TABLE 2. THE EFFECT OF β ON TRANSFER COEFFICIENTS

λ	$N_{Nu}(\alpha, \infty)$	$N_{Nu}(\alpha, \beta)$	$N_{Nu}(\alpha, \infty)/2\beta$	$N_{Nu}/N_{Nu\text{app}}$	α	β
10^6	1,128.4	756.0	0.5642	1.048	0	1,000.0
10^4	112.84	108.0	0.05642	1.011	0	1,000.0
10^2	11.284	11.23	0.005642	1.001	0	1,000.0
10^6	1,132.0	757.5	0.5660	1.048	4	1,000.0
10^4	117.0	111.5	0.05848	1.009	4	1,000.0
10^2	16.90	16.77		1.001	4	1,000.0
10^6	1,132.0	556.6	1.132	1.048	4	500.0
10^4	117.0	106.13	0.1170	1.013	4	500.0
10^2	16.90	16.64	0.01690	1.001	4	500.0

$$N_{Nu\text{app}} = \left[\frac{1}{N_{Nu}(\alpha, \infty)} + \frac{1}{2\beta}\right]^{-1}$$

However available correlations, and the assumption of additivity of separately calculated resistances, will be satisfactory for many purposes and will probably lead to conservative design in most cases.

NOTATION

D = equivalent diameter of laminar stream

h_l = average heat transfer coefficient for the laminar stream, based on inlet temperature difference

k_l = thermal conductivity of fluid in laminar stream

U_l = corresponding overall heat transfer coefficient

Greek Letters

α = measure of relative capacities

β = transfer resistances of two streams

ζ = reduced distance in the direction of flow of the laminar stream

η = reduced distance into laminar stream

λ = reduced length of apparatus, that is the value of ζ at the laminar-stream outlet

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A Test of the Assumption of Interfacial Equilibrium in Measurements of the Gas Film Mass Transfer Coefficient

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Rates of interphase mass transfer have attracted the attention of most chemical engineers at one time or another. Concurrent with this interest has been the concern with the assumption of interfacial equilibrium at the phase boundary where the transfer of mass is occurring. It has usually been assumed that the concentrations existing at a gas-liquid interface where mass transfer occurs are those that would be present if no mass were transferring and the system were maintained at the same conditions of temperature and pressure. However most of the concern has been qualitative for two main reasons, namely the deviations were expected to be small, if not undetectable, and the deviation itself depended on a quantity which was somewhat in doubt, the condensation coefficient α. The recent activity in this field among chemical engineers (*3, 9, 10, 11, 13*) confirms the interest in the problem. The following is an attempt to make a quantitative evaluation of the deviations from interfacial equilibrium in the case of vaporization of pure liquids and solids into a foreign gas.

THEORY

The basis of the discussion of rates of vaporization of pure liquids is the Hertz-Knudsen equation

$$\frac{dn}{dt} = \frac{p}{(2\pi\, m\, kT)^{1/2}} \qquad (1)$$

where $(dn)/(dt)$ is the number of molecules per unit time passing through an arbitrary plane of 1 sq. cm. area randomly placed in the gas phase in which the molecules have a Maxwellian distribution. If the reference plane is placed at the gas-liquid interface, Equation (1) with $p = p_i$ gives the number of molecules striking the liquid surface from the gas phase. At equilibrium this also gives the number of molecules leaving the surface by reflection and by evaporation. If one assumes that a certain fraction α of the molecules striking the liquid surface actually condenses, then at equilibrium $\alpha\, p_s/(2\pi\, m\, kT)^{1/2}$ molecules enter and leave the liquid per square centimeter of surface per second. This expression is a function only of the nature of the liquid surface and will represent the rate that molecules leave the liquid under nonequilibrium conditions as well as at equilibrium. The net flux N_A will then be given by the difference in the opposing rates of mass transfer:

$$N_A = \frac{\alpha P_s}{(2\pi MRT_s)^{1/2}} - \frac{\alpha P_i}{(2\pi MRT_i)^{1/2}} \approx \frac{\alpha(P_s - P_i)}{(2\pi MRT)^{1/2}} \qquad (2)$$

Use of Equation (2) is often made difficult by confusion concerning units, and this problem will be deferred until Equation (2) is used to obtain Equation (4).

