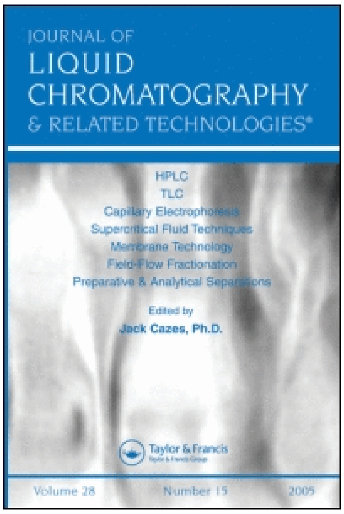

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A THERMODYNAMIC ANALYSIS OF THE DISPERSIVE INTERACTIONS BETWEEN ATOMS OF HYDROGEN, CARBON, CHLORINE, AND BROMINE AND THE STATIONARY PHASE *n*-OCTADECANE

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ABSTRACT

The standard enthalpies and entropies of hydrogen, carbon, chlorine, and bromine atoms, when interacting dispersively with *n*-octadecane, are calculated from retention measurements made on some substituted methanes. A clean linear correlation between the standard enthalpy and standard entropy of interaction is demonstrated and it is also shown that there is a linear relationship between the standard free enthalpy of interaction of the elements investigated and their atomic polarizability. The results also indicate that there is another factor, independent of the element polarizability that contributes to the standard enthalpy of interaction. It is postulated that this factor may be a function of some property of the stationary phase.

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INTRODUCTION

The standard energy of distribution of a solute between two phases can be assigned in two ways, either by allotting portions to the different types of interaction[1–3] (e.g., dispersive, polar, ionic, hydrogen bonding etc.) or to the different atoms or groups that are interacting[4–6] (e.g., methylene, methyl, or phenyl groups). If an appropriate series of solutes are chosen (e.g. the substituted methanes) containing different elements (e.g., H, Cl, and Br) and different numbers of atoms of each element (i.e., 1, 2, 3, and 4), then gas chromatographic retention measurements of these substituted methanes, taken at different temperatures, can yield the standard enthalpies and entropies for the interaction of each substituent element with the stationary phase. Such data will, in turn, help elucidate the nature of the interactions and how they may differ from one element to another and influence phase selectivity.

To obtain the required thermodynamic data, however, at this time, only one kind of interaction can be present, otherwise, the number of unknown parameters exceed the number of pertinent equations that can be derived for the distribution system. Under such circumstances, a practical mathematical solution would be precluded. Dispersive interaction (interaction resulting from London's Dispersion Forces) is the only type of interaction that can proceed in the absence of any other. Polar interactions will always be accompanied by dispersive interactions and ionic interactions are usually accompanied by both polar interactions and dispersive interactions. It follows, that until the mechanism of dispersive interactions are fully understood, they cannot be easily separated from other types of interactions. Consequently, polar interactions or ionic interactions would be difficult to isolate and their interactive mechanism difficult to individually investigate.

If a dispersive stationary phase is chosen for thermodynamic analysis (e.g., an aliphatic hydrocarbon) then solute retention will be controlled solely by dispersive interactions and all thermodynamic data obtained from the distribution system will refer to dispersion interactions only. This assumption is generally accepted and is supported further by the results discussed in this paper. Direct evidence for this assumption is apparent from the early work of Adlard[7] and that of Martire and Reidel,[8] who showed that methanol was eluted with a specific retention value equivalent to about a C_{10} alkane on polyethylene glycol, whereas, on *n*-heptadecane methanol was eluted with a specific retention volume equivalent to about C_{25} (see Fig. 1). Considering that the dispersive interaction of a hydroxyl group is likely to be a little greater than one methylene group, this confirms that, if there is any polar or induced polar interactions between methanol and an alkane stationary phase then they would be negligible compared with those from dispersive interactions. This being true for the highly polar methanol, it will certainly be true for the halogen substituted methanes examined in this paper.

