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## THE CHROMATOGRAPHIC DETERMINATION OF THE PARAMETERS IN THE LENNARD-JONES 12-6 POTENTIAL

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### SUMMARY

The chromatographic determination of the temperature dependence of binary diffusion coefficients is shown to be of sufficient precision to permit the calculation of intermolecular force constants. With peak widths restricted to manual measurement, the precision in  $\epsilon/k$  and  $\sigma$  is of the order of 20%.

### INTRODUCTION

In principle, both the parameters  $\epsilon/k$  and  $\sigma$  in the Lennard-Jones 12-6 potential function of intermolecular distance  $r$

$$\varphi = 4\epsilon \left[ \left( \frac{\sigma}{r} \right)^{12} - \left( \frac{\sigma}{r} \right)^6 \right] \quad (1)$$

can be determined exactly from measurement of the diffusion coefficients at two different temperatures. The well-depth,  $\epsilon$ , is first determined by solving for  $\epsilon/k$  from the expression for the ratio  $\xi$  of the collision integrals (let  $T_2 > T_1$ ):

$$\xi = \frac{\Omega_1}{\Omega_2} = \left( \frac{D_2}{D_1} \right) \left( \frac{T_1}{T_2} \right)^{3/2} \left( \frac{P_2}{P_1} \right) \quad (2)$$

The collision integrals,  $\Omega_i$  ( $i = 1, 2$ ), are the reduced (1, 1) collision integrals and are functions of the reduced temperatures:

$$\Omega_i = [\Omega_{12}^{(1,1)*}]_i = [\Omega_{12}^{(1,1)*}(T_{12}^*)]_i \quad (i = 1, 2) \quad (3)$$

The value of  $\epsilon/k$  thus obtained is inserted in the expression for the diffusion coefficient,  $D_2$ , and solved for  $\sigma$ , i.e.

$$\sigma = \left\{ \frac{0.002628 T_2^{3/2} \left[ \frac{(M_1 + M_2)}{2 M_1 M_2} \right]^{1/2}}{P D_2 \Omega(T_2^*)} \right\}^{1/2} \quad (4)$$

where

$$\begin{aligned}
 P &= \text{pressure (atm);} \\
 M_i &= \text{molecular mass of species } i; \\
 T_2 &= \text{temperature (}^\circ\text{K)} \\
 T_2^* &= kT_2/\varepsilon
 \end{aligned}$$

In practice, this information is neither easily extracted nor, in general, can it be unambiguously extracted, particularly  $\varepsilon/k$ .

The ratio  $\xi = \Omega_1/\Omega_2$  is a unique function of  $\varepsilon/k$  but depends on the functional form of the potential. It is well known that the simple Lennard-Jones 12-6 potential can be regarded only as an approximation of the true potential and that its applicability becomes increasingly inexact with increasing size and non-sphericity of the molecular pairs. This implies an ill-defined envelope of uncertainty around the theoretical line in Fig. 1, which in turn gives rise to an uncertainty  $\Delta(\varepsilon/k)_t$  in the  $\varepsilon/k$  values obtained as the ordinate in the intersection of these lines with the experimentally determined right-hand side of eqn. 2. In addition, there is the uncertainty  $\Delta(\varepsilon/k)_e$  that results from the measurements of  $D_i$ ,  $T_i$  and  $P_i$  ( $i = 1, 2$ ).  $\Delta(\varepsilon/k)_e$  increases with decreasing slope in the theoretical line.  $\Delta(\varepsilon/k)_t$  and  $\Delta(\varepsilon/k)_e$  together result in an uncertainty  $\Delta(\varepsilon/k)$ , as indicated in Fig. 1. The present concern is not with the theoretical uncertainties but an important consequence should be kept in mind, *viz.*, that different pairs of temperatures can yield different values for  $\varepsilon/k$  even if the experimental data are exact.

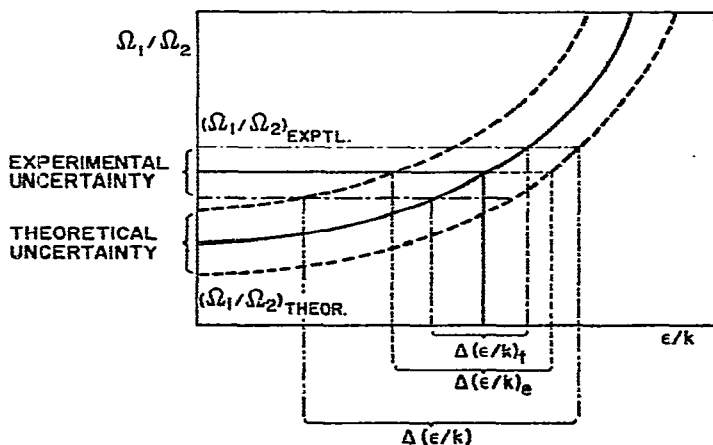


Fig. 1. Illustration of uncertainties in the determination of  $\varepsilon/k$ .

