Mass Transfer from a Single Sphere in Stokes' Flow with a Homogeneous Chemical Reaction

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Many investigators have studied the classical problem of mass or heat transfer for creeping flow past a single solid sphere. It is the intent of this theoretical investigation to continue the study of transfer from spheres and to develop an expression for the Sherwood number for mass transfer with an irreversible, first-order, homogeneous chemical reaction taking place in the flowing medium. The analysis gives mass transfer results in a reactive system at low Reynolds numbers for which experimental investigations are made difficult by the disturbing effects of natural convection. Although the results are for Reynolds numbers lower than generally found in industrial chemical reactors, the mathematical technique employed in this study may be advanced to incorporate an expression for the velocity field which is consistent with higher Reynolds numbers. Also, this study of single spheres may provide a basis for the study of reaction accompanied mass transfer in assemblages of particles such as suspensions or packed beds by including the "free surface model" considered by Pfeffer and Happel (*1*).

Solutions to the related mass transfer problem without chemical reaction have been obtained with some success by perturbation techniques such as those employed by Kronig and Bruijsten (*2*), by Acrivos and Taylor (*3*), and by Yuge (*4*). A singular perturbation technique with "inner" and "outer" expansions similar to that employed by Acrivos and Taylor was used by Hartunian and Liu (*5*) to obtain a solution for mass transfer from a single sphere with a heterogeneous first-order reaction on the surface of the sphere. Recently, Johnson and Akehata (*6*) solved the problem with a first-order, homogeneous chemical reaction by numerical evaluation of finite-difference methods and by an extension of Yuge's method to include the homogeneous chemical reaction.

OUTLINE OF METHOD

The mathematical technique employed for the solution of the problem considered in this analytical work is based on the technique developed by Kronig and Bruijsten (*2*) to solve the related problem without a chemical reaction. These investigators, after having demonstrated the failure of a straightforward perturbation technique, reasoned that a point of source of mass (or heat) might serve as an adequate representation of a spherical source at large distances from the source. Thus following their established procedure, we solved exactly the concentration profile for the case of streaming flow past a point source of mass with which the fluid undergoes a first-order, homogeneous reaction. This result was used to formulate an expression for the concentration profile around a solid sphere.

The assumed expression for the concentration profile included an unknown function to be subsequently determined to account for the difference between a point source of mass and a solid sphere. The basis for the perturbation technique was established by assuming the unknown function to be expressible in terms of a power series in the Peclet number. Substitution of this series expression for the concentration profile into the basic differential equation and combination of terms of similar power in the Peclet number resulted in a set of partial differential equations, each containing a successively higher order term of the unknown function which defined the concentration profile. These equations were solved to the second order to obtain an expression for the average Sherwood number for mass transport from the sphere.

THEORETICAL DEVELOPMENT

The case of mass transfer from a single solid sphere to a slowly flowing stream in the Stokesian flow regime, in which the removed material undergoes an irreversible, first-order, homogeneous chemical reaction, is considered. It is presumed for this development that steady state has been reached and physical properties are constant. Also, the concentration of the dissolving species comprising the solid spherical particle is small and the presence of the reaction product does not interfere with the diffusion of the dissolving species through the flowing medium. The basic equation for mass transfer with a first-order chemical reaction can be written in dimensionless form as

$$\nabla^2 c - \epsilon \mathbf{v} \cdot \nabla c - \beta^2 c = 0 \tag{1}$$

with boundary conditions.

$$\begin{aligned} c &= 1 \quad \text{at} \quad r = 1 \\ c &= 0 \quad \text{when} \quad r = \infty \end{aligned} \tag{2}$$

The well-known velocity field of Stokes may be used as an adequate representation of the velocity near the sphere (which is the important region for mass transport) for the low values of the Reynolds number ($N_{Re} < 1$) considered in this study. The components in the r and θ directions in this regime are

$$\begin{aligned} v_r &= \left(1 - \frac{3}{2r} + \frac{1}{2r^3}\right) \cos\theta \\ v_\theta &= -\left(1 - \frac{3}{4r} - \frac{1}{4r^3}\right) \sin\theta \end{aligned} \tag{3}$$

