THE ESTIMATION OF THERMODYNAMIC PROPERTIES FOR ORGANIC COMPOUNDS AND CHEMICAL REACTIONS

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The thermodynamic calculation of free-energy changes for compounds and chemical reactions can be used as a criterion of the thermodynamic stability and feasibility of the processes considered. The theoretical calculation of thermodynamic properties from molecular parameters, spectroscopic data, and statistical mechanics is well established. Owing to the inherent mathematical difficulties and the lack of experimental information, the results for polyatomic molecules established by this method are limited. A number of semi-empirical and empirical methods for the calculation of the thermodynamic data for organic compounds have been proposed since the classical work of Parks and Huffman.[1] A purpose of this Review is to outline the thermodynamic approach, the sources of data, and to survey the methods of calculation with particular reference to organic compounds.

The calculation of the free-energy change for a chemical reaction requires a knowledge of the heat of reaction and the entropy change at the temperature in question. Ordinarily the calculations are referred to the ideal state by means of the well-known relation :

$$\Delta G^0_{298} = \Delta H^0_{298} - T\Delta S^0_{298} \quad . \quad . \quad . \quad (1)$$

If the data are available for calculation of the heat of reaction and entropy change at 25° c, and the heat-capacity data are known over the temperature range in question, the free-energy change, and equilibrium constant, can be readily calculated at a number of temperatures with the modified form of the van't Hoff isochore :

$$\Delta G^0_T = I_H + (\Delta a - I_S)T - \Delta aT \ln T - 1/2\Delta bT^2 - 1/6\Delta cT^3 \quad (2)$$

where I_H and I_S are constants of integration evaluated from the equations

$$\Delta H^0_T = I_H + \Delta aT + 1/2\Delta bT^2 + 1/3\Delta cT^3 \quad . \quad . \quad (3)$$

$$\Delta S^0_T = I_S + \Delta a \ln T + \Delta bT + 1/2\Delta cT^2 \quad . \quad . \quad (4)$$

by using ΔH^0_{298} and ΔS^0_{298} respectively. The constants Δa, Δb, and Δc are the differences of the constants of the heat-capacity equations, *i.e.* :

$$\Delta a = \sum (a)_p - \sum (a)_r \quad . \quad . \quad . \quad . \quad (5)$$

where the heat capacity is expressed as function of temperature by

$$C_P = a + bT + cT^2 \quad . \quad . \quad . \quad . \quad (6)$$

and the subscripts p and r refer to products and reactants respectively.

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[1] Parks and Huffman, " The Free Energies of Some Organic Compounds ", F. C. S. Monograph No. 60, The Chemical Catalogue Co., Inc., New York, 1932.

When the thermodynamic functions from statistical thermodynamic calculations :

Heat-content function, $(H^0 - H^0_0/T)$; entropy, S^0 ;
Free-energy function, $-(G^0 - H^0_0/T)$; heat capacity, C^0_P

are available for both reactants and products, the free-energy change can be calculated precisely without recourse to the van't Hoff isochore. A knowledge of the heat of reaction is still essential to evaluate the zero-point energy, ΔH^0_0, *i.e.* :

$$\Delta H^0_0 = \Delta H^0_{298} - \Delta(H^0_{298} - H^0_0) \quad . \quad . \quad . \quad (7)$$

where ΔH^0_{298} is the heat of reaction at 25° C and $\Delta(H^0_{298} - H^0_0)$ is the difference of heat content for products and reactants. ΔH^0_0 is not purely an experimental quantity, but is calculated by using the values of $(H^0_{298} - H^0_0)$ and as such is subject to the errors in the latter.

It follows from the free-energy function that :

$$\Delta G^0/T = \Delta H^0_0/T + \Delta[(G^0 - H^0_0)/T] \quad . \quad . \quad (8)$$

where $\Delta = \sum_p - \sum_r$ for that function, and p and r are the products and reactants of the process under consideration.

Comprehensive tabulations of the separate thermodynamic functions over a temperature range up to 1500° K have been published by Rossini and his associates [2] as part of a programme of research for the American Petroleum Institute. A survey of the entropies, statistical calculations, and thermochemistry covering the past fifteen years has also appeared recently.[3]

The combined functions, $*G^0/T$ and $*H^0_T$, defined by the equations :

$$-*G^0/T = -[(G^0 - H^0_0)/T] - H^0_0/T \quad . \quad . \quad (9)$$

$$*H^0_T = (H^0_T - H^0_0) - H^0_0 \quad . \quad . \quad . \quad (10)$$

have also been recommended [4] for free-energy calculations, having the advantage of some simplicity in use over the separate functions (*e.g.*, the heat-content function and the free-energy content function). These are not in general use today. Pitzer [5] has pointed out that in any revision of the tabulated data, owing to more precise heats of combustion data, only the H^0_0 values need be changed in the tables of the separate functions, whereas with the combined functions the whole tables of $-*G^0/T$ and $*H^0_T$ would require change. The values of combined functions also are generally larger than the separate functions, and change more rapidly with temperature. Graphical treatment and interpolations are less difficult with the separate thermodynamic functions.

Statistical Thermodynamic Calculations

The calculation of the thermodynamic functions for polyatomic systems from molecular and spectroscopic data and statistical thermodynamics is

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[2] " Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds ", Carnegie Press, Pittsburgh, 1953.

[3] Rossini, Wagman, Evans, and Prosen, *Ann. Rev. Phys. Chem.*, 1950, **1,** 1.

