Phase and Area Contributions to Mass Transfer Kinetics

A. J. TELLER

University of Florida, Gainesville, Florida

A relationship has been developed describing quantitatively the factors affecting packed column performance. The relationship, based on the Colburn equation, is proposed within the limits of a consistent flow regime in the liquid phase.

Via separation of the effects of packing geometry on diffusion rates and the effect of area variation with flow rate, single phase transfer rates can be obtained from over-all mass transfer data. The appearance of a maximum in the relationship of H_{oa} vs. G in the range of 60% of flooding is explained by the large increase of the term H_{oa}/a_{i} ($\partial a_{i}/\partial G_{m}$) relative to the term $1/a_{i}$ ($\partial H_{0}a_{i}/\partial G_{m}$). The ammonia-air-system behavior is analyzed via this relationship. It is found that the gas phase resistance varies between 72 and 94% of the over-all resistance as a function of flow rate.

Mass transfer characteristics in packed columns are functions of the following behavior factors: physical properties of the streams, flow characteristics of the streams, and effective area of phase contact.

The first factor has been evaluated quantitatively by many investigators, resulting in the development of the Schmidt number concept. The second factor has been evaluated effectively for many surface shapes for the vapor phase for conditions of constant area of interphase contact by Powell and others (13, 14) and Von Karman (24), Sherwood (16), and Chilton and Colburn (2).

In recent years there has been an effort on the part of many investigators to establish the effect of flow mechanisms in packed towers on the wetted area and the area of interphase contact.

It is apparent that these two phenomena are not the same in that the effective area of interphase contact consists not only of wetted area but the surface of rivulets of liquid flow and that of the dynamic interstitial holdup as indicated by Sherwood (10) and Teller (22), the equivalent area effect of surface renewal described by Danckwerts (3), and the effective penetration time of Higbie (9).

The importance of the effect of flow characteristics of the process streams and the effective area of interphase contact that are interrelated by the geometry of the packing is indicated by the following mathematical analysis based on the original Chilton and Colburn (1) equation for dilute systems.

$$H_{og} = H_g + \left(\frac{mG_m}{L_m}\right) H_L \qquad (1)$$

If the two film theory is to be utilized as the interpretive procedure, then via differentiation of Equation (1) at constant liquid flow conditions

$$\left(\frac{\partial H_{oG}}{\partial G_{m}}\right)_{L} = \left(\frac{\partial H_{G}}{\partial G_{m}}\right)_{L} + \left(\frac{mG_{m}}{L_{m}}\right) \left(\frac{\partial H_{L}}{\partial G_{m}}\right)_{L} + \frac{mH_{L}}{L_{m}} \tag{2}$$

From Equation (1)

$$\frac{mH_L}{L_m} = \frac{H_{oG} - H_G}{G_m} \tag{3}$$

Substituting Equation (3) in Equation (2) one obtains

$$\left(\frac{\partial H_{oG}}{\partial G_m}\right)_L = \left(\frac{\partial H_G}{\partial G_m}\right)_L + \left(\frac{mG_m}{L_m}\right) \left(\frac{\partial H_L}{\partial G_m}\right)_L + \frac{H_{oG} - H_G}{G_m} \tag{4}$$

The height of a transfer unit may be divided into the effects of the constant area coefficient and the area for transfer, analogous to treatment of the overall mass transfer coefficient:

$$H_a = \frac{G_m}{k_a} \frac{1}{a_i} = H_a a_i \frac{1}{a_i} \qquad (5)$$

where

$$H_{a}a_{i} = \frac{G_{m}}{k_{a}} \tag{6}$$

or the measure of the difficulty of mass transfer independent of the variation of area of interphase contact.