DISCUSSION

Equation (2) will be used subsequently to test data from runs in which there was a rather large temperature difference between the bulk gas phase and the liquid. Nevertheless the temperature difference between the liquid surface and the gas at the surface must be small. These temperatures enter as the half power of the absolute temperature, and the error caused by assuming $T_s = T_i$ is neglected as indicated by the right side of the equation. Equation (2) has been given by many authors (*6, 9, 11*) and is derived here principally to bring out this assumption, which is traditionally overlooked but which some might regard as worthy of discussion.

Equation (2) was derived for the case of the vaporization of a pure liquid or solid into a vapor space containing its own vapor only. In the case of a binary mixture the flux of one component is given correctly by Equation (1), and hence (2), if the partial pressure of that component is used in place of p. This can be shown by adapting the derivation of Equation (1), as given for example by Loeb (*7*), to the binary case. The additional assumption required is that the P-V-T relation for the mixture may be expressed by the perfect gas law. In subsequent use of Equation (2) it will be understood that the partial pressure is to be used for mass transfer in a binary mixture. Another assumption required in the use of Equation (2) is that α, often measured in the absence of an inert gas, has the same value when an inert gas is present.

Equation (2) indicates that, when liquids vaporize at a net finite rate p_s is greater than p_i, and an interfacial resistance to vaporization exists, however small. It has been the basis of numerous investigations of mass transfer studies, both of liquids and solids.

The development of correlations for the gas phase mass transfer coefficients in a variety of experimental conditions has depended on the validity of the assumption that the pressure existing at the interface is equal to the saturated vapor pressure of the liquid at the surface. Equation (2) shows that this assumption can only be an approximation if there is to be a net transfer of mass in one direction. The design of experiments to measure the gas phase mass transfer coefficients has been based on the concept of the additivity of individual resistances in passing from the bulk of one phase to the bulk of the other. The use of a pure liquid eliminates the liquid phase resistance, and if the assumption of interfacial equilibrium is made, the total resistance to mass transfer resides in the gas phase. Most of the investigations of the gas phase mass transfer coefficients in wetted-wall towers, packed columns, liquid jets, open pans, etc. have used a pure liquid vaporizing into a foreign gas, and almost without exception the assumption of interfacial equilibrium has been made.

DEPARTURE FROM INTERFACIAL EQUILIBRIUM

The calculation of the experimentally determined mass transfer coefficient k_G is made with

$$N_A = k_G(p_i - p_G) \qquad (3)$$

If the point values of the driving force vary during the time of the measurement or with position, the log mean driving force is used. In making the assumption of interfacial equilibrium p_i is replaced by p_s in the calculation of k_G with Equation (3).

To allow for the possibility of p_i being different from p_s the following development is used. Equating the rate of phase transition to the rate of transport across the film one gets[*]

$$k_G(P_i - P_G) = \frac{7.45 \times 10^9 \alpha (P_s - P_i)}{(2\pi MRT)^{1/2}} \qquad (4)$$

Solving Equation (4) for p_i and substituting into Equation (3) one obtains

$$N_A = \frac{k_G(p_s - p_G)}{1 + (2\pi MRT)^{1/2} k_G / 7.45 \times 10^9 \alpha} \qquad (5)$$

Equation (5) is important because it shows the relationship between the experimentally determined gas phase mass transfer coefficient based on the assumption of interfacial equilibrium and the actual mass transfer coefficient:

$$K_G = \frac{k_G}{1 + (2\pi MRT)^{1/2} k_G / 7.45 \times 10^9 \alpha} \qquad (6)$$

where K_G is based on $p_s - p_G$, and k_G is based on the actual driving force $p_i - p_G$.