[4] " International Critical Tables ", 1929, **3—5,** McGraw Hill Co., New York.

[5] Pitzer, *Chem. Rev.*, 1940, **27,** 39.

well established and described in most advanced text-books in physical chemistry. Attention is directed in this section to the results and equations in this field founded on this theoretical treatment, for comparison with the empirical methods to be discussed in the next part.

Rigid Rotator–Simple Vibrator.—A clear discussion of the treatment of a polyatomic molecule as a rigid rotator–simple vibrator, based on the partition function and the energy distribution in an assembly of particles and energy levels, can be found in the books by Herzberg,[6] Rossini,[7] and Gurney.[8] Tables of equations with the numerical constants used in practice for calculating the data for the monatomic, linear, and non-linear polyatomic molecules have been compiled by Rossini and his associates.[2] Inspection of the equations, summarised in Table 1, for the most general case, the non-linear polyatomic molecule, shows the basic principle underlying all the empirical and semi-empirical methods for the calculation of thermodynamic properties.

TABLE 1. *Equations for calculating the translational, rotational (rigid rotator), and vibrational (harmonic oscillator) contribution to the thermodynamic functions for non-linear polyatomic molecules in the ideal-gas state at atmospheric pressure*

(a) *Translation contributions*

(i) $[(H^0 - H^0_0)/T]_t = 4{\cdot}9680$

(ii) $-[(G^0 - H^0_0)/T]_t = 6{\cdot}8635 \log M + 11{\cdot}4392 \log T - 7{\cdot}282$

(iii) $(C_p)_t = 4{\cdot}9680$

(b) *Rotation contributions*

(i) $[(H^0 - H^0_0)/T]_r = 2{\cdot}9808$

(ii) $-[(G^0 - H^0_0)/T]_r = 2{\cdot}2878 \log (I_A \times I_B \times I_C \times 10^{117}) + 6{\cdot}8635 \log T - 4{\cdot}5757 \log s - 3{\cdot}0140$

(iii) $(C_p)_r = 2{\cdot}9808$

(c) *Vibration contributions*

(i) $[(H^0 - H^0_0)/T]_v = 1{\cdot}9872 \sum_i [x_i/(e^{x_i} - 1)]$

(ii) $-[(G^0 - H^0_0)/T]_v = -1{\cdot}9872 \sum_i [\ln (1 - e^{-x_i})]$

(iii) $(C_p)_v = 1{\cdot}9872 \sum_i [x_i^2 e^{x_i}/(e^{x_i} - 1)^2]$

where $x_i = (w_i hc/kt)$, w_i being one of the fundamental frequencies (in wave-numbers)

In the translational contributions, the only parameter specific for each molecule is the molecular mass (M). It follows that a contribution relating to a structural modification by a simple group or atom would thus be additive with reference to the translational contribution.

The vibrational contributions are calculated with reference to standard

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[6] Herzberg, " Infrared and Raman Spectra ", D. Van Nostrand Co., New York, 1945.

[7] Rossini, " Chemical Thermodynamics ", J. Wiley & Sons, Inc., New York, 1950.

[8] Gurney, " Introduction to Statistical Mechanics ", McGraw Hill Co., New York, 1951.

tables of Einstein functions in term of the fundamental vibrational modes (w_i). The fundamental vibrations of a polyatomic system are, in the first approximation, the modes of a simple harmonic oscillator, in which the displacements of the atoms about any bond are governed by the force constant for that bond and the atomic masses. It has been recognised for some time that certain bond vibrational modes, and even group frequencies, are constant, independently of the rest of the polyatomic system. This is basically related to the invariance of the force constants for the bonds in the system under consideration. Therefore the vibrational contribution to the thermodynamic property introduced by a simple structural change would be additive in the first approximation, especially if the group contribution has been derived from an environment quite similar to that in which it is found in the final molecule. Structural modification such as the introduction of double-bond conjugation, or strong polar groups, will influence the force constants of a particular group.

Inspection of the rotational contribution to the thermodynamic properties shows that its value is dependent on the products of the moments of inertia ($I_AI_BI_C$), and the symmetry number (s), both specific parameters for each polyatomic system. Structural modifications by atomic or group increments would be essentially additive in nature with reference to the products of the moments of inertia since the mass changes for such increments are only a small part of the total mass of the parent polyatomic system. The structural increments, however, are obtained from lower members or related compounds in the class under consideration. The symmetry number of each polyatomic system under consideration must be taken into account in this calculation. Thus the rotational contributions to the thermodynamic properties are additive providing cognisance is taken of the differences in the symmetry numbers, and in the potential barriers restricting internal rotation. This correction is considered in more detail in a later section of this Review dealing with the estimation of thermodynamic properties by the method of group equations.

The calculation of the thermodynamic functions from the statistically derived equations (Table 1) requires a knowledge of the vibrational frequencies associated with the fundamental modes of the polyatomic systems as well as the molecular parameters of bond angles and bond lengths. With these data, the vibrational contribution is obtained by reference to standard tables [9, 10] listing the contributions to the thermodynamic functions for a Planck–Einstein oscillator in one degree of freedom. The secular equation suggested by Hirschfelder [11] provides a general method for calculation of the products of the moments of inertia for unsymmetrical molecules.

Restricted Internal Rotation.—In the earlier treatments, completely free rotation was assumed about single C–C or similar skeletal bonds in a poly-

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[9] Sherman and Ewell, *J. Phys. Chem.*, 1942, **46**, 641.

[10] Dole, " Introduction to Statistical Thermodynamics ", Prentice Hall Inc., New York, 1954.

