

(B), and  $\gamma_{\pm}$  is the mean ionic molal activity coefficient for the KCl solution.

The left-hand side of Eq. (1) can be determined experimentally if cell (B) is arranged by maintaining known concentration differences between the two half-cells. The thermoelectric powers are obtained in practice by dividing the measured emfs by the corresponding temperature differences. The right-hand side of Eq. (1) can be calculated provided that transport number and activity coefficient data are available for KCl solutions. Transport number data have been published by Allgood, le Roy, and Gordon.<sup>4</sup> The quantity  $(\partial \ln \gamma_{\pm} / \partial m)$  may be obtained from Spencer's experimental values<sup>5</sup> of  $\gamma_{\pm}$  for KCl. In practice,  $(dm/dT)$  is equated to  $(\Delta m / \Delta T)_{t=t}$ , i.e., finite temperature and concentration differences replace the corresponding infinitesimal quantities.

The cell used in this study was similar to the non-isothermal cell described by Tyrrell and Hollis.<sup>6</sup> It consisted essentially of two jacketed glass electrode vessels connected by an inverted Y piece in which liquid junction between the two half-cells can be made. A positive nitrogen pressure on the Y piece was used to keep the KCl solutions in the two electrode vessels apart until it was desired to take readings. The KCl concentrations were the same in both half-cells for cell (A) and slightly different for cell (B). The calomel electrodes were prepared according to the method of Hills and Ives.<sup>1</sup> Temperatures in the half-cells were controlled to within  $\pm 0.01^{\circ}\text{C}$ . A Vernier Potentiometer was used to measure the cell potentials in conjunction with a galvanometer, (sensitivity: 1.05 mm scale deflection per microvolt), as a null-point detector. This instrument gave readings correct to one microvolt.

Table I shows some selected experimental results for  $\Delta(dE/dT) \equiv (dE/dT)_{t=t} - (dE/dT)_{t=0}$  compared with the corresponding theoretical values calculated from Eq. (1). The mean molality of the KCl solutions used was kept constant at 0.1. The half-cell at the lower temperature was maintained at  $0.45^{\circ}\text{C}$  throughout.  $\Delta m$  represents the difference in molality of the KCl solutions in cell (B),  $E_t$  the emf corresponding to a temperature difference  $\Delta T$  in cell (B), and  $E_0$  is the emf corresponding to the same temperature difference in cell (A).

From Table I, we find in general that comparison between theory and experiment is satisfactory, particularly when the temperature interval is small, i.e.,  $\Delta T < 10^{\circ}$ . The table also indicates that it should be possible to apply the theory to the determination of Soret coefficients and heats of transfer using temperature differences smaller than  $10^{\circ}$ . These general conclusions are perhaps to be expected since infinitesimal quantities in the theory are replaced in practice by finite values.

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<sup>6</sup> H. J. V. Tyrrell and G. L. Hollis, *Trans. Faraday Soc.* **48**, 893 (1952).

### Comparison of Exp-6, L.-J.(12,6), and Sutherland Potential Functions Applied to the Calculation of Differential Scattering Cross Sections\*

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**D**IFFERENTIAL elastic scattering cross sections  $G(\chi)$ , as observed in molecular beam scattering experiments, may be calculated for different assumed intermolecular potential functions by standard methods of classical collision theory. The deflection angle  $\chi$  as a function of the impact parameter  $b$  is calculated for the given initial relative kinetic energy.  $G(\chi)$  is given by  $b | db/d\chi | / \sin\chi$ .

Mason<sup>1</sup> has applied the 3-parameter exponential-six potential function to the scattering of hydrogen by mercury and compared with the experimental results of Knauer.<sup>2</sup> In the present note calculations based on the exp-6 function are compared with those employing the 2-parameter Lennard-Jones (12,6) and Sutherland functions.

Table I lists the constants used in the calculations.

The exp-6 parameters are those used by Mason<sup>1</sup>; the L.-J. parameters are from Hirschfelder.<sup>3</sup> The constants for the Sutherland potential were evaluated graphically to produce the same viscosity (and its temperature dependence) at  $300^{\circ}\text{K}$  as the L.-J. parameters. The table<sup>4</sup> of  $\Omega^{(2,2)*}$  integrals for the Sutherland potential based on Kotani's<sup>5</sup> calculations was used. The potential constants for the binary system were approximated using the usual combination rules. To maintain consistency with Mason's calculations,  $(kT/\epsilon) = 1.60$  was used (convenient in view of existing tables) for both exp-6 and L.-J., and 0.65 for Sutherland calculations; this corresponds to  $T = 285^{\circ}\text{K}$ . Figure 1 compares the calculations with the data of Knauer<sup>2</sup> ( $295^{\circ}\text{K}$ ). Sample computations showed that the  $10^{\circ}\text{K}$  difference is inconsequential (i.e., results in a negligible shift of the scattering curve). The cross sections for the exp-6 function were calculated using Mason's<sup>1</sup> tables.

