COMMUNICATIONS TO THE EDITOR

On the Calculation of Catalytic Cracking Reactor-Regenerator Units with Permanent and Temporary Deactivation

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This communication concerns the article entitled "On the Interdependence of Temporary and Permanent Deactivation in a Reactor-Regenerator System," by J. E. Gwyn and J. D. Colthart (*1*). The main point of this article is correct in principle, namely, that "catalyst particles that undergo an appreciable degree of permanent deactivation per cycle cannot be considered to have time independent temporary and permanent deactivation." I believe the authors perform a service in pointing out this fact lest the equations derived by Petersen (*2*) be applied to a case where this is true.

What the article does not make clear and what prompts this response is that the hypothetical example at the end of their article indicates an error of 25% in the use of Petersen's equations. This is far different from the result one would obtain if more realistic values for catalytic cracking are substituted for the parameters. In the nomenclature of their article, the constants for catalytic cracking have "first-order" values of the order of:

$P \approx 10^{-6}$/sec.	Assume inventory of, say, 80 tons and makeup of about 1 ton/day.
$\lambda \approx 10^{-3}$/sec.	120 tons/hr. recirculation 40 tons or half of catalyst in the reactor.
$k_r = 10$/sec.	See Blanding (*3*). Although Blanding does not assume a first-order process, this value serves as an order of magnitude.

If these numbers are substituted into their Equation (2), one obtains

$$\bar{A}_0 = \frac{\lambda}{p + k_r + \lambda} = \frac{10^{-3}}{10^{-6} + 10^{-3} + 10} \approx 10^{-2}$$

whereas if the numbers are substituted into Equation (4), one obtains

$$\bar{A}_0 = \frac{\lambda}{p + \lambda} \cdot \frac{\lambda}{k_r + \lambda} = \frac{10^{-3}}{10^{-6} + 10^{-3}} \cdot \frac{10^{-3}}{10^{-3} + 10} \approx 10^{-2}$$

Certainly the answers obtained above are the same to the degree that any of the parameters are known. Hence, for catalytic cracking, which is the system Petersen was analyzing, both sets of equations give the same numerical result.

A note of interest also is that from Blanding's data of $k_r = 10$/sec., if $p = k_r = \lambda$ as assumed in an example by the authors, the total catalyst inventory would have to be replaced on the order of every 10^{-1} sec. in the reactor-regenerator unit.

It should be made clear that while the authors are correct mathematically, the magnitudes of the parameters for catalytic cracking lead to the same numerical results by using either the equations of Gwyn and Colthart or Petersen.

This may not be true, however, in all other catalytic systems.

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Determination of a Single Set of Unlike Pair Potential Interaction Force Constants from Dilute Gas Thermodynamic and Transport Property Data

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Previous work (*1*) has shown that interaction parameters for the pair potential for pure substances can be systematically evaluated by simultaneous solution of transport coefficients and second virial coefficients. An extensive discussion on property estimation techniques by Reid (*22*) noted the multiplicity of (σ,ϵ) sets which would satisfy viscosity data on pure substances. He showed that log ϵ/k vs. σ gave a straight line for each gas. He also noted that the (σ,ϵ) parameters from second virial coefficient data gave quite different lines and sug-

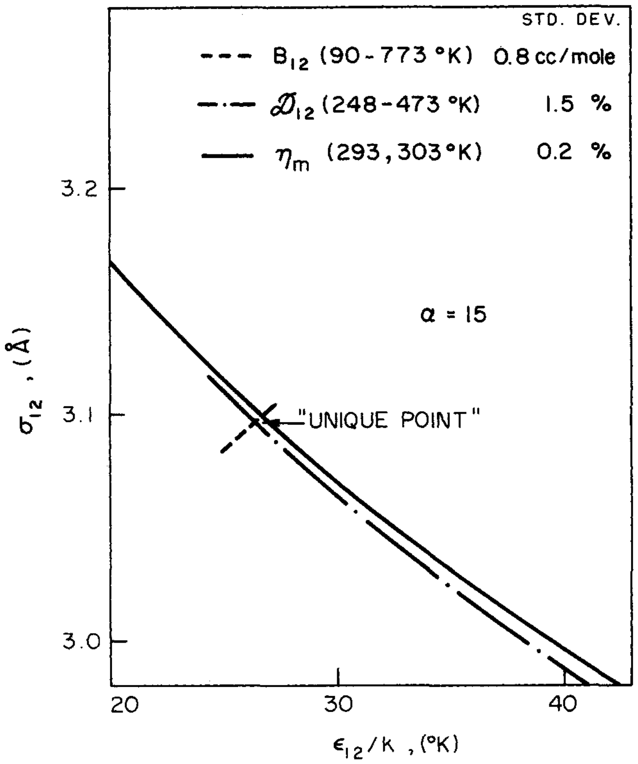

Fig. 1. Simultaneous determination of force constants of exp-6 potential for argon-helium system.

