perature Properties of Liquid *n*-Alkanes at Elevated Pressures," *Proc. of the Fifth Symp. on Thermophys. Properties*, ASME (1970).
Yen, L. C., and S. S. Woods, "A Generalized Equation for Computer Calculation of Liquid Densities," *AIChE J.*, **12**, 95 (1966).

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# Unlike Pair Potential Interaction Force Constants for Hydrogen-Light Hydrocarbon Systems

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A similar earlier study by Hu, Chappelear, and Kobayashi (1970) following the suggestion by Reid (1968) determined unlike pair potential interaction force constants for the argon-helium and nitrogen-helium systems from diffusivity, viscosity, and second virial data. That study showed that the Buckingham Exp-6 potential gives a better fit than the two parameter Lennard-Jones (L-J) 12-6 potential for this combination of thermodynamic and transport properties. The present study for the four hydrogen-light hydrocarbon systems uses the data sources listed in Table 1.

Evaluations are presented here for two potential functions, the Lennard-Jones (12-6) and the Modified Buckingham Exp-6. The tables of Klein and Smith (1968) for the L-J (12-6) potential were used to evaluate the collision integrals $\Omega^{(1,1)*}$ and $\Omega^{(2,2)*}$ and the function $B^*_{12}$. For the Modified Buckingham Exp-6 potential, the tables in Hirschfelder, Curtiss, and Bird (1964) were used. The correlation functions $f_D$ and $f_\mu$ were nearly unity for the systems studied in this work. In the calculations of transport properties, the lowest temperature was well above 200°K so that the quantum corrections were always negligible in comparison with the experimental error.

## METHOD OF CALCULATION

At each experimental condition, values for $B_{12}$ were calculated from

$$B_M = x_1^2\, B_{11} + 2x_1x_2\, B_{12} + x_2^2\, B_{22} \qquad (1)$$

and values for $\mu_{12}$ were calculated from the Chapman-Enskog theory (Hirschfelder, Curtiss, and Bird, 1964). Evaluations of the results of the computations were based on two considerations: (1) evaluation of the intermolecular parameters $\epsilon_{12}/k$ vs. $\sigma_{12}$ should give the same curve independent of the particular experimental temperature, and (2) the values of $\mu_{12}$ should be independent of the concentration as required by the theoretical model.

The calculations for three systems were straightforward; however, calculations for the $H_2$-$C_3H_8$ system seemed to indicate a concentration dependence in $\mu_{12}$. This contradicts the model so the average $\mu_{12}$ was selected as a first trial. However, this gave different $\epsilon_{12}/k$ vs. $\sigma_{12}$ for the four experimental temperatures. The diffusivity experiments were conducted with the hydrocarbon at infinite dilution in hydrogen; hence, a value for $\mu_{12}$ in the hydrogen rich region was selected. This gave a single curve for the $\epsilon_{12}/k$ vs. $\sigma_{12}$ and formed an internally consistent set with the homologous series.

Finally, the least-squares method was used on all experimental temperature conditions (except as noted above) to evaluate the best $\epsilon_{12}/k$ vs. $\sigma_{12}$ for each property. The standard deviation was 5% for $B_{12}$, 1% for $D_{12}$, and 0.5% for $\mu_{12}$ for the four systems.

## COMPARISON OF POTENTIAL FUNCTIONS

The results of the calculations outlined above are presented in Figures 1 and 2. The values of $\sigma_{12}$ and $\epsilon_{12}/k$ selected as nearest to the intersection of the three loci are given in Table 2 for the L-J (12-6) and Exp-6 potentials.

If the potential function correctly and uniformly represents the three properties, the three lines will have a single mutual intersection of values for $\sigma_{12}$ and $\epsilon_{12}/k$. However, the loci for $\mu_{12}$ and $D_{12}$ for the L-J (12-6) potential are spread apart over a wide range, as shown in Figure 1. A region of intersection is defined by the intersection of the line for $B_{12}$ with these loci. On the other hand, Figure 2 shows a much smaller region of intersection for the three loci. This, and specific computations given in the following section, show that the three parameter Exp-6 model, perhaps owing to the extra parameter to adjust the repulsive portion of the potential, is better than the two parameter L-J model for the properties and systems studied here.

The figures show that $\epsilon_{12}/k$ is determined by $B_{12}$. Preliminary calculations showed that the third parameter $\alpha$ shifted the line for $B_{12}$ but did not change its orientation. A larger $\alpha$ gives a larger value for $\epsilon_{12}/k$. The comparisons here are presented at $\alpha = 12$.

