This Week's Citation Classic

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Franklin J L. Prediction of heat and free energies of organic compounds. *Ind. Eng. Chem.* 41: 1070-6, 1949.

This paper shows that the thermodynamic properties of gaseous organic molecules can be expressed as the sum of constants characteristic of the various groups that make up the molecule. Tables of group values for the important thermodynamic functions are included. [The *SCI*® indicates that this paper has been cited over 160 times since 1961.]

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"This paper was the result of a need for thermodynamic data on several hydrocarbons. I was a member of the research staff of Humble Oil & Refining Co. and had been requested to evaluate a process that seemed to have some promise of commercial application. In order to do this, I needed enthalpies and entropies of several compounds, mainly hydrocarbons. However, to my disappointment some of these data were not available. I was faced with the alternatives of giving up or developing empirical relationships that would enable me to obtain at least reasonable approximations of the needed properties. I elected the latter approach.

"Upon examining the available data, it became evident that the heats of formation of normal paraffin changed by approximately -5 kcal/mol with each addition of a methylene group. Further, successive additions of methylene groups to aromatics, olefins and several hydrocarbon derivatives, also caused an incremental change of about -5 kcal/mol.

"From this, I inferred that other characteristic groups of organic molecules might exhibit similar additive behavior. Pitzer had shown from statistical mechanical considerations that the heat and free energy functions of gaseous normal paraffins could be expressed as additive functions of the number of carbon atoms and constants characteristic of the temperature, symmetry, bond stretching, bending, etc.[1] I was able to show that these relations could be modified to include branched paraffins and extended to enthalpies, and heats and free energies of formation.

"From these considerations it was evident that for each of these thermodynamic properties it would be possible to assign characteristic values to the various groups that make up a molecule. The sum of the group values would be the thermodynamic property of the molecule. I accordingly computed from available data, constants for various hydrocarbon groups at several temperatures for the functions:

$$\frac{H^0-H^0_0}{T}, \quad \frac{F^0-H^0_0}{T}, \quad H^0-H^0_0, \quad F^0-H^0_0$$

$\Delta H°_f$ and $\Delta F°_f$. In addition, group constants for $\Delta H°_f$ and $\Delta F°_f$ for several nonhydrocarbon groups were computed. Tables of group constants for the various thermodynamic functions were prepared and included in a company report.

"This study was undertaken to provide thermodynamic constants for my own use. It seemed evident, however, that it might also be useful to others and, accordingly, the results were submitted as a paper for publication. I have found the method to be useful over the ensuing years. I presume that the reason the paper has been cited frequently is that others have also found the method useful."

Reference

1. **Pitzer K S.** The vibration frequencies and thermodynamic functions of long chain hydrocarbons.J. *Chem. Phys.* 8:711-20, 1940.