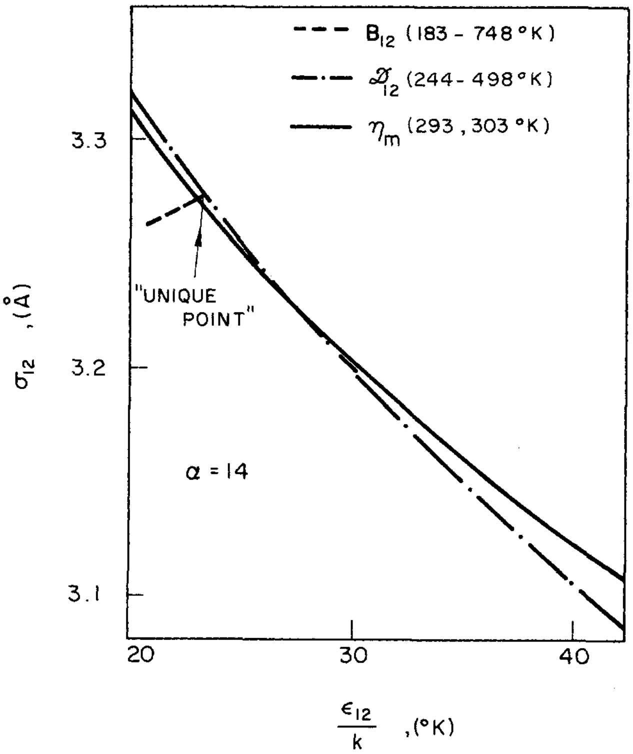

Fig. 2. Simultaneous determination of the force constants of exp-6 potential for nitrogen-helium system.

gested that the intersection of viscosity lines and virial lines would yield single interaction parameter sets suitable for both properties. However, the solution for unlike pair potential force constants and the potential which would satisfy both transport and thermodynamic properties has remained obscure, although the desirability for such an analysis has long been recognized (*19*). It has become possible to carry out a simultaneous solution for the unlike (ϵ_{12},σ_{12},α_{12}) parameters by using recent, more accurate measurements of the diffusivity for dilute and moderately dense binary gaseous systems and existing experimental data.

The sources and ranges of the experimental data used in this study [first approximation diffusivity (*2*), the viscosity, and the second virial coefficients] are listed in Table 1. Based on the Chapman-Enskog kinetic theory for dilute gases, values were obtained for the $\mathcal{D}_{12}$ from dilute and moderately dense gas diffusivity data and the fact that the product density-diffusivity is nearly constant with density. Interaction force parameters for the viscosity were calculated from the Chapman-Enskog relationship (*18*).

Statistical calculations to minimize the error for each property were then made to determine the force constants. All data for each property were used to determine the family of interaction force constants which would satisfy the particular data set for each property: diffusivity, viscosity, and interaction second virial coefficients. The standard deviations from these calculations were 4% for the second virial coefficient data, 1.5% for the diffusivity data, and 0.3% for the viscosity data. No weighting factors for the experimental error were included. Only two potentials for which the collision integrals are available were investigated. For the three parameter Buckingham exp-6 potential, an intermediate value between the pure component values for the third parameter α was selected for each system.

Figures 1 and 2 give an example of results of calculations for the argon-helium and helium-nitrogen systems with the modified Buckingham exp-6 potential. The lines shown could be shown as narrow bands, particularly for the second interaction virial coefficient. The uncertainty in the mixture viscosity and diffusivity with their improved accuracies are such that the width of the lines appropriately includes the uncertainties of the parameters. The figures show three lines through the points for the unlike force constants as determined by using the least-squares method on all the data for each of the three properties. It is evident that one set determined by the intersection of the three lines serves as a common set of unlike pair interaction force constants for *all* three properties, applicable to the temperature ranges of the experimental data.

Although an exact statistical calculation to minimize the sum of the errors for all three properties could be made, a close approximation can be made graphically; these values at the "unique" point are reported in Table 2 with the average deviation for each property by using these parameters.

The results of the Lennard-Jones potential calculations are shown in Figures 3 and 4. An intermediate value on the second virial coefficient between the diffusivity and

TABLE 1. RANGE AND SOURCE OF EXPERIMENTAL DATA

	Temperature, °K.	Number of datum	References
Argon-helium			
B_{12}	90 to 773	15	*3* to *7*
η_m	293 and 303	11	*8*
$\mathcal{D}_{12}$	248 to 473	11	*9, 10, 20*
Nitrogen-helium			
B_{12}	90 to 748	17	*7, 11* to *15*
η_m	293 and 303	15	*16*
$\mathcal{D}_{12}$	244 to 497	12	*9, 10, 17*

