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In an investigation of the film condensation of methanol in the presence of small quantities of air Baer and McKelvey (1) measured heat transfer rates lower than the theoretical Nusselt values. They stated that the data could not be explained satisfactorily on the basis of a diffusion controlled resistance to mass transfer. The explanation was presented that, under the conditions of the experiments, the interfacial resistance to mass transfer was controlling.

However Harriott (2) has shown that these data can be correlated with a diffusion equation if one makes the assumption that the interfacial resistance to mass transfer is negligible and that  $k_{\sigma}$  is a constant. The purpose of this note is to present a more complete analysis of the original data to show that the experimental data are clearly incompatible with a diffusion controlled resistance to mass transfer.

The experimental data for runs I through V are shown in Table I. In these runs the partial pressure of the air was constant, but the total pressure was varied. The measured quantities are  $\Delta T_1$  and  $\Delta T_2$ .

Since the thickness and the thermal conductivity of the condenser plates are known, the heat flux is calculated directly from the  $\Delta T_2$  values. The rate of mass transfer is then calculated by dividing the heat flux by the latent heat of vaporization of methanol. Mass transfer rates are shown in the third column of the table.

 $\Delta P$  is defined as  $(P_o - P_1)$ . Therefore

$$\frac{\Delta P}{P_a} = 1 - \frac{P_1}{P_a} \tag{1}$$

If the pressures  $P_o$  and  $P_1$  are related to temperatures  $T_o$  and  $T_1$  through the Clausius-Clapyron equation, and if  $T_oT_1 \approx T^*_{o_0}$  one obtains

$$\frac{\Delta P}{P} = 1 - e^{-\lambda M \Delta T_o/RT^2_o} \qquad (2)$$

where

$$\Delta T_o = (T_o - T_1).$$

If  $\Delta T_s$  represents the temperature drop across the condensate film, then

$$\Delta T_a = \Delta T_1 - \Delta T_3 \tag{3}$$

Since the heat flux is known, values of  $\Delta T_s$  can be calculated directly with the Nusselt equation. Values of  $(\Delta P/P_o)$  can then be calculated with Equation

(2). They are shown in the last column of Table 1.

Figure 1 is a plot of the data. The mass transfer rate is plotted against the dimensionless quantity  $(\Delta P/P_o)$ . The points fall on straight lines with the possible exception of run V, where there appears to be a slight bending of the curve.

A test of the diffusion mechanism is provided by analyzing the effect of air on the mass transfer rate. Consider, for example, runs II and V when  $\Delta P/P_o = 0.06$ . With 0.9% air the mass transfer rate is about 7 times greater than when 1.8% air is present.

For a diffusion controlled process the increase in the rate of mass transfer can be calculated. The process to be considered is the steady state unidirectional diffusion of methanol vapor through air. The rate is given by the equation

$$r = \frac{MDP}{RT\Delta z} \ln \left[ \frac{P_o - P_1 (1 - x)}{x P_o} \right]$$
(4)

Since (x << 1), Equation (4) can be written

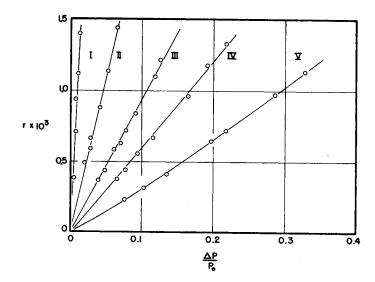
$$r = \frac{MDP}{RT\Delta z} \ln \left[ \frac{\Delta P}{xP_{s}} \right]$$
 (5)

The effect of temperature and pressure on  $\Delta z$  can be estimated by using the standard correlations (3) for natural convection heat transfer. The result is that the diffusion rate at 0.9% air is

TABLE 1

- (0G)		$r \times 10^3$ (g./sq.	. n /n	
$\Delta T_1(^{\circ}C_{\cdot})$	$\Delta T_2(^{\circ}C.)$	cmsec.)	$\Delta P/P_o$	
1.21	0.59	0.56	0.0038	Run I
1.77	0.75	0.71	0.0076	$T_{\circ} = 333^{\circ} \text{K}.$
2.45	1.00	0.94	0.0084	P = 0.82  atm.
3.10	1.19	1.12	0.0107	x = 0.008
3.84	1.60	1.51		
4.12	1.48	1.40	0.0134	
1.48	0.53	0.49	0.0203	Run II
1.95	0.64	0.59	0.0283	$T_{\circ} = 330^{\circ} \text{K}.$
2.23	0.73	0.67	0.0278	P = 0.73  atm.
2.95	0.88	0.81	0.0418	x=0.009
4.30	1.23	1.14	0.0532	
5.70	1.56	1.44	0.0650	
1.70	0.40	0.37	0.0395	Run III
2.07	0.47	0.43	0.0476	$T_{\circ} = 327^{\circ} \text{K}.$
2.84	0.64	0.59	0.0604	P = 0.64  atm.
3.20	0.68	0.63	0.0703	x=0.010
3.70	0.78	0.72	0.0785	
4.43	0.91	0.84	0.0920	
6.00	1.19	1.10	0.119	
6.86	1.33	1.23	0.125	
2.26	0.40	0.37	0.065	Run IV
2.76	0.46	0.44	0.077	$T_{\circ} = 314^{\circ} \text{K}.$
3.56	0.59	0.56	0.094	P = 0.49  atm.
4.45	0.73	0.67	0.116	x = 0.014
6.72	1.03	0.96	0.165	
8.25	1.26	1.18	0.191	
9.60	1.44	1.33	0.218	
2.21	0.26	0.24	0.076	Run V
3.00	0.34	0.31	0.102	$T_o = 314$ °K.
4.06	0.45	0.41	0.135	P = 0.37 atm.
6.40	0.70	0.64	0.196	x=0.018
7.20	0.78	0.72	0.217	
10.10	1.06	0.97	0.285	
12.00	1.23	1.13	0.327	

Thickness of condenser plate: 0.56 cm. Conductivity of condenser plate: 0.14 cal./cm.-sec.-°C.