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Table 1. Summary of Data Sources*

| System | $B_{12}$ | Number of data | $\mu_{12}$ | Number of data | $D_{12}$** |
|---|---|---|---|---|---|
| $H_2$-$CH_4$ | Mueller (1959)<br>Mueller et al. (1961)<br>Pope (1971) | 5 $T$ | Chuang (1972) | 4 $M$ at 4 $T$ each | 4 $T$ |
| $H_2$-$C_2H_6$ | Mason and Eakin (1961) | 1 $T$ | Trautz and Sorg (1931) | 4 $M$ at 4 $T$ | 3 $T$ |
| $H_2$-$C_3H_8$ | Brewer (1967) | 3 $T$ | Trautz and Kurz (1931) | 6 $M$ at 4 $T$ | 3 $T$ |
| $H_2$-n$C_4H_{10}$ | Mason & Eakin (1961) | 1 $T$ | Ghosh (1971) | 1 $M$ at 1 $T$ | 2 $T$ |

$T$ = temperature condition, $M$ = mixture composition.

* Detailed tabulation of the data are available as a supplement and in the thesis (Chu, 1972).

** The experimental work which led to these calculations: Chu (1972), Chu et al. (1974).

### Diffusion Comparison

The parameters in Table 2 were used to correlate the density-diffusivity product $\rho D_{12}$ at the experimental conditions. The percent deviation in $\rho D_{12}$ for the L-J (12-6) calculations are two to four times the magnitude of the deviations for the three-parameter Exp-6 calculations, for all four systems at all temperatures. The overall deviation was 1.75% for the L-J and 0.08% for the Exp-6 potentials.

A second comparison was made by examining the progression with carbon number. This showed that the results with the Exp-6 parameters more closely approximates the experimental results. Both tests show that the three parameter function is better for diffusivity than the two parameter function.

### Second Virial Coefficient Comparison

The experimental and calculated values for $B_{12}$, along with the absolute deviation, were compared. The deviations are approximately the same for both potentials. This might be expected since the second virial coefficient is essentially determined only by the $\epsilon_{12}/k$ parameter (Figures 1 and 2). The larger deviations for the $H_2$-$C_3H_8$ system may reflect the larger experimental error of that system.

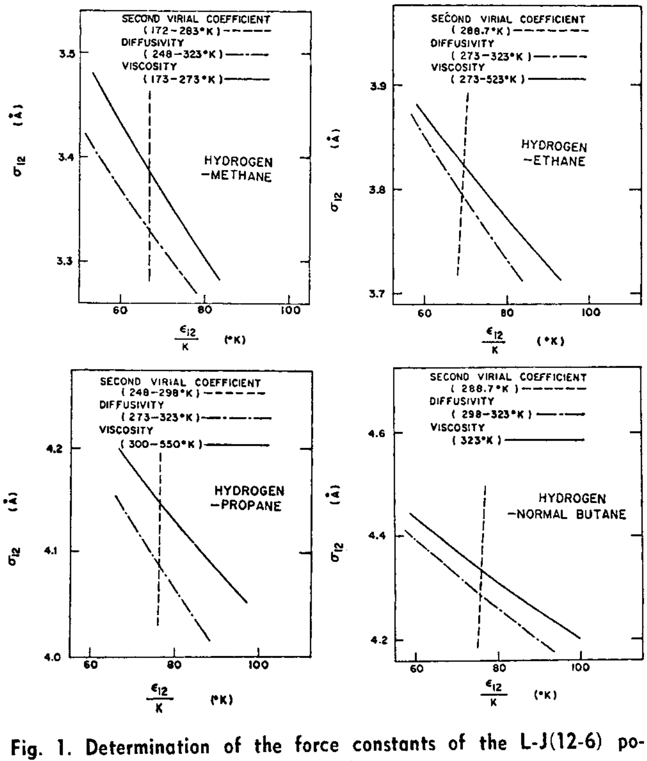

Fig. 1. Determination of the force constants of the L-J(12-6) potential.

Table 2. Interaction Force Constants Determined by Multiproperty Analysis

| System | $\epsilon_{12}/k$ (°K) | $\sigma_{12}$ (Å) |
|---|---|---|
| Lennard-Jones (12-6) Potential | | |
| $H_2$-$CH_4$ | 66.7710 | 3.36 |
| $H_2$-$C_2H_6$ | 69.1659 | 3.811 |
| $H_2$-$C_3H_8$ | 76.4416 | 4.118 |
| $H_2$-n$C_4H_{10}$ | 75.8153 | 4.312 |
| Modified Buckingham Exp-6 Potential ($\alpha = 12$) | | |
| $H_2$-$CH_4$ | 58.1849 | 3.484 |
| $H_2$-$C_2H_6$ | 60.3874 | 3.966 |
| $H_2$-$C_3H_8$ | 66.6901 | 4.28 |
| $H_2$-n$C_4H_{10}$ | 66.0752 | 4.472 |

