coordinates for system i
r_{ij} = reaction rate of moment i for species j
R_{ij} = reaction rate of species j in concentration system i
t = time
$\mathbf{v}_i$ = average velocity of material in system i
$\mathbf{v}_j$ = velocity of species j with respect to stationary coordinates
x_{ij} = fraction of species j with respect to system i

Greek Letters

ν_{ij} = moment i of species j
ν_i = total moment of system $i = \sum_{J=1}^{n} \nu_{ij}$

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Optimal Truncation of the Virial Equation

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The virial equation represents compressibility factor isotherms for gases as an infinite series in density

$$Z - 1 = \sum_{k=2}^{\infty} B_k \rho^{k-1} \tag{1}$$

where Z is the compressibility factor, ρ is the density, and the B_k are virial coefficients. This equation has a precise theoretical basis in statistical mechanics and relationships exist between the B_k and intermolecular forces. These characteristics make the virial equation a useful predictive tool in thermodynamic analyses (for example, Prausnitz, 1969; Van Ness, 1964).

Because Equation (1) is an infinite series, it must be approximated by a finite polynomial the degree of which is not known a priori. The degree of the optimal polynomial is a function of temperature and density, but the function is unknown. Michels et al. (1960) and Hall and Canfield (1967) suggested truncation criteria to determine the optimal polynomial.

In this note, we use the Hall-Canfield criterion to make an extensive study of the T, ρ dependence of the optimal polynomial degree. The results appear as areas on a reduced plot with ranges $1 \leqq T_R < 60$ and $0 \leqq \rho_R < 4$.

PROCEDURE

We collected several sets of $P\rho T$ data from the literature covering some common gases: argon, helium, hydrogen, nitrogen, methane, carbon dioxide, and propene (the classical limit critical properties are used for helium and hydrogen, not the true critical values).* We used least squares with equal weighting for all data points and the Hall-Canfield truncation criterion to analyze each isotherm for its optimal number of parameters.

Specifically, we chose an isotherm, determined the optimal number of parameters in Equation (1) from the Hall-Canfield criterion, eliminated the highest density datum and re-fit the isotherm, and continued this process until only four data remained. We then plotted the optimal number of parameters for each fit on a $T_R - \rho_R$ plot and chose a new isotherm for the same analysis. The resulting chart defined regions on the $T_R - \rho_R$ surface requiring various numbers of parameters.

RESULTS

Figure 1 presents our results. The contours separating regions requiring different numbers of parameters are broad to indicate that there is no sharp delineation. The Hall-Canfield criterion becomes flat and somewhat uncertain in regions of overlap so some subjectivity enters the analysis. However, by incorporating multiple sets of data, we were able to establish definite trends and thus the contours. Terminating the T_R axis at 1.0 was necessary be-

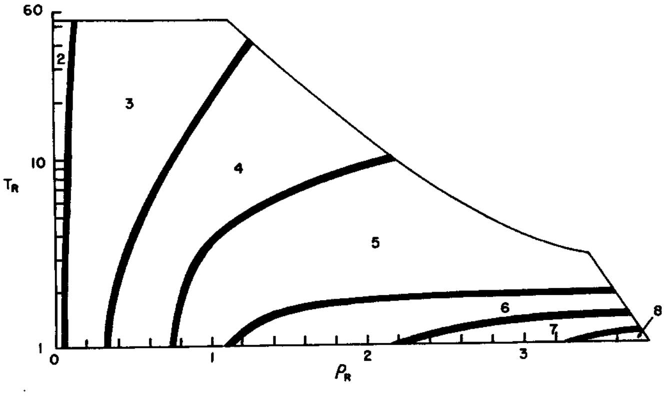

Fig. 1. Optimal parameter ranges for the truncated virial equation.

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* The tabulation of the properties of the gases has been deposited as Document No. 02523 with the National Auxiliary Publications Service (NAPS), c/o Microfiche Publications, 305 E. 46 St., New York, N. Y. 10017 and may be obtained for $1.50 for microfiche or $5.00 for photocopies.

cause of the paucity of low temperature data.