From Equation (5)

$$\left(\frac{\partial H_o}{\partial G_m}\right)_L = \frac{1}{a_i} \left(\frac{\partial H_o a_i}{\partial G_m}\right)_L$$

$$-\frac{H_{\theta}a_{i}}{a_{i}^{2}}\left(\frac{\partial a_{i}}{\partial G_{m}}\right)_{L} \tag{7}$$

By analogy to Equation (5)

$$H_L = \left(\frac{L_m}{k_L}\right) \frac{1}{a_i} = (H_L a_i) \frac{1}{a_i}$$
 (8)

Therefore

$$\left(\frac{\partial H_L}{\partial G_m}\right)_L = \frac{1}{a_i} \left(\frac{\partial H_L a_i}{\partial G_m}\right)_L - \frac{H_L a_i}{a_i^2} \left(\frac{\partial a_i}{\partial G_m}\right)_L \tag{9}$$

Under conditions of a constant flow regime the liquid phase mass transfer coefficient or its equivalent $H_L a_i$ is independent of gas rate. The relationship developed by Hatta and Katori (8)

$$k_{L} = \sqrt{\frac{6}{\pi}} \sqrt{\frac{D_{L} \tau}{\rho_{L} B_{F} Z}}$$
 (10)

is indicative of this behavior. Inasmuch as the flow pattern in packed towers in the preloading zone is laminar in nature, it is anticipated that the flow regime is constant in this region of flow. Substantiation of this hypothesis is indicated by the fact that $k_L \propto D_L^{0.5}$ in this region in accordance with the prediction of the laminar penetration theory of Higbie. An additional substantiation may be obtained from the fact that the product of H_L obtained from Sherwood and Hollaway (17) data for oxygen absorption in water at L=2,000 lb./hr. sq. ft. and the Shulman and de Gouff (19) estimation of a_i for the same 1-in. Raschig ring packing at L = 2,000 lb./hr. sq. ft. results in a constant $H_{G}a_{i}$ for values of G below 500 lb./hr. sq. ft. and varies only from 16.0 in the laminar zone to 16.5 in the loading zone. It must be noted however that these are based on curve values of a_i .

The accuracy of the values of a_i in the loading zone are also subject to question, since they were obtained via

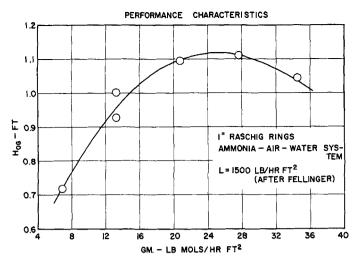


Fig. 1. Performance characteristics of 1-in. Raschia rings.

application of the Chilton and Colburn j factor type of relationship which does not consider the Nikuradse (12) transition from laminar to turbulent behavior. Thus the use of k_L independent of the gas rate is limited to flows below loading.

Under these restricted conditions

$$\left(\frac{\partial H_L a_i}{\partial G_m}\right)_L = 0 \tag{11}$$

Substitution of

$$\left(\frac{\partial H_L}{\partial G_m}\right)_L = -\frac{H_L a_i}{a_i^2} \left(\frac{\partial a_i}{\partial G_m}\right)_L \tag{12}$$

Substituting Equations (7) and (12) in Equation (4) one gets

$$\left(\frac{\partial H_{oG}}{\partial G_m}\right)_L = \frac{1}{a_i} \left(\frac{\partial H_{oG_i}}{\partial G_m}\right)_L \\
-\frac{H_{oG_i}}{a_i^2} \left(\frac{\partial a_i}{\partial G_m}\right)_L \tag{13}$$

$$+\frac{mG_{\scriptscriptstyle m}}{L_{\scriptscriptstyle m}}\left[-\frac{H_{\scriptscriptstyle L}a_{\scriptscriptstyle 1}}{{a_{\scriptscriptstyle i}}^2}\,\frac{\partial a_{\scriptscriptstyle i}}{\partial G_{\scriptscriptstyle m}}\right]_{\scriptscriptstyle L}+\frac{H_{\scriptscriptstyle oG}-H_{\scriptscriptstyle G}}{G_{\scriptscriptstyle m}}$$