[11] Hirschfelder, *J. Chem. Phys.*, 1940, **8**, 431.

atomic system. The results obtained were too high to agree with the experimental data for these molecules. This problem was resolved in the recognition by Pitzer [12] and by Pitzer and Gwinn [13] of a state of hindered or restricted internal rotation about single bonds. The status of the problem of hindered rotation about single bonds in hydrocarbons and related molecules has been the subject of recent reviews by Pitzer [14] and Aston.[15] In ethane, the simplest molecule with restricted internal rotation, it is concluded that the barrier is very close to a three-fold cosine-type function in shape, and about 2750—3200 cal./mole in magnitude. For the more complex systems the cosine shape of barrier is ordinarily assumed. Where several equivalent rotations are possible, the barriers are assumed in practice to be equal and independent. The stable configuration in these systems is the staggered position. The origin of the potential barriers seems to lie in a repulsive interaction of the electron pairs of two single bonds in adjacent multivalent atoms. At present no satisfactory theoretical treatment or explanation for this has been achieved. In complex hydrocarbons the exact solution of the problem is even more difficult owing to additional possibilities of internal rotational isomers or tautomers corresponding to non-equivalent configurations of different energies. The simplest example of this was found with *n*-butane,[16] where, owing to restricted rotation about the middle bond, three configurations of minimum energy, one *trans*, and two *gauche* or skew forms, are present.

In the calculation of the precise thermodynamic functions for the simpler polyatomic systems, the tables of Pitzer [12] and Pitzer and Gwinn,[13] based on the simple cosine type of potential barrier, provide a very convenient reference for the contributions associated with the hindered rotation of a given group. Halford [17] and Blade and Kimball [18] have discussed methods by which these contributions can be calculated for other shapes of barriers.

The contributions due to nuclear spins cancel between the products and reactants, and contributions due to electronic excitations are negligible except for systems undergoing changes of very high energies. It follows from this outline that, when the spectroscopic data and molecular parameters are known, the thermodynamic functions can be calculated, leading to values frequently more accurate than those hitherto measured. This approach is not very satisfactory for the more complex molecules since a knowledge of the normal co-ordinates of vibration and the assignment of fundamental frequencies is required. Owing to the inherent mathematical difficulties in the former and lack of spectroscopic data the application of this rigorous treatment to polyatomic molecules has been limited.

Long-chain Hydrocarbons.—The problem of calculating the thermodynamic functions for long-chain molecules, with particular attention to

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[12] Pitzer, *J. Chem. Phys.*, 1937, **5**, 469, 473, 752.

[13] Pitzer and Gwinn, *ibid.*, 1942, **10**, 428.

[14] Pitzer, *Discuss. Faraday Soc.*, 1951, **10**, 66.

[15] Aston, *ibid.*, p. 73.

[16] Szasz, Sheppard, and Rank, *J. Chem. Phys.*, 1948, **16**, 704.

[17] Halford, *ibid.*, 1947, **15**, 645; 1948, **16**, 410, 560.

[18] Blade and Kimball, *ibid.*, 1950, **18**, 630.

normal and branch-chain paraffins, has been considered by Pitzer[19] and by Person and Pimentel.[19a] A vibrational analysis of the skeletal modes, based on the treatment of the long-chain hydrocarbon by an infinite chain approximation method, established that the skeletal frequencies fall into two groups, a narrow band near 1000 cm.$^{-1}$ and a broad band from 0 to 460 cm.$^{-1}$. The partition function was set up as a product of the complete classical functions. The correcting factors for the contributions arising from the hydrogen atom vibrations were added later. The resulting formula:

$$X = [F_0(T)] + n_1[\mathrm{C{-}C_{str.}}] + n_2[\mathrm{C{-}C_{bend.}}] + n_3[I\cdot\mathrm{Rot}] + n_4[\mathrm{CH_3}] + n_5[\mathrm{CH_2}] + n_6[\mathrm{CH}] + F_{\mathrm{steric}} + F_\sigma \quad . \quad . \quad (11)$$

expresses the thermodynamic functions of these complex systems as additive functions of the number of carbon atoms, N, and constants characteristic of temperature, bond stretching and bending, internal rotation, and steric and symmetry factors. The exact nature of these additive increments is shown in Table 2. $F_0(T)$ is a function of temperature and pressure only; $[\mathrm{C{-}C_{str.}}]$, $[\mathrm{C{-}C_{bend.}}]$, and $[I\cdot\mathrm{Rot}]$ are dependent on the generalised 1000-cm.$^{-1}$ stretching frequency, temperature, and the restricted rotor functions.[12] The term F_{steric} is a correction for steric repulsions not taken into account by the $[I\cdot\mathrm{Rot}]$ term owing to the simplifying assumption of treating the potential barriers in these long-chain molecules as the simple symmetrical threefold cosine type observed in ethane. The partition function in F_{steric} is calculated from the number of positions of steric interaction obtained by direct inspection of a molecular model of the specific paraffin in question. The remaining terms in equation (11) represent the contributions to the thermodynamic function for the methyl, methylene, and methylidene groups, and are calculated from a knowledge of the generalised vibrational frequencies for the appropriate bending and stretching modes in these groups. For a normal paraffin of N carbon atoms, n_1, n_2, n_3, n_4, n_5, and n_6 are equal to $N - 1$, $N - 2$, $N - 3$, 2, $N - 2$, and 0 respectively. The values for the additive terms in equation (11) above have been calculated, and are tabulated in units of cal./deg. for the temperature range from 298·1 to 1500° K for the heat-content function and free-energy function.[5, 19] Ready application of these results to the estimation of these data for the more complex hydrocarbon molecules is thus possible. Pitzer has shown that the entropies calculated from this generalised equation agree within experimental error (± 1 cal./deg.) with the observed entropies as far as *n*-octane, the highest member for which an accurate experimental entropy has been reported. The method is thus capable of yielding approximate values with the expectation of considerable accuracy.

