sulfur, and oxygen, the following three independent linear combinations are found:

$$\Delta N_{\mathrm{OC}} + \Delta N_{\mathrm{MC}} + \Delta N_{\mathrm{OCS}} + \Delta N_{\mathrm{MCS}} = 0 \qquad (18)$$

$$\Delta N_{\mathrm{acid}} + \Delta N_{\mathrm{OCS}} + \Delta N_{\mathrm{MCS}} = 0 \qquad (19)$$

$$\Delta N_{\mathrm{OC}} + \Delta N_{\mathrm{MC}} + 4\Delta N_{\mathrm{acid}} + 4\Delta N_{\mathrm{OCS}} + 4\Delta N_{\mathrm{MCS}} + \Delta N_{\mathrm{water}} = 0 \qquad (20)$$

The material balance over hydrogen is dependent of these three equations since the rank $R = 3$. However, since only the two reactions (16) and (17) occur, the following equations, which cannot be obtained from the material balances over the elements, must be satisfied

$$\Delta N_{\mathrm{OC}} + \Delta N_{\mathrm{OCS}} = 0 \qquad (21)$$

$$\Delta N_{\mathrm{MC}} + \Delta N_{\mathrm{MCS}} = 0 \qquad (22)$$

Thus there are two linear combinations in excess. However, only four of the Equations (18) to (22) are independent equations. Equation (22), for example, can be obtained by combining (18) and (21). Therefore, the number of independent linear combinations in excess, $NLCE = 1$. This means that Equation (15) gives the right number of independent reactions also in this case.

NOTATION

$\Delta N_{al}, \Delta N_{ac} \ldots \Delta N_{\mathrm{OC}}$ etc. = change in number of moles
$NLCE$ = the number of independent linear combinations of ΔN-values, which remain zero during reaction, in excess over those derived from material balances over the elements.
NRX = number of independent reactions
NSP = number of species
R = rank of the elements-by-species matrix
x_i = molar extent of the ith reaction

LITERATURE CITED

Amundson, N. R., *Mathematical Methods in Chemical Engineering*, pp. 50-54, Prentice-Hall, Englewood Cliffs, N. J. (1966).

Aris, R., "The Fundamental Arbitrariness in Stoichiometry," *Chem. Eng. Sci.*, **18**, 554 (1963).

Bulygin, M. G., E. A. Blyumberg, and L. A. Al'tschuler, "The Liquid-phase Oxidation of Propane," *Intern. Chem. Eng.*, **12**, 50 (1972).

Whitwell, J. C., and S. R. Dartt, "Independent Reactions in the Presence of Isomers," *AIChE J.*, **19**, 1114 (1973).

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Reply to Björnbom's Note

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The case described by Björnbom, where the number of independent reactions exceeds the difference between the numbers of species and the rank of the element-by-species matrix, contains kinetic constraints on ratio of product species. The equality

$$NRX = NSP - NC$$

should be replaced by

$$NRX \leq NSP - NC$$

as noted by Aris (1963).

In our original paper (1973) we did not consider compositional constraints in cases that did not involve isomeric species. These constraints can, however, easily be added to the program by defining a new variable (for example, CONSTR), which takes on integer values equal in number to the constraints of the type described by Björnbom. This variable would be subtracted from Equation (3) in our original paper.

We wish to thank Dr. Björnbom for bringing this interesting case to our attention.

LITERATURE CITED

Aris, R. B., and R. H. S. Mah, "Independence of Chemical Reactions," *Ind. Eng. Chem. Fundamentals*, **2**, 90 (1963).

Mass Transfer to the Free Interface in a Stirred Vessel

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A turbulent, free interface occurs at the liquid surface with liquid and gas phases in a mechanically stirred vessel. At low stirring speeds in baffled vessels, the interface is not broken by gas entrapment and the turbulence at the interface appears to correspond to the turbulence in the stream generated by the impeller. This note presents an analysis of the mechanism of liquid phase mass transport at this free interface by comparison of the impeller stream turbulence to that for turbulent flow in a circular pipe.

PIPE FLOW

Transition region turbulence in pipe flow appears similar to that for a free interface because both show a penetration model response. Hughmark (1973) has shown that the

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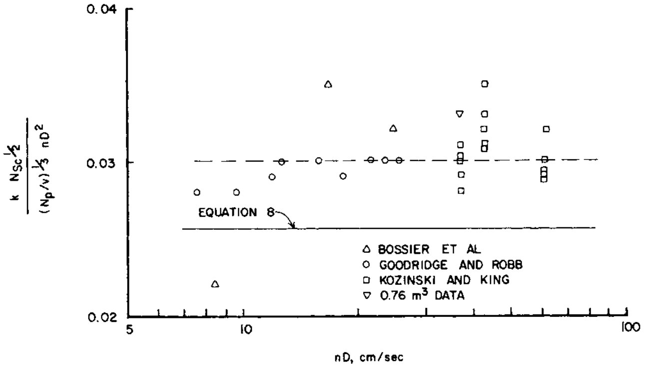

