# RESPONSE PREDICTION OF THE THERMAL CONDUCTIVITY DETECTOR WITH LIGHT CARRIER GASES

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## SUMMARY

In gas chromatography the response of thermal conductivity detectors is dependent on the physical properties of the solute. This investigation determined that signal strengths represented as relative molar response factors can be calculated from the critical properties of both the chromatographic fraction and a carrier gas of low molecular weight. The approach suggested by LITTLEWOOD has been adopted and appropriately modified with the incorporation of a molecular weight term. The equation is applicable to both polar and non-polar compounds when helium or hydrogen are carrier gases. More significantly, the decrease in response with increased molecular symmetry for isomeric compounds is accurately predicted.

## INTRODUCTION

Investigations[1-4] have confirmed that the signal strength arising from the presence of an eluted solute in a typical detector depends primarily on the nature of the solute. MESSNER et al.[2] reported that these relative molar response (RMR) factors were nearly a linear function of molecular weight within a homologous series and that the relative response of a branched hydrocarbon is less than the RMR of the normal (*n-*) isomer.

Several attempts have been made to calculate RMR factors theoretically. The path most frequently chosen utilizes an appropriate thermal conductivity mixture formula derived from the kinetic theory of gases. However, difficulties are encountered because thermal conductivities of the components in a gaseous binary mixture (eluted solute and carrier gas) are usually not additive. Furthermore the thermal conductivity of a mixture cannot be accurately determined in all cases by empirical equations.

HOFFMANN[5] employed the thermal conductivity relationship proposed by WASSILJEWA[6] and suggested that cell response is proportional to $(K_1 - K_{12})/K_{12}$. $K_1$ and $K_{12}$ represent the thermal conductivity of the carrier gas and the mixture of solute and carrier gas, respectively. Similarly, LITTLEWOOD[7,8], LUY[9] and MECKE AND ZIRKER[10] proposed applications of the rigorous Chapman–Enskog theory[11,12]. Relevant to the present study is the extension of the Chapman–Enskog theory which was

adopted by LITTLEWOOD[7]. For the case where the mole fraction of one component is small $(X_2)$, LITTLEWOOD derived the following equation:

$$\frac{1}{K_1}\frac{dK_m}{dX_2} \cong -2.30\frac{\sigma_{12}^2}{\sigma_1^2} \tag{1}$$

where $\sigma_{12} = (\sigma_1 + \sigma_2)/2$. The molecular diameters of the carrier gas and solute are designated by $\sigma_1$ and $\sigma_2$, respectively. There were four assumptions made by LITTLE-WOOD[8] in the derivation of this equation.

(1) $X_2$ must be much less than 1.

(2) The molecular weight of the solute $(M_2)$ must be at least twenty times that of the carrier gas $(M_1)$.

(3) Organic molecules may be regarded as rigid spheres.

(4) The validity of the Chapman–Enskog theory is unaffected by the internal structure of the solute.

LITTLEWOOD's equation illustrates how the thermal conductivity of the carrier gas is altered by the presence of solute molecules. As the carrier gas is responsible for the heat dissipation in the sensing filament, the solute vapor interferes with this process to the extent of their total cross-sectional area, namely, $X_2\sigma_{12}^2$. The resulting decrease in thermal conductivity is indicated by the minus sign.

LITTLEWOOD[8] stated that collision diameters for only a few compounds are available in the literature and also that the concept of a molecular diameter is not precise enough to make such values applicable in all circumstances. To alleviate these difficulties, he believed that it is feasible that the cross-sectional area of an organic molecule is approximately equal to the sum of the cross-sectional areas of its structural units. Analyzing the RMR data reported by ROSIE AND GROB[1], LITTLEWOOD found that the RMR factors of these compounds can be determined by addition of the RMR values assigned to each structural unit. However, this procedure is unsatisfactory for very symmetrical molecules, such as 3-ethylpentane.

Recently, NOVAK et al.[13] chose to predict RMR values through consideration of both conductive and convective heat effects. With hydrogen as the carrier gas, the calculated response factors agreed well with the experimental data, but theoretical predictions were inadequate with nitrogen as carrier gas due to the non-linear response of the detector and peak distortion for both the internal standard and the compound under consideration.