Semi-empirical Calculations

The principal effort in the semi-empirical approach has been to predict the properties of substances from a knowledge of the data for a relatively small number in any homologous series or class of compounds. The

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[19] Pitzer, *J. Chem. Phys.*, 1940, **8**, 711.

[19a] Person and Pimentel, *J. Amer. Chem. Soc.*, 1953, **75**, 532.

TABLE 2. *Generalised additive factors in the Pitzer formula for calculating thermodynamic functions of long-chain paraffin hydrocarbons*

	$-\left(\frac{G^0 - H^0_0}{T}\right)$	$\left(\frac{H^0 - H^0_0}{T}\right)$	C
$F_0(T)$	$4{\cdot}274 + \boldsymbol{R} \ln T - \boldsymbol{R} \ln P$	$4\boldsymbol{R}$	$4\boldsymbol{R}$
$[\mathrm{C{-}C}]_{\mathrm{str.}}$	$0{\cdot}75 + \mathrm{Ein}\left(\frac{\boldsymbol{h}v_1'}{\boldsymbol{k}T}\right)$	$\mathrm{Ein}\left(\frac{\boldsymbol{h}v_1'}{\boldsymbol{k}T}\right)$ where $v_1'/c = 1000$ cm.$^{-1}$	$\mathrm{Ein}\left(\frac{\boldsymbol{h}v_1'}{\boldsymbol{k}T}\right)$
$[\mathrm{C{-}C}]_{\mathrm{bend.}}$	$-\,11{\cdot}275 + \boldsymbol{R} \ln T + \frac{413}{T} - \frac{14{,}200}{T^2}$	$\boldsymbol{R} - \frac{413}{T} + \frac{28{,}400}{T^2}$	$\boldsymbol{R} - \frac{28{,}400}{T^2}$ $(T \geqslant 250)$
$[I{\cdot}\mathrm{Rot}]$	$\frac{1}{2}\boldsymbol{R} \ln T - 0{\cdot}55 + \frac{170}{T}$ $- \frac{F - F_f}{T}\left(\frac{3600}{\boldsymbol{R}T}\right)$	$\frac{H}{T}\left(\frac{3600}{\boldsymbol{R}T}\right) - \frac{170}{T}$	$C\left(\frac{3600}{\boldsymbol{R}T}\right)$
F_σ	$-\,\boldsymbol{R} \ln \sigma$	0	0
$F_{\mathrm{steric.}}$	$\boldsymbol{R} \ln Q$ $Q = \exp(-\,E_i/\boldsymbol{k}T)$	$\boldsymbol{R}(Q'/Q)$ $Q' = (E_i/\boldsymbol{k}T)[\exp(-\,E_i/\boldsymbol{k}T)]$	$RQ''/Q - (Q'/Q)^2$ $Q'' = (E_i/\boldsymbol{k}T)^2[\exp(-\,E_i/\boldsymbol{k}T)]$

regularity and systematisation found in organic compounds applies to both chemical and physical properties to a very large extent. With reference to thermodynamic data, the interest has been to apply this systematisation empirically, seeking correlations that enable the prediction of free energies, heats of formation, entropies, and heat capacities for compounds for which experimental data or statistical thermodynamic data do not exist. The contributions in this field are covered under three basic topics in this section : (i) Modifications in molecular structure and thermodynamic properties, (ii) estimation of thermodynamic properties of organic compounds from group contributions, and (iii) the use of group equations for estimating thermodynamic properties. In addition, methods proposed specifically for the estimation of heats of formation and heat capacities are reviewed. The contributions are discussed in historical order. The various methods are compared later.

Modification in Molecular Structure and Thermodynamic Properties.—Parks and Huffman's work is classic in this field.[1] Stimulated by the publication of several earlier theoretical papers, and the increasing interest in the thermodynamics of hydrocarbons, these authors undertook the task of extending experimental data, and correlating systematically the published data with molecular structure.

Paraffin hydrocarbons were considered to be derived from a lower member in the series by substitution of an appropriate number of methylene groups into the chain. Likewise by substitution of an alkyl group for one or more of the hydrogen atoms attached to the main chain of the normal paraffin, the appropriate branched-chain hydrocarbon was formulated. Substitution of chlorine for hydrogen led to an alkyl halide. A comprehensive investigation of the thermodynamic data for the hydrocarbons and organic compounds containing oxygen, halogens, sulphur, and nitrogen was made by these investigators. Tabulated regularities of the data with structural modifications were compiled for use in estimating the free energies and entropies for compounds for which no experimental results were available.

In summary, Parks and Huffman's method is purely empirical in its approach. It is based on the increments obtained by comparison of the data for related compounds, assuming that these may be applied quite simply by mathematical addition for a corresponding structural modification in another molecule. No cognisance is taken in this approach of the influence of the symmetry of the molecule, hindered internal rotation, and products of the moments of inertia which influence additivity of free-energy function and entropy (Tables 1 and 2). The increments are thus likely to be rather specific, and should be applied only in estimating the data for quite comparable molecular species.