Following the procedure established by Kronig and Bruijsten, we first obtained an expression for the concentration profile for a point source of mass. This expression is analytically obtained by solving the basic equation, Equation (1), with the velocity field taken to be parallel (stream flowing). The concentration profile for this case is found to be

$$c = \frac{k}{r} \exp\left[-\frac{\epsilon r}{2}(\gamma - \mu)\right] \tag{4}$$

With the form of the point source solution in Equation (4), the following expression suggests itself for the concentration profile with a spherical source of mass

$$c = \kappa(r, \mu) \exp\left[-\frac{\epsilon r}{2}(\gamma - \mu)\right] \tag{5}$$

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where $\kappa(r, \mu)$ is a new dependent variable, which can be expressed in series form as

$$\kappa = \kappa_0 + \kappa_1\epsilon + \kappa_2\epsilon^2 + \ldots \tag{6}$$

Also the variable γ is expanded in series form to give

$$\gamma = \left(1 + \frac{4\beta^2}{\epsilon^2} \right)^{1/2}$$

$$= \frac{2\beta}{\epsilon} \left(1 + \frac{1}{2^3\beta^2}\epsilon^2 - \frac{1}{2^7\beta^4}\epsilon^4 + \ldots \right)$$

$$\left[\frac{\epsilon^2}{4\beta^2} < 1 \right] \tag{7}$$

The use of the above series expansion for γ limits all the results to cases for which $\epsilon^2/4\beta^2 < 1$ or its equivalent $N_{Pe}/\beta < 4.0$. Substituting Equations (6) and (7) into Equation (5), and expanding the exponential term in powers of ϵ, we developed the following form for the concentration profile up to the second-order approximation in ϵ

$$c = \exp(-\beta r) \left\{ \kappa_0 + \left(\frac{\mu r}{2}\kappa_0 + \kappa_1 \right)\epsilon + \left[\frac{1}{8}\left(r^2\mu^2 - \frac{r}{\beta} \right)\kappa_0 + \frac{r\mu}{2}\kappa_1 + \kappa_2 \right]\epsilon^2 + \ldots \right\} \tag{8}$$

The problem equations are obtained by substituting the velocity components, Equations (3); the assumed expression for the concentration profile, Equation (5); and the series expansions for the variables κ and γ, Equations (6) and (7), into the basic equation for reaction accompanied mass transfer, Equation (1), to obtain

Zeroth order in ϵ

$$(\nabla^2 + F)\kappa_0 = 0$$

First order in ϵ

$$(\nabla^2 + F)\kappa_1 + G\,\kappa_0 = 0 \tag{9}$$

Second order in ϵ

$$(\nabla^2 + F)\kappa_2 + G\,\kappa_1 + H\,\kappa_0 = 0$$

n^{th} order in ϵ

$$(\nabla^2 + F)\kappa_n + G\,\kappa_{n-1} + H\,\kappa_{n-2} = 0$$

In terms of the dependent variable κ, boundary conditions (2) become

$$\left.\begin{aligned} \kappa_0(1,\mu) &= \exp(\beta)\,P_0(\mu) \\ \kappa_1(1,\mu) &= \frac{1}{2}\exp(\beta)\,P_1(\mu) \\ \kappa_2(1,\mu) &= \frac{1}{8}\exp(\beta)\left[\frac{\beta+3}{3\beta} + P_2(\mu) \right] \end{aligned}\right\} \text{ for } r = 1 \tag{10}$$

where P_i are Legendre polynomials

and

$$\kappa_0(\infty,\mu) = \kappa_1(\infty,\mu) = \kappa_2(\infty,\mu) = \kappa_n(\infty,\mu) = 0$$
$$\text{for } r = \infty$$

The problem equations, Equations (9) and boundary conditions, Equations (10), are fulfilled by

$$\kappa_0 = \frac{1}{r}\exp(\beta)$$

$$\kappa_1 = \mu\left[\left\{ \frac{3}{4\beta}\left(\frac{1-\beta}{1+\beta} \right)\exp(\beta)\,[1 + \exp(2\beta)] \right.\right.$$