TABLE I.

	Exp-6			L.-J.(12,6)		Sutherland	
	$\epsilon/k(^{\circ}\text{K})$	$r_m(\text{A})$	$\alpha$	$\epsilon/k(^{\circ}\text{K})$	$\sigma(\text{A})$	$\epsilon/k(^{\circ}\text{K})$	$\sigma(\text{A})$
H <sub>2</sub>	37.3	3.337	14	38.0	2.915	163.	2.50
Hg	851.	3.253	14	851.	2.898	1185.	3.33
H <sub>2</sub> +Hg	178.	3.30	14	178.	2.91	439.	2.91

For the L.-J. (12, 6) function, Hirschfelder's table<sup>6</sup> for  $\chi(b)$  was employed. In the low-angle region additional values of  $\chi$  were calculated using an approximate analytical formula.<sup>7</sup> For large  $b$  values the slopes of the  $\chi(b)$  curve were obtained by differentiation of these formulas; otherwise  $db/d\chi$  was evaluated graphically. The Sutherland potential has been treated by Kotani.<sup>5</sup> The calculation of  $\chi(b)$  involves an elliptic integral; evaluation of  $\chi(b)$ ,  $db/d\chi$ , and  $G(\chi)$  was carried out using an IBM 650 computer.

Knauer's data are given in terms of his scattering function  $f(\theta)$ , equivalent<sup>8</sup> to  $G(\chi)/kT$ . The data originate from two sets of experiments and show a break in the curve near  $20^{\circ}$  ( $\log \chi$  (deg) = 1.3).

It is well known that transport properties and virial coefficients may be fitted over a wide temperature range using the exp-6 and L.-J. (12, 6) potentials and over a limited range with the Sutherland function. All of these potentials include the theoretically sound inverse sixth-power long-range attraction. The differing repulsion terms would be expected to yield differences in the scattering at large angles, whereas the small-angle scattering is determined primarily by the form and magnitude of the attraction term.

As seen in Fig. 1, the L.-J. and exp-6 curves are indistinguishable except near the discontinuity,<sup>1</sup>  $\chi_s$ . The Sutherland curve differs only slightly from these

curves; the difference is greater for large angles, presumably due to the unrealistic repulsion term. For the small angles the deviation is due to the wrong magnitude of the attraction term which arises as compensation for the overly steep repulsion in making a fit to viscosity.

Within Knauer's experimental error all three calculated curves fit the data. The deviation between experiment and calculations at the very low angles is due to quantum effects; classically calculated cross sections are known to be high at small angles.

In summary, for the present example at least, it appears that the calculated angular dependence of the scattering for the exp-6 and L.-J. (12, 6) potentials is virtually indistinguishable, while that for the Sutherland function differs only slightly. Data of extremely high precision (presumably from experiments with crossed monochromatic beams) would be required in order to discriminate among different potential functions with inverse sixth-power long-range attraction terms.

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<sup>1</sup> E. A. Mason, *J. Chem. Phys.* **26**, 667 (1957).

<sup>2</sup> F. Knauer, *Z. Physik* **80**, 80 (1933); **90**, 559 (1934).

<sup>3</sup> Hirschfelder, Curtiss, and Bird, *Molecular Theory of Gases and Liquids* (John Wiley & Sons, Inc., New York, 1954), Table I-A, p. 1110.

<sup>4</sup> Reference 3, Table V, p. 1157.

<sup>5</sup> M. Kotani, *Proc. Phys.-Math. Soc. Japan* (3) **24**, 76 (1942).

<sup>6</sup> Reference 3, Table I-R, p. 1140.

<sup>7</sup> Hirschfelder, Bird, and Spatz, *J. Chem. Phys.* **16**, 968 (1948), Eqs. (45), (49), and (50).

<sup>8</sup> In reference 1, an erroneous relation  $G(\chi) = 2kTf(\theta)$  was employed [E. A. Mason (private communication, July 15, 1958)]; this led to the necessity of altering the value of  $r_m$  from 3.3 to 3.8 Å to fit Knauer's data. Here the correct relation and the value of  $r_m = 3.30$  Å have been used.

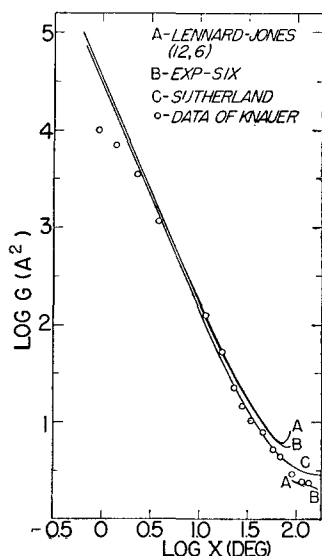


FIG. 1.

## “Free Volumes” in Liquids

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**T**HE concept of “free volume” in liquids has been stated in various ways. Bondi<sup>1</sup> has differentiated