When one combines terms in Equation (13), the following relationship results:

$$\left(\frac{\partial H_{oa}}{\partial G_{m}}\right)_{L} = \frac{H_{oo} - H_{a}}{G_{m}} + \frac{1}{a_{i}} \left(\frac{\partial H_{a}a_{i}}{\partial G_{m}}\right)_{L} - \left(\frac{\partial a_{i}}{\partial G_{m}}\right)_{L} \\
\left[\frac{1}{a_{i}^{2}} \left(H_{a}a_{i} + \frac{mG_{m}}{L_{m}}H_{L}a_{i}\right)\right] \tag{14}$$

$$H_{sG}a_i = H_Ga_i + \frac{mG_m}{I}H_La_i \quad (15)$$

and

$$H_{oG}a_i = H_{oG} \times a_i \tag{16}$$

Then substituting Equations (15) and (16) in Equation (14) one gets

$$\left(\frac{\partial H_{oG}}{\partial G_m}\right)_L = \frac{H_{oG} - H_G}{G_m} + \frac{1}{a_i} \left(\frac{\partial H_G a_i}{\partial G_m}\right)_L - \frac{H_{oG}}{a_i} \left(\frac{\partial a_i}{\partial G_m}\right)_L \tag{17}$$

Thus a knowledge of the behavior of the quantities $1/a_i(\partial H_a a_i/\partial G_m)_L$ and $H_{\sigma G}/\hat{a}_i(\partial a_i/\partial G_m)_L$, both functions of the flow behavior in packed columns, can lead to an understanding of overall mass transfer behavior in packed columns and also the evaluation of the resistances in each film from over-all mass transfer data.

For example data relating to $H_{\circ G}$ and G_m can be used to determine H_G and therefore H_L ; the existence of the term $H_{og}/a_i(\partial a_i/\partial G_m)_L$ indicates the reason for the inversion of slope in the plot $H_{\circ g}$ vs. G_m (Figure 1). Apparently the rate of area increase in this zone of operation is greater than the rate of increase of $H_{g}a_{i}$ with G_{m} , so that the over-all mass transfer rate increases. The mass rate of flow at which this inversion occurs will obviously be affected by the effect of the geometry of the packing on the flow mechanism which in its turn affects $(\partial a_i/\partial G_m)_L$ and $(\partial H_{\sigma}a_{\iota}/\partial G_{m})_{L}$. Elgin and Jesser

(2) and Teller (13) have discussed qualitatively the change of flow mechanism from a predominantly surface film flow to that of surface film-dynamic interstitial holdup in the region of the

slope inversion. The value of $(\partial H_0 a_s/\partial G_m)_L$ is controlled by the shape factor of the packing. The exponent n in the equation (j

factor form)

$$\frac{k_{c} P_{BM} (N_{Sc})^{2/3}}{G_{m}} = K (N_{Re})^{n}$$
(18)

has been found by many investigators (6, 18, 19, 20) to be a function of surface geometry under conditions of constant area in the turbulent region.

For a low solute concentration sys-

$$k_{g} \; ({
m const} \; L) = rac{K}{(N_{Sc})^{2/3}} \, G_{m}^{-n+1} \ \ \, (19)$$

Thoenes and Kramers (23) indicate that this relationship is not rigorous for prediction of behavior of packed columns and that the relationship of k_{σ} with Nse is a function of the relative degrees of turbulent flow, laminar flow, and stagnant pockets. However for the entire range of their experimental work, where $0.25 < \epsilon < 0.50$, $40 < N_{Re} < 4,000$, $1 < N_{Se} < 4,000$, the relationship $N_{Sh} = 1.0N_{Re}^{-1/2}N_{Se}^{-1/8}$ described the operation characteristics of their packings within a deviation limit of 10%.

Inasmuch as

$$H_o a_i = \frac{G_m}{k_c} \tag{20}$$

then

$$H_{G}a_{i} = \frac{(N_{so})^{2/3}}{K} G_{m}^{-n} \qquad (21)$$

or via differentiation

$$\left[\frac{\partial (H_{a}a_{i})}{\partial G_{m}}\right] = \frac{-n(N_{sc})^{2/3}}{K}G_{m}^{-(1+n)}$$
(22)

It has been established that the exponent n varies with the geometry of the surface involved as shown in Table 1.

