LETTERS TO THE EDITOR

TO THE EDITOR

In a recent paper Whitwell and Dartt (1973) present a method of calculating the number of "independent reactions in the presence of isomers." I now wish to show that the relations derived by these authors represent an unnecessary complication of a problem which was solved long ago and that, in some cases, they even lead to erroneous results. There exists no system of reactions for which the equation presented by Aris (1963) is invalid. Aris gives

$$R \leq S - (N - P) \qquad (1)$$

where S is the number of distinguishable chemical species, N the number of atomic species, $N - P$ is the rank of the "element-by-species-matrix," and R is the number of reactions needed to describe the system completely. This equation corresponds to Equation (1) in the paper of Whitwell and Dartt

$$NRX = NSP - NC. \qquad (2)$$

Aris, however, gives an upper limit to the number of reactions: in Equation (1), $\leq$ (less than) must be used if one or several independent reactions (for example, isomerizations) are chemically impossible. This is a question of kinetics rather than one of stoichiometry.

The term *distinguishable chemical species* used by Aris includes isomers because they are distinguishable by their physical and chemical properties. The usefulness of the distinction made by Whitwell and Dartt between the basic number of species (number of different empirical formulae) and the overall number of species (including isomers) is by no means evident. If this distinction is really desired, the calculation of the latter from the former is simple and there is no need for the definition of 3 different cases.

As to the number of reactions, Equation (1) will give in every case a correct result for the upper limit. Of course for the rank of the element-by-species-matrix it does not matter whether it is defined as a $N \times S$- or $N \times BNSP$-matrix. It may be of interest to know the difference between the actual R and its upper limit if isomerization is forbidden. If there are n independent isomers of the same compound, the number of independent isomerization reactions will be $n - 1$ (compare case c of Whitwell and Dartt). The same number ($n - 1$) results for case b, where two groups with different empirical formulae, each containing n isomers are related by n independent reactions. However, in this latter case Equation (3) of Whitwell and Dartt yields erroneous results for the upper limit, that is, if isomerization is allowed (compare example 6 discussed below). With $NC = 3$, $BNSP = 4$, $ISOMR = 2$, $TYPES = n$, $XCHNG = n$, Equation (3) yields

$NRX = 1 + n - 1 + n\,(n - 1) = n^2$.

For $n \geq 2$ this value is too large when compared with the correct result, obtained from Equation (1) with $S = 2n + 2$, $N - P = 3$;

$$R = 2n + 2 - 3 = 2n - 1,$$

where n equations are needed for reactions of the isomers of the first group to those of the second and $n - 1$ for isomerizations within one group. Application of Equation (1) to the seven examples presented by Whitwell and Dartt gives correct results in all cases:

Example 1:
$S = 4, N - P = 2, R \leq 2$;
$R = 2$, all independent reactions are allowed; the isomerization is a linear combination of the two formation reactions.

Example 2:
$S = 5, N - P = 2, R \leq 3$;
$R = 3$, see example 1.

Example 3:
$S = 6, N - P = 3, R \leq 3$;
$R = 2$, no isomerization between OC and MC (or OCS and MCS).

Example 4:
$S = 12, N - P = 4, R \leq 8$;
$R = 6$, the two isomerizations between the $n = 3$ isomers are forbidden.

Example 5:
$S = 10, N - P = 4, R \leq 6$;
$R = 5$, the isomerization between the $n = 2$ isomers is forbidden.

Example 6:
$S = 10, N - P = 4, R \leq 6$;
$R = 6$, isomerization between the $n = 2$ isomers is allowed.

As a consequence of the term $(XCHNG) \neq (TYPES - 1)$, the result of Whitwell and Dartt ($R = 7$) is incorrect. One possibility for the matrix of the stoichiometric coefficients for six independent reactions is the following:

$$\begin{array}{cccccc}
H_2SO_4 & H_2O & IB & OC & MC & (IB)_x \\
-1 & 1 & & -1 & & \\
-1 & 1 & & & -1 & \\
 & & -1 & -1 & & \\
 & & -1 & & -1 & \\
 & & & -1 & 1 & \\
 & & -x & & & 1
\end{array}$$

$$\begin{array}{cccc}
OCS & MCS & OCB & MCB \\
1 & & & \\
 & 1 & & \\
 & & 1 & \\
 & & & 1
\end{array}$$

all other reactions in this system are linear combinations of the above six.

Example 7:
$S = 4, N - P = 2, R \leq 2$;
$R = 1$, the isomerization between glucose and fructose is impossible.

Other than consideration of the number of independent isomerization reactions within a single group of isomers, no further alteration to Aris' Equation (1) is needed. The fact that Whitwell and Dartt derive their equations empirically rather than by the rules of linear algebra leads to erroneous results.

