

INTERFACIAL MASS TRANSFER IN TURBULENT FLOW ACCOMPANIED BY IRREVERSIBLE FIRST ORDER CHEMICAL REACTION

Václav KOLÁŘ and Zdeněk BROŽ

*Institute of Chemical Process Fundamentals,
Czechoslovak Academy of Sciences, 165 02 Prague 6-Suchbát*

Received March 1st, 1978

Relations describing the mass transfer accompanied by an irreversible first order chemical reaction are derived, based on the formerly published general theoretical concepts of interfacial mass transfer. These relations are compared with experimental results taken from literature.

Mass transfer accompanied by an irreversible first order chemical reaction is one of few cases of mass transfer accompanied by chemical reaction amenable to analytical treatment. The problem was solved several times both theoretically and experimentally. More information can be found in Danckwerts¹ and Astaritas² monographies.

In this study the formerly published³ general concepts of mechanism of mass transfer across the interface in turbulent medium are applied, which are based on the known parameters characterizing hydrodynamic conditions close to the interface and in the bulk of fluid.

THEORETICAL

In the case of mass transfer accompanied by an irreversible first order chemical reaction only the laminar and transition regions are taken into account. The effect of the turbulent region is significant only at low values of the Schmidt number. Also, for the same reason, the mass transport in the transition region is not treated as in a slab of finite thickness as in the original paper³ but the transport with reaction in a semiinfinite space is assumed. This has no significant quantitative effect on the solution which is formally much simpler because the relations published in literature for the film and penetration theories can be applied.

According to the physical model the reaction species crossing the interface diffuses and reacts in the laminar region of the thickness δ_1 in a steady fashion. The remaining unreacted species in the laminar region proceeds to the transition region of the thickness λ_p . In this region there is assumed an unsteady diffusion and reaction in a semi-

infinite space for a time period t_p equal to the time scale of turbulence in the transition region ($t_p = \lambda_p^2/\nu$).

The flux of species A across the interface G_i is given by

$$G_i = -D(dc/dx)_{x=0}. \quad (1)$$

The corresponding concentration gradient is obtained from the concentration profile by solving the differential equation

$$D(d^2c/dx^2) = kc \quad (2)$$

for the boundary conditions

$$c(0) = c_i \quad \text{and} \quad c(\delta_1) = c_1. \quad (3), (4)$$

In this way the relation has been obtained⁴

$$G_i = (D/\delta_1)(c_i \cosh M - c_1) M/\sinh M, \quad (5)$$

where

$$M = (k\delta_1^2/D)^{1/2}. \quad (6)$$

Similarly the flux of reaction species leaving the laminar region G_1 is obtained upon introducing the concentration gradient at $x = \delta_1$ in Eq. (1) which results in the relation

$$G_1 = (D/\delta_1)(c_i - c_1 \cdot \cosh M) M/\sinh M. \quad (7)$$

The overall flux of the reaction species leaving the laminar region comes into the transient region where there exists the unsteady diffusion with reaction. The corresponding concentration profile of the species for this physical model is obtained by solving the equation

$$D(\partial^2 c/\partial x^2) = \partial c/\partial t + kc \quad (8)$$

for the boundary conditions

$$c(\delta_1, t) = c_1 \quad c(\infty, t) = 0 \quad \text{and} \quad c(x, 0) = 0. \quad (9)-(11)$$

For the mentioned conditions the relation for the flux of reaction species between the laminar and transient regions is obtained⁵ which after introducing $t_p = \lambda_p^2/\nu$ and rearrangement has the form

$$G_1 = (D/\lambda_p)(\nu/D)^{1/2} c_1 [(N + 1/(2N)) \operatorname{erf} N + \pi^{-1/2} \exp(-N^2)] \quad (12)$$

where

$$N = (k\lambda_p^2/\nu)^{1/2}. \quad (13)$$

It follows from Eqs (7) and (12) for the unknown concentration of reaction species c_1 on the boundary between the laminar and transition regions the relation

$$c_1 = c_i / \{ \cosh M + \sinh M [(N + 1/(2N)) \operatorname{erf} N + \pi^{-1/2} \exp(-N^2)] / N \}. \quad (14)$$