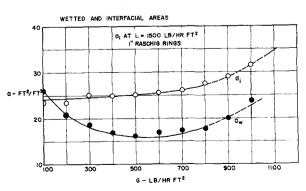


Fig. 2. Wetted and interfacial areas, 1-in. Raschig rings.

Inasmuch as packing shapes are, in effect, combinations of single shapes, it is anticipated, and thus far corroborated, that the exponent n for packings will have a value -0.5 < n < -0.2, representing the two extremes of surface characteristics: the plane normal to gas flow and the plane parallel. The value n for packings is therefore essentially a characterization factor of the mass transfer characteristics of the unirrigated packing.

The study of the effect of packing geometry and flow conditions on area of interphase contact has not been as extensive as that of effect of geometry under constant area conditions. The effect of packing geometry is significant inasmuch as a large number of contact points among packing units will affect the relationship of appearance and the magnitude of the dynamic interstitial holdup (with flow rate). The presence of curved surfaces rather than plane surfaces permits greater exposure of surface to flow changes and therefore greater variation of area with flow changes.

Unfortunately the study of area has been of two types, wetted area and area of interphase contact. These two are not necessarily the same, and this may explain the disagreement in the conclusions of investigators in this field of study.

Historically it was Mayo et al. (10) who determined the effects of flow on wetted area with Raschig rings via the dye wetting procedure. This group found that a_w was independent of gas rate and proportional to Lo. 45. However only very low gas rates were investigated, G < 67 lb./hr. sq. ft.

Grimley (7) estimated the wetted area for %-in. Raschig rings at gas

flows below 20 lb./hr. sq. ft.

Weisman and Bonilla (25), using k_{σ} data for constant area developed by Taeker and Hougen (14) and mass transfer data for the air-water system of McAdams et al. (7), proposed that

$$\frac{a_i}{a_t} = 0.044 \ G^{0.31} \ L^{0.07} \tag{23}$$

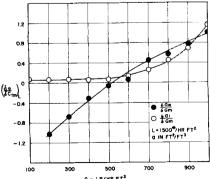


Fig. 3. Rate of change of wetted and interfacial areas with gas flow, 1-in Raschig rings.

TABLE 1. EFFECT OF SURFACE GEOMETRY ON GAS FILM BEHAVIOR

	n	Source
Plane surface parallel to gas flow	-0.2	(18)
Plane surface normal to gas flow	-0.5	(18)
Cylinders—axis parallel to gas flow	0.28	(18)
Cylinders—axis normal to gas flow	-0.46	(18)
Single spheres	-0.43	(18)
Random packed spheres	-0.41	(6)
Random packed 1-in. Raschig rings	0.41	(20)
1 0 0	0.35	(19)
Random packed 1-in. Berl saddles	-0.34	(20)

for 1-in. Raschig rings where 540 <

L < 2,600 and 350 < G < 1,000. Shulman and de Gouff (19), using mass transfer of naphthalene from constant area of naphthalene Raschig rings and then irrigated rings, determined the wetted area of a hydrophobic packing. The a_w was found to be proportional to $L^{(0.64 \text{ to } 0.84)}$ as a function of gas velocity. The effect of gas flow was found to be complex, with a slope inversion that may be related to the slope inversion observed by Fellinger (5) in H_{gg} vs. G plots.

Shulman further attempted to find a_i by using Fellinger's ammonia data. However the procedure used involved an assumption of the relative resistances to diffusion of each phase.

Pratt (15) developed the concept of the minimum effective liquid rate (MELR) at which the entire packing surface becomes effective in mass transfer. This effective interphase contact area was determined relative to a value obtained by extrapolating the level portion of the curve relating $K_{\circ 6}$ $(N_{8c})^{2/3}$ vs. a surface irrigation rate to the zero rate. Pratt assumed a constant surface beyond the MELR in contradiction to Shulman's results and recorded observations of development of interstitial holdup. Pratt, because of limited mass transfer data on single phase controlling systems, had to assume, as did Shulman, the relative transfer resistances of the phases.