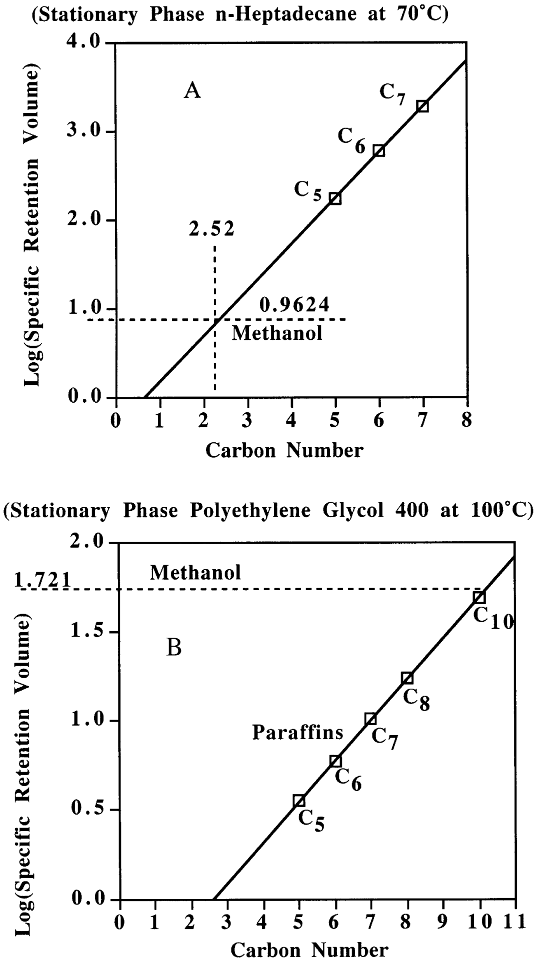

Figure 1. (A) Graph of log (specific retention volume) against carbon number for a series of alkanes and methanol. (B) Graph of log (specific retention volume) against carbon number for a series of alkanes and methanol. Stationary phase: polyethylene glycol 400 at 100°C.

Fortunately, there is a prolific amount of retention data available in the literature and, in particular, the period between the mid-sixties and the mid-seventies produced a plethora of very accurate and precise data, e.g., that reported by Purnell and his group from Cambridge University, England, Martire and his group from Georgetown University, Washington USA, Lochmüler and his group from Duke University, Durham, USA, and Karger and his group from Northeastern University, Boston, USA. In fact, research in the thermodynamics of chromatography can be carried out very comprehensively and inexpensively because of the precise and accurate data that is already readily available in the literature. The data for this work was taken from a publication by Martire et al.[9] that gives results for the retention of a number of substituted methanes on *n*-octadecane over a range of column temperatures.

THEORETICAL CONSIDERATIONS

The solutes of interest in the study of Martire et al.[9] and that are pertinent to this thermodynamic analysis, are the following:

1. Dichloromethane
2. Chloroform
3. Carbon tetrachloride
4. Dibromomethane
5. Bromoform
6. Carbon tetrabromide
7. Chlorobromomethane
8. Dichlorobromomethane
9. Trichlorobromomethane
10. Dibromochloromethane

Now, the distribution coefficient is proportional to the negative exponent of the standard energy of distribution (ΔG^0), thus,

$$\mathrm{R}T\ln(K) = -\Delta G^0$$

Thus,

$$\log(K) = -\frac{\Delta G}{2.303\mathrm{R}T} = \Delta G'$$

For mathematical convenience, initially, ($\Delta G'$) will be used in the algebraically arguments instead of (ΔG).

Let ($\Delta G'$) be partitioned between (m) substituent atoms or groups (e.g. H, Br, CH_2, etc.).

Then,

$$\log(K) = n_1\Delta G'_1 + n_2\Delta G'_2 + n_3\Delta G'_3 + \cdots + n_r\Delta G'_r + \cdots + n_m\Delta G'_m$$
$$= \sum_{r=1}^{r=m} n_r\Delta G'_r \qquad (1)$$

where ($\Delta G'_r$) pertains to the element (r) and (n_r) is the number of atoms of element (r) in the solute molecule.

Developing the above equation by analogy, for each of the solutes,

$$\text{Dichloromethane } \log(K_1) = \Delta G'_{\text{C}} + 2\Delta G'_{\text{H}} + 2\Delta G'_{\text{Cl}} \tag{2}$$
$$\text{Chloroform } \log(K_2) = \Delta G'_{\text{C}} + \Delta G'_{\text{H}} + 3\Delta G'_{\text{Cl}} \tag{3}$$
$$\text{Carbon tetrachloride } \log(K_3) = \Delta G'_{\text{C}} + 4\Delta G'_{\text{Cl}} \tag{4}$$
$$\text{Dibromomethane } \log(K_4) = \Delta G'_{\text{C}} + 2\Delta G'_{\text{H}} + 2\Delta G'_{\text{Br}} \tag{5}$$
$$\text{Bromoform } \log(K_5) = \Delta G'_{\text{C}} + \Delta G'_{\text{H}} + 3\Delta G'_{\text{Br}} \tag{6}$$
$$\text{Carbon tetrabromide } \log(K_6) = \Delta G'_{\text{C}} + 4\Delta G'_{\text{Br}} \tag{7}$$
$$\text{Chlorobromomethane } \log(K_7) = \Delta G'_{\text{C}} + 2\Delta G'_{\text{H}} + \Delta G'_{\text{Br}} + \Delta G'_{\text{Cl}} \tag{8}$$
$$\text{Dichlorobromomethane } \log(K_8) = \Delta G'_{\text{C}} + \Delta G'_{\text{H}} + \Delta G'_{\text{Br}} + 2\Delta G'_{\text{Cl}} \tag{9}$$
$$\text{Trichlorobromomethane } \log(K_9) = \Delta G'_{\text{C}} + \Delta G'_{\text{Br}} + 3\Delta G'_{\text{Cl}} \tag{10}$$
$$\text{Dibromochloromethane } \log(K_{10}) = \Delta G'_{\text{C}} + \Delta G'_{\text{H}} + 2\Delta G'_{\text{Br}} + \Delta G'_{\text{Cl}} \tag{11}$$

where ($\Delta G'_{\text{H}}$) is associated with interaction between a hydrogen atom and the stationary phase,

($\Delta G'_{\text{C}}$) is associated with interaction between a carbon atom and the stationary phase,

($\Delta G'_{\text{Cl}}$) is associated with interaction between a chlorine atom and the stationary phase,

and ($\Delta G'_{\text{Br}}$) is associated with interaction between a bromine atom and the stationary phase.