The tables of structural modifications and thermodynamic increments reported in Parks and Huffman's work are based on early data and are restricted to 25° C ; in some cases, only one or two structural comparisons were possible to gain these owing to the limited data available. The use of these data for anything but estimating very tentative values for ΔG^0 and S^0 at 25° C is not recommended in practice. The recent literature [2, 3] should be consulted to obtain better values for the increments in thermodynamic data accompanying a modification in structure of the molecule in any application of this approach today.

Estimation of Thermodynamic Properties of Organic Compounds by Group Contributions.—Four systematic correlation methods for the prediction of thermodynamic data on the basis of the additivity of group contributions have been published since the work of Parks and Huffman. A description of these in chronological order follows.

Anderson, Beyer, and Watson. These authors' method [20] is a comprehensive one whereby the thermodynamic properties of organic compounds of many types can be estimated at 25° C and higher temperatures. A basic or parent compound is selected from which, by substituting the appropriate groups for atoms in it, the complex molecule in question is built. The increments in thermodynamic properties corresponding to these group contributions are summed, and together with the data for the basic compound give the estimated values ; *e.g.*, methane, benzene, dimethyl ether, and formamide are recommended as the " base groups " for the more complex molecules of the aliphatic hydrocarbons, aromatic compounds, ethers, and amides.

The base group chosen should be the one having the largest entropy contribution. This group is then modified to build the carbon skeleton of the final molecule, the longest straight chain being built up before side chains are added. The increments for modifications resulting from multiple-bond contributions, and from replacement of methyl groups by substituent groups, *e.g.*, CN, OH, Cl, NO_2, are added in the final steps.

The greatest uncertainty in the tables of increments compiled by these investigators lies in the heat-capacity data. Because of the lack of high-temperature data, Anderson, Beyer, and Watson used the semi-empirical estimation methods based on generalised bond vibrational frequencies to calculate the heat-capacity data for several of the non-hydrocarbon groups. Some of the vapour pressures and critical constants required to correct the heats of formation and entropies to the ideal-gas state were also estimated. No detailed information is given by these investigators to distinguish between the increments based on precisely established data and the approximated values. It is estimated that the limits of error are ± 4 kcal./mole and ± 2 e.u. for heats of formation and entropies respectively calculated from these tables as a guide, and best values for the increments. The data on heat capacities are more uncertain, the estimated results deviating from better experimental data by ± 5% at moderate temperatures. The tables of increments, however, are specific, and make it possible to take into account the differences between isomers.

Franklin. This method [21] is an extension of the relations developed by Pitzer [19] for the long-chain paraffins. According to the latter, it was shown

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[20] Anderson, Beyer and Watson, *Nat. Petroleum News*, 1944, **36,** R476 ; Hougen and Watson, " Chemical Process Principles ", Vol. 2, p. 762, J. Wiley & Co., New York, 1943.

[21] Franklin, *Ind. Eng. Chem.*, 1949, **41,** 1070.

from theoretical considerations that the heat-content function and free-energy functions for gaseous normal paraffins can be expressed as additive functions of the number of carbon atoms, and constants characteristic of temperature, bond stretching, bending, internal rotation, and the symmetry number for the molecule. To extend this approach to branched-chain paraffins, Franklin revised Pitzer's basic equation (11) in the form:

$$\begin{aligned}X = F^0 + (n_1 + n_2 + n_3 + n_4 - 1)S + (2n_1 + n_2 + n_3 + n_4 - 4)B \\ + (n_1 + n_2 - n_4 - 3)I + n_1V_1 + n_2V_2 + n_3V_3 + n_4V_4 + F_{\text{steric}} + F_\sigma \quad (12)\end{aligned}$$

to account for the CH and C (*i.e.*, n_3 and n_4) groups as well as the CH_3 and CH_2 groups (*i.e.*, n_1 and n_2) which occur in such molecules: S, B, I, V_2, V_3, and V_4 are the empirical constants for C–C stretching, bending, internal rotation, C–H, and the quaternary C group within the molecule. On rearrangement, this gives:

$$\begin{aligned}X = 2(F^0/2 + S/2 - I/2 + V_1) + (n_1 - 2)(S + 2B + I + V_1) \\ + n_2(S + B + I + V_2) + n_3(S + B + V_3) + n_4(S + B - I + V_4) \\ + F_{\text{steric}} + F_\sigma \quad . \quad . \quad . \quad (13)\end{aligned}$$

which expresses the thermodynamic function (free-energy function, heat-content function) as an additive function of the CH_3, CH_2, CH, and C groups for each molecule plus the constants F_{steric} and F_σ. Owing to the additive nature of these thermodynamic functions, group values can be established from the heat-content and free-energy functions of molecules containing these groups.

Franklin calculated the group values for the free-energy function, after first deducting the symmetry correction, $-R \ln \sigma$, for the molecule in question from this function. The steric factor term, F_{steric}, was assumed negligible in compiling these data. The functions, $(H^0-H^0_0)$, $(G^0-H^0_0)$, ΔH^0_f, and ΔG^0_f are tabulated up to 1500° K at 100°-intervals for the characteristic hydrocarbon groups. Most of these data are based on the compilation of the properties of hydrocarbons by the American Petroleum Institute.[22] To account for constant deviations found from simple additivity found for certain molecular forms, Franklin compiled a table of correction factors. Thus for each ethyl side chain, a factor of 0·8 kcal. was proposed to correct for the deviation from additivity over the whole temperature range from 298° K to 1500° K. The principle of this method can be summarised by the equation:

$$X = \sum \begin{matrix}\text{contributions of} \\ \text{structural groups}\end{matrix} + RT \ln \sigma + \sum \begin{matrix}\text{deviation cor-} \\ \text{rection factors}\end{matrix} \quad . \quad (14)$$

The increments listed for the non-hydrocarbon groups by Franklin are based on the early data of Parks and Huffman,[1] the International Critical Tables,[4] and a compilation by Aston.[23] These values must be recognised as highly tentative. Anderson, Beyer, and Watson's compilation of group

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[22] "Collection, Analysis, and Calculation of Data on the Properties of Hydrocarbons," A.P.I. Research Project 44, 1947.