$$\left. + \frac{3}{8(1+\beta)}\exp(\beta) \right\} \frac{1+\beta r}{r^2}$$

$$+ \frac{3}{4\beta}\exp[\beta(1+2r)]\,E_1(2\beta r)$$

$$- \frac{3}{4\beta}\left(\frac{1+\beta r}{r^2} \right)\exp(\beta)\ln(r)$$

$$\left. - \exp(\beta)\left(\frac{3}{4\beta}\frac{1}{r^2} + \frac{1}{8r^3} \right) \right] \tag{11}$$

where

$$E_1(x) = \int_x^\infty e^{-u}\,u^{-1}\,du$$

$$\kappa_2 = W(r)\,P_2(\mu) + \frac{\exp(\beta)}{8r}\left(\frac{\beta+3}{3\beta} \right)$$

$$+ \frac{\exp(2\beta)}{2\beta r}\int_1^\infty s\,h(s)\exp(-2\beta s)\,ds$$

$$- \frac{\exp(2\beta r)}{2\beta r}\int_r^\infty s\,h(s)\exp(-2\beta s)\,ds$$

$$- \frac{1}{2\beta r}\int_1^r s\,h(s)\,ds$$

where

$$h(s) = \frac{\exp}{8\beta}[\beta(1+2s)]\,E_1(2\beta s)\left[\frac{-3\beta^2}{s^2} \right.$$

$$\left. + \frac{3\beta}{s^3} + \frac{(\beta^2-3)}{s^4} - \frac{3\beta}{s^5} - \frac{3}{s^6} \right]$$

$$+ \left\{ \frac{\exp}{8\beta}\left[\exp(2\beta)\left(\frac{1-\beta}{1+\beta} \right)E_1(2\beta) \right.\right.$$

$$\left.\left. - \ln(s) \right] \right\} \left[\frac{3\beta^2}{s^2} + \frac{3\beta}{s^3} + \frac{(3-\beta^2)}{s^4} \right.$$

$$\left. - \frac{3\beta}{s^5} - \frac{3}{s^6} \right] + \frac{\exp(\beta)}{1+\beta}\left[\left(\frac{-3\beta^2}{16} \right.\right.$$

$$\left. - \frac{\beta}{8} - \frac{1}{2} \right)\frac{1}{s^2} + \left(\frac{3\beta}{16} + \frac{3}{4} \right)\frac{1}{s^3}$$

$$+ \left(\frac{-3\beta}{16} - \frac{9}{16} \right)\frac{1}{s^4} + \left(\frac{-\beta}{16} - \frac{5}{8} \right)\frac{1}{s^5}$$

$$\left. + \left(\frac{\beta^2}{48} + \frac{\beta}{48} + \frac{9}{16} \right)\frac{1}{s^6} + \left(\frac{\beta}{12} + \frac{1}{12} \right)\frac{1}{s^7} \right]$$

thus determining the expression for the concentration profile, Equation (8), completely to the first-order approximation and only partially to the second order. The term $W(r)$, which would complete the second-order approximation of the concentration profile, was not determined due to the excessive amount of calculation required. The term $W(r)$ does not, however, contribute to the second-order approximation of the Sherwood number due to the orthogonality relation of the Legendre polynomials. Thus the incomplete expression for κ_2 does permit the determination of the average Sherwood number complete to the second-order approximation.

The Sherwood number averaged over the surface of the spherical particle is expressed as

$$N_{Sh} = -\int_{-1}^{1} \left.\frac{\partial c}{\partial r}\right|_{r=1} du \tag{12}$$

Making use of the expression developed for the concentration profile in Equation (12), we find the final expression for the average Sherwood number to the second-order approximation to be