Equations (2) to (11) need to be defined in detail, as it will be seen that they are necessary to solve for ($\Delta G'_{\text{H}}$), ($\Delta G'_{\text{C}}$), ($\Delta G'_{\text{Cl}}$), and ($\Delta G'_{\text{Br}}$). However, it is clear that Eqs. (2) to (4) can be replaced by a general equation for the chlorine substituted methanes; likewise Eqs. (5) to (7) can be replaced by a general equation for the bromine substituted methanes and Eqs. (8) to (10) can be replaced by a general equation for the chlorine substituted bromomethanes. Similarly, Eqs. (8) and (11) are members of the bromine substituted monochloromethanes.

Thus, the general equation for the chlorine substituted methanes will be,

$$\begin{aligned}\log(K) &= \Delta G'_{\text{C}} + (4-n)\Delta G'_{\text{H}} + n\Delta G'_{\text{Cl}} \\ &= \Delta G'_{\text{C}} + 4\Delta G'_{\text{H}} + n(\Delta G'_{\text{Cl}} - \Delta G'_{\text{H}})\end{aligned} \tag{12}$$

the general equation for the bromine substituted methanes will be,

$$\begin{aligned}\log(K) &= \Delta G'_{\text{C}} + (4-n)\Delta G'_{\text{H}} + n\Delta G'_{\text{Br}} \\ &= \Delta G'_{\text{C}} + 4\Delta G'_{\text{H}} + n(\Delta G'_{\text{Br}} - \Delta G'_{\text{H}})\end{aligned} \tag{13}$$

the general equation for the chlorine substituted monobromomethanes will be,

$$\begin{aligned}\log(K) &= \Delta G'_{\mathrm{C}} + \Delta G'_{\mathrm{Br}} + (3-n)\Delta G'_{\mathrm{H}} + n\Delta G'_{\mathrm{Cl}} \\ &= \Delta G'_{\mathrm{C}} + \Delta G'_{\mathrm{Br}} + 3\Delta G'_{\mathrm{H}} + n(\Delta G'_{\mathrm{Cl}} - \Delta G'_{\mathrm{H}}) \qquad (14)\end{aligned}$$

and the general equation for the bromine substituted monochloromethanes will be,

$$\begin{aligned}\log(K) &= \Delta G'_{\mathrm{C}} + \Delta G'_{\mathrm{Cl}} + (3-n)\Delta G'_{\mathrm{H}} + n\Delta G'_{\mathrm{Br}} \\ &= \Delta G'_{\mathrm{C}} + \Delta G'_{\mathrm{Cl}} + 3\Delta G'_{\mathrm{H}} + n(\Delta G'_{\mathrm{Br}} + \Delta G'_{\mathrm{H}}) \qquad (15)\end{aligned}$$

It is seen that Eqs. (12)–(14) are linear functions of (n) and thus, curves of $\log(K)$, taken at a given temperature, against (n) for a series of substituted methanes will give a straight line with slopes and intercepts that are predicted by Eqs. (12)–(14). It should be noted that Eq. (15) is for the bromine substituted monochloro-methane and data for only two members of this series are available.

EXPERIMENTAL

The data of Martire et al.[9] are included in Table 1. The actual data published was the specific retention volume of each solute at four different temperatures, 30°C, 40°C, 50°C, and 60°C, respectively, and was reported to have been determined with a precision of better than ±2%. However, by multiplying each specific retention volume by the density of the stationary phase (*n*-octadecane) at the respective temperature, the retention volume per mL of each solute could be obtained, which is numerically equal to the distribution coefficient. The density of *n*-octadecane was obtained by direct measurement with a hydrometer at 30°C, 40°C, 50°C, and 60°C, respectively. The dielectric constant of graphite was obtained from its refractive index obtained by determining the Brewster angle where the light reflected from a polished surface is polarized. Using light from a helium/neon laser, (632.8 nm) which was plane polarized, the Brewster angle was identified as that position where the reflected light had minimum intensity (in practice, virtually zero). Then, knowing the angle between the reflected light and the refracted light is $\pi/2$, the refractive index can be determined. Finally, assuming the simple Maxwell relationship between refractive index and dielectric constant, viz.,

$$\varepsilon = \mu^2$$

where (μ) is the refractive index of the material, and (ε) is the dielectric constant of the material, the dielectric constant can then be calculated.

It should be noted that, theoretically, the Maxwell relationship is only true for lights of long wavelength, but will give a reasonably close relationship to the true value of the dielectric constant with lights of visible wavelength (cf. 632.8 nm).