After substitution for c_1 from Eq. (14) into Eq. (5) and some rearrangements the final relation results

$$G_i = c_i (kD)^{1/2} [N \operatorname{tgh} M + (N + 1/(2N)) \operatorname{erf} N + \pi^{-1/2} \exp(-N^2)] / \{ N + [(N + 1/(2N)) \operatorname{erf} N + \pi^{-1/2} \exp(-N^2)] \operatorname{tgh} M \}. \quad (15)$$

For the case $\delta_1 = 0$ and thus for $c_1 = c_i$ Eq. (15) changes into Eq. (12) because then $G_i = G_1$. For the case $k = 0$, $\delta_1 \neq 0$, $\lambda_p \neq 0$ ($M = N = 0$) Eq. (15) changes into an expression for physical mass transport

$$G_i = Dc_i [\delta_1 + (\sqrt{\pi/2}) (D/\nu)^{1/2} \lambda_p], \quad (16)$$

where the zero concentration of diffusing species in turbulent bulk is assumed.

RESULTS

In order to verify the theoretical relation it is necessary to know aside from the physico-chemical properties (ν , D , k , c_i) also the hydrodynamic parameters δ_1 and λ_p . It appears to be very suitable for the mentioned purpose to use the paper by Pohorecki^{6,8} who studied the mass transfer accompanied by chemical reaction during absorption of gas into liquid on a sieve plate. In that case we can assume that $\delta_1 = 0$ and $\lambda_p = \lambda_t$, where there holds for λ_t

$$\lambda_t = (\nu_1^3/\bar{\epsilon}_1)^{1/4}. \quad (17)$$

This means that we assume uniform energy dissipation in the liquid phase on the plate, so that the turbulent eddies³ for which Eq. (17) holds are also assumed to exist at the gas-liquid interface.

The energy of gas flowing through the gas-liquid mixture on the plate is dissipated both in gas and liquid phases. For this case the relation has been derived⁷ between the mean rate of energy dissipation per unit mass of fluid in both phases

$$\bar{\varepsilon}_1 v_1 \rho_1^2 = \bar{\varepsilon}_g v_g \rho_g^2 \quad (18)$$

and therefore

$$\bar{\varepsilon}_1 = g u_g / [1 + e \mu_1 / (1 - e) \mu_g] . \quad (19)$$

According to experimental conditions and data in the mentioned papers^{8,6} the hydrodynamic parameters $\lambda_p = \lambda_t$ were calculated from Eqs (17) and (19). Then for individual reaction rate constants k the values of N and corresponding functions of N and finally the values of $G_i^2 / [(c_i - c_r)^2 D]$ were calculated. Using these values and experimentally determined values $X_F = (G_i a_F)^2 / [(c_i - c_r)^2 D]$ the interfacial areas per unit froth volume a_F were calculated.

It is necessary to mention that in Pohorecki's⁶ paper is not treated the irreversible reaction but the reversible reaction with the equilibrium concentration c_r which is assumed to be uniform all over the liquid phase. It embodies the assumption that reaction species and product concentration in liquid phase are much higher than the concentration of absorbed gas. In that case the solution for irreversible and reversible reaction differs only in that, that the relation contains instead of the interface concentration the difference between the interface and equilibrium concentrations.

In the paper by Pohorecki^{6,8} there are eight series of measurements of carbon dioxide absorption in two absorbers using two chemical systems with and without catalyst addition. For the purpose of comparison of experimental data with theoretically derived relations are used three series of measurements of the system with a catalyst $\text{CO}_2\text{-K}_2\text{CO}_3/\text{KHCO}_3/\text{KCl} + \text{NaOCl}$. The author⁶ expressed his data in a form of the Danckwerts' plot and determined both the interfacial area per unit volume of liquid and froth on the sieve plate a_1 , a_F and also the mass transfer coefficient k_1 . The averaged value of carbon dioxide diffusivity in solution $D(\text{solution}) = 1.4 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ was calculated from published values of mass transfer coefficient k_1 and surface renewal rate⁸ s (Table I). The solution viscosity $\mu_1 = 0.00125 \text{ Nsm}^{-2}$ was calculated from the relation $D\mu = \text{constant}$ and the values of viscosity of water $\mu_1(\text{water}) = 0.000981 \text{ Nsm}^{-2}$ and diffusivity of CO_2 in water $D(\text{water}) = 1.784 \cdot 10^{-9} \text{ m}^2 \text{ s}^{-1}$ at the temperature 21°C . Densities of the solution were determined experimentally and corrected for the catalyst addition ($\rho_1 = 1170 \text{ kgm}^{-3}$). The air viscosity was chosen $\mu_g = 1.8 \cdot 10^{-5} \text{ Nsm}^{-2}$. Introducing the values in Eqs (17) and (19) the $\bar{\varepsilon}_1$ and λ_t were determined and the mass transfer coefficient without chemical reaction