[23] Aston, "Thermodynamic Data on Hydrocarbons", Standard Oil Development Co., 1944.

increments is more comprehensive for the non-hydrocarbon species than Franklin's work in this publication.

Franklin's work provides group increments useful for predicting the heat-content function and free-energy function, ΔH^0 and ΔG^0, for the majority of typical hydrocarbons up to 1500° K. The accuracy of the calculated values is estimated to be ± 1 kcal. in most instances. For non-hydrocarbon molecules, this approach also seems applicable; however, increments for the non-hydrocarbon groups are less accurate. A comprehensive extension of this method to non-hydrocarbons was not attempted by Franklin in this publication.

Souders, Matthews, and Hurd. The estimation method and tables of group increments developed by these investigators appeared in two publications,[24] the first dealing with heat capacities and heat contents, and the second with entropies of formation and heats of formation. The tables of increments for the group contributions relating to heat capacities and heat contents are correlated with the Fahrenheit scale rather than the Centigrade. The entropy data are compiled for the estimation of entropies of formation as distinct from the entropy contents of the molecules. The method as described in these papers is restricted to hydrocarbon molecules, no attempt being made to generalise the approach to other types of organic compounds. The group contributions were determined from the rigorously calculated or experimental data of the simpler hydrocarbons available up to 1945 when this work was completed.

The heat-capacity contributions were tabulated separately from − 250° to 3000° F for (i) translational and external rotation of the group as a whole, (ii) the vibrational contribution of the structural group, and (iii) the internal rotational contributions. It was observed that the presence of a double or triple bond in conjugation alters the vibrational contributions since these were estimated from unconjugated systems. For simplicity, the differences between conjugated and unconjugated contributions were included in the internal-rotational contribution increments. A series of nine types of groups characteristic of rotation in the simpler hydrocarbon molecules are tabulated. By choosing the internal-rotational contribution most like those in the molecule under consideration, a better value can be estimated for the desired property. The correlations were constructed by comparison of the data for the lower members of the molecules in the normal paraffin, branched-chain, and aromatic homologous series. These are briefly described by the investigators.

In application of this approach to the entropy data, values for all the hydrocarbons were recalculated to entropies of formation by the equation

$$\Delta S^0{}_f = S^0 - 1{\cdot}36m - 15{\cdot}615n \quad . \quad . \quad . \quad (15)$$

where m and n are the number of carbon and hydrogen atoms, and 1·36 and 15·615 are the entropies of solid graphite and atomic hydrogen, respectively. The group contributions were set up by comparison of these entropies of formation. Souders, Matthews, and Hurd indicate that the

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[24] Souders, Matthews, and Hurd, *Ind. Eng. Chem.*, 1949, **41**, 1037, 1048.

correction term ($-R\ln\sigma$) must be applied to take into account contributions due to changes in symmetry. In the group increment for CH_3, the effect of the internal symmetry is already included. The symmetry number used in the correction term is thus that of the system treated as a rigid rotator with no free internal rotation. In the event of optical isomerism, an additional correction term, $+R\ln 2$, must be added to the entropy being estimated. This term corrects for the increased number of probable orientations within this system. The increments for the heat of formation were calculated in a similar manner. In addition to the structural increments, a table of increments correcting for conjugation and adjacency effects is given.

Souders, Matthews, and Hurd extended the method to higher temperatures by calculating the contributions to the functions: $(\Delta S^0{}_f)_T - \Delta S^0{}_{f,298}$, and $(\Delta H^0{}_f)_T - \Delta H^0{}_{f,298}$, using the group increments to the heat capacities to calculate the desired values. These data are tabulated from 300° to 2000° K. Thus $\Delta S^0{}_{f,298}$ and $[(\Delta S^0{}_f)_T - \Delta S^0{}_f]$ are estimated for the molecule at 298° K and at T by summing the contributions of the various structural groups, and corrections for conjugation, optical isomerism, and symmetry. The entropy of formation at temperature T is gained by simple addition of these two values.

Standard entropies of formation and heats of formation predicted by this method are believed to be within ± 1·0 e.u. and ± 0·5 kcal./mole of the correct value regardless of the complexity of the hydrocarbon molecule. The effect of temperature on each of these properties predicted by this method has an uncertainty less than 3%. The structural formula must be studied for the characteristic type of internal rotation, symmetry, and optical isomerism in application of this method for a best estimate.