Table 1. log(K) Experimentally Determined and Calculated from Enthalpy and Entropy Values

	log(K)							
Solute	Actual[a]	Calculated[a]	Actual[b]	Calculated[b]	Actual[c]	Calculated[c]	Actual[d]	Calculated[d]
Dichloromethane	1.857	1.880	1.725	1.747	1.601	1.624	1.484	1.505
Chloroform	2.326	2.285	2.172	2.133	2.027	1.992	1.891	1.856
Carbon tetrachloride	2.661	2.690	2.492	2.519	2.332	2.360	2.182	2.207
Dibromomethane	2.671	2.704	2.502	2.533	2.343	2.373	2.192	2.221
Bromoform	3.556	3.521	3.344	3.312	3.147	3.116	2.959	2.930
Carbon tetrabromide	4.310	4.338	4.063	4.091	3.831	3.859	3.613	3.639
Chlorobromo-methane	2.267	2.292	2.118	2.140	1.977	1.998	1.845	1.863
Dichlorobromo-methane	2.745	2.697	2.572	2.526	2.409	2.367	2.256	2.214
Trichlorobromo-methane	3.080	3.102	2.891	2.912	2.713	2.735	2.546	2.565
Dibromochloro-methane	3.150	3.109	2.956	2.919	2.774	2.741	2.603	2.572

[a] 30°C; [b] 40°C; [c] 50°C; [d] 60°C.

CALCULATIONS

The curves relating log(K), measured at 30°C, to the number of substituent groups that correspond to each series given by Eqs. (12)–(14) are shown in Fig. 2 and the values for the slopes and intercepts of each curve are included. It is seen that all the nine points fall on the predicted three straight lines and the indices of determination are 0.995, 0.999, and 0.995, respectively. It is also seen that Eqs. (12) and (14) should have the same slopes equivalent to $(\Delta G'_{\mathrm{Cl}} - \Delta G'_{\mathrm{H}})$ but different intercepts. In Fig. 2 they are shown to have very similar slopes of 0.402 and 0.406 but significantly different intercepts (1.193 and 2.002). Comparing Eqs. (12) and (13), it is seen that each curve should exhibit the same intercepts, namely $(\Delta G'_{\mathrm{C}} + 4\Delta G'_{\mathrm{H}})$ but different slopes $(\Delta G'_{\mathrm{Cl}} - \Delta G'_{\mathrm{H}})$ and $(\Delta G'_{\mathrm{Br}} - \Delta G'_{\mathrm{H}})$. The calculated values of the intercepts are indeed similar (1.193 and 1.173), whereas the slopes again, are very different vis. 0.402 and 0.819. The clear linear

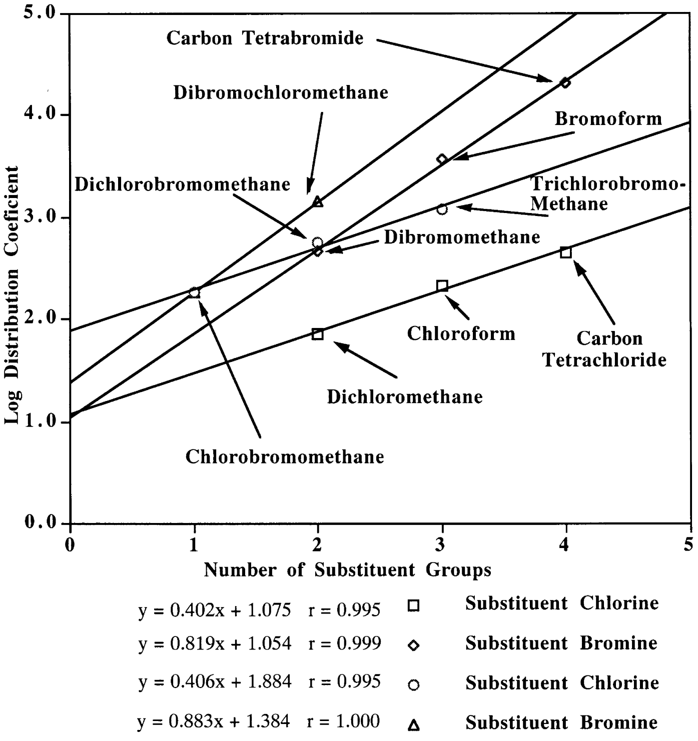

Figure 2. Graph of log(distribution coefficient) against number of substituent groups in methane (30°C).

nature of the three curves, together with the fit of the experimental data to that predicted by the equations, supports the validity of the original concepts from which the three equations were derived.

The distribution coefficients measured at different temperatures was then used to identify the thermodynamic parameters {i.e., $(\Delta G'_{\mathrm{H}})$, $(\Delta G'_{\mathrm{C}})$, $(\Delta G'_{\mathrm{Cl}})$, and $(\Delta G'_{\mathrm{Br}})$} with the aid of a computer and a simple iterative program. Values for each parameter were taken over a wide numerical range and used in Eqs. (2) to (11) to calculate the log(K). Each calculated value was subtracted from that obtained experimentally and the difference squared and summed for all the ten equations. Each time the sum was reduced, the particular values of each parameter were noted, and the process was continued until those values for the parameters that provide the minimum sum of squares was obtained. The value of each parameter for the minimum sum of squares was then recorded and the results are reported in Table 2. Subsequently, this data was used to determine the different enthalpies and entropies for each type of dispersive interaction. Using the values obtained for the different parameters the log (distribution coefficient) was calculated using Eqs. (1) to (10) and the calculated data, so obtained, are included with those experimentally determined in Table 1.