The present study is a test of the theory at a prescribed level of uncertainty and is not an example of the best that the chromatographic method has to offer, but should rather be regarded as an exploration of its potential. It is hoped that correspondence of the experimental results with the theoretical predictions will provide the justification for an attempt to realize its full potential within the limits of current technology.

It was shown earlier<sup>1</sup> that a maximum slope in  $\Omega_1/\Omega_2$  is obtained for pairs of temperatures corresponding to reduced temperatures  $T_1^* \approx 0.7$  and  $T_2^* > 10$ . Under these conditions,  $\varepsilon/k$  can be expected to be about an order of magnitude more uncertain than the uncertainties in the measurements of the diffusion coefficients. Unfortunately, this ideal is not readily attainable in practice and a considerably higher amplification factor is the rule rather than the exception.

In order to appreciate the difficulties involved, it is useful to consider some pertinent examples. The work of Bunde<sup>2</sup> on  $H_2-N_2$ , Rumpel<sup>3</sup> on  $He-N_2$  and Strunk<sup>4</sup> on  $He-Ar$ ,  $He-air$ ,  $CO_2-He$ ,  $CO_2-air$  and  $CO_2-Ar$  gave no unique solutions for  $\varepsilon/k$  and  $\sigma$ . Indeed, Rumpel was unable to obtain any intersections and Strunk was unable to obtain intersections for four of the gas pairs he studied. If the semi-empirical correlations recommended by Marrero and Mason<sup>5</sup> are used, at temperatures of about 300 and 500 °K, values of  $\varepsilon/k$  obtained for the gas pairs  $N_2-Ar$  and  $CH_4-He$  are 112 °K and 85 °K, respectively, in comparison with the values of 82 °K and 39 °K, respectively, obtained from the application of combination rules to force constants obtained from viscosity values<sup>6</sup>.

It follows from eqn. 2 that

$$\frac{d\xi}{\xi} = \frac{dD_2}{D_2} - \frac{dD_1}{D_1} + \frac{3}{2} \left[ \frac{dT_1}{T_1} - \frac{dT_2}{T_2} \right] + \frac{dP_2}{P_2} - \frac{dP_1}{P_1} \quad (5)$$

and

$$\frac{\text{Var } \xi}{\xi^2} = \frac{\text{Var } D_2}{D_2^2} + \frac{\text{Var } D_1}{D_1^2} + \frac{9}{4} \left( \frac{\text{Var } T_1}{T_1^2} + \frac{\text{Var } T_2}{T_2^2} \right) + \frac{\text{Var } P_2}{P_2^2} + \frac{\text{Var } P_1}{P_1^2} \quad (6)$$

where  $\text{Var}$  = variance. Eqns. 5 and 6 apply to systematic and random errors, respectively. In contrast to the determination of diffusion coefficients *per se*,  $\varepsilon/k$  is seen to be less sensitive to systematic errors. As these are also difficult to quantify, attention will be restricted to the random errors. Both  $\text{Var } P/P^2$  and  $\text{Var } T/T^2$  are expected to be substantially less than  $\text{Var } D/D^2$ .

Using the experimental results from a recent paper<sup>7</sup> with the values  $T_1 \approx 300$  °K,  $T_2 \approx 500$  °K and  $(\text{Var } D)/D^2 \approx 5 \cdot 10^{-5}$ ,  $(\text{Var } \xi)/\xi^2$  is obtained as approximately  $10^{-4}$ . This corresponds to a deviation in  $\varepsilon/k$  of about 20% based on an actual plot of the information in Fig. 1.

## RESULTS

The results obtained are summarized in Table I. The empirical combining laws relating force constants between unlike molecules to those between like molecules are<sup>6</sup>