$$N_{Sh} = 2 + 2\beta + j\epsilon^2 + 0(\epsilon^3) \tag{13}$$

where

$$\begin{aligned} j = {} & \frac{1}{4(1+\beta)} \left[\frac{5\beta}{12} + \frac{7}{24} + \frac{1}{4\beta} - \frac{1}{2}\beta^2 \exp(2\beta)\, E_1(2\beta) \right] \\ & + \frac{1}{16}\exp(2\beta) \int_1^\infty \left\{ E_1(2\beta r) \left[\frac{-3\beta^2}{r} + \frac{3\beta}{r^2} + \frac{(\beta^2-3)}{r^3} - \frac{3\beta}{r^4} + \frac{3}{r^5} \right] + \exp(-2\beta r) \right. \\ & \left[\exp(2\beta) \left(\frac{\beta-1}{\beta+1}\right) E_1(2\beta) + \ln(r) \right] \left(\frac{-3\beta^2}{r} - \frac{3\beta}{r^2} + \frac{(\beta^2-3)}{r^3} + \frac{3\beta}{r^4} + \frac{3}{r^5} \right) \\ & + \exp(-2\beta r) \frac{\beta}{1+\beta} \left[\left(\frac{-3\beta^2}{2} - \beta - 4 \right) \frac{1}{r} + \left(\frac{3\beta}{2} + 6 \right) \frac{1}{r^2} - \left(\frac{3\beta}{2} + \frac{9}{2} \right) \frac{1}{r^3} - \left(\frac{\beta}{2} + 5 \right) \frac{1}{r^4} \right. \\ & \left. \left. + \left(\frac{\beta^2}{6} + \frac{\beta}{6} + \frac{9}{2} \right) \frac{1}{r^5} + \left(\frac{2\beta}{3} + \frac{2}{3} \right) \frac{1}{r^6} \right] \right\} dr \end{aligned}$$

It should be recalled that the above expression is subject to the restriction $N_{Pe}/\beta < 4$. A computer program was written to evaluate the average Sherwood number, since the integral in Equation (13) cannot be integrated analytically.

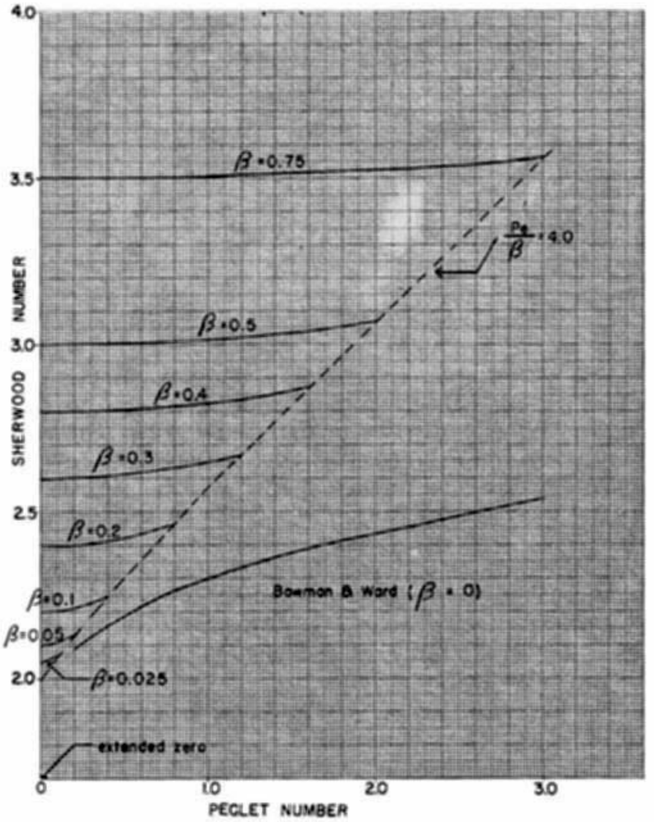

Fig. 1. Average Sherwood number as a function of the Peclet number with β as a parameter ($\beta < 1$).

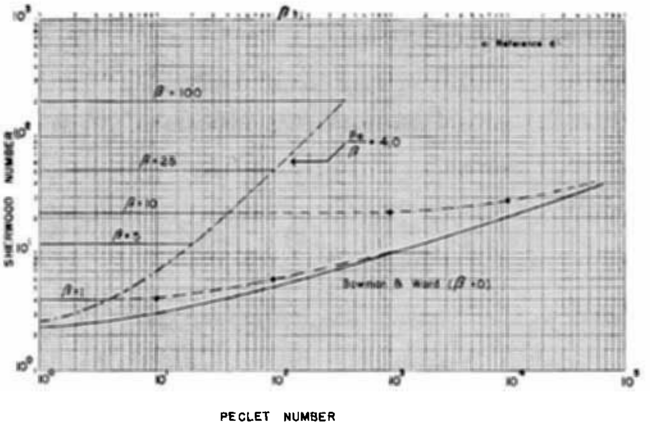

Fig. 2. Average Sherwood number as a function of the Peclet number with β as a parameter ($\beta \geqq 1$).