CONCEPT OF A MOLECULAR DIAMETER

The thermal conductivity of a vapor is dependent upon its molecular weight and distance of closest approach in addition to other molecular properties. The distance of closest approach may be defined by the $\sigma$ term in the Lennard–Jones (12 — 6) intermolecular potential energy function,

$$V(r) = 4e_0\left[\left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6\right] \tag{2}$$

in which $e_0$ is the maximum energy of attraction of two colliding molecules. The param-

eters $\sigma$ and $e_0$ have been related to the viscosity and thermal conductivity of a gas near atmospheric pressure by the rigid Chapman–Enskog theory[12]:

$$N = \frac{0.002669\,(MT)^{1/2}}{\sigma^2 \Omega^{(2,2)*}(T^*)} \qquad [cP] \tag{3}$$

$$K = \frac{1.989 \times 10^{-4}(T/M)^{1/2}}{\sigma^2 \Omega^{(2,2)*}(T^*)} \qquad [cal/(cm)\,(sec)\,(°K)] \tag{4}$$

where $M$ is the molecular weight of the gas and $T$ is absolute temperature. The collision integral, $\Omega^{(2,2)*}(T^*)$, in which $T^* = kT/e_0$, is the resultant of a complex set of integrals after the potential function and temperature have been selected.

Since viscosity and thermal conductivity are a function of the Lennard–Jones parameters, these constants may be determined from the experimental measurements by choosing the set of $\sigma$ and $e_0$ which fits the data most accurately. Complications

TABLE I

LENNARD–JONES PARAMETERS DETERMINED FROM VISCOSITY DATA

| Compound | $\sigma\,(\mathring{A})$ | $e_0/k\,(°K)$ | Reference |
|---|---|---|---|
| n-Butane | 4.687 | 531 | 14 |
|  | 4.997 | 410 | 15 |
|  | 5.339 | 310 | 16 |
|  | 5.869 | 208 | 17 |
| Benzene | 5.349 | 412 | 14 |
|  | 5.443 | 387 | 16 |
|  | 5.628 | 412 | 17 |
|  | 5.270 | 440 | 18 |

TABLE II

LENNARD–JONES PARAMETERS CALCULATED FROM VISCOSITY DATA FOR VARIOUS COMPOUNDS IN A HOMOLOGOUS SERIES

| Compound | $\sigma\,(\mathring{A})$ | $e_0/k\,(°K)$ | Reference |
|---|---|---|---|
| Methane | 3.808 | 140 | 17 |
| Ethane | 4.384 | 238 | 17 |
| Propane | 5.240 | 206 | 17 |
| Butane | 5.869 | 208 | 17 |
| Pentane | 6.099 | 269 | 17 |
| Hexane | 5.916 | 423 | 17 |
| Heptane | — | — | no values reported |
| Octane | 7.407 | 333 | 17 |
| Nonane | 8.302 | 266 | 17 |
| Methanol | 3.666 | 452 | 19 |
| Ethanol | 4.370 | 415 | 19 |
| Dimethyl ether | 4.264 | 412 | 19 |
| Diethyl ether | 5.539 | 351 | 19 |
| Methyl acetate | 5.054 | 417 | 19 |
| Ethyl acetate | 5.163 | 531 | 19 |

arise in this procedure as there are often multiple sets of $\sigma$–$e_0$ values which will reproduce the same viscosity data. Pairs of $\sigma$–$e_0$ values for $n$-butane and benzene are presented in Table I. In addition to the existence of several sets of parameters for a given compound, irregularities in reported values are common. The data in Table II show that the addition of a methylene group does not contribute a constant amount to either the collision diameter or the energy of interaction.

## DETERMINATION OF COLLISION DIAMETERS

To eliminate irregular trends and multiple sets of $\sigma$–$e_0$ values, collision diameters have been calculated by the empirical expressions reported in the literature. In particular, TEE et al.[16] found that the following relations accurately reproduced experimental viscosity data for fourteen non-polar, non-associated substances:

$$\sigma = 2.36 \ (T_c/P_c)^{1/3} \tag{5}$$

$$e_0/k = 0.774 \ T_c \tag{6}$$

where $T_c$ and $P_c$ are the critical temperature (°K) and pressure (atm), respectively. Only the additional diameter expressions employed in the present investigation and the appropriate designation by which they will be subsequently referred to are presented in Table III.

