = solution film heat transfer coefficient at membrane, B.t.u./hr. sq.ft. °F., assumed equal to water film coefficient, h_{wf}
K_m = mass transfer coefficient in lb./hr. sq.ft. in. Hg.
K_{m1} = mass transfer coefficient in lb./hr. sq.ft. = $N_AP_{Blm}/P_s - P_w$.
k_x = mass conductivity, lb./hr. sq.ft. in. Hg./unit of X, = K_mX
k = thermal conductivity based on units of X, B.t.u./hr. sq.ft. °F./unit of X
k_1, k_2 = constants
M = transfer rate in lb./hr.
N_A = mass transfer flux in lb./hr. sq.ft.

$N_{A'}$ = mass transfer flux in lb. mol./hr. sq.ft.
P = vapor pressure of water, in. Hg.
P_{Blm} = log-mean partial pressure of stagnant components
$P_{Bavg.}$ = total pressure minus average of P_s and P_w assumed approximately equal to P_{Blm}
P_s = vapor pressure on solution side, in. Hg. = $a\,P_{ws}$
P_w = vapor pressure on water condensate side, in. Hg.
P_{ws} = vapor pressure of pure water at T_s, in. Hg.
P_1, P_2 = vapor pressures at membrane interfaces, solution and coolant sides
q_c = heat conducted through membrane, B.t.u./hr. sq.ft.
q_v = heat transferred through membrane with vapor as latent heat, B.t.u./hr. sq.ft.
q_t = total heat transferred = $q_c + q_v$
R = gas constant
T_w = coolant-condensate bulk temperature, °F.
T_s = solution bulk temperature, °F.
T_1 = solution-membrane interface temperature, °F.
T_2 = coolant-condensate (water)-membrane interface temperature, °F.
$\overline{T}$ = average of T_s and T_w converted to °R.
Wg = weight of glass fiber in g. per sq.ft. of membrane
X = wt. of glass fiber in g. per 111 sq.cm. of membrane or wt. glass fiber, g./12 sq.ft., used as a measure of thickness
X' = membrane thickness in ft.
ΔT = $T_s - T_w$
λ = latent heat of vaporization, B.t.u./lb.
π = total pressure in in. Hg. (Atmospheric throughout this study)

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Cyclic Steady State Diffusion

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Analytic equations describing cyclic steady state diffusion in which the diffusivity depends on the direction of transfer, as well as on the system, have been obtained.

By imposing the cyclic steady state constraint, of periodically repetitive concentration profiles, simultaneous solution of separate Fick's diffusion equations for the on-off segments of the cycle results in the desired equations. The method of solution can be extended to more complex diffusion problems, such as coupled diffusion processes. Shallow bed experiments have been performed on particle-diffusion controlled, cyclic steady state ion exchange. Agreement between the predicted and experimental transfer was obtained. Variables and parameters affecting cyclic steady state diffusion are discussed.

Many unit processes, operated in a cyclic steady state* have been shown to be superior to the noncyclic analogues. Steady state operations such as distillation and extraction have been made cyclic, leading to improved throughputs and efficiencies (*2, 5, 14, 18, 19, 23*). These controlled cyclic operations have generally been treated mathematically in a similar manner to their noncyclic analogues (*1, 12, 15, 17*), and analysis has shown that the noncyclic steady state operation is a special case of the cyclic operation.

Even a process, such as ion exchange, commonly operated in a transient state, has been operated at a cyclic steady state resulting in improved performance (*13, 20, 21*). The mathematical problems involved in the latter case are complex, due, not only to the column dynamics, but also to the diffusional process within the ion exchange material (*9*).

Since many processes are diffusion controlled (for example cyclic steady state ion exchange), a fundamental examination of cyclic steady state diffusion was felt to be necessary for a complete understanding of such processes.

THEORETICAL ANALYSIS

Diffusion Controlled Processes

Processes which have diffusion controlled steps (for example ion exchange, adsorptions) may have diffusivities which are functions of the dependent and/or independent variables. In the analysis of such operations, nonlinear partial differential equations, which have not admittted to analytic solutions, are frequently encountered (*3a, 4*). To overcome this problem, numerical or approximate solutions are necessary. A striking example is the numerical solution of the nonlinear partial differential equation describing ion exchange diffusion (*10, 11*).

An approximate analytic solution can sometimes be obtained for such systems by assuming a constant effective diffusivity which will be dependent upon the direction of transfer as well as on the system (*3b, 4*).

Cyclic Steady State Diffusion

If the diffusivity is constant, but not dependent on the direction of transfer, a cyclic steady state diffusion equation is readily solved (*3c*). The method of solution involves one partial differential equation, with a specified time varying boundary condition. In order to solve the cyclic steady state diffusion problem with different diffusivities for the on and off portions of the cycle, a different approach is necessary.

The following method of solution is similar to that used

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* Definition: If a periodic boundary condition is imposed on a body, with a given initial condition, the cyclic steady state is the condition existing after the transient involving the initial conditions has died away. In the cyclic steady state, the dependent variable is periodically repetitive with time.