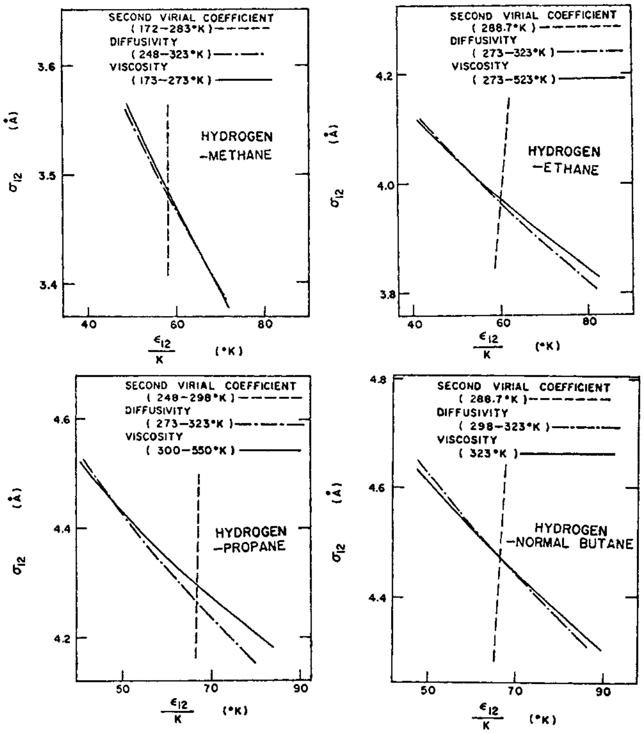

Fig. 2. Determination of the force constants of the Exp-6 potential.

### Viscosity Comparison

Experimental and calculated values for $\mu_{12}$ with percent deviation were compared. In one case, $H_2$-$CH_4$ at 0°C, the values from the L-J calculations (0.24%) are three times better than from the Exp-6 (0.92%); however, nine of the other twelve comparisons show that the Exp-6 values are up to six times better than the L-J, with three cases about equal (for example, at −75°C for $H_2$-$CH_4$,

