

## Thermal Diffusion in HydrogenHydrocarbon Mixtures

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temperature alone and is small relative to the volume, the fugacity, defined by the relation  $F = RT \ln f$ , can be expressed as

$$f = p^2/p(\text{ideal}) = pV/V(\text{ideal}). \quad (5)$$

The fugacity can be calculated from vapor densities or from the volumes obtained by means of the Clapeyron equation and, since this property must represent the pressure at which the hypothetical

perfect gas would be at equilibrium with the liquid, it follows, if the liquid volume is negligible, that

$$\Delta S^* = RT d \ln f / dT. \quad (6)$$

Equation (6) gives the entropy of vaporization to the ideal gas at the pressure  $f$ , and its use should be the practical equivalent of the usual separate evaluation of the entropies of vaporization and of gas imperfection.

## Thermal Diffusion in Hydrogen-Hydrocarbon Mixtures

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Thermal diffusion data have been obtained on a series of mixtures of hydrogen plus hydrocarbons. The results indicate that "collision diameter" for these unlike molecules is considerably smaller than the mean collision diameter of the pure compounds. This is consistent with the high critical pressure of such mixtures.

### NOMENCLATURE

- $\alpha$ —Thermal diffusion ratio  
 $D_{12}$ —Coefficient of ordinary diffusion  
 $\epsilon$ —Difference between energy of separated molecules and configuration for which they have maximum attraction  
 $E$ —Potential energy  
 $m$ —Molecular mass  
 $M_1$ —( $m_1/m_1 + m_2$ )  
 $r$ —Intermolecular distance  
 $r_0$ —"Collision diameter"—distance of separation from zero interaction energy  
 $T_1, T_2$ —Temperatures of upper and lower bulb respectively  
 $T_m$ —Average temperature  
 $v_1, v_2$ —Convection velocities of species 1, 2  
 $W^i r$ —Integral involving collision cross sections  
 $x_1, x_2$ —Mole fractions of species 1, 2

### THEORY

THE thermal diffusion ratio  $\alpha$  is defined by the equation,

$$x_1 x_2 (v_1 - v_2) = D_{12} (-\text{grad } x_1 + x_1 x_2 \alpha \text{ grad } \ln T). \quad (1)$$

From the kinetic theory of gases Chapman and Cowling<sup>1</sup> give the following relationship for  $\alpha$ :

$$\alpha = 5(c-1) \frac{x_1 S_1 + x_2 S_2}{x_1 Q_1 + x_2 Q_2 + x_1 x_2 Q_{12}} \quad (2)$$

which for 50-50 mixtures of gases reduces to

$$\begin{aligned} \alpha &= 10(c-1) \frac{S_1 + S_2}{Q_1 + Q_2 + Q_{12}} \\ &= 10(c-1)G, \end{aligned} \quad (2')$$

<sup>1</sup> S. Chapman and T. G. Cowling, *Mathematical Theory of Non-uniform Gases* (Cambridge University Press, Teddington, 1939).

where

$$S_1 = \frac{M_1}{M_2^{\frac{1}{2}}} \left( \frac{r_{01}}{r_{012}} \right)^2 \frac{W_1^{(2)}(2)^{\sqrt{2}A}}{W_{12}^{(2)}(2)} - M_2 \{ 3(M_2 - M_1) + 4M_1 A \}, \quad (3)$$

$$Q_1 = \frac{\sqrt{2}A}{M_2^{\frac{1}{2}}} \left( \frac{r_{01}}{r_{012}} \right)^2 \frac{W_1^{(2)}(2)}{W_{12}^{(2)}(2)} \times \{ 6M_2^2 + 5M_1^2 - 4M_1^2 B + 8M_1 M_2 A \}, \quad (4)$$

$$\begin{aligned} Q_{12} &= (M_1 - M_2)^2 (5 - 4B) + 4M_1 M_2 A (11 - 4B) \\ &\quad + 4 \left( \frac{r_{01}}{r_{012}} \right)^2 \left( \frac{r_{02}}{r_{012}} \right)^2 \\ &\quad \times \frac{A^2}{(M_1 M_2)^{\frac{1}{2}}} \frac{W_1^{(2)}(2) W_2^{(2)}(2)}{(W_{12}^{(2)}(2))^2}, \end{aligned} \quad (5)$$

$$A = (W_{12}^{(2)}(2) / 5 W_{12}^{(1)}(1)), \quad (6)$$

$$B = (5 W_{12}^{(1)}(2) - W_{12}^{(1)}(3) / 5 W_{12}^{(1)}(1)), \quad (7)$$

$$C = (2 W_{12}^{(2)}(2) / 5 W_{12}^{(1)}(1)). \quad (8)$$

$S_2, Q_2$  can be obtained by reversing subscripts.