The theoretically calculated parameters are plotted against those obtained experimentally in Fig. 3 for all solutes and at all four temperatures. It is seen, that a closely linear curve is obtained with a slope very close to unity (0.998) and an intercept very close to zero (0.005). The curve shown in Fig. 3 is further evidence that validates the original concepts used to derive Eqs. (2) to (11) and the procedure by which the data was calculated. It is also seen, that the slopes and intercepts given in Fig. 2 can be calculated from the parameters obtained from the iteration program, and the comparison is shown in Table 3 for the data obtained at 30°C. It is seen, that good agreement between the two procedures is again obtained. It should be noted, that the slope and intercept values, obtained by the curve fitting procedure shown in Fig. 2, involves the use of only three data points from each series. In contrast, the values for the slope and intercepts obtained from the iteration program utilizes all the values obtained for the distribution system at 30°C, 40°C, 50°C, and 60°C, respectively.

Table 2. $(\Delta G')$ Values for the Elements Hydrogen, Carbon, Chlorine, and Bromine from Retention Data for Some Substituted Methanes

Element	$(\Delta G')$ 20°C	$(\Delta G')$ 30°C	$(\Delta G')$ 40°C	$(\Delta G')$ 50°C
Hydrogen	0.189	0.170	0.155	0.139
Carbon	0.314	0.295	0.269	0.247
Chlorine	0.594	0.556	0.523	0.490
Bromine	1.006	0.949	0.897	0.848

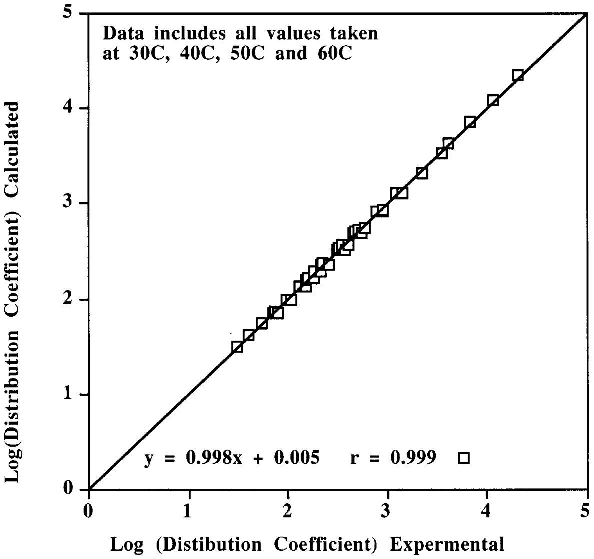

Figure 3. Graph of log(distribution coefficient) calculated against log(distribution coefficient) experimental.

Table 3. Dispersion Parameters Calculated by the Computer Program Compared with Those Obtained by the Curve Fitting Procedure Shown in Fig. 1

Series	From Fig. 1	By Iteration
Chlorine substituted methanes		
Slope $(\Delta G'_{Cl} - \Delta G'_{H})$	0.402	0.405
Intercept $(\Delta G'_{C} + 4\Delta G'_{H})$	1.075	1.070
Bromine substituted methanes		
Slope $(\Delta G'_{Br} - \Delta G'_{H})$	0.819	0.817
Intercept $(\Delta G'_{C} + 4\Delta G'_{H})$	1.054	1.070
Chlorine substituted monobromomethanes		
Slope $(\Delta G'_{Cl} - \Delta G'_{H})$	0.406	0.405
Intercept $(\Delta G'_{C} + 3\Delta G'_{H} + \Delta G'_{Br})$	1.884	1.887
Bromine substituted monochloromethanes (straight line through only two points)		
Slope $\Delta G'_{Br} - \Delta G'_{H}$	0.883	0.817
Intercept $(\Delta G'_{C} + 3\Delta G'_{H} + \Delta G'_{Cl})$	1.384	1.475

THERMODYNAMIC PROPERTIES OF THE INTERACTIVE ATOMS

Having evaluated the contribution of each atom to log(K), the standard enthalpy and standard entropy of each interacting atom can now be assessed.

Now, as already stated

$$\mathrm{R}T\ln(K) = -\Delta G^0$$

From a classical thermodynamics

$$\Delta G^0 = \Delta H^0 - T\Delta S^0$$

where (ΔH^0) is the standard enthalpy change; and (ΔS^0) is the standard entropy change.

The standard enthalpy term represents the energy involved when the solute molecule interacts by electrical forces, with the stationary phase. However, when the solute interacts with the stationary phase, it also suffers a change in freedom of movement and, thus, can no longer move in the same random manner. In the gas (mobile phase), the solute molecules have high velocities and can travel in any direction. However, when in the liquid phase, they are held by interacting molecular forces to the molecules of stationary phase and can no longer travel through the phase at high velocities, or with the same directional freedom of movement. This new motion restriction is measured as a standard entropy change. Thus, the standard energy change is made up of an actual energy change resulting from the intermolecular forces between solute and stationary phase and an entropy change that reflects the resulting restricted movement, or loss in randomness, of the solute while preferentially interacting with the stationary phase.