$$k_1 = (2/\sqrt{\pi})(D/\lambda_t)(v/D)^{1/2} \quad (20)$$

was calculated from Eq. (20) for the Schmidt number $\text{Sc} = v/D = 763.1$.

In Table I only one value of the mass transfer coefficient k_1 could be calculated for each series from Eq. (20) even though the physical properties of liquid phase are influenced to some extent by the $\text{CO}_3^{2-}/\text{HCO}_3^-$ ratio and by the catalyst addition.

TABLE I
Comparison of Experimental and Calculated Gas Absorption Rates in the System $\text{CO}_2\text{-K}_2\text{CO}_3/\text{KHCO}_3/\text{KCl} + \text{NaOCl}$ on the Sieve Plate^a

Experiment	Results of Pohoreckj ^{6,8}										Calculated results		
	u_g ms ⁻¹	h m	e	a_F m ⁻¹	a_1 m ⁻¹	k_1 10 ⁻⁴ ms ⁻¹	$k_1 a_F$ s ⁻¹	s s ⁻¹	D 10 ⁻⁹ m ² s ⁻¹	ϵ_1 m ² s ⁻³	λ_t 10 ⁻⁵ m	k_1 10 ⁻⁴ ms ⁻¹	Deviation %
a	0.86	0.069	0.63	300	822	6.9	0.207	341	1.396	0.07074	6.443	6.77	1.9
b	0.90	0.091	0.60	225	552	10.9	0.245	844	1.408	0.08396	6.173	7.07	35.1
c	1.44	0.069	0.70	250	863	7.4	0.185	381	1.437	0.08665	6.125	7.13	3.6

^a Rectangular sieve plate 305 × 305 mm, thickness 2.38 mm, hole diameter 5.56 mm situated in triangular pitch 19 mm. On the plate circumference a strip was left without perforations, 25.4 mm wide, to reduce liquid weeping through the plate. Free plate area was 5.5%.

TABLE II
Computation of Interfacial Area and Mass Transfer Coefficient k_1 in the Series a

k s ⁻¹	X_F 10 ⁴ m ⁻² s ⁻¹	μ_1 10 ⁻³ Nsm ⁻²	ν_1 10 ⁻⁶ m ² s ⁻¹	λ_t 10 ⁻⁵ m	Sc	k_1 10 ⁻⁴ ms ⁻¹	N	$\frac{G_i^2}{(c_i - c_i^*)^2 D}$ s ⁻¹	a_F m ⁻¹
2 537	25 910	1.363	1.158	6.993	902	6.22	3.273	2 779	305
1 707	17 220	1.326	1.131	6.824	857	6.39	2.651	1 959	297
1 227	15 510	1.303	1.114	6.717	830	6.49	2.229	1 486	323
840	11 800	1.287	1.101	6.643	810	6.57	1.834	1 108	326
446	8 860	1.269	1.089	6.561	790	6.67	1.328	730	348
178	4 770	1.258	1.081	6.511	777	6.72	0.835	482	315
96	3 140	1.254	1.078	6.492	772	6.74	0.613	409	277
$\text{CO}_3^{2-}/\text{HCO}_3^- = 2.4$									
891	10 670	1.323	1.126	6.797	852	6.41	1.912	1 151	304
607	9 140	1.299	1.108	6.685	823	6.52	1.565	878	323
288	7 360	1.270	1.087	6.583	789	6.67	1.067	581	356
213	6 210	1.265	1.084	6.533	783	6.69	0.916	512	348
82	2 730	1.253	1.075	6.477	769	6.75	0.566	396	263
$\text{CO}_3^{2-}/\text{HCO}_3^- = 1.0$									