Rearranging Equation (6) one gets Equation (7) from which k_G could readily be computed from K_G and R_i:

$$\frac{1}{K_G} = \frac{1}{k_G} + R_i \qquad (7)$$

CRITERION OF IMPORTANCE FOR INTERFACIAL RESISTANCE

One can develop a criterion of importance for the interfacial resistance by defining E as the interfacial resistance R_i, divided by the sum of R_i and $1/k_G$. In terms of partial pressures E is defined as

$$E = \frac{p_s - p_i}{p_s - p_G} \qquad (8)$$

E is also the error (expressed as a fraction of k_G) introduced by assuming that $k_G = K_G$ in the interpretation of experimental data. This is seen by introducing the definition of K_G and k_G into Equation (8) and making use of Equation (7) to give

$$E = \frac{k_G - K_G}{k_G} = R_i K_G \qquad (9)$$

The right-hand side of Equation (9) is used to determine E from mass transfer data presented in terms of K_G. If $E = 0.1$ in a particular case, it would be proper to conclude that the interfacial resistance was 10% of the overall gas phase resistance and that a gas film coefficient based on p_s rather than p_i would be in error by 10%. Similarly if it is desired to be sure that the error is less than a particular value E_c, then K_G must be less than E_c/R_i.

The equations presented above apply to data obtained in any type of mass transfer equipment where vaporization occurs from a pure liquid or solid. The value of the condensation coefficient for liquids lies generally in the range 0.01 to 1.0. Comprehensive listings (*5, 8, 13*) of experimental values for several liquids have been reported. The values for many of the liquids used in vaporization studies such as water, methanol, ethanol are in the range 0.02 to 0.04. Values of R_i for some substances are given in Table 1. In referring to Table 1 it is seen that the largest values of R_i are about 0.01. Thus the experimentally measured K_G will differ from the true gas phase mass transfer coefficient by less than about 1% if the former is less than 1.0 lb. mole/(hr.) (sq. ft.) (atm.). It may be desirable however to correct for the deviations of p_i from p_s when the value of K_G *is greater than* 1.0. A lower critical value of K_G would apply at substantially higher temperatures or for substances with lower values for α.

Similar criteria have been suggested by Scala and Vidale (*9*) and by Spalding (*11*). The Scala and Vidale criterion is based on an equation equi-

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[*] In converting from mk in Equation (1) to MR in equation (2) one uses the relations $M = mN_{av}$ and $R = kN_{av}$. The indicated substitution leaves N_{av} in the numerator on the right side, but dividing both sides by N_{av} converts the flux from molecules per (square centimeter) (second) to moles per (square centimeters) (second). Thus N_A in Equation (2) is in gram moles per (square centimeter) (second). If the value for R of 8.317×10^7 erg./(mole) (°K.) is used in Equation (2), the proper units for p are dynes/sq. cm. The conversion factor desired is to allow p to be expressed in atmospheres and also to result in the flux being in engineering units of pound mole per (square feet) (hour). Thus $(1.013 \times 10^6)(3{,}600)(929)/(454) = 7.45 \times 10^9$, and with this conversion constant in equation (4) k_G has its conventional units and the partial pressures are properly expressed in atmospheres, if R has the value given above and T is in °K.

TABLE 1. INTERFACIAL RESISTANCE FOR VARIOUS SUBSTANCES

Substance	Temperature, °C.	α	Ref. for α	$R_i \times 10^3$, (hr.)(sq. ft.)(atm.)/lb. mole
Water	25	0.04	(*6*)	5.64
Water	100	0.02	(*6*)	14.1
Methanol	25	0.045	(*6*)	6.62
Carbon tetrachloride	25	1.0	(*6*)	0.66
Ethanol	25	0.036	(*6*)	12.0
Naphthaline	25*	0.2	(*5*)	3.02

Actually the value of 0.2 for α was measured at about 3°C.

valent to Equation (8) for the special case of $p_G = 0$ which applied in their problem. There is an interesting difference between the criterion suggested by Spalding, namely $K_{\text{vap}} < 0.1$, and that developed here. K_{vap} is proportional to the flux N_A times R_i rather that $K_G R_i$ as given in Equation (9). The Spalding criterion was based on the observation that the curve for $K_{\text{vap}} = 0.1$ was close to the curve for $K_{\text{vap}} = 0$ (equilibrium at the interface) on an enthalpy-concentration diagram for the air-water system, but the relative importance of a given distance on such a diagram depends on the distance G-S (Spalding nomenclature) for the process. Hence a criterion such as $K_{\text{vap}} = 0.1$ would correspond to somewhat different errors for different experiments. This is not a general criticism of the Spalding paper, since the graphical method suggested would clearly show the importance, if any, of the interfacial resistance in each case.