Now bearing in mind that

$$\Delta G' = -\frac{\Delta G^0}{2.303\mathrm{R}T}$$

Then,

$$\log K = \Delta G' = -\frac{\Delta G^0}{2.303\mathrm{R}T} = -\left(\frac{\Delta H^0}{2.303\mathrm{R}T} - \frac{\Delta S^0}{2.303\mathrm{R}}\right)$$

$$\Delta G' = -\frac{\Delta H^0}{2.303\mathrm{R}T} + \frac{\Delta S^0}{2.303\mathrm{R}} \qquad (16)$$

Further, if ($\Delta G'$) is plotted against ($1/T$) a straight line will be produced with a slope of $-\Delta H^0/2.303\mathrm{R}$ and an intercept of $\Delta S^0/2.303\,\mathrm{R}$.

The calculated values of ($\Delta G'_{\mathrm{H}}$), ($\Delta G'_{\mathrm{C}}$), ($\Delta G'_{\mathrm{Cl}}$) and ($\Delta G'_{\mathrm{Br}}$) for each element were plotted against the reciprocal of the absolute temperature, and the linear curves obtained are shown in Fig. 4. The indices of determination were 0.999, 0.997, 1.000, and 1.000 for hydrogen, carbon, chlorine, and bromine,

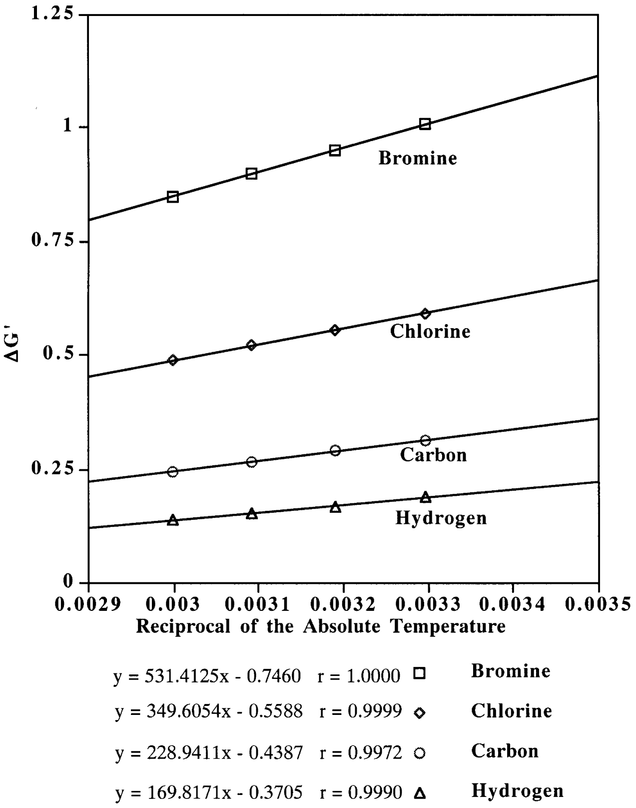

Figure 4. Graph of ($\Delta G'$) for each element against the reciprocal of the absolute temperature.

respectively. The numerical results are summarized in Table 4. A value of $1.987\,\mathrm{kcal\,K^{-1}\,mol^{-1}}$ was taken as the value for (R) and was used to calculate the values of (ΔH^0) and (ΔS^0) for each element, which are also included in Table 4. The linear curves shown in Fig. 4 not only provide additional support for the theoretical concepts postulated, but also confirm that the experimental measurements were made with great care, accuracy, and precision.

It is seen from Eq. (16) and the results shown in Table 4, that (ΔH^0) and (ΔS^0) for each element are both negative. A negative value for (ΔS^0) means that the entropy is reduced when the atom moves into the environment of the stationary phase from the gas phase and the atoms are more organized and less random. A negative value or (ΔH^0) means that heat is evolved when interaction takes place in the stationary phase as a result of the forces between the atom and the *n*-octadecane.

Table 4. Standard Free Enthalpies and Entropies for the Elements Hydrogen, Carbon, Chlorine, and Bromine

Element	Slope $\Delta H^0/2.303\mathrm{R}$	Intercept $\Delta S^0/2.303\mathrm{R}$	ΔH^0 kcal mol^{-1}	ΔS^0 kcal $\mathrm{K}^{-1}\mathrm{mol}^{-1}$
Hydrogen	169.8	−0.3705	−777	−1.695
Carbon	228.9	−0.4387	−1,047	−2.007
Chlorine	349.6	−0.5588	−1,600	−2.557
Bromine	531.4	−0.7460	−2,432	−3.413

In addition, it is clear from Table 4 that the standard entropy term increases with the standard enthalpy term. This relationship between standard entropy and standard enthalpy has been reported many times in the literature (e.g. Ref. 1). A graph of (ΔH^0) against (ΔS^0) for each element is shown in Fig. 5. It is seen that, again, there is excellent linear correlation between (ΔH^0) and (ΔS^0) (index of determination 1.000). The excellent linear correlation again brings credit to the experimental work of Martire and his group. In addition, it demostrates the need to deal exclusively with one type of interaction, only, if a true linear correlation between (ΔH^0) against (ΔS^0) is to be achieved.