Therefore we recalculated the experimental data of series *a* which were plotted in Figs 15 (ref.⁶) and 16 (ref.⁸) in a form of Danckwerts' plot for different values of $\text{CO}_3^{2-}/\text{HCO}_3^-$ ratio. Physical properties, length scale of turbulence λ_t , mass transfer coefficient k_1 and interfacial area per unit froth volume a_F , for each experimental measurement defined by X_F and k , are tabulated in Table II. Deviations from the value $a_F = 300 \text{ m}^{-1}$ specified by the author are lowest for the highest reaction rate constants where the scatter around the Danckwerts' plot straight line is also low. The relative deviation 5% of the average interfacial area $a_F = 315 \text{ m}^{-1}$ is rather low if we take into account that the length scale of turbulence λ_t was calculated theoretically. It follows from results that the values of mass transfer coefficients vary according to variations of physical properties of the system and also that the values of k_1 from Table I refer to the zero reaction rate. It also follows from Table II that the values of interfacial area calculated for the lowest reaction rate constants $k = 96$ and 82 s^{-1} are in a good agreement with the others. Their somewhat lower value can be explained by the rise of an unreacted carbon dioxide concentration in a liquid bulk over its equilibrium value. This effect has been not accounted for in the derivation and we do not treat it here in a more detail.

DISCUSSION

Pohorecki⁶ in his experimental paper, whose results are used to verify our theoretical predictions treated the experimental data using the Danckwerts' plot in order to evaluate the mass transfer coefficient without chemical reaction and the value of interfacial area. In this discussed case of the absorption in a gas-liquid layer on a sieve plate we can expect with a sufficient accuracy the validity of Danckwerts' model particularly the assumption that the turbulent eddies reach the interface which means that there is no laminar region at the interface. Therefore, under the assumption of constant physical properties of the system during the experiment the obtained values of mass transfer coefficient and interfacial area can be expected to be the real ones approximately* to that extent to which correspond each other the solutions of unsteady diffusion accompanied by the first order chemical reaction according to Higbie and Danckwerts models. As has been demonstrated the numerical solutions of unsteady diffusion accompanied by the first order chemical reaction according to both models are so close^{1,2} that it has not been proved which hydrodynamic concept better agrees with the experimental data. From the agreement between the results obtained from the Danckwerts plot and theoretical predictions results, that the new model correctly describes the relation between hydrodynamics and mass

* "Approximately" is introduced because it is necessary to compare the numerical solution for unknown real distribution function of surface ages with the solution for the distribution function according to the Danckwerts' model.

transport. Further, from the model the relation for the Danckwerts intensity of surface renewal s is obtained in the form

$$s = (4/\pi) (v/\lambda_1^2) \quad (21)$$

i.e. the value which the author has not been able to determine and circumvented it by using the mass transfer coefficient without chemical reaction. It follows from Eq. (21) that s is inversely proportional to the time scale of turbulence. In our treatment the time scale of turbulence was obtained from the theoretical equation using no adjustable parameters. The k_1 values in Table II were calculated directly from Eqs (17), (19) and (20).

It is interesting to discuss in a more detail the case where the assumptions of Danckwerts' model are not met, that is the case where there exists the laminar region of thickness δ_1 at the interface resisting the turbulent eddies to reach the interface. The mentioned close agreement of numerical solutions of unsteady diffusion accompanied by the first order chemical reaction according to different mass transfer models makes it possible to replace Eq. (12) by corresponding solution according to Danckwerts model

$$G_1 = c_1 \sqrt{D(s + k)} \quad (22)$$

and to introduce the unknown concentration c_1 resulting from Eqs (22) and (7) into Eq. (15). The resulting final relation in variables of the Danckwerts plot has a form

$$(G_1 a)^2 / c_1^2 D = a^2 k [(tgh M + \sqrt{(1 + s/k)}) / (1 + \sqrt{(1 + s/k)} tgh M)]^2. \quad (23)$$

It follows from Eq. (23) that the linear course of Danckwerts parameters $(G_1 a)^2 / c_1^2 D$ versus k is linear only if $\delta_1 = M = 0$. Therefore the experimental data with a curved shape of the dependence in the Danckwerts plot should be checked for the existing laminar region resisting the turbulent eddies in reaching the interface. This effect is called "the surface rejuvenation" contrary to "the surface renewal" in case in which the turbulent eddies reach the interface.

