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Influence of Interatomic Forces on Paraffin Properties

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EMPIRICAL formulas giving excellent agreement with observed molecular refractions, molecular volumes, heats of formation, and boiling points of the paraffin isomers have recently been reported by Platt[1] in this journal. The variables used in these formulas are based on the assumptions of additivity of bond properties and of interaction between different bonds in a molecule. The agreement between observed and calculated values should, however, not be taken as evidence for the influence, additive or constitutive, of bonds upon physical properties; the same basic formula may be derived by a different approach.

The forces acting between two atoms will depend on their kind and distance. Without any assumption as to the nature of these interactions, the sum of the forces acting between n pairs of atoms, of kind x and y, all of which are separated by an equal distance j, will be $k_{xyj}n$. For a paraffin, let n_j be the number of C−C pairs separated by j carbon-carbon bonds, P_{j+1} the number of C−H pairs separated by one carbon-hydrogen and j carbon-carbon bonds, and q_{j+2} the number of H−H pairs separated by two carbon-hydrogen and j carbon-carbon bonds. The sum of all these interactions, or atom-pair contributions to the property G, is

$$G-a_0=\sum_j a_jn_j+\sum_k b_kp_{k+1}+\sum_i c_iq_{i+2}.$$

The structure of paraffins is sufficiently defined by the relations of the carbon atoms, so that the p and q terms may be omitted. If N is the number of carbon atoms, $n_1=N-1$. Platt's coefficients are related to the variables n_j by $\Sigma_\alpha f_\alpha(j-1)=2n_j$. This gives:

$$G=a_0+\sum_j a_jn_j=a_0+a_1(N-1)+\frac{\partial_2}{2}\sum_\alpha f_{\alpha 1}+\frac{\partial_3}{2}\sum_\alpha f_{\alpha 2}+\cdots.$$

This equation is identical, except for the form of the constants, with the equation developed by assuming bond interactions. The difference is essentially one of terminology, but it is believed that the viewpoint presented here is clearer and more firmly founded upon physical experience.

A simple empirical equation, based on the variables defined above, is $G=C_N+(k/N^2)\,\Sigma_j\, j\cdot n_j+b\cdot n_3$, where C_N is a function of N and therefore constant within each group of isomers. C_N may be eliminated by confining the calculations to the differences ΔG between the value of a property for a branched paraffin and its normal isomer. Values of k and b have been evaluated by the method of least squares from the observed data for the paraffins C_5 to C_8, as compiled in the API tables.[2] The average deviations between calculated and observed values for these paraffins are compared for the methods given by Platt,[1] by Taylor, Pignocco, and Rossini,[3] and in this report. (See Table I.)

TABLE I.

	Rp^{20} Molecular refraction ml/mole	V^{20} Molecular volume ml/mole	t^{760mm} Boiling point °C	$\Delta Hf°(gas)$[2] Heat of formation kcal./mole
Empirical constants				
k	−0.45	−14.2	+98	+20.7
b	−0.152	− 2.58	+ 5.5	+ 1.3
Average deviations				
Platt	±0.0106	± 0.22	± 0.67	± 0.19
TPR	±0.013	± 0.16	± 0.55	—
Wiener	±0.013	± 0.23	± 0.53	± 0.33

The accuracy of all three equations is seen to be of the same order of magnitude, except for the heat of formation, where Platt's formula is greatly preferable to the equation discussed here. It should be noted, however, that the latter employs only two empirical parameters, as compared to six and seven in the methods used by Platt and by Taylor, Pignocco, and Rossini, respectively. This gives this equation the advantage of simplicity and ready evaluation; furthermore, the addition of one or two well-chosen structural variables will probably increase its accuracy, while keeping the number of parameters below five.

The calculations for the boiling points have been reported,[4] the symbols used being w for $\Sigma_j\, j\cdot n_j$ and p for n_3. Details of the work on the other properties will be published later.

[1] J. R. Platt, J. Chem. Phys. 15, 419 (1947).
[2] American Petroleum Institute Research Project 44 at the National Bureau of Standards. *Selected Values of Physical and Thermodynamical Properties of Hydrocarbons.*
[3] W. J. Taylor, J. M. Pignocco, and F. D. Rossini, J. Research Nat. Bur. Stand. 34, 413 (1945), RP 1651.
[4] H. Wiener, J. Am. Chem. Soc. 69, 17 (1947).