RESULTS

The average Sherwood number as expressed by Equation (13) was evaluated numerically with a computer program written in FORTRAN-63 for the CDC-1604A computer. The average Sherwood number was obtained for a range of Peclet numbers for several values of the dimensionless group β, which accounts for the mass transfer effects of the chemical reaction. The inequality which arises in the development, that is, $N_{Pe}/\beta < 4$, limited the range of the Peclet number considered for each value of the parameter β.

The calculated values of the average Sherwood number are presented graphically in Figures 1 and 2. For $\beta > 1$ the average Sherwood number is essentially independent of Peclet number, over the range of Peclet number considered. The results of the analysis of Bowman and Ward (7) are also presented for comparison with the present results. Their results correspond to the extreme case of $\beta = 0$, or no chemical reaction.

A curve of the second-order approximation j, which appears in Equation (13), is presented in Figure 3 to facilitate the calculation of the average Sherwood number from this equation. A more complete listing of the results obtained appears in reference *8*.

DISCUSSION

The average Sherwood number for a reactive and nonreactive case differs most for zero Peclet number. With increasing Peclet number for constant β, the mass transfer from convective effects soon predominates and the average Sherwood number approaches that for the case of no chemical reaction. The inequality which arises in the mathematical development restricts the range of validity of the results to $N_{Pe}/\beta < 4$. Thus the mathematical technique employed in this analysis is useful where reactive effects predominate.

Numerical results of this analysis indicate that for $N_{Pe}/\beta < 1$, the expression for the average Sherwood number, Equation (13), reduces effectively to

$$N_{Sh} = 2 + 2\beta \tag{14}$$

This simple expression for the average Sherwood number is the complete solution for the case in which there is no convection, and should therefore apply at least to a good approximation when reactive effects predominate.

A recent paper published by Johnson and Akehata (*6*) after the completion of this work also considered the same problem. By an extension of the theoretical analysis de-

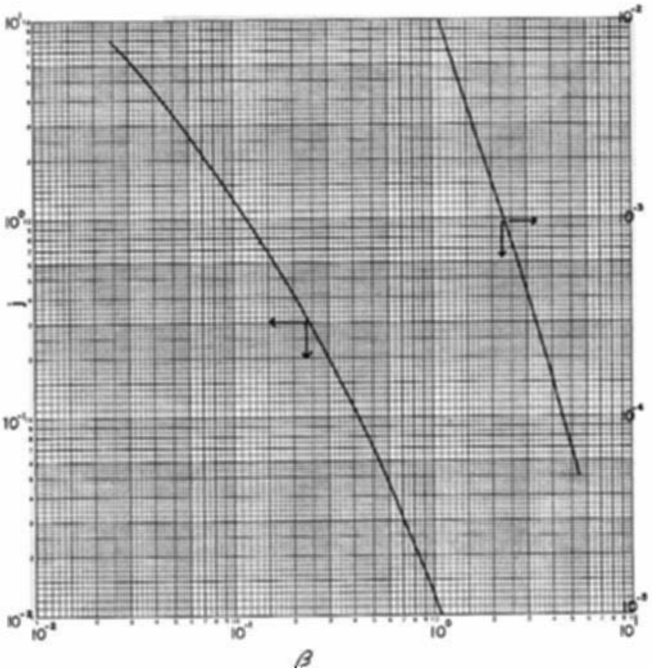

Fig. 3. Second-order approximation term j in Equation (13).

veloped by Yuge (*4*), the authors were able to determine the relationship between the Sherwood and Peclet numbers numerically over a range of Peclet numbers between 1 and 10^4. They also solved Equation (1) directly with a relaxation procedure; however, results could only be obtained in the low Peclet number range because of instability difficulties. A comparison of the results of this work with those of Johnson and Akehata show very close agreement even at $N_{Pe}/\beta = 10$ ($N_{Pe} = 10$ and $\beta = 1$) which is outside of the range of validity of the present analysis. For $N_{Pe}/\beta^2 > 10^3$ the average Sherwood number for the nonreactive case can be used as a good approximation. This is shown in Figure 2 based on the Sherwood numbers computed by Johnson and Akehata at high Peclet numbers for $\beta = 1$ and $\beta = 10$.