The application of information to the utilization of Equation (17)

$$\left(\frac{\partial H_{oG}}{\partial G_{m}}\right)_{I} = \frac{H_{oG} - H_{G}}{G_{m}}$$

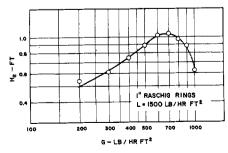


Fig. 4. Height of transfer unit gas phase, ammonia-air-water system.

$$+\frac{1}{a_{i}}\left(\frac{\partial H_{G}a_{i}}{\partial G_{m}}\right)_{L}-\frac{H_{GG}}{a_{i}}\left(\frac{\partial a_{i}}{\partial G_{m}}\right)_{L}$$
(17)

is as follows.

Shulman and de Gouff (19) in work with naphthalene Raschig rings (1 in.) established that for a constant area sys-

$$k_{\rm G}=0.0137~{
m G}^{
m 0.65}~(N_{\rm Sc})^{-2/3}~(24)$$

Thus for gas phases consisting primarily of air

$$k_o = 0.122 \; G_m^{0.65} \; (N_{Sc})^{-2/3} \; \; \; (25)$$

$$H_{o}a_{i} = \frac{G_{m}}{k_{o}} = 8.2 \ (N_{Sc})^{2/8} \ G_{m}^{0.85}$$
 (26)

and

$$\left(\frac{\partial H_0 a_i}{\partial G_m}\right) = \frac{2.87 (N_{Sc})^{2/3}}{G_m^{0.65}} (27)$$

It was indicated by Shulman and de Gouff (19) that Equation (24) is in agreement with that obtained by Taeker and Hougen (14). No other data of an extensive nature are available for mass transfer rate determinations for packed columns under constant area conditions.

The work on contact area variation with flow and packing geometry is less consistent than that of mass transfer. The work applicable to utilization in the basic equation developed was done by Taeker and Hougen (21) and Shulman and de Gouff (19).

Weisman and Bonilla (25) established the mechanism for determination of area and area variation with flow. Data for constant area k_{θ} taken from the work of Taeker and Hougen was applied to mass transfer data in irrigated packing for the single phase control-I'ng water-air system obtained by Mc-Adams et al. (8). Thus for a totally vapor phase controlling system

$$\frac{k_0 a_i}{k_a} = a_i \tag{28}$$

However the data of McAdams (11) for the air-water system was quite scattered.

Although Weisman and Bonilla (25) found the k_ca obtained from the Mc-Adams data to vary with $L^{\circ,07}$, Sher-

Table 2. Interfacial and Wetted Area for 1-in. Raschic Rings $L=1{,}500\ lb./hr.\ sq.\ ft.$

		H_{G}		k_{G}			$\frac{\partial a_w}{\partial a_w}$	∂a₁
\mathbf{G}	G_m	(McAdams)	$k_{\sigma}a$	(Shulman)	a_i	a_w	$\partial \mathbf{G}_m$	∂G_m
100	3.45	0.316	9.18	0,39	23.5	26.2		0.0755
200	6.90	0.465	14.8	0.63	23.5	20.8	-1.03	0.0755
300	10.35	0.528	19.6	0.78	25.1	18.7	-0.667	0.0755
400	13.80	0.581	23.7	0.95	24.9	16.9	-0.319	0.0755
500	17.25	0.625	27.6	1.10	25.1	16.1	-0.0725	0.0755
600	20.7	0.657	31.5	1.23	25.6	17.0	+0.0638	0.1305
700	24.1	0.680	35.4	1.36	26.0	17.4	+0.447	0.2495
800	27.6	0.680	40.7	1.48	27.5	17.7	+0.566	0.4410
*900	31.0	0.670	46.3	1.60	29.0	20.0	0.760	0.6910
*1000	34.5	0.643	53.7	1.71	31.4	23.8	0.902	0.976

^e Extrapolated values. No great significance can be attached to these values since the flow regime of the liquid changes with gas velocity.