TABLE III

COLLISION DIAMETER EXPRESSIONS

$T_c$ = critical temperature (°K); $P_c$ = critical pressure (atm); $V_c$ = critical volume (cm³/gmole); $W$ = acentric factor.

| Desig-nation | Expression | Reference |
|---|---|---|
| 1 | $\sigma = 2.3647 \ (T_c/P_c)^{1/3}$ | 16 |
| 2 | $\sigma = (2.3454 + 0.2972 \ W) \ (T_c/P_c)^{1/3}$ | 16 |
| 3 | $\sigma = 2.3442 \exp (0.1303 \ W) \ (T_c/P_c)^{1/3}$ | 16 |
| 4 | $\sigma = (0.8123 + 0.1678 \ W) \ V_c^{1/3}$ | 16 |
| 5 | $\sigma = 0.5894 \ V_c^{0.4006}$ | 20 |
| 6 | $\sigma = (2.3551 - 0.0874 \ W) \ (T_c/P_c)^{1/3}$ | 16 |
| 7 | $\sigma = 0.785 \ V_c^{1/3}$ | 21 |
| 8 | $\sigma = 0.561 \ V_c^{5/12}$ | 17 |
| 9 | $\sigma = 0.618 \ V_c^{1/3} T_c^{1/18}$ | 17 |

The acentric factor, $W$, appearing in Table III was introduced by PITZER[22,23] as a correlating parameter to characterize the acentricity of a molecule and is mathematically written as:

$$W = -\log P_{v \cdot p_r} - 1.00/T_{r=0.7} \tag{7}$$

where $T_r$ and $P_{v.p_r}$ are the reduced temperature and reduced vapor pressure, respectively. This technique of defining $W$ results from the fact that it is sensitive to the value of the reduced vapor pressure near the normal boiling point. It has been found that for spherically symmetric species, such as argon, the value of $P_{v.p_r}$, at a reduced

TABLE IV

COLLISION DIAMETERS (Å) OF SELECTED COMPOUNDS

| Compound | Collision diameter expression | | |
|---|---|---|---|
| | 1 | 3 | 8 |
| n-Pentane | 5.71 | 5.85 | 6.13 |
| n-Hexane | 6.07 | 6.25 | 6.58 |
| n-Heptane | 6.41 | 6.66 | 6.99 |
| n-Octane | 6.73 | 7.03 | 7.39 |
| n-Nonane | 7.04 | 7.39 | 7.74 |
| 2,2-Dimethylbutane | 5.94 | 6.10 | 6.51 |
| 2-Methylpentane | 6.02 | 6.20 | 6.57 |
| 3-Methylpentane | 6.00 | 6.17 | 6.55 |
| 2-Methylhexane | 6.36 | 6.59 | 7.00 |
| 3-Methylhexane | 6.31 | 6.53 | 6.94 |
| 3-Ethylpentane | 6.29 | 6.50 | 6.92 |
| 2,2,3-Trimethylbutane | 6.17 | 6.33 | 6.77 |
| Benzene | 5.34 | 5.45 | 5.69 |
| Toluene | 5.73 | 5.89 | 6.17 |
| o-Xylene | 6.16 | 6.35 | 6.59 |
| m-Xylene | 6.17 | 6.38 | 6.64 |
| p-Xylene | 6.22 | 6.41 | 6.65 |
| 1,3,5-Trimethylbenzene | 6.40 | 6.70 | 7.02 |
| Diethyl ether | 5.57 | 5.69 | 5.82 |
| Acetone | 5.23 | 5.40 | 5.22 |
| Methanol | 4.42 | 4.71 | 4.09 |
| Ethanol | 4.76 | 5.13 | 4.73 |
| Helium | 3.14 | 3.11 | 3.04 |
| Hydrogen | 3.25 | 3.22 | 3.19 |

temperature equal to 0.7, is approximately 0.1; thus, $W = 0$. More significantly, the acentric factor is a convenient measure of the difference between a given molecule and an inert gas.