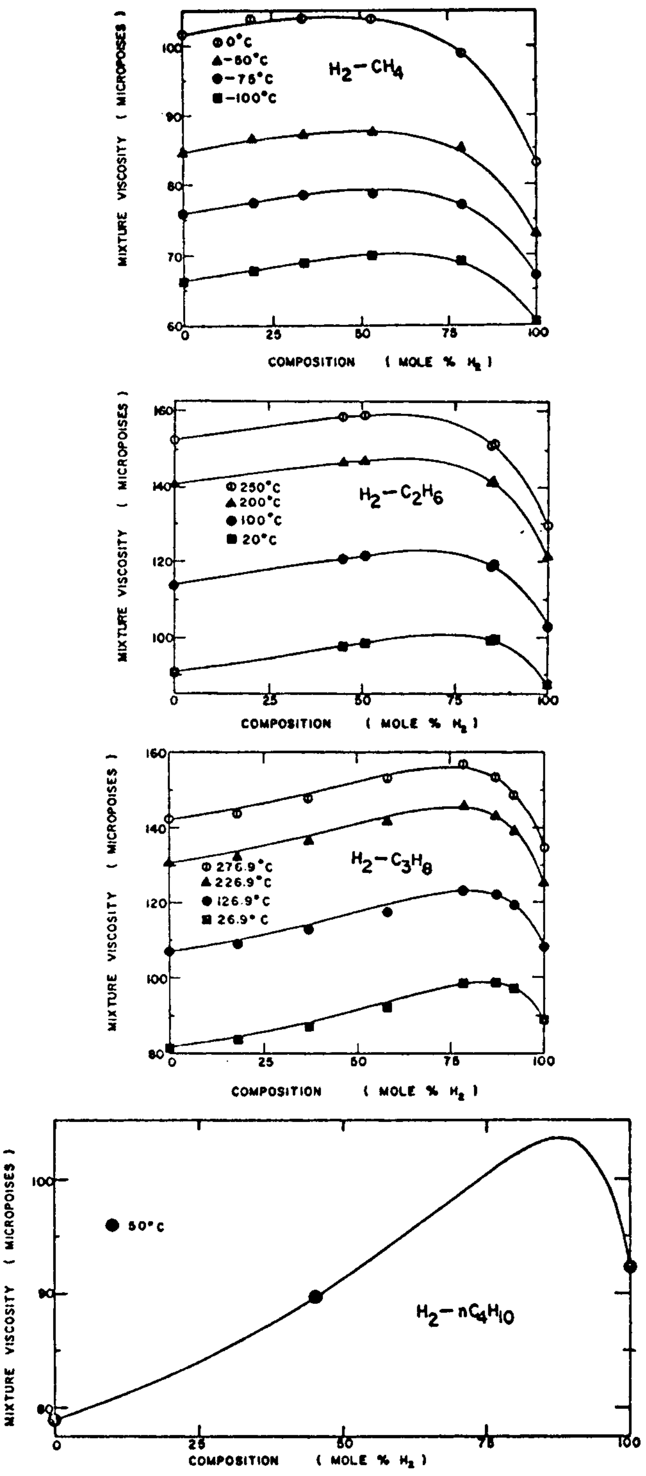

**Fig. 3. Comparison of experimental viscosity with values predicted from multiproperty analysis.**

L-J = 2.15% and Exp-6 = 0.56%). No claims, however, can be made as to the literal superiority of one potential to the other.

### Viscosity Hump

Figure 3 shows the calculation of mixture viscosity for the four systems with the Exp-6 parameters compared with the experimental values. The progression of the maximum in the mixture viscosity appears to behave in a continuous fashion from all aspects: temperature, mole % $H_2$, and carbon number. The pronounced effect calculated for the heaviest system would not be expected from an examination of only the three viscosity data points shown.

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Dr. Arun Ghosh provided his results on the dilute gas viscosities of propane and *n*-butane and of hydrogen-propane and hydrogen-*n*-butane mixtures. The National Science Foundation and the Columbia Gas Systems Service Corporation provided financial support.

## NOTATION

$B$ = second virial coefficient
$D$ = diffusivity
Exp-6 = Buckingham potential function
L-J = Lennard-Jones potential function
$M$ = subscript denoting mixture
$T$ = temperature
$x$ = mole fraction
12 = subscript for interaction of component 1 with component 2
$\epsilon/k$, $\sigma$ = molecular interaction parameters
$\mu$ = viscosity

## LITERATURE CITED

Brewer, Jerome, "Determination of Mixed Virial Coefficients," final report Air Force Office of Scientific Research, Contract No. AF49 (638)—1620 (1967).

Chu, Teh-Cheng, "Diffusivity in Hydrogen-Light Hydrocarbon Systems," Ph.D. thesis, Rice University, Houston, Texas (1972).

Chu, T.-C., Patsy S. Chappelear, and Riki Kobayashi, "Diffusivity of Light Hydrocarbons into Hydrogen," *J. Chem. Eng. Data*, **19**, (1974).

Chuang, Sheng-Yi, "Viscosity of Methane-Hydrogen System from −100°C to 0°C at Pressures up to 500 Atmospheres," Ph.D. thesis, Rice University, Houston, Texas (1972).

Ghosh, Arun K., private communication, Rice University, Houston, Texas (1972).

Hirschfelder, Joseph O., Charles F. Curtiss, and R. Byron Bird, *Molecular Theory of Gases and Liquids*, Wiley, New York (1964).

Hu, Alexander T., Patsy S. Chappelear, and Riki Kobayashi, "Determination of a Single Set of Unlike Pair Potential Interaction Force Constants from Dilute Gas Thermodynamic and Transport Property Data," *AIChE J.*, **16**, 490 (1970).

Klein, M., and F. J. Smith, "Tables of Collision Integrals for the (m, 6) Potential for Ten Values of m," AEDC-TR-68-92 (1968).

Mason, D. McA., and B. E. Eakin, "Compressibility Factor of Fuel Gases at 60°F. and 1 Atm," *J. Chem. Eng. Data*, **6**, 499 (1961).

Mueller, William H., "Volumetric Properties of Gases at Low Temperatures by the Burnett Method," Ph.D. thesis, Rice University, Houston, Texas (1959).

———., T. W. Leland, Jr., and Riki Kobayashi, "Volumetric Properties of Gas Mixtures at Low Temperatures and High Pressures by the Burnett Method: The Hydrogen-Methane System," *AIChE J.*, **7**, 267 (1961).

Pope, Gary Arnold, "Calculation of Argon, Methane, and Ethane Virial Coefficients at Low Reduced Temperature Based on Data Obtained by Isochorically Coupled Burnett Experiments," Ph.D. thesis, Rice University, Houston, Texas (1971).

Reid, R. C., "Present, Past, and Future Property Estimation Techniques," *Chem. Eng. Progr. Monograph Ser. No. 5*, **64** (1968).

Trautz, M., and F. Kurz, "Reibung, Wärmeleitung und Diffusion in Gasmischungen XV," *Ann. Phys.*, 9, 981 (1931).

Trautz, Max, and Karl Georg Sorg, "Reibung, Wärmeleitung und Diffusion in Gasmischungen XVI. Die Reibung von $H_2$, $CH_4$, $C_2H_6$, $C_3H_8$ und ihren binären Gemischen," *ibid.*, **10**, 81 (1931).

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