wood and Pigford (18) indicate that k_0a is proportional to $L^{0.33}$ by plotting the McAdams data with other mass transfer data. The McAdams information fits the relationship

$$H_{\sigma} = \frac{1.01 \, G^{0.81}}{L^{0.33}} \tag{29}$$

for the air-water system indicated by Sherwood and Pigford (II) to be applicable for G 600 lb./(hr.) (sq. ft.). For general application therefore

$$k_{c}a = 0.184 G_{m}^{0.69} L^{0.33} N_{Sc}^{-2/8}$$
 (30)

Beyond this flow rate there is a slope inversion similar to that obtained by Fellinger (4). These smoothed $k_{\sigma}a$ data of McAdams (11) were then divided by k_{σ} proposed by Shulman and de Gouff to fit their naphthalene vaporization data and the water vaporization data of Taeker and Hougen (21), as indicated in Equation (25).

From these data the interfacial area for 1-in. Raschig rings was determined.

The wetted area was obtained by multiplying the wetted area for naphthalene rings of Shulman and de Gouff (19) by 1.12. The authors indicated that mass transfer rates over napthalene rings were lower, by this quantity, than they were over ceramic rings. This is reasonable inasmuch as the naphthalene is hydrophobic and there is a tendency for rivulet flow rather than film flow. In fact this behavior

can explain the unusual decrease in wetted area for the range 300 < G < 600 indicated in the paper by Shulman and de Gouff.

The data representing a_w , a_i , $\partial a_w/\partial G_m$, and $\partial a_i/\partial G_m$ are indicated in Table 2 and Figures 2 and 3.

It is to be noted that the wetted and interfacial areas are essentially equal at G=100 lb./(hr.)(sq. ft.). The interfacial area is almost constant below G=600 lb./(hr.) (sq. ft.) and then rises in the same range where the wetted area rises. The slopes of both curves (Figure 3) are of equal magnitude during the zone of rise in area. It is possible that this phenomenon is reflective of the development of a dynamic interstitial holdup proposed by Elgin and Jesser (4) and Teller (22).

The interfacial area data indicated in Table 2 and the H_{oc} data indicated in Figure 1 were combined with k_{o} data from Equation (25) to calculate H_{o} in the ammonia-air-water system. The results of the calculation are shown in Table 3 and Figures 4 and 5.

Examination of Table 3 and Figure 4 indicates that the rate of variation of interfacial area significantly affects the mass transfer phenomenon at gas flows above 500 lb./(hr.) (sq. ft.).

This quantity $(a_i/G_m)_L$ has a negative value in Equation (17)

$$\left(\frac{\partial H_{oG}}{\partial G_m}\right)_L = \frac{H_{oG} - H_o}{G_m}$$

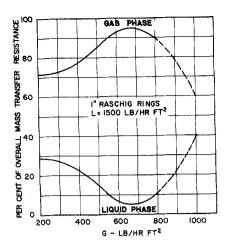


Fig. 5. Fractional resistances of liquid and gas phases in the ammonia-air-water system.

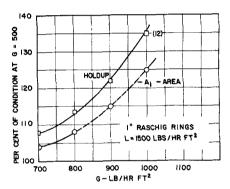


Fig. 6. Variation of holdup and (extrapolated) interfacial area with gas flow in the loading-

$$+\frac{1}{a_i}\left(\frac{\partial H_G a_i}{\partial G_m}\right)_L - \frac{H_{oG}}{a_i}\left(\frac{\partial a_i}{\partial G_m}\right)_L$$
(17)

and contributes to the slope inversion in the plot of H_{oG} vs. G. Thus the rate of area change in this zone overcomes the anticipated loss in transfer efficiency described by the relationship under constant area conditions where $H_G \ a \ G_m^{0.35}$.