These diameter expressions generate a consistent set of diameters on which response prediction can be based. Diameters calculated by expressions 1, 3, and 8 are illustrated in Table IV for a few selected compounds. By inspection of Table IV it can be seen that collision diameters increase linearly with molecular weight for compounds belonging to a homologous series. Also, the diameter of a branched compound is smaller than that of the corresponding normal isomer, e.g., 2-methylpentane and hexane. Furthermore, a decrease in collision diameter is associated with increased molecular symmetry as a comparison of 2-methylhexane, 3-methylhexane, and 3-ethylpentane indicates.

Critical constants and acentric factors for many organic compounds have been tabulated[24]. For compounds whose molecular constants are unavailable, their critical temperature and volume were estimated by LYDERSEN's method[25], the critical pressure by RIEDEL's procedure[26] and the acentric factor by the technique proposed by EDMISTER[27].

## FORMULATION OF AN RMR EXPRESSION

When helium and hydrogen are employed as carrier gases, response behavior for compounds of vastly different functionalities can be predicted very well by the following equation:

$$RMR_i = \left[\frac{\dfrac{\sigma_i + \sigma_1}{\sigma_1}}{\dfrac{\sigma_\phi + \sigma_1}{\sigma_1}}\right]^2 \left[\frac{M_i - M_1}{M_\phi - M_1}\right]^{1/4} \times 100 \tag{8}$$

The subscripts $i$, $1$, and $\phi$ refer to the solute under consideration, the carrier gas, and benzene (the internal standard), respectively. The first bracketed term in the expression has been proposed by LITTLEWOOD[7], whereas the second term was incorporated in the present study to explain the increase in response with a corresponding increase in molecular weight. The factor of 100 represents the response of benzene, arbitrarily assigned a value of 100 response units per mole. In the calculation of an RMR value, the collision diameters of the substances indicated in the above equation were computed from the same diameter expression.

### EXPERIMENTAL

Although this investigation was not designed to be experimentally oriented, the RMR of selected compounds were measured with helium as a carrier gas. Hydrogen was not employed as a carrier gas with the thermal conductivity detector.

*Apparatus*

The injection port and column were located in a Wilkens aerograph Model 600-B. The detector oven connected externally to the column exit was a Research Specialties Model 1601-2 equipped with a proportioning temperature controller capable of maintaining a temperature to $\pm 0.1°$. The column exit and the thermal conductivity cell were connected by stainless steel tubing tightly wrapped in a Briskeat heating tape. The temperature of the heating tape was controlled by a Variac autotransformer and maintained at 100°. Two partitioning columns were used: (1) a 6 ft. × 1/8 in. O.D. stainless steel column containing 20 % dinonyl phthalate on 60–80 mesh Chromosorb P; (2) a 6 ft. × 1/4 in. O.D. aluminum tubing containing 5.5 % Carbowax 20M on Fluoropak 80.

A Gow-Mac Model 9677 thermal conductivity detector was operated at 100° and with a bridge current of 10 mA supplied by a Gow-Mac power unit Model 9999-D1616. The detector elements were matched glass bead thermistors having a resistance (cold) of 8000 $\Omega$. The flow rate of helium was controlled at 37 ml/min by a rotameter (Matheson Company). Peak areas were measured by a Nester Faust Summatic 1501 digital electronic integrator and the chromatographic signals were observed on a Leeds and Northrup Speedomax H recorder with a 0–1 mV range and a chart speed of 30 in./h. Injected sample size was less than 1 $\mu$l. The selected compounds were obtained from Matheson, Coleman and Bell and their purity was greater than 99 mole %.

Each compound was mixed with a known weight of benzene or toluene from which the mole % of each component could be calculated. Each mixture was chromatographed a minimum of three times and two mixtures were prepared for each compound.