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

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TO THE EDITOR

We are indebted to Dr. Schubert for noting an error in Example 6 of the Whitwell-Dartt (1973) paper. The error is due to improper logic in defining of the variable *XCHNG*. This variable can take on only two integer values, zero and unity. If there are no compositional constraints, the value is unity to allow for the material balance equations, in number equal to (*TYPES-1*), which account for the total changes in isomeric ratios. If the kinetic constraints allow no variation in isomeric ratios, the value of *XCHNG* is zero.

This correction has been incorporated into the documentation of the program (No. 02250, National Auxiliary Publications (NAPS), c/o Microfiche Publications, 305 East 46th Street, New York, N. Y. 10017). An additional logical-IF statement (Fortran IV) will also be added to test the number of independent reactions *NRX* against the difference between the number of species *NSP* and the rank of the element-by-matrix *NC*. If *NRX* exceeds this difference, as was the case in Example 6, the program will terminate, and a warning will be printed indicating that the user has an error in input data. Users who already have copies of the program may obtain the necessary corrections by writing the undersigned.

LITERATURE CITED

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

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TO THE EDITOR

A recent paper by Miller (1974) describes an empirical factor k_L^* [Equation (27)] which the author concludes can be used to correct values of the liquid-phase mass transfer coefficient k_L computed from penetration theory type models for the effect of varying bubble average diameter D_{BM} in stirred-tank gas-liquid dispersions. The results indicate that k_L in such contactors is rather strongly dependent upon D_{BM}. The author claims that the application of this correction factor will improve scale-up procedures.

Although the conclusion that k_L is dependent upon bubble diameter is directionally in agreement with some aspects of some previous works (Robinson and Wilke, 1974; Calderbank and Moo-Young, 1961), in our opinion the reported values of k_L^* (Figure 6) may be subject to several sources of error arising from assumptions made by Miller. He computed $k_{L\text{exp}}$ by combining measured values of k_La with values of the specific area a computed from previous correlations obtained in systems of different geometry and/or geometric ratios. Miller's stirred tanks were each equipped with a paddle impeller having four flat blades. Mechanical power input P_m in the sparged systems used by the author was calculated using the correlation [Equation (17)] of Michel and Miller (1962) which was obtained using 6-blade turbine impellers; these authors state that "the value of the coefficient probably depends importantly on the geometry of the impeller" and, hence, its applicability to Miller's system seems questionable. Miller's estimated values of P_m were then used with Equations (13) and (15) from which he obtained his values of D_{BM} and a (and, hence, $k_{L\text{exp}}$ and k_L^*), respectively. However, these equations are modified versions of the correlations of Calderbank (1958) which were also obtained using 6-blade turbines in tanks with geometric ratios different from the author's vessels.

In addition, two empirical correction terms—C_1 (power input correction) and C_2 (surface aeration correction)—obtained by trial and error data fitting are implicitly included in Equations (13) and (15); apparently, the validity of neither of these factors was checked by independent experimental methods. The author's conclusion about the effect of tank size on the C_2 factor is contrary to the results of Calderbank (1958).

Since reliable correlations are lacking for the prediction of k_L in all the types of bubble size regimes commonly found in stirred-tank gas dispersions, it seems unfortunate that the author relied on correlations of undemonstrated applicability to his system to determine a number of the key parameters involved. Experimental measurement of D_{BM} to confirm the validity of the computed results (and from which, in conjunction with measured gas holdup, the interfacial area could be evaluated) would have been most useful. The relationship between k_L and D_{BM} in various systems appears to be not yet completely resolved.

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Robinson, C. W., and C. R. Wilke, "Simultaneous Measurement of Interfacial Area and Mass Transfer Coefficients for a Well-Mixed Gas Dispersion in Aqueous Electrolyte Solutions," *ibid.*, 285.

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TO THE EDITOR: COMMENTS ON THE LETTER FROM HASSAN AND ROBINSON

It is true that the correlations of Michel and Miller and Calderbank [Equations (17) and (13) to (15) in the paper by Miller] were obtained with *six*- rather than four-blade impellers. The geometric coincidence of the vessels is also not exact in every detail. These particular correlations were used as part of the network of relationships characterizing scale-up, however, because they are the closest and most broadly based, for their respective purposes, of any available in the literature. The complete scale-up analysis is fitted directly, of course, to experimental data on aeration and mass transfer. The information extracted on D_{BM}, a and k_L is therefore consistent, representative, and reliable within reasonable bounds of experimental accuracy.

Surface aeration in sparged, agitated systems becomes less and less a significant contributor to overall aeration with increased tank size. For tanks above 100 gal. in size, for all practical purposes, it ceases to be important. Calderbank's original work on aeration was done in 5- to 25-gal. vessels and his correlation does not recognize this important scale-up consideration. Hence, the need for the improved correlation including the C_2 correction for surface aeration in small vessels.

The correspondents have missed an important point in their commentary. This work was undertaken to identify the appropriate scale-up criteria for gas-liquid mass transfer. It is through recognition and understanding of these criteria that improvement in scale-up procedures can be achieved. The k_L^* factor, although it can indeed be quantitatively helpful in scale-up, is only part of the overall development.

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