Fig. 1. Mass transfer data.

penetration model applies to the transition region of pipe flow with a contact time corresponding to the mean period of fluctuations in the wall region. This is represented by

$$\frac{u^{*2}t}{\nu} = 338 \qquad (1)$$

The fluctuating velocity in the transition region is related to the shear velocity by

$$u_i = 0.8\ u^* \qquad (2)$$

So the contact time can be expressed in terms of the fluctuating velocity

$$t = 218\ \nu/u_i^2 \qquad (3)$$

IMPELLER STREAM MASS TRANSFER

Equation (3) can then be applied to the impeller stream of a stirred vessel. Levins and Glastonbury (1972) report fluctuating velocity data for baffled, stirred vessels which indicate

$$u_i = (\epsilon D)^{1/3}/3 \qquad (4)$$

Thus combination of Equations (3) and (4) provides an estimate of the mean contact time for the impeller stream.

$$t = 1962\ \nu/(\epsilon D)^{2/3} \qquad (5)$$

The penetration model provides the mass transfer coefficient:

$$k = 2\sqrt{\frac{\mathfrak{D}}{\pi t}} \qquad (6)$$

Substitution of Equation (5) yields

$$k = 0.0256\ (\epsilon \mathfrak{D})^{1/3}\ N_{Sc}^{-1/2} \qquad (7)$$

Average energy dissipation for a stirred vessel is

$$\epsilon = \frac{N_p\ n^3\ D^5}{v}$$

Substitution in Equation (7) then provides

$$k = 0.0256\ \frac{N_p^{1/3}\ n\ D^2}{v^{1/3}}\ N_{Sc}^{-1/2} \qquad (8)$$

EXPERIMENTAL DATA

Experimental mass transfer data for an unbroken interface in a stirred vessel are reported by Goodridge and Robb (1965) for CO_2 absorption in water; Kozinski and King (1966) for helium, hydrogen, oxygen, argon, and carbon dioxide desorption from water; and Bossier et al. (1973) for two organic systems with the Schmidt number range of 150 to 690. The Goodridge and Robb and Bossier et al. data were obtained with six-bladed impellers and the Kozinski and King data with a four-bladed impeller. The impeller diameters were from 4 to 6.35 cm and were all about one-half the tank diameter. A 0.76 m³ (200 gal.) vessel of 100-cm diameter with a 50-cm diameter, six-bladed impeller was used to obtain surface mass transfer with a large impeller. Water was degassed under reduced pressure followed by air absorption at 21.5°C and 43 rev./min. to provide mass transfer corresponding to $k = 0.057$ cm/sec. Figure 1 shows the experimental data in the form indicated by Equation (8) with a power number of 4. The data are shown as a function of impeller tip speed and the data indicate a coefficient of 0.030 for Equation (8) rather than the value derived from the pipe flow-impeller stream analogy with the assumption of equal energy dissipation in the liquid phase of a stirred vessel. The coefficient of 0.030 corresponds to an energy dissipation for the impeller stream at the surface 60% greater than the average value for the vessel. Cutter (1966) reports that the energy dissipation in the impeller plane at the vessel wall is about three times the average value for the vessel. The indicated surface value is consistent with this observation since the free surface of the liquid can be thought of as a containing wall deflecting the flow of the impeller stream. Thus the experimental data indicate that the pipe flow-impeller stream analogy for surface turbulence is valid.

NOTATION

D = impeller diameter
$\mathfrak{D}$ = molecular diffusivity
g = acceleration due to gravity
k = mass transfer coefficient
N_p = power number, $Pg/n^3D^5\rho$
N_{Sc} = Schmidt number
n = impeller speed
P = power input
t = contact time
u^* = friction velocity
u_i = fluctuating velocity
v = vessel liquid volume

Greek Letters

ϵ = energy dissipation
ν = kinematic viscosity
ρ = density

LITERATURE CITED

Bossier, J. A., R. E. Farritor, G. A. Hughmark, and J. T. F. Kao, "Gas-Liquid Interfacial Area Determination for a Turbine Agitated Reactor," *AIChE J.*, **19**, 1065 (1973).

Cutter, L. A., "Flow and Turbulence in a Stirred Tank," *ibid.*, **12**, 35 (1966).

Goodridge, F., and I. D. Robb, "Mechanism of Interfacial Resistance in Gas Absorption," *Ind. Eng. Chem. Fundamentals*, **4**, 49 (1965).

Hughmark, G. A., "Additional Notes on Transfer in Turbulent Pipe Flow," *AIChE J.*, **19**, 1054 (1973).

Kozinski, A. A., and C. J. King, "The Influence of Diffusivity on Liquid Phase Mass Transfer to the Free Interface in a Stirred Vessel," *ibid.*, **12**, 109 (1966).

Levins, D. M., and J. R. Glastonbury, "Particle-Liquid Hydrodynamics and Mass Transfer in a Stirred Vessel. Part I—Particle-Liquid Motion." *Trans. Inst. Chem. Engrs.*, **50**, 32 (1972).

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