## PREDICTED RMR DATA WITH HELIUM AS CARRIER GAS

The predicted response factors of 68 compounds have been calculated by eqn. 8 and are presented in Table V as a function of the particular collision diameter expression employed in the calculations. Included for comparison are the experimental RMR factors reported by MESSNER et al.[2]. The experimental RMR data in parentheses were determined in the present investigation. Several conclusions may be drawn from the inspection of Table V. The predicted RMR values reflect the fact that relative

TABLE V

PREDICTED RMR FACTORS WITH HELIUM AS CARRIER GAS

| Compound | RMR experimental | RMR predicted | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1[b] | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Pentane | 105 (106) | 107 | 107 | 107 | 107 | 108 | 106 | 106 | 108 | 105 |
| Hexane | 123 (122) | 121 | 123 | 123 | 122 | 123 | 120 | 119 | 125 | 120 |
| Heptane | 143 (136) | 135 | 139 | 139 | 137 | 139 | 134 | 132 | 141 | 134 |
| Octane | 160 (151) | 149 | 155 | 155 | 153 | 155 | 148 | 145 | 157 | 148 |
| Nonane | 177 (164) | 164 | 171 | 171 | 167 | 170 | 162 | 157 | 173 | 162 |
| 2,2-Dimethylbutane | 116 | 118 | 119 | 119 | 119 | 122 | 117 | 118 | 123 | 118 |
| 2,3-Dimethylbutane | 116 | 118 | 119 | 119 | 119 | 122 | 118 | 117 | 123 | 118 |
| 2-Methylpentane | 120 | 120 | 121 | 122 | 122 | 123 | 119 | 119 | 124 | 119 |
| 3-Methylpentane | 119 | 119 | 121 | 121 | 121 | 123 | 119 | 119 | 124 | 119 |
| 2,2-Dimethylpentane | 133 | 130 | 132 | 132 | 132 | 135 | 130 | 129 | 137 | 130 |
| 2,3-Dimethylpentane | 135 | 130 | 133 | 133 | 132 | 135 | 130 | 129 | 137 | 131 |
| 2,4-Dimethylpentane | 129 | 132 | 135 | 135 | 135 | 138 | 132 | 131 | 140 | 133 |
| 2-Methylhexane | 136 | 134 | 137 | 137 | 137 | 139 | 133 | 132 | 141 | 134 |
| 3-Methylhexane | 133 | 132 | 135 | 135 | 135 | 138 | 132 | 131 | 139 | 133 |
| 3-Ethylpentane | 131 | 132 | 134 | 135 | 134 | 137 | 131 | 130 | 139 | 132 |
| 2,2,3-Trimethylbutane | 129 | 129 | 130 | 130 | 129 | 133 | 128 | 127 | 135 | 129 |
| 2,2,4-Trimethylpentane | 147 | 144 | 147 | 147 | 148 | 154 | 144 | 144 | 157 | 147 |
| Cyclopentane | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 | 97 |
| Methylcyclopentane | 115 | 111 | 112 | 112 | 112 | 114 | 111 | 111 | 114 | 112 |
| Ethylcyclopentane | 126 | 125 | 127 | 127 | 126 | 129 | 125 | 124 | 130 | 126 |
| Cyclohexane | 114 (110) | 110 | 110 | 110 | 109 | 111 | 110 | 109 | 112 | 110 |
| Methylcyclohexane | 120 | 124 | 125 | 125 | 121 | 123 | 124 | 119 | 124 | 121 |
| Ethylene | 48 | 56 | 55 | 55 | 54 | 53 | 57 | 56 | 52 | 52 |
| Propylene | 63 | 73 | 72 | 72 | 72 | 71 | 73 | 73 | 70 | 70 |
| Isobutylene | 82 | 88 | 88 | 88 | 87 | 87 | 88 | 88 | 87 | 86 |
| 1-Butene | 81 | 88 | 88 | 88 | 88 | 88 | 88 | 89 | 88 | 86 |
| cis-2-Butene | 87 | 89 | 90 | 90 | 89 | 87 | 89 | 88 | 87 | 86 |
| trans-2-Butene | 85 | 87 | 88 | 88 | 89 | 88 | 87 | 89 | 88 | 87 |
| 1,3-Butadiene | 80 | 85 | 85 | 85 | 84 | 83 | 85 | 85 | 83 | 83 |
| Benzene | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Toluene[a] | 116 (114) | 114 | 115 | 115 | 115 | 116 | 114 | 113 | 116 | 115 |
| o-Xylene[a] | 130 (124) | 130 | 132 | 132 | 129 | 130 | 129 | 126 | 132 | 129 |
| m-Xylene[a] | 131 (128) | 130 | 133 | 133 | 131 | 132 | 130 | 127 | 133 | 129 |
| p-Xylene[a] | 131 | 132 | 134 | 134 | 130 | 132 | 131 | 127 | 133 | 130 |
| Ethylbenzene[a] | 129 | 127 | 129 | 130 | 130 | 131 | 126 | 126 | 133 | 129 |