Van Krevelin and Chermin. This method [25] considers the temperature dependence of the structural group contribution to the free energy to be given by the function:

$$\Delta G^0{}_{f,\text{group}} = A + 10^{-2}BT \quad . \quad . \quad . \quad . \quad (16)$$

where A and $10^{-2}B$ are, by approximation, equal to the heats and entropies of formation. These investigators found it possible to describe the temperature dependence up to 1500° K by two linear equations, the first covering the range 300—600° K, and the second 600—1500° K. The values of the constants A and B for these equations are reported for the various structural groups for hydrocarbons and non-hydrocarbons. The equation for the free energy of formation of a complex molecule is readily obtained by summation of the contributions for structural groups of the molecule. Whereas the other methods necessitate interpolation methods to calculate the free-energy change at any temperature other than those for which the data were tabulated, Van Krevelin and Chermin's method gives the result in equation form enabling a direct calculation of the free-energy change at any desired temperature.

The sources of data and procedures for compiling the data for these

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[25] Van Krevelin and Chermin, *Chem. Eng. Sci.*, 1951, **1**, 66.

correlations are discussed by these investigators. Some of these are of interest for comparison with the earlier methods. The free energy of formation was calculated by the equation :

$$\Delta G^0_f = T\Delta\left(\frac{G^0 - H^0_0}{T}\right)_f + \Delta H^0_f - \Delta(H^0 - H^0_0)_f \;. \quad (17)$$

where

$$\Delta\left(\frac{G^0 - H^0_0}{T}\right)_f = \left(\frac{G^0 - H^0_0}{T}\right)_{\text{compound}} - \sum\left(\frac{G^0 - H^0_0}{T}\right)_{\text{elements}} \quad (18)$$

and $\Delta(H^0 - H^0_0)_f$ is defined by a similar expression. The free-energy function and heat-content function are as a rule fairly accurate, being based on statistical thermodynamic calculation. If no experimental data existed for calculating ΔH^0_f, Anderson, Beyer, and Watson's method was used by Van Krevelin and Chermin to estimate both $\Delta H^0_{f,298}$ and the heat-capacity equation necessary for calculating ΔH^0_f up to 1500° K.

The structural group increments are made quite specific in the correlations of this method ; *e.g.*, seven group increments for the olefinic double bond are listed, each for a slightly different environment. To avoid the correction factors for conjugation effects proposed by Franklin, and Souders *et al.*, the present investigators report contributions for characteristic resonance groups of the aliphatic and aromatic type compounds. The influence of side chains or branching in hydrocarbons on the additivity of the free-energy correlation is tabulated to give greater accuracy to this estimation method.

Values of the parameters A and B are reported for twenty-two groups containing oxygen, nitrogen, or sulphur, to extend this approach to non-hydrocarbons. The method thus is more comprehensive than the three preceding methods. A point differing from the previous investigators is with reference to the hydroxyl group contributions. Parks and Huffman, Anderson *et al.*, and Franklin reported several values, the exact value to be used depending on whether the hydroxyl group appeared as a primary, secondary, tertiary, or aromatic substituent. In the present work, only one hydroxyl group increment is given, the positional effect having already been taken into account by the more specific nature of the groups for the hydrocarbons. Again, owing to lack of data, the non-hydrocarbon group increments have been estimated in many instances by reference to data reported for only one compound, and frequently at only one temperature. These then have been generalised to a wider temperature range by reference to the estimation method of Anderson *et al.* as indicated earlier.

It can be concluded that, whereas Van Krevelin and Chermin's method presents a more direct approach for the estimation of ΔG^0_f as a function of temperature, the accuracy to be expected, especially for the non-hydrocarbon species, is probably only that of the earlier methods.[20, 21] An agreement of ± 0·6 kcal. for ΔG^0_f between the estimated and observed values is reported by Van Krevelin and Chermin for a number of compounds used as reference for establishing the group increments. For complex molecules closely related structurally to these reference standards, a mean deviation of the estimated value of this magnitude can be expected.

Group Equations.—In the method of group equations, the thermodynamic functions are estimated for a desired molecule by referring it to other compounds containing the same numbers and types of groups. Thus the properties for *n*-pentane would be calculated from a knowledge of the data for *n*-butane, propane, and ethane, *e.g.*:

$$X(n\text{-pentane}) = X(n\text{-butane}) + X(\text{propane}) - X(\text{ethane}) \quad . \quad (19)$$

where X is the free-energy content, the heat content, or some desired thermodynamic function. Equations such as (19), in which there is an identity of groups, are termed group equations. This approach can be used to estimate the data for higher members of a homologous series very accurately provided the data for the lower members are well established, and cognisance is taken, where necessary, of differences in the symmetry numbers and potential barriers restricting internal rotation.

Bremner and Thomas. The method of group equations was applied by Bremner and Thomas [26] to demonstrate the additive nature of the thermodynamic properties of the aliphatic hydrocarbons, and to the use of these data for estimating the values for the alicyclic and aromatic series. These investigators do not take into account the correction to the free energy of formation necessary where differences in symmetry numbers arise in the group equations for the aliphatic series. Thus 2 : 4-dimethylhexane is represented by the group equation:

$$(2:4\text{-dimethylhexane}) = 2(iso\text{butane}) + 2(\text{propane}) - 3(\text{ethane}) \quad . \quad (20)$$

The symmetry numbers for 2 : 4-dimethylhexane, *iso*butane, propane, and ethane, treated as rigid rotators, are 1, 2, 2, and 2 respectively. To account for the differences in the symmetry numbers on the two sides of the equation, the free energy and entropies should be corrected by a factor of $- \boldsymbol{R} \ln 2$. Accordingly, the actual deviation of the estimated values from the literature values for the free energy of dimethylhexane are less by a term of $-$ 1·38 kcal./mole than those reported by Bremner and Thomas.