We do not intend to imply that using fewer parameters than indicated by Figure 1 will produce unsatisfactory correlations. We do imply that using the indicated number of parameters will produce correlations more nearly approximating the data and that the polynomial parameters will be more nearly identifiable with virial coefficients.

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Mass Transfer Coefficients and Interfacial Areas in Agitated Dispersions

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The recent article by Robinson and Wilke (1974) reports some interesting results and conclusions on liquid-phase mass transfer coefficients in an agitated vessel involving gas-liquid dispersion. The authors claim a new technique for the simultaneous evaluation of the liquid mass transfer coefficients and gas-liquid interfacial areas for gas-liquid dispersions in an agitated vessel. The success claimed by the authors and the results reported may lead many workers interested in this topic to conclude that therein lies the answer to a long search in trying to understand gas-liquid mass transfer in an agitated vessel. It is therefore pertinent at this point to examine the results obtained by these workers.

Robinson and Wilke reached the unexpected conclusion that the mass transfer coefficient k_L in an agitated dispersion decreases with increasing energy dissipation (power input) in the agitated vessel. They state that the mass transfer coefficient in physical absorption decreases in value as the bubbles decrease in size and the bubbles decrease in size as the power input in the system increases and as the ionic concentration increases. The result of the decrease in bubble size is presumably to change the character of the gas-liquid interface from a somewhat free interface to a somewhat rigid (fixed) interface as the bubble decreases in size. This definitely alters the boundary conditions at the interface, but to claim that the mass transfer coefficient in the liquid phase decreases with increasing energy dissipation goes counter to any known theory in mass transfer. Lamont (1970), solving the problem of transfer in a turbulent field in terms of the eddies in the equilibrium range for the case of both the fixed interface (solid-liquid) and the free (gas-liquid) interface, obtained similar expressions for the mass transfer coefficient in the form

$$k_L = \alpha N_{Sc}^{-m} (\epsilon\nu)^{1/4} \tag{1}$$

where m is 2/3 for the rigid interface and 1/2 for the case of the free interface. Calderbank (1961) confirmed the variation of k_L with energy dissipation in case of transfer from submerged solid surfaces to liquid in agitated vessels for a limited range of energy dissipation [$k_L = 0.13 N_{Sc}^{-2/3} (\epsilon\nu)^{1/4}$]. In the case of solid-liquid transfer, the increase in k_L with energy input in agitated vessels has been established by a number of workers (Harriott, 1961; Keey, 1966; Sykes and Gomezplata, 1967; Nienow, 1969; Miller, 1971; Levins, 1972; and others), although some of them found that some geometrical parameter is also needed to correlate k_L. In view of this, it is desirable to examine critically the technique that has been used to evaluate the results in the study by Robinson and Wilke and others.

Robinson and Wilke calculated their results by simultaneously conducting the absorption of CO_2 from a CO_2-N_2 mixture into an [OH^-] solution and the desorption of O_2 from the solution into a CO_2-N_2 mixture. From the theory of diffusion with reaction, for a fast reaction the rate of absorption with reaction is given by (Danckwerts, 1951)

$$R^r = a_r C_I^* \, (k_{L3}^2 + D_{L3} k_2 C_B)^{0.5} \tag{2}$$

where $k_{L3}^2 << D_{L3} k_2 C_B$ and hence the rate in Equation (2) is independent of hydrodynamics. For the case of physical absorption or desorption of species 4 R is given by

$$R = a_p \Delta C \; k_{L3} \left(\frac{D_{L4}}{D_{L3}} \right)^{0.5} \tag{3}$$

Equation (2) has been used by Wilke and Robinson to describe the rate of CO_2 uptake by the [OH^-] solution and Equation (3) for the desorption of O_2 into the gas bubbles. They further assumed that the effective interfacial area in the case of the reacting system is equal to the effective interfacial area a_p in the case of physical desorption. A little reflection about the dynamics of the agitated vessel will intuitively indicate that this assumption is open to serious doubt. In the case of the absorption system with a fast chemical reaction, the mass transfer coefficient is independent of the hydrodynamics. Hence all the interfacial area distributed in all parts of the agitated vessel