CONCLUSIONS

The perturbation technique developed by Kronig and Bruijsten was found to be useful for determining the relation between the Sherwood number and Peclet number for the case of mass transfer from a solid sphere in creeping flow. The resulting expression for the average Sherwood number, Equation (13), however, is restricted by the inequality $N_{Pe}/\beta < 4$.

For $N_{Pe}/\beta < 1$ the average Sherwood number is essentially independent of the Peclet number and is adequately expressed by the solution for chemical reaction with no convection, that is

$$N_{Sh} = 2 + 2\beta \tag{14}$$

For $N_{Pe}/\beta > 1$, the mass transfer from convective effects becomes significant and the average Sherwood number for $N_{Pe}/\beta < 4$ is determined from the complete expression for the average Sherwood number, Equation (13). The average Sherwood number for $N_{Pe}/\beta > 4$ (not determined in the analysis) can be approximated, since the Sherwood number with chemical reaction for a given value of the dimensionless group β continuously approaches that for the case of no reaction with increasing values of the Peclet number. For a given value of β, the curve for the average Sherwood number is approximated by extending the curve from the known value at $N_{Pe}/\beta = 4$ such that it continuously approaches the curve for the average Sherwood number with no reaction ($\beta = 0$) and merges with this curve when the ratio N_{Pe}/β^2 is about 10^3.

The mathematical technique developed here could be extended for flow at higher Reynolds numbers by using a suitable velocity profile and to multiparticle systems by employing a unit cell model as described in reference *1*.

ACKNOWLEDGMENT

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NOTATION

a = radius of spherical particle
c = dimensionless concentration of dissolving reactive species comprising spherical particle relative to concentration at surface of sphere
D = binary diffusivity

$$F = -2\beta\left(\frac{\partial}{\partial r} + \frac{1}{r}\right)$$

$$G = \left(\frac{3}{2r} - \frac{1}{2r^3}\right)\mu\frac{\partial}{\partial r} + \left(\frac{3}{4r^2} + \frac{1}{4r^4}\right)(1-\mu^2)\frac{\partial}{\partial \mu} + 2\beta\mu\left(-\frac{3}{4r} + \frac{1}{4r^3}\right)$$

$$H = -\frac{1}{4\beta}\left(\frac{\partial}{\partial r} + \frac{1}{r}\right) + \frac{3}{8}r + \frac{1}{8r^3} + \mu^2\left(\frac{3}{8r} - \frac{3}{8r^3}\right)$$

h = function defined in Equation (11)
j = second-order approximation in Sherwood number, Equation (13)
k = constant dependent on source strength
k''' = first-order chemical rate constant
N_{Pe} = Peclet number
N_{Re} = Reynolds number
N_{Sh} = Sherwood number
r = dimensionless radial distance relative to radius of sphere
U_∞ = velocity of free stream
$\mathbf{v}$ = dimensionless velocity vector relative to free stream velocity
W = function in Equation (11)

Greek Letters

β^2 = $k''' a^2/D$, dimensionless
γ = $(1 + 4\beta^2/\epsilon^2)^{1/2}$, dimensionless
ϵ = ½ Peclet number = $U_\infty a/D$, dimensionless
θ = angle made with polar axis, dimensionless
κ = auxiliary variable used in Equation (5), dimensionless
μ = $\cos\theta$, dimensionless

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A New Gas-Gas Equilibria Prediction Method

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The phenomenon of gas-gas equilibrium—limited mutual solubility of gases at temperatures above the critical point of the least volatile component—was predicted by van der Waals (*1*) in 1894 on the basis of fold theory, but was not observed experimentally until 1940, when Krichevski (*2*) determined that homogeneous ammonia-nitrogen mixtures decompose into two gas phases at elevated pressures. At present, seventeen binary and two ternary systems are known to exhibit the phenomenon.

Two types of gas-gas equilibria are possible, designated as type I or type II, depending on whether the $P(T)$ critical curve, starting from the critical point of the least volatile component, has a positive or negative slope, respectively. More detailed discussions of gas-gas equilibria are given in references *3* and *4*.

