LETTERS TO THE EDITOR

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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 $n \geqq 2$ 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:

H_2SO_4	H_2O	IB	OC	MC	$(IB)_x$	OCS	MCS	OCB	MCB
−1	1		−1			1			
−1	1			−1			1		
		−1	−1					1	
		−1		−1					1
			−1	1					
		−x			1				

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.

LITERATURE CITED

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

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

ECKART SCHUBERT
INST. TECHNISCHE CHEMIE I
DER UNIVERSITÄT ERLANGEN-NÜRNBERG
ERLANGEN, W. GERMANY

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