The nomenclature has been modified slightly to correspond to that used by Hirschfelder, Bird, and Spotz.<sup>2</sup>

The evaluation of the integrals  $W^{(i)}(r)$  involves the use of the collision cross section and therefore depends on the intermolecular force law assumed. Hirschfelder *et al.*,<sup>2</sup> have evaluated these integrals

<sup>2</sup> J. O. Hirschfelder, R. B. Bird, and E. Spotz, *J. Chem. Phys.* 16, 968 (1948).

TABLE I.

100°C—Boiling water
20°C—Tap water
−40°C—Alcohol plus dry ice
−80°C—Chloroform and carbon tetrachloride plus dry ice

for the Lennard Jones model

$$E(r) = 4\epsilon[-(r_0/r)^6 + (r_0/r)^{12}]. \quad (9)$$

As is discussed in the above paper, it is possible to evaluate  $\epsilon$  and  $r_0$  for pure compounds from viscosity data. Using Eq. (2') and experimental values of  $\alpha$  it is possible to evaluate  $\epsilon_{12}$  and  $(r_0)_{12}$  for collisions between unlike molecules. The factor  $G$  is relatively insensitive to the value of  $\epsilon_{12}$  and to  $T$ , but depends more strongly on the ratios  $r_{01}/r_{012}$  and  $r_{02}/r_{012}$ . On the other hand  $(C-1)$  is very strongly dependent on the value of  $\epsilon_{12}$  and  $T$ , but independent of the ratios  $r_{01}/r_{012}$  and  $r_{02}/r_{012}$ . This simplifies the evaluation of these quantities from experimental  $\alpha$ 's.

Before comparison with experiment is possible it is necessary to obtain the temperature corresponding to the experimental  $\alpha$ .

For the steady state (1) reduces to

$$\frac{1}{x_1(1-x_1)} \text{grad} x_1 = \alpha \text{ grad} \ln T. \quad (10)$$

TABLE II.

Methane-Hydrogen						
$T_1$	$T_2$	$\bar{T}_m$	CmHg	Pressure % H <sub>2</sub>		$\alpha$
	$^{\circ}\text{K}$			Upper	Lower	
537°	372°	445	102.7	51.34	48.66	0.292
537°	372°	445	96.3	51.34	48.66	0.292
523°	299°	391	97.4	52.01	47.99	0.288
523°	299°	391	94.7	52.00	48.00	0.288
474°	299°	353	100.5	51.14	48.86	0.261
470°	300°	352	98.9	51.16	48.84	0.267
363°	195°	262	104.0	51.90	48.10	0.231
299°	190°	236	89.2	51.22	48.78	0.222
299°	189°	236	87.9	51.18	48.82	0.212
Ethylene-Hydrogen						
532°	372°	443	95.9	51.33	48.66	0.299
523°	301°	392	97.8	51.89	48.11	0.274
523°	301°	392	112.1	51.94	48.06	0.281
364°	194°	262	90.7	51.94	48.06	0.250
363°	195°	262	102.6	51.90	48.10	0.243
302°	192°	239	92.1	51.37	48.63	0.242
301°	191°	239	92.7	51.34	48.66	0.239
Propylene-Hydrogen						
530°	372°	442	105.1	51.47	48.53	0.321
523°	299°	390	93.9	52.18	47.82	0.308
523°	293°	386	86.7	52.11	47.89	0.302
417°	295°	349	97.3	51.18	48.82	0.279
375°	230°	290	92.1	51.75	48.25	0.282
376°	232°	293	89.5	51.72	48.28	0.284
Propane-Hydrogen						
531°	372°	442	81.5	51.48	48.52	0.323
523°	299°	391	105.0	52.18	47.82	0.315
524°	294°	387	97.6	52.30	47.70	0.318
476°	300°	354	93.1	51.22	48.78	0.283
375°	231°	292	93.2	51.78	48.22	0.291

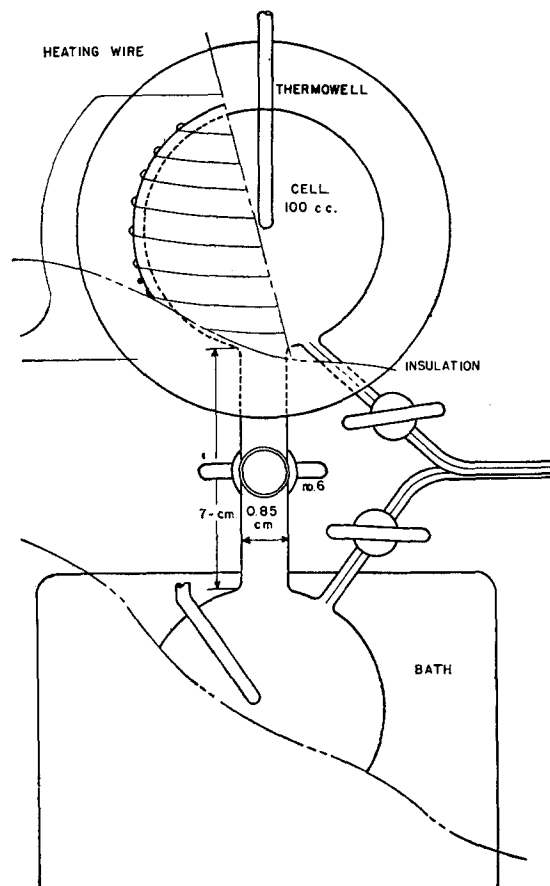


FIG. 1. Thermal diffusion equipment.