Kreglewski (*5*) showed that the greater the differences in the D^2 values of the components of a binary system ($D^2 = 3\ RT_c/2\ V_c$), the greater is the probability that gas-gas equilibrium will occur. The D^2 parameter equation was obtained when Hildebrand's (*6*) equation, $D^2 = -E/V$, was combined with van Dranen's (*7*) hypothesis that $E = -3\ RT_c/2$,* which results from his assumption that the potential energy equals the negative of the kinetic energy at the critical point.

Arranging systems in order of increasing D^2 difference and thereby predicting that all systems with a D^2 difference greater than that of the first system—the one with the least D^2 difference that does exhibit gas-gas equilibria—show the phenomenon (and conversely, that all systems with a D^2 difference less than that of the last system—the one with the largest D^2 difference that does not exhibit the equilibria—will not show the phenomenon) is not an acceptable way to predict systems; because, although no system with a D^2 parameter difference of less than 159 atm. has shown the phenomenon, there are systems with larger D^2 differences that fail to exhibit this behavior (for example, hydrogen-carbon dioxide with a 333-atm. difference and hydrogen-benzene with a 203-atm. difference).

If, however, the components are arranged in a table in order of increasing D^2 values toward the right and toward the bottom, the systems formed by the intersecting horizontal rows and vertical columns can be predicted to exhibit the phenomenon or not on the basis of experimental findings, and the rule that in a series of systems containing one compound or element in common, the greater the D^2 differences between the components, the greater is the probability that gas-gas equilibrium will occur. This slight alteration of the Kreglewski concept is a logical one, since it helps to eliminate any large molecular interaction differences between the components of the two systems whose D^2 differences are being compared.

The following are examples of the method: since nitrogen-sulfur dioxide (D^2 difference = 263 atm.) shows gas-gas equilibria, nitrogen-methanol (D^2 difference = 362 atm.) is predicted to exhibit the behavior. But, since hydrogen-hexane (D^2 difference = 107 atm.) does not show this type equilibrium, hydrogen-octane (D^2 difference = 80 atm.) is predicted not to exhibit this type of behavior.

Four tables have been formulated. The first includes only those systems that have been studied experimentally and attests to the validity of the method by the fact that no system violates the D^2 difference trend. The second contains those systems from the previous table and predictions made on the basis of the first table. The third contains those systems from the previous tables and predictions made on the basis of the second table (predictions based on the first predictions, and therefore, perhaps, are not as reliable as the first predictions). The fourth lists the predictions made for as yet unstudied systems. Due to space limitations, only Tables 3 and 4 are presented here.†

These tables are limited to only those elements and compounds that have been experimented upon in gas-gas equilibria studies, plus oxygen and octane, which are included because they are components of systems that have been predicted to show the phenomenon by other methods. Among the systems formed by these components, twenty-seven new binaries are predicted to exhibit the behavior and seventy new binaries are predicted not to exhibit this type of equilibrium (see Table 4).

The Temkin (*8*) criteria for gas-gas equilibrium correctly predict only a few of the systems that exhibit this phenomenon and all such systems also are predicted by the D^2 method. However, whereas the Temkin criteria have forecast no gas-gas equilibria incorrectly in numerous cases (that is, helium-propane, helium-benzene, helium-

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* This approximate relation may be derived by using a corrected van der Waals approach in the following manner: with the van der Waals equation

$$P = \left(\frac{RT}{V-b}\right) - \frac{a}{V^2}$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{R}{V-b}$$

Therefore

$$\left(\frac{\partial E}{\partial V}\right)_T = T\left(\frac{\partial P}{\partial T}\right)_V - P = \left(\frac{RT}{V-b}\right) - \left(\frac{RT}{V-b}\right) + \frac{a}{V^2} = \frac{a}{V^2}$$

or

$$E = -\frac{a}{V}$$

By the familiar van der Waals relation

$$a = \frac{27\ R^2T_c^2}{64\ P_c}$$

Thus

$$E = -\frac{27\ R^2T_c^2}{64\ P_cV_c} = -\frac{27\ RT_c}{64\ Z_c}$$

Since Z_c for a real gas is approximately 0.27, $E \cong 100/64\ RT_c \cong 3/2\ RT_c$.

† Tables 1 and 2 have been deposited as document 9167 with the American Documentation Institute, Photoduplication Service, Library of Congress, Washington 25, D. C., and may be obtained for $1.25 for photoprints or 35-mm. microfilm.