$$\sigma_{12} = (\sigma_1 + \sigma_2)/2 \quad (7)$$

and

$$\varepsilon_{12} = (\varepsilon_1 \varepsilon_2)^{\frac{1}{2}} \quad (8)$$

TABLE I  
LENNARD-JONES 12-6 FORCE CONSTANTS

Gas pair	This study			From viscosity			From second virial coefficient		
	$\epsilon/k$ ( $^{\circ}\text{K}$ )	Deviation ( $\pm$ )	$\sigma$ ( $\text{\AA}$ )	$\epsilon/k$ ( $^{\circ}\text{K}$ )	$\sigma$ ( $\text{\AA}$ )	Ref.	$\epsilon/k$ ( $^{\circ}\text{K}$ )	$\sigma$ ( $\text{\AA}$ )	Ref.
$\text{N}_2$ -Ar	68	16	3.7	107	3.550	8, 9	108	3.555	11
				82	3.670	10			
$\text{CH}_4$ -He	41	10	3.1	37	3.199	8, 9, 12	30	3.224	13, 14
				39	3.155	10			
$\text{C}_2\text{H}_6$ -Ar	205	14	3.6	169	3.918	8, 12	171	3.680	15, 16
				142	3.993	10			
$\text{C}_3\text{H}_8$ -Ar	141	34	4.3	177	4.240	8, 12	170	4.521	15, 16
				149	4.330	10			
$\text{C}_2\text{H}_{10}$ -Ar	257	35	4.0	225	4.208	8, 17	189	4.188	15, 16
				223	4.115	10			
$\text{C}_2\text{H}_6$ - $\text{N}_2$	105	6	4.0	145	4.050	9, 12	153	3.832	11, 16
				124	4.121	10			
$\text{C}_4\text{H}_{10}$ - $\text{N}_2$	158	8	4.4	181	4.373	17-19	168	4.335	16, 20
				195	4.243	10			

These rules were applied to the literature values. The  $\epsilon/k$  values found in the literature often show striking differences. For butane, for instance, Flynn and Thodos<sup>21</sup> list  $\epsilon/k = 208$   $^{\circ}\text{K}$ , Svehla<sup>10</sup> 531.4  $^{\circ}\text{K}$  and Hirschfelder *et al.*<sup>6</sup> 410  $^{\circ}\text{K}$ . In other comparisons the differences might be less pronounced, but are often as large as 50  $^{\circ}\text{K}$ <sup>22</sup>.

In the comparison of  $\epsilon/k$  values from different data sources, some considerations should be kept in mind. Firstly, the Lennard-Jones potential is an approximation only of the true intermolecular potential. Further, the use of different properties for the determination of the force constants often results in appreciable differences in the values obtained. Even if the same experimental data are used, differences in two sets of  $\epsilon/k$  and  $\sigma$  values might result from the use of different averaging procedures<sup>22</sup>. Lastly, the combination rules applied in Table I might not be valid. Eqn. 7 is exact only for rigid spherical molecules, while eqn. 8 follows from a simple interpretation of the dispersion forces in terms of the polarizabilities of the individual molecules<sup>6</sup> and is subject to the limitations imposed by that approach.

It is interesting to note that when a large positive difference in  $\epsilon/k$  is reported between different sets of force constants, the value of  $\sigma$  usually shows a large negative difference<sup>22</sup>. That this would be expected can be seen from eqn. 3. This compensation effect often causes calculated macroscopic properties to be almost the same. Reid and Sherwood<sup>22</sup> noted the case of *n*-butane, where, as pointed out above, Flynn and Thodos<sup>21</sup> and Svehla<sup>10</sup> reported very different  $\epsilon/k$  and  $\sigma$  values, while only slight differences are obtained in the calculated gas viscosity curves.

The temperatures at which the  $D$  determinations were made are those reported in Table II of ref. 7. The reported  $\epsilon/k$  values often show large standard deviations, partly because the number,  $n$ , of diffusion coefficient values used in the calculation of the ratio  $\xi = \Omega_1/\Omega_2$  was usually small. For the butane-argon system, a value of  $n = 10$  yielded a relative standard deviation of 17.8%, which is the order of precision to be expected from the present method. Note that eqn. 2 can be written in the form

$$\xi = \frac{\Omega_1}{\Omega_2} = \left[ \frac{(\Delta w_{p\pm}^2)_2}{(\Delta w_{p\pm}^2)_1} \right] \left[ \frac{(u_C^2)_2}{(u_C^2)_1} \right] \left[ \frac{T_1}{T_2} \right]^{3/2} \left[ \frac{P_2}{P_1} \right] \quad (9)$$

where  $\Delta w_{p\pm}$  is the measured increase in the square of the peak width at half-height as measured on the recorder paper and  $u_C$  is the linear gas flow velocity in the column<sup>7</sup>. The chart paper speed,  $u_p$ , and the time,  $t_2$ , during which flow is stopped are regarded as constant for temperatures  $T_1$  and  $T_2$ . If the dimensions of the column are independent of temperature, and the retention time flow method is used, eqn. 3 reduces to

$$\xi = \frac{\Omega_1}{\Omega_2} = \left[ \frac{(\Delta w_{p\pm}^2)_2}{(\Delta w_{p\pm}^2)_1} \right] \cdot \left[ \frac{(t_R^2)_1}{(t_R^2)_2} \right] \cdot \left[ \frac{T_1}{T_2} \right]^{3/2} \left[ \frac{P_2}{P_1} \right] \quad (10)$$

For one determination of  $\epsilon/k$ , only four measured values are required at each temperature:  $\Delta w_{p\pm}$ , retention time ( $t_R$ ),  $T$  and  $P$ . The determination of force constants is therefore not subject to possible uncertainties in column dimensions, as was the case in the determination of diffusion coefficients.

Inspection of Table I shows that the present method has definite possibilities and that, once the necessary refinements have been made, it could become a standard procedure for the determination of intermolecular force constants.

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