To integrate this the dependence of  $\alpha$  on  $T$  must be known. The actual dependence is somewhat complicated for the Lennard Jones model, but it can be approximated reasonably well in the temperature range considered below by the formula:

$$\alpha = A - (B/T). \quad (11)$$

Brown<sup>3</sup> has shown that using the relationship (11)

$$\bar{T}_m = \frac{T_1 T_2}{T_1 - T_2} \ln \frac{T_1}{T_2}. \quad (12)$$

#### EXPERIMENTAL PROCEDURE AND RESULTS

While Eqs. (2) and (2') were derived specifically for spherically symmetrical molecules, nevertheless it was felt that it would be of interest to obtain values of  $(r_0)_{12}$  and  $\epsilon_{12}$  for hydrogen-hydrocarbon systems.

The essential features of the experimental apparatus are shown in Fig. 1. The temperatures in the upper bulb were obtained by use of the heating wire. For the lower bulb the temperatures were obtained as shown in Table I.

<sup>3</sup> H. Brown, Phys. Rev. 58, 661 (1940).

TABLE III.

	$\epsilon$	$r_0$
H <sub>2</sub>	33	2.97
CH <sub>4</sub>	136	3.88
C <sub>2</sub> H <sub>4</sub>	200	4.27
C <sub>3</sub> H <sub>6</sub>	245	4.83
C <sub>3</sub> H <sub>8</sub>	250	4.94

TABLE IV.

	$\epsilon_{12}$	$r_{012}$	$(\epsilon_{12})^\dagger$
H <sub>2</sub> -CH <sub>4</sub>	88±3	2.90	67
H <sub>2</sub> -C <sub>2</sub> H <sub>4</sub>	81±2	2.62	81
H <sub>2</sub> -C <sub>3</sub> H <sub>6</sub>	84±3	2.75	90
H <sub>2</sub> -C <sub>3</sub> H <sub>8</sub>	80±3	2.70	91

In general it was possible to maintain the temperature in the lower bulb within  $\pm 2^\circ\text{C}$  while that in the upper bulb was maintained within  $\pm 5^\circ\text{C}$ .

The pressure in the bulbs during the runs was about 1.5 atmospheres. It was maintained constant during each run, but no effort was made to reproduce precisely the same pressure from run to run.

The systems investigated were hydrogen-methane, hydrogen-ethylene, hydrogen-propylene, and hydrogen-propane.

The binary mixtures were made up to contain fifty percent of each gas by pressure. Analyses were performed by measuring the difference in refractive index between the samples in the top and bottom bulbs on a Zeiss laboratory interferometer with a 25-cm cell. All runs were made in duplicate and for different lengths of time to insure that steady state had been reached. The experimental results are shown in Table II.

In Table III are given the values of  $\epsilon$  and  $r_0$  obtained for the pure components from viscosity data. To evaluate  $\epsilon_{12}$  and  $r_{012}$  from experimental values of  $\alpha$  it was first assumed that the ratios

$r_{01}/r_{012}$  and  $r_{02}/r_{012}$  would be independent of temperature. Then, for any assumed value of these ratios the value of  $\epsilon_{12}$  could be established by trial, evaluating  $A$ ,  $B$ ,  $C$ , and  $W^{(1)}(r)$  from the work of Hirschfelder *et al.*<sup>2</sup>

For most assumed values of  $r_{012}$  the  $\epsilon_{12}$  obtained were temperature dependent. In Table IV are shown the values of  $r_{012}$  and corresponding values of  $\epsilon_{12}$  for the particular value of  $\epsilon_{12}$  which are independent of the temperature. It can be seen that the effective collision diameter for hydrogen-hydrocarbon collisions is slightly less than the collision diameter for hydrogen-hydrogen collisions, also,  $\epsilon_{12}$  is considerably less than the geometric mean of the  $\epsilon$  values.

The precise significance of these results for molecules which are so far from spherically symmetrical is open to considerable question. At least one physical fact can be pointed out which is consistent with these values. Hydrogen-hydrocarbon mixtures are known to have a critical pressure considerably higher than the critical pressure of the pure gases which would correspond to interaction only at very small separations.