TABLE V (continued)

| Compound | RMR experimental | RMR predicted | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 1[b] | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Propylbenzene[a] | 145 | 143 | 147 | 147 | 145 | 148 | 142 | 140 | 150 | 144 |
| Isopropylbenzene[a] | 142 | 143 | 149 | 149 | 149 | 148 | 141 | 140 | 150 | 144 |
| p-Ethyltoluene[a] | 150 | 144 | 148 | 148 | 145 | 147 | 142 | 139 | 148 | 143 |
| 1,2,4-Trimethylbenzene[a] | 150 | 143 | 147 | 147 | 146 | 147 | 141 | 139 | 148 | 143 |
| 1,3,5-Trimethylbenzene[a] | 149 (143) | 142 | 147 | 147 | 147 | 147 | 140 | 139 | 148 | 143 |
| Ethyl acetate[a] | 111 (108) | 111 | 114 | 114 | 112 | 108 | 111 | 107 | 109 | 107 |
| Isopropyl acetate[a] | 121 | 121 | 124 | 125 | 124 | 123 | 120 | 120 | 124 | 120 |
| Butyl acetate[a] | 135 | 137 | 141 | 141 | 139 | 139 | 136 | 133 | 140 | 135 |
| Isoamyl acetate[a] | 145 | 149 | 153 | 154 | 150 | 153 | 148 | 144 | 155 | 148 |
| Diethyl ether | 110 (107) | 104 | 104 | 104 | 101 | 101 | 104 | 101 | 101 | 100 |
| Dipropyl ether[a] | 131 | 129 | 133 | 134 | 134 | 133 | 128 | 127 | 135 | 129 |
| Diisopropyl ether | 130 | 129 | 132 | 132 | 131 | 132 | 128 | 126 | 133 | 127 |
| Butyl ether[a] | 160 | 157 | 165 | 165 | 164 | 163 | 155 | 151 | 166 | 156 |
| Ethyl butyl ether[a] | 130 | 130 | 134 | 134 | 134 | 133 | 128 | 127 | 135 | 129 |
| Argon | 44 | 51 | 49 | 49 | 49 | 47 | 51 | 52 | 45 | 45 |
| Nitrogen | 42 | 49 | 47 | 47 | 48 | 45 | 49 | 50 | 44 | 43 |
| Oxygen | 40 | 47 | 46 | 46 | 46 | 44 | 48 | 49 | 42 | 43 |
| Carbon monoxide | 42 | 49 | 48 | 48 | 48 | 46 | 50 | 51 | 45 | 44 |
| Carbon dioxide | 48 | 57 | 59 | 59 | 60 | 53 | 57 | 58 | 51 | 53 |
| Methanol | 55 (55) | 62 | 65 | 65 | 62 | 53 | 61 | 57 | 52 | 55 |
| Ethanol | 72 (72) | 75 | 80 | 80 | 80 | 70 | 74 | 73 | 69 | 71 |
| Propanol | 83 (86) | 90 | 95 | 96 | 95 | 85 | 88 | 87 | 85 | 86 |
| Isopropanol[a] | 85 (85) | 91 | 99 | 99 | 99 | 86 | 88 | 87 | 85 | 86 |
| Butanol[a] | 95 (99) | 103 | 110 | 110 | 111 | 101 | 101 | 101 | 102 | 101 |
| sec.-Butanol[a] | 97 | 103 | 110 | 110 | 109 | 100 | 102 | 100 | 100 | 100 |
| tert.-Butanol[a] | 96 (96) | 103 | 110 | 111 | 111 | 101 | 101 | 101 | 102 | 100 |
| 3-Methyl-1-butanol[a] | 107 | 115 | 123 | 124 | 121 | 109 | 112 | 108 | 109 | 108 |
| Acetone | 86 (83) | 90 | 91 | 91 | 87 | 83 | 90 | 85 | 83 | 84 |
| Methyl ethyl ketone | 98 | 103 | 105 | 105 | 102 | 99 | 102 | 99 | 99 | 99 |
| Diethyl ketone | 110 | 115 | 118 | 118 | 119 | 117 | 114 | 114 | 118 | 115 |
| 3,3-Dimethyl-2-butanone[a] | 118 | 127 | 129 | 129 | 127 | 127 | 126 | 123 | 128 | 124 |
| Methyl amyl ketone[a] | 133 | 143 | 150 | 150 | 147 | 145 | 141 | 137 | 147 | 140 |
| Methyl hexyl ketone[a] | 147 | 156 | 165 | 166 | 162 | 159 | 154 | 149 | 162 | 154 |