ERROR IN ASSUMING INTERFACIAL EQUILIBRIUM IN GAS FILM COEFFICIENT MEASUREMENTS

The conditions which seem to favor high values of K_G are those in which the transfer is most rapid as caused by low inert partial pressure, high temperature, or high gas velocity. The recent attempts to operate wetted-wall columns at very high liquid temperatures by Cairns and Roper (*1*) and open pan experiments at greatly reduced pressures by Severson, Madden, and Piret (*12*) indicate the need for a more careful analysis of the data with respect to interfacial equilibrium. Table 2 lists the calculated corrections for selected runs from the papers mentioned above, as well as the highest value from Gilliland and Sherwood (*4*) on the air-water system. Values of α used in preparing Table 2 were taken from a summary of the data for water by Delaney (*2*). These values as well as those used in Table 1 are thought to be reliable, but one should realize that there are serious experimental difficulties associated with the measurement of α. In addition surface contamination may alter the value of α markedly so that the measured α may be in error, or, if α is correctly measured for a clean surface, it might not be properly applied in a given mass transfer experiment where a small amount of surface contamination may be practically unavoidable. It does not seem possible to estimate the error in E or R_i, if any, caused by these factors, but the reader should realize that the values reported may be only approximately correct and conceivably could be in error by a rather large amount.

CONCLUSIONS

The assumption of interfacial equilibrium has been shown to be adequate for most studies on the vaporization of pure liquids or solids into an inert gas stream. However when the rate of mass transfer is such that the experimental gas phase mass transfer coefficient becomes larger than 1.0 lb. mole/(hr.)(sq. ft.) (atm.), it may be worth while to correct for deviations from interfacial equilibrium. On the other hand many workers would conclude that even the maximum error of about 7% is negligible compared with other uncertainties usually present in mass transfer studies.

TABLE 2. CALCULATED ERRORS IN THE GAS FILM COEFFICIENT FOR SELECTED DATA

System	Reference & run no.	Values used for R_i T, °K.	α	Experimental, K_G	% Error $= 100E$
Air-water	(*4*) P75p	324.8	0.0260	2.92	2.6
Air-water	(*1*) 10	369.0	0.0196	3.50	4.5
	(*1*) 12	367.0	0.0198	3.16	4.0
	(*1*) 17	365.0	0.0201	2.75	3.5
Air-water	(*12*) 88	288.4	0.0354	5.32	3.3
	(*12*) 114	285.5	0.0360	7.66	4.7
	(*12*) 119	290.3	0.0348	1.96	1.3
	(*12*) 120	295.6	0.0330	3.21	2.2
Helium-water	(*12*) 90	284.8	0.0361	11.4	7.0

Units for K_G are lb. mole/(hr.)(sq. ft.)(atm.)

NOTATION

k = Boltzmann constant, 1.3804×10^{-16} erg./(°K.) (molecule) = (g.) (sq. cm.)/(sec.)^2 (molecule)
m = molecular mass, g./molecule
M = molecular weight
N_{av} = Avogadro's number
p = pressure existing in the gas phase, dynes/sq. cm. = g./(cm.) (sec.)^2
p_G = partial pressure in bulk of gas
p_i = pressure existing at the interface
p_s = saturated vapor pressure of liquid
R = gas constant
R_i = $(2\pi MRT)^{1/2}/7.45 \times 10^9 \alpha$, the interfacial resistance
T = absolute temperature
T_s, T_i = absolute temperature of liquid and gas at the interface, respectively
α = condensation coefficient

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