In the preloading, where the anticipated decrease in H_{σ} occurs owing to a rapid increase in interfacial area, there appears to be an increase in $H_{\scriptscriptstyle L}$. Although the area increases and surface renewal increases, the holdup of liquid also increases rapidly (Figure

Table 3. Determination of Hg and HL from Equation (15) Ammonia-Air-Water System-1 in. Raschig rings L = 1,500

G	G	$H_{oG} \ (ext{Figure 1})$	$\left(\frac{\partial H_{\partial G}}{\partial G_m}\right)_L$	$ \left(\frac{\partial H_{Gai}}{\partial G_m} \right)_L $ [Equation (19)]	$\frac{1}{a_i} \left(\frac{\partial H_G a_i}{\partial G_m} \right)_{i}$	$\frac{H_{oG}}{a_i} \left(\frac{\partial a_i}{\partial G_m} \right)_L$	$\frac{H_{oG}-H_{G}}{G_{m}}$	$H_{oG} - H_L$	H_G	H_L	€% Phase Vapor	
200 300 400 500 600 700 800 *900	6.90 10.35 13.80 17.25 20.7 24.1 27.6 31.0 34.5	0.72 0.86 0.97 1.05 1.10 1.12 1.10 1.08 1.04	0.0480 0.0398 0.0282 0.10185 0.0106 0.0020 -0.0054 -0.0111 -0.0163	0.589 0.453 0.375 0.314 0.294 0.261 0.239 0.222 0.207	0.0241 0.0184 0.0151 0.0125 0.0115 0.0099 0.0088 0.0077 0.0066	0.0022 0.0026 0.0029 0.0032 0.0056 0.0107 0.0178 0.0250 0.0322	0.0261 0.024 0.0160 0.0092 0.0035 0.0028 0.0046 0.0063 0.0093	0.18 0.25 0.22 0.16 0.07 0.07 0.13 0.19 0.32	0.54 0.61 0.75 0.89 1.03 1.05 0.97 0.89 0.62	5.42 5.07 3.3 1.93 0.71 0.61 0.98 1.27 1.93	75 71 77 85 94 98 88 83 60	25 29 23 15 6 12 17 40

Extrapolated values only.

6). Only a postulation of behavior can be made for this region of flow. It may be that the rate of increase in holdup exceeds the rate of increase in area and surface renewal resulting in an over-all increase in H_L due to a greater effective depth of penetration required. This hypothesis is based on the observation of columns in this zone of operation where the gas tends to channel and bubble and where large masses of liquid flow in a laminar regime.

The change in the relative contributions of the gas and liquid phases to mass transfer kinetics is highly dependent on the variation of interfacial area with gas flow at constant liquid flow at rates below loading. The increase in H_a with gas flow is moderated by the rate of increase of interfacial area in the preloading zone. This phenomenon is causative of the slope inversion of the plot of $H_{\sigma\sigma}$ vs. \tilde{G} generally encountered in systems where the gas phase provides a major portion of the resistance to mass transfer.

NOTATION

= area, sq. ft./cu. ft. = interfacial area a_i

= wetted area

= thickness of liquid film, ft. B_F

D= diffusivity, sq. ft./hr.

= gas phase flow rate, lb./(hr.) (sq. ft.)

= gas phase flow rate, lb. moles/(hr.) (sq. ft.) Η

= height of transfer unit, ft. = transfer rate, lb. moles/(hr.) (sq. ft.) (mole fraction driving force)

= liquid phase mass transfer coefficient

= liquor flow rate, lb./(hr.) (sq. ft.)

= liquor flow rate, lb. moles/

(hr.) (sq. ft.) = slope of equilibrium curve m

= unirrigated packing characterization factor

= Schmidt number, dimension-

= Reynolds number, dimension-

log means partial pressure of inerts, atm.

length of surface, ft.

= density, lb./cu. ft.