[a] Estimation of critical constants.
[b] The numbers 1–9 refer to the collision diameter expressions as given in Table III.

response is indeed a linear function of molecular weight for compounds of a homologous series. In the case of the alkanes, slightly better agreement is obtained when the experimental factors of our study serve as the basis for comparison. The calculated RMR factors of branched compounds are less than the response factors of their corresponding normal isomer. An example of this effect is the isomeric pair 2,2-dimethylbutane and n-hexane. Moreover, eqn. 7 can also account for the decrease in response associated with increased molecular symmetry for isomers, e.g., 2-methylhexane, 3-methylhexane, 3-ethylpentane, and 2,2,3-trimethylbutane.

Other trends in response are very adequately predicted as can be observed by a comparison of the computed and experimental factors of 1,3-butadiene with those of the isomeric butenes. In addition, surprisingly good agreement between the two sets of RMR values is achieved for the aromatics, acetates and ethers although their critical constants have been estimated. For the permanent gases studied, the calcu-

TABLE VI

PREDICTED RMR FACTORS WITH HYDROGEN AS CARRIER GAS

| Compound | Range of experimental factors[a] | | RMR predicted | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ref. 5 | Ref. 28 | 1[b] | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
| Methane | 41 | — | 44 | 42 | 42 | 43 | 41 | 44 | 45 | 40 | 41 |
| Ethane | 58 | — | 61 | 60 | 60 | 60 | 59 | 61 | 62 | 58 | 59 |
| Propane | 73 | — | 77 | 76 | 76 | 76 | 75 | 77 | 77 | 75 | 74 |
| Butane | 87 | — | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 91 | 90 |
| Pentane | 104 | 102 | 106 | 107 | 107 | 106 | 107 | 106 | 105 | 107 | 104 |
| Hexane | 118 | 123 | 120 | 122 | 122 | 121 | 122 | 120 | 118 | 124 | 118 |
| Heptane | 133 | 132 | 134 | 138 | 138 | 136 | 138 | 133 | 131 | 140 | 132 |
| Octane | 150 | 152 | 148 | 153 | 154 | 151 | 153 | 147 | 143 | 156 | 145 |
| Nonane | — | 185 | 162 | 169 | 169 | 165 | 168 | 160 | 155 | 171 | 158 |
| Benzene | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 | 100 |
| Toluene | 112 | 116 | 113 | 115 | 115 | 115 | 115 | 113 | 113 | 115 | 114 |
| Cyclohexane | 106 | 105 | 109 | 109 | 109 | 108 | 111 | 109 | 109 | 111 | 109 |
| Diethyl ether | 112 | 101 | 103 | 104 | 104 | 101 | 101 | 103 | 100 | 101 | 99 |
| Acetone | 86 | 89 | 90 | 91 | 91 | 87 | 83 | 89 | 85 | 83 | 84 |
| Dichloromethane | — | 85 | 91 | 91 | 91 | 91 | 89 | 91 | 92 | 88 | 90 |
| Chloroform | — | 99 | 104 | 104 | 104 | 107 | 107 | 104 | 107 | 106 | 107 |
| Carbon tetrachloride | — | 112 | 122 | 121 | 121 | 121 | 122 | 122 | 121 | 122 | 121 |
| Carbon disulfide | — | 84 | 81 | 80 | 80 | 81 | 80 | 81 | 83 | 79 | 82 |
| Methanol | 62 | 59 | 63 | 66 | 66 | 62 | 54 | 62 | 58 | 53 | 56 |
| Ethanol | 75 | 69 | 75 | 80 | 80 | 80 | 70 | 74 | 73 | 69 | 71 |
| Propanol | — | — | 89 | 95 | 95 | 95 | 85 | 88 | 87 | 85 | 86 |
| Isopropanol | — | — | 90 | 98 | 99 | 99 | 86 | 88 | 87 | 85 | 86 |
| Butanol | — | — | 103 | 109 | 110 | 110 | 101 | 101 | 100 | 101 | 101 |
| Isobutanol | — | — | 103 | 109 | 110 | 110 | 101 | 101 | 100 | 101 | 100 |
| Pentanol | — | — | 116 | 122 | 123 | 123 | 117 | 115 | 114 | 117 | 115 |
| Ethyl acetate | — | — | 111 | 113 | 114 | 111 | 108 | 110 | 107 | 108 | 106 |