If we compare Figs 8 and 9 (ref.⁶) for the same gas velocity and the clear liquid height on the sieve plate we can see that the experimental measurements expressed by the absorption rate per unit of foam volume X_F are in the Danckwerts plot separated according to the concentration of sodium hydroxide. The situation is similar in Figs 10 and 11 (ref.⁸) of the series *b* of the system with the catalyst. The conclusion can be thus made that during the experiment porosity of the foam changes. The application of theoretical conclusions on intensity of surface renewal s can elucidate the cause of separation of dependences in the Danckwerts plot. If we neglect the value

one in the denominator in Eq. (19) and substitute for s from Eq. (21) into Eq. (23) we obtain at the assumption $\delta_1 = 0$ the relation

$$(G_1 a)^2 / c_1^2 D = (4/\pi) [(1 - e) g u_g \mu_g / (e \rho_1 v_1^2)]^{1/2} a^2 + a^2 k. \quad (24)$$

From this equation results that the effects of physical properties of the system, porosity and gas velocity can be the reason of the considerable scatter and separation of individual dependences in the variables of the Danckwerts plot. This was perhaps also the case for large values k_1 in the series b (Table I) which does not correspond to the dependences of k_1 on the clear liquid height and the gas velocity in Figs 10 and 11 (ref.⁶) as given by the author.

LIST OF SYMBOLS

a	interfacial area per unit volume (m^{-1})
c	concentration (kmol m^{-3})
D	diffusivity ($\text{m}^2 \text{s}^{-1}$)
e	porosity of foam (—)
g	gravitational acceleration (ms^{-2})
G	flux of mass per unit of cross sectional area per unit of time ($\text{kmol m}^{-2} \text{s}^{-1}$)
h	clear liquid height on the plate (m)
k	reaction rate constant of the first order (s^{-1})
k_1	mass transfer coefficient without chemical reaction (ms^{-1})
M	defined by Eq. (6) (—)
N	defined by Eq. (13) (—)
s	intensity of surface renewal according to Danckwerts (s^{-1})
Sc	Schmidt number (—)
t	time (s)
u_g	gas velocity in the column (in free cross-sectional area) (ms^{-1})
x	distance from the interface (m)
$X_1 = (G_1 a_1)^2 / [(c_1 - c_r)^2 D]$	coordinate of the Danckwerts plot evaluated per unit of liquid volume on the plate ($\text{m}^{-2} \text{s}^{-1}$)
$X_F = (G_1 a_F)^2 / [(c_1 - c_r)^2 D]$	coordinate of the Danckwerts plot evaluated per unit of foam volume on the plate ($\text{m}^{-2} \text{s}^{-1}$)
δ_1	thickness of the laminar region (m)
$\bar{\epsilon}$	dissipation of energy per unit of time per unit of mass ($\text{m}^2 \text{s}^{-3}$)
λ_p	thickness of the transition region (m)
λ_t	length scale of turbulence (m)
μ	dynamic viscosity ($\text{kg m}^{-1} \text{s}^{-1}$)
ν	kinematic viscosity ($\text{m}^2 \text{s}^{-1}$)
ρ	density (kg m^{-3})

Subscripts

F	foam
g	gas
i	interface

l	liquid; laminar region
p	transition region
r	equilibrium
t	turbulent

REFERENCES

1. Danckwerts P. V.: *Reakce v soustavě plyn-kapalina*. Published by SNTL, Prague 1975.
2. Astarita G.: *Mass Transfer with Chemical Reaction*. Elsevier, New York 1967.
3. Kolář V.: This Journal 42, 1310 (1977).
4. Hatta S.: Technol. Repts. Tohoku Imp. University 10, 119 (1932).
5. Danckwerts P. V.: Trans. Faraday Soc. 46, 300 (1950).
6. Pohorecki R.: Chem. Eng. Sci. 31, 637 (1976).
7. Kolář V.: This Journal 35, 3678 (1970).
8. Pohorecki R.: Prace Naukowe Politechniki Warszawskiej, Chemia, No 5, 1970.

Translated by M. Rylek.