= linear rate of liquid flow, lb./(hr.) (ft. of wetted perimeter)

Subscripts

= interfacial

G= gas phase

L= liquid phase

oGoverall based on gas phase compositions or equivalent

= total physical dry

= wetted

LITERATURE CITED

I. Chilton, T. H., and A. P. Colburn,

- Ind. Eng. Chem., 27, 255 (1935). Ibid., 26, 1183 (1934). Danckwerts, P. V., ibid., 43, 1460 (1951).
- 4. Elgin, J. C., and B. W. Jesser, Trans. Am. Inst. Chem. Engrs., 39, 277 (1943).
- 5. Fellinger, L. L., Thesis, Mass. Inst. Technol., Cambridge, Massachusetts

- 6. Gamson, B. W., George Thodos, and O. A. Hougen, Trans. Am. Inst. Chem.
- Engrs., 39, (1943). 7. Grimley, S. S., Trans. Inst. Chem. Engrs. (London), 23, 228 (1945).
- 8. Hatta, S, and M. Katori, J. Soc. Chem. Ind. (Japan), 37, 820B (1934).
- Higbie, Ralph, Trans. Am. Inst. Chem. Engrs., 31, 365 (1935).

 10. Mayo, F., T. G. Hunter, and A. W.
- Nash, J. Soc. Chem. Ind. (London), 44, 375T (1935).
- 11. McAdams, N. H., J. B. Pohlenz, and R. C. St. John, Chem Eng. Progr., **45**, 241 (1949).
- 12. Nikuradse, J., Forschungsheft, No. 356 (1932); No. 361 (1933).
- 13. Powell, R. W., Trans. Inst. Chem. Engrs. (London), 18, 36 (1940).
- and E. Griffiths, ibid., 13, 175 (1935)
- 15. Pratt, ibid., 29, 195 (1951).
- 16. Sherwood, T. K., Trans. Am. Inst. Chem. Engrs., 36, 817 (1940).
 17. ——, and F. A. L. Holloway, ibid.,
- 21 (1940).
- 18. Sherwood, T. K., and Robert Pigford, "Absorption and Extraction," McGraw-Hill, New York (1952).
- Shulman, H. L., and J. J. de Gouff, Ind. Eng. Chem., 44, 1915 (1952).
- 20. Shulman, H. L., C. F. Ulrich, and N. Wells, A.I.Ch.E. Journal, 1, 247
- 21. Taeker, R. G., and O. A. Hougen, Chem. Eng. Progr., 45, 188 (1949).
- 22. Teller, A. J., ibid., 50, 65 (1954).
- Thoenes, D., and H. Kramers, Chem. Eng. Sci., 8, 271 (1958).
- 24. von Karman, T., Trans. Am. Soc. Mech. Engrs., 61, 705 (1939).
- 25. Weisman, Joel, and C. F. Bonilla, Ind. Eng. Chem., 42, 1099 (1950).

Manuscript received July 16, 1959; revision received May 4, 1960; paper accepted May 5, 1960. Paper presented at A.I.Ch.E. Atlantic City

Vapor-Liquid Equilibrium in Ammonia

Complex Systems

C. H. MUENDEL, H. B. LINFORD, and W. A. SELKE

Columbia University, New York, New York

The vapor-liquid equilibrium in ammonia complex systems has been studied with a view toward design methods for separational and leaching processes. It is felt that the previously reported equilibrium constants for these systems are subject to considerable question with regard to the method used to measure the activity of the free ligand, or coordinating species. It is shown how this difficulty can be surmounted by the use of ammonia vapor pressure measurements and fugacities. A method of correlating complex equilibrium data from measurements of over-all metal concentration and free metal ion concentration is proposed. Vapor liquid equilibrium measurements have been made on the systems copper hydroxide, ammonia, water, nitrogen and nickel hydroxide, ammonia, water, nitrogen at 40° and 60°C. under 1 atm. total pressure with a continuously recirculating batch contactor. The correlation method is illustrated with the data of these measurements.

It has long been known that aqueous

C. H. Muendel is with E. I. du Pont de Nemours & Company, Newport, Delaware; W. A. Selke is with Peter I. Schweitzer Division, Kimberly-Clark Corporation, Lee, Massachusetts.

complex systems with volatile ligands, or complexing groups such as ammonia, involve equilibrium not only within the liquid phase but also between the solution and the vapor over it. When an excess of an insoluble compound of the complexed metal ion is present, equilibria in three phases are involved. Systems of this type are becoming increasingly important in the metallurgical industry. In order to study the behavior of such systems and develop