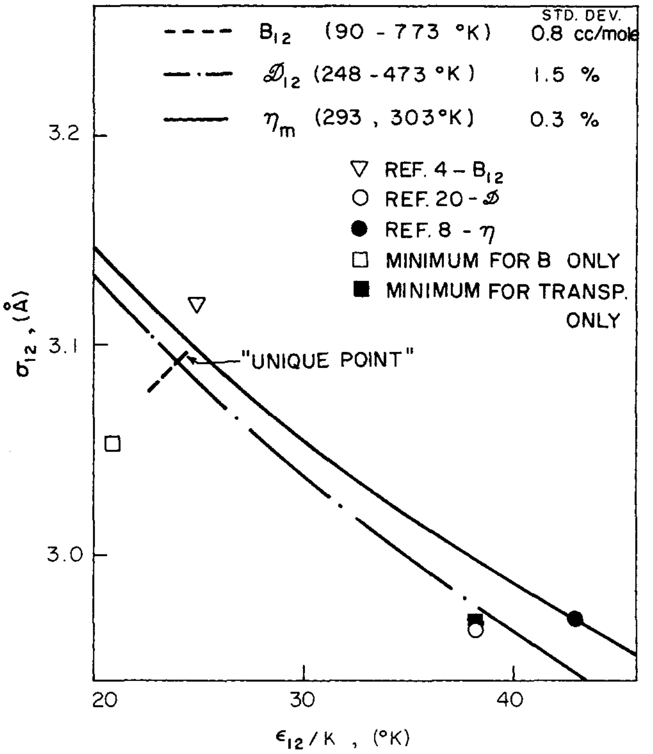

Fig. 3. Simultaneous determination of the force constants of Lennard-Jones (12-6) potential for argon-helium system.

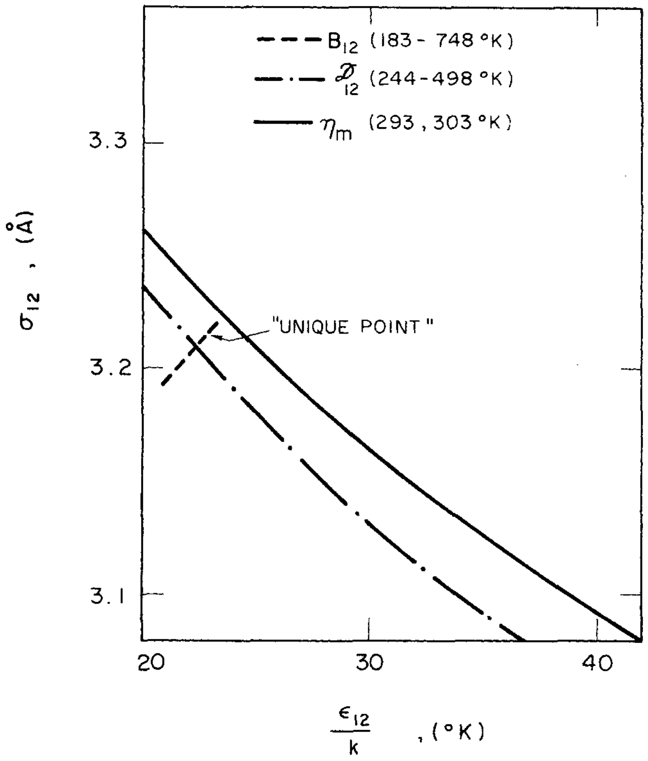

Fig. 4. Simultaneous determination of the force constants of Lennard-Jones (12-6) potential for nitrogen-helium system.

viscosity lines was chosen as the best approximation, and, as would be expected, the deviations for the Lennard-Jones potential are higher. It is evident that the three parameter Buckingham exp-6 potential is somewhat superior to the two parameter Lennard-Jones (12-6) potential to serve for both thermodynamic and transport properties for these particular systems.

This method of analysis of data for various systems has several implications. It may provide a tool for critical analysis of particular potential functions. Any deficiencies of a particular potential for a specific system will readily appear, as indicated by Figures 3 and 4. The method does not, however, uniquely determine the adequacy of the various potential functions.

Perhaps the major application of the method might be some guidance in the solution of the difficult problem for the selection of the best mixing rules for ϵ, σ, etc. A manuscript (*21*) in preparation includes the application of this type of analysis to other systems for which data are being obtained.

TABLE 2. INTERACTION FORCE CONSTANTS FROM DIFFUSIVITY, VISCOSITY, AND SECOND VIRIAL DATA

	Lennard-Jones (12-6)		Buckingham exp-6*	
	Ar-He	N_2-He	Ar-He	N_2-He
Parameter				
α			15	14
ϵ_{12}/k, °K.	24.5	23.2	26.6	24.2
σ_{12}, Å	3.095	3.212	3.096	3.267
Deviation				
$^{\delta}B_{12}$, cc./mole	0.8	0.7	0.8	0.5
$^{\delta}\eta_m$, %	0.3	0.8	0.2	0.2
$^{\delta}\mathfrak{D}_{12}$, %	1.5	3.0	1.5	1.5

* The Buckingham potential calculations did not include two B_{12} data points for argon-helium and six B_{12} data points for nitrogen-helium which were below 273°K., since the quantum effect is significant at low temperature.

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