From a theoretical point of view, this linear relationship between standard enthalpy and standard entropy is to be expected. An increase in enthalpy indicates

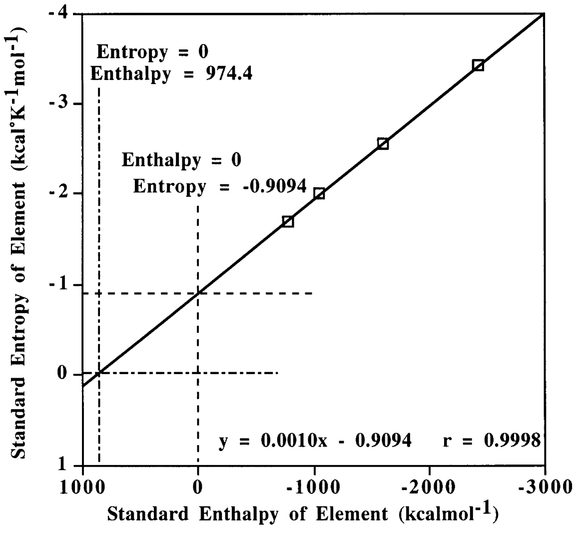

Figure 5. Graph of the standard entropy against standard enthalpy for each element.

that more energy is used up in the interaction of the atom with the molecules of the stationary phase. This means that the inter-atomic/molecular forces are stronger and, thus, the stationary phase molecules hold the atoms more tightly. In turn, this would reduce the freedom of movement and random nature of the atom, which will result in a corresponding change in standard entropy. It follows that, unless other significant retentive factors are present, any change in standard enthalpy will be accompanied by a proportional change in standard entropy. The simple proportional relationship between (ΔH^0) and (ΔS^0) shown in Fig. 5 can be expressed as follows,

$$\Delta S^0 = \phi \Delta H^0 + \psi$$

where (ϕ) and (ψ) are constants.

For the specific elements examined,

$$\Delta S^0 = 0.00104\,\Delta H^0 - 0.9094 \qquad (18)$$

Equation (18) is quite informative. It is seen that when (ΔH^0) is zero, that is when, theoretically, there are no forces between the element and the stationary phase the standard entropy is -0.9094. This reflects the change in entropy that occurs when the environment of the element changes from a gas to a liquid. Consequently, in this case (ψ) represents, what might be termed, the standard phase transfer entropy.

Alternatively, if there is no change in entropy, then from Eq. (18),

$$\Delta H^0 = \frac{0.9094}{0.00104} = 874.4$$

This means, that to ensure there is no standard energy change when transferring from one phase to the other, 874.4 kcal mol^{-1} must be given to the system to counteract the natural change in entropy. This situation could never occur in GC, but is conceivably possible in LC. It is also seen that (ϕ) is the incremental increase in entropy for unit increase in enthalpy.

In due course, this relationship may be useful in predicting the standard free energy of a given distribution and, thus, predict retention after having established the magnitude of the standard enthalpy. It should be emphasized, however, that this simple linear relationship has only been demonstrated for dispersive interactions and for four elements only. At this time, the relationship cannot be assumed to be true for other elements (although it would appear likely) or for other types of interaction.

It now remains to determine if the standard free enthalpy can be related to other physical properties of the distribution system for the elements concerned. The interactions are solely dispersive, as determined by the conditions of the experiments. As a first approximation, the interaction energy involved with dispersive forces between like molecules has been shown to be[9] a function of the molar polarizability.

Now, the polarizability (α_p) can be expressed by the function

$$\frac{\varepsilon - 1}{\varepsilon + 2} = \frac{4}{3}\pi n_v \alpha_p$$

where (ε) is the dielectric constant of the material, and (n_v) is the number of molecules per unit volume.

In addition,

$$\frac{4}{3}\pi N_A \alpha_p = \frac{(\varepsilon - 1)}{(\varepsilon + 2)}\frac{M}{\rho} = P_M$$

where (ρ) is the density of the medium, (M) is the molecular or atomic weight, (N_A) is Avogadro's Number, and P_M is the molar (or atomic) polarizability, noting that the number of molecules per unit volume is $N\rho/M$.

If the dispersive interactive energy, is directly related to the standard enthalpy of interaction, then, consequently,

$$\Delta H^0 \propto P_M$$

The physical constants of the elements necessary to calculate their atomic polarizability are given in Table 5[9,10] The standard enthalpy for hydrogen, carbon, chlorine, and bromine were plotted against their atomic polarizability and the resulting linear curve is shown in Fig. 6 (index of determination 0.996). There was some uncertainty with respect to the choice of pertinent data for carbon. Although, the dielectric constants of graphite and diamond are very similar, the densities of graphite and diamond are significantly different. It was necessary to decide which material was more likely to simulate the carbon atom in methane. It would appear that the carbon in graphite more accurately simulated the carbon in an aromatic ring, such as benzene, than an aliphatic carbon similar to that in methane. The data for diamond was, therefore, chosen for the