[a] Indicates absence of experimental data.
[b] The numbers 1–9 refer to the collision diameter expressions as given in Table III.

lated RMR factors are slightly greater than the experimental ones. However, it is quite possible that these deviations may be attributed to techniques by which RMR values of gaseous substances are determined.

Conceding an error of 3 % in the experimental measurement of a response factor, the overall agreement can be considered excellently, especially for those compounds whose molecular constants have been estimated. Essentially the accuracy of the predicted factors depends on the accuracy of the molecular constants and the validity of the exponent of the molecular weight term in eqn. 7. An exponent of 1/2 produces slightly better agreement for the permanent gases but a value of 1/4 is satisfactory for the overall molecular weight range considered.

PREDICTED RMR DATA WITH HYDROGEN AS CARRIER GAS

Although hydrogen is not ordinarily used as a carrier gas in conjunction with the thermal conductivity detector, a limited amount of RMR data has been reported[5,28] and is presented in Table VI together with the computed factors of twenty

compounds. The ability of a given collision diameter expression to accommodate both polar and non-polar substances is again demonstrated. In addition, the experimental and calculated RMR data are almost identical with those determined with helium as carrier gas. This agreement can be justified by considering the molecular weight and collision diameters of these gases. Since the molecular weight of both carrier gases is much less than that of most organic compounds, the magnitudes of the molecular weight term in the RMR equation are nearly identical for a particular solute with each carrier gas. Moreover, the collision diameters of helium and hydrogen are approximately equal, as can be seen in Table IV.

## CONCLUSIONS

This investigation has determined that the concept of a collision diameter, which is specified in the Lennard–Jones potential function, may be successfully utilized in the calculation of response factors for a typical thermal conductivity detector. Because the diameter expressions are a function of molecular properties, the computed diameters provide a measure of the size of the solute vapor relative to the size of the carrier gas. However, these calculated diameters should not be confused with the concept of a "true" molecular diameter.

The independence of the computed RMR on molecular polarity can be explained by consideration of the environment of the chromatographic solute. In a gas chromatographic analysis, the mole fraction of eluted solute is much less than unity; thus, solute–solute interactions are minimized whereas solute–carrier gas interactions predominate. Consequently, the calculation of diameters for both non-polar and polar compounds by the same expression is justified because the appropriate molecular constants serve as a relative measurement of size. Furthermore, molecular interactions, such as hydrogen bonding and dipole–dipole effects, are essentially absent for polar substances under conventional gas chromatographic conditions.

With nitrogen as carrier gas, our RMR equation failed to predict the experimental data. Response prediction with this carrier gas will be the subject of a later communication.

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