1.6 times greater than that at 1.8% air. It is apparent that some other factor than diffusion is involved.

Now consider the possibility that the diffusional process operates in series with the interfacial process. In this case the resistances are additive and

$$R_t = R_a + R_i \tag{6}$$

Equation (6) can be rearranged to give

$$\frac{R_d}{R_i} = \frac{1}{1 + \frac{R_i}{R_d}} \tag{7}$$

The quantities  $R_i$  and  $R_d$  are defined by the equations

$$R_i = (P^* - P_1)/r \tag{8}$$

$$R_a = (P_o - P^*)/r \tag{9}$$

Equations (7), (8), and (9) can be combined to eliminate r. One obtains

$$\frac{R_i}{R_d} = \frac{P^* - P_1}{P_o - P^*} \tag{10}$$

The rate equation for the diffusional process can be written

$$r = \frac{MDP}{RT\Delta z} \ln \left[ \frac{P_o - P^{\circ} (1 - x)}{x P_o} \right]$$
(11)

which can be rearranged to give

$$\frac{P^{\bullet}}{P_o} = \left(\frac{1 - xe^{r\gamma}}{1 - x}\right) \quad (12)$$

where  $\gamma = RT\Delta z/MDP$ .

Now combining Equations (1), (7), (10), and (12) one obtains

$$\frac{R_d}{R_t} = \frac{x}{1-x} \left( \frac{e^{r\gamma}-1}{\Delta P/P_o} \right) (13)$$

In the limit when  $r \to 0$  the right side of Equation (13) reduces to the indeterminate form (0/0). It can be evaluated with L'Hospital's rule:

$$\lim_{r\to 0} \left(\frac{R_d}{R_t}\right) = \left(\frac{x}{1-x}\right) \gamma m_o$$
(14)

where

$$m_o = \left[\frac{dr}{d(\Delta P/P_o)}\right]_{r=0}$$

which is seen to be the slope of the rvs.  $(\Delta P/P_o)$  curve evaluated at r=0.

Equations (13) and (14) would enable one to calculate the relative importance of diffusion, if one knew the value of  $\Delta z$ . Unfortunately  $\Delta z$  values are not known, and because of the complex shape and flow conditions in the apparatus it is unlikely that anything more than an order-of-magnitude estimate of  $\Delta z$  can be made.

The vapor in the apparatus follows a path from the surface of the boiling liquid, past the condenser plate where some of it condenses, and upward to the walls of the bell jar which encloses the apparatus where more of it condenses. The condensate then drips back into the boiling liquid. In a sense then the vapor is in a state of forced convection, and since the condenser surface is located directly above the boiling liquid, it is probable that eddies disrupt any steady flow pattern. Therefore if one calculates the effective film thickness based on correlations for natural convection heat transfer, one should have an estimate of the maximum possible film thickness.

Now consider for example run V. The value of  $m_o$  is 3 x  $10^{-3}$  g./sq.cm.sec. and x = 0.018. The diffusivity of methanol vapor under the conditions of the run is about 0.48 sq.cm./sec. The Nusselt number is estimated to be about 7.4 with the correlation for natural convection heat transfer to short vertical plates used. The characteristic length was taken as 3.5 cm. (the radius of the disk), and  $\Delta T$  is taken as 10 deg. The substitution of

these numbers into Equation (14) shows that at very low heat flux the diffusion process could contribute 12% of the total resistance to mass transfer.

In run V, in which the air content was about 1.8%, the heat flux ranged from about 700 to 3,500 B.t.u./sq.ft.hr. Previous investigations of condensation have been carried out at higher heat flux. For example Othmer (4) investigated the condensation of steam containing 1.9% air but with the heat flux in the range of 6,000 to 24,000 B.t.u./sq.ft.-hr. Under these conditions it is quite likely that diffusion could be the controlling factor for mass transfer.

#### NOTATION

 $k_g$ = mass transfer coefficient

= slope of r vs.  $(\Delta P/P_o)$  curve  $m_{s}$ at r=0

= mass transfer rate r

mole fraction air in bulk of  $\boldsymbol{x}$ vapor

D= diffusion coefficient

M = molecular weight of methanol P

= total pressure

 $P_{o}$ = partial pressure of methanol in bulk of vapor

 $P_1$ = partial pressure of methanol at liquid side of interface

= partial pressure of methanol at vapor side of interface

R = gas constant

= total resistance to mass trans- $R_t$ 

= diffusional resistance to mass  $R_d$ transfer

= interfacial resistance to mass  $R_i$ transfer

= temperature in bulk of vapor  $T_{o}$ = temperature at liquid side of  $T_1$ 

interface

## **Greek Letters**

= quantity defined by Equation

= latent heat of vaporization of methanol

= effective film thickness for diffusion

= temperature drop from bulk of vapor to condenser plate

= temperature drop through condenser plate

= temperature drop through condensate film

 $\Delta P = (P_o - P_1)$  $\Delta T_o = (T_o - T_1)$ 

# LITERATURE CITED

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