Table 5. The Physical Constants of the Elements Necessary to Calculate Their Atomic Polarizability

Element	Atomic Weight	Density (g/mL)	Dielectric Constant	Atomic Polarizability
Hydrogen	1.00	1.78(8) (20.4K)	1.228(8) (20.4K)	0.040
Carbon	12.00	3.20(8) (Diamond)	5.5 (20°C) (Diamond)	2.25
Chlorine	35.45	1.557(8) (−34°C)	2.10(8) (−50°C)	6.11
Bromine	79.91	3.12(8) (20°C)	3.09(8) (20°C)	10.51

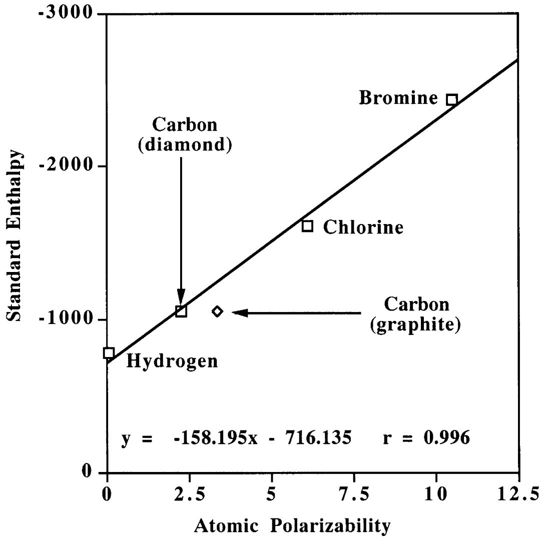

Figure 6. Graph of standard enthalpy against atomic polarizability.

correlation but the point for graphite is included in Fig. 6. The simple linear relationship between standard free enthalpy and atomic polarizability might lead to the calculation of standard enthalpy, standard entropy, and, thus, retention data from basic physical and electrical properties of solute and phase system.

From Fig. 5,

$$\Delta H^0 = \varphi \alpha_p + \xi \qquad (19)$$

where (φ) and (ξ) are constants.

It should be noted, that although there appears to be a linear relationship between polarizability and standard free enthalpy of interaction, there is a constant of significant magnitude in the equation (ξ). This indicates that there is a contribution to the standard free enthalpy that is independent of the atomic polarizability of the element concerned.

CONCLUSIONS

Apportioning the standard free energy of a distribution system between the atoms, or groups of a solute molecule, allows the different interactive character of each group or atom to be identified. If this is carried out for a distribution system in which solely dispersive interactions are active, some of the factors that control the dispersive interaction can be disclosed. A thermodynamic analysis of the distribution of some substituted methanes in this manner has demonstrated a linear relationship between the standard free enthalpy and standard free entropy of the interactive contribution from each substituent atom. This indicates, that if either the standard enthalpy or standard entropy was known, the other could be calculated. In addition, it is shown that there is a linear relationship between the atomic polarizability of the interacting atom and its standard free enthalpy of interaction. This also leads to the possibility of calculating the standard enthalpy, hence, the standard entropy and, thus, the retention of a solute, from its molecular structure and the physical and electrical properties of it component atoms. However, there appears to be a relatively large contribution to the standard enthalpy of interaction that is independent of the polarizability of the interacting atom. This may indicate that either there is some other physical property that adds to the standard enthalpy, other than that predictable from the polarizability of the atom. Alternatively, the constant may be a function of some property of the stationary phase with which the atom is interacting. Reiterating Eq. (1),

$$\log(K) = \sum_{r=1}^{r=m} n_r DG'_r$$

thus,

$$\ln(K) = -\sum_{r=1}^{r=m} n_r \Delta G_r$$

where the symbols have the meaning previously ascribed to them.
Expanding,

$$\ln(K) = -\sum_{r=1}^{r=m} n_r \left(\frac{\Delta H_r{}^0}{\mathrm{R}T} - \frac{\Delta S_r{}^0}{\mathrm{R}} \right)$$

substituting for (ΔS^0) from Eq. (16) and factoring,

$$\ln(K) = -\sum_{r=1}^{r=m} n_r \frac{\Delta H_r{}^0}{\mathrm{R}} \left(\frac{1}{T} - \phi \right) - \frac{\psi}{\mathrm{R}}$$

Substituting for (ΔH^0) from Eq. (18),

$$\ln(K) = -\sum_{r=1}^{r=m} n_r \frac{(\varphi \alpha_{p(r)} + \xi)}{\mathrm{R}} \left(\frac{1}{T} - \phi \right) - \frac{\psi}{\mathrm{R}} \tag{20}$$

where, (ψ) is the standard phase-transfer entropy, (ϕ) is the change in standard entropy for unit change in standard enthalpy, (φ) is the proportionality constant relating polarizability to standard enthalpy, and (ξ) is that part of the standard enthalpy that is independent of the polarizability of the interacting component.

Equation (20) could be the first fragment of an alternative preliminary model for predicting the magnitude of a distribution coefficient. The equation needs, however, much more development and equations that account for polar and ionic interactions included.

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