Extension of the method of group equations to the alicyclic and aromatic series in the same paper illustrates several important points. It is demonstrated that for the estimation of thermodynamic data for an alicyclic hydrocarbon from an aliphatic compound, heats of formation are additive even though ring closure occurs. In the formation of an aromatic ring, the estimated heat is too great by a term equal to the resonance energy or resonance heat of the aromatic compound. Bremner and Thomas suggest that the method of group equations offers a process for calculating the resonance energy at any temperature, whereas the more conventional method based on bond energies only permits calculation of this energy at the temperature for which the bond energies have been established. Resonance energies, calculated over the temperature range up to 1000° K, are shown to be temperature-independent. The entropy changes are examined when the thermodynamic properties of these ring compounds are estimated

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[26] Bremner and Thomas, *Trans. Faraday Soc.*, 1947, **43**, 779.

from the data of the aliphatic compounds. Bremner and Thomas thus show that for the alicyclic compounds, if the changes in entropy of translation and the complete symmetry numbers for the molecules are taken into account, the entropy can be estimated by the method of group equations. When these factors are all considered in the case of aromatic molecules, an additional small decrease still remains necessary, *e.g.*, 4 e.u. for benzene. It is suggested that this small term, if real, is the entropy changes associated with resonance effects (*i.e.*, the resonance entropy of the aromatic molecule).

Rossini, *Pitzer*, et al. The method of group equations has been developed and applied by Rossini, Pitzer, and their associates [27, 28, 29] in compiling the tables of the American Petroleum Institute [2] for the thermodynamic properties of hydrocarbons. The symmetry number enters in the statistical formulæ for the free-energy function (Tables 1 and 2), the entropy $\{i.e., [(H^0 - H^0_0)/T - (G^0 - H^0_0)/T]\}$, and the free energy of formation, but not in the expressions for heat content, heat capacity, and heat of formation. In the application of the method of group equations to calculate rather accurate data for hydrocarbons, these investigators modified the basic equation (19) to correct for symmetry factors and internal rotation. Some examples illustrating the use of the method of group equations by Rossini, Pitzer, and their co-workers in this field are summarised in Table 3.

TABLE 3. *Group equations used in the calculation of* $(H^0 - H^0_0)/T$, S^0, $-(G^0 - H^0_0)/T$, *and* C^0_p *by Rossini, Pitzer,* et al.

No.	Compound	Group equation *
1	Pent-1-ene	But-1-ene + *n*-butane − propane
2	3 : 3-Dimethylbut-1-ene	Propene + 2 : 2-dimethylbutane − propane − $\boldsymbol{R} \ln 2$
3	Penta-1 : 4-diene	2(But-1-ene) − propane − $\boldsymbol{R} \ln 4$
4	2-Methylbuta-1 : 3-diene	*iso*Butene + buta-1 : 3-diene − propene + $\boldsymbol{R} \ln 4$ − 0·3
5	*iso*Propylbenzene	Ethylbenzene + *iso*butane − propane + $\boldsymbol{R} \ln \frac{3}{2}$
6	1-Ethyl-4-methylbenzene	1 : 4-Dimethylbenzene + ethylbenzene − toluene + $\boldsymbol{R} \ln 2$

* The term involving $\boldsymbol{R}$ ln is to be included for the entropy and the negative of the free-energy function but disregarded for the heat-content function and heat capacity.

The constant terms, $\boldsymbol{R} \ln 2$, etc., appearing in these equations are corrections for the differences in the symmetry numbers. These are readily obtained by an inspection of the complete symmetry numbers for the desired compound and the internal symmetry numbers conferred on each by the presence of the symmetrical-top substituents in the carbon skeleton of the parent molecule. Thus the complete symmetry numbers for pent-1-ene, but-1-ene, *n*-butane, and propane are 3, 3, 18, and 18, respectively. In the group equation for pent-1-ene (Table 3, No. 1), no correction for symmetry

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[27] Kilpatrick, Prosen, Pitzer, and Rossini, *J. Res. Nat. Bur. Stand.*, 1946, **36**, 559.
[28] Taylor, Wagman, Williams, Pitzer, and Rossini, *ibid.*, 1946, **37**, 95.
[29] Kilpatrick, Beckett, Prosen, Pitzer, and Rossini, *ibid.*, 1949, **42**, 225.

enters since the net contribution of the symmetry correction for the components is $-\boldsymbol{R}\ln 3$, *i.e.*, the same as for pent-1-ene. The complete symmetry number of penta-1 : 4-diene is 2. The net contribution of the symmetry correction for the components in this group equation (Table 3, No. 3) is $+\boldsymbol{R}\ln 2$. Therefore an additional term of $-\boldsymbol{R}\ln 4$ is required to bring the symmetry into correspondence with that of the desired compound, penta-1 : 4-diene. In the case of isoprene, the calculated additional term, $-0{\cdot}3$, was added to the increment equation to bring the calculated value to within $\pm 0{\cdot}2$ e.u. of the experimental value [29] at 298·16° K. Presumably this change gives better extrapolated values at higher temperatures.

The corrections arising from differences in the potential barriers restricting internal rotation require more special consideration. For example in but-1-ene, owing to the steric interference of the methyl and ethylenic groups, the rotational potential becomes almost constant from 240° to 360° and passes through a symmetrical two-fold minimum from 0° to 240° in the angle of rotation. These requirements are satisfied by the expression

$$\begin{aligned} V &= \tfrac{1}{2}(1 - \sin\phi)V^0 \text{ cal./mole}; \quad 0^\circ < \phi < 240^\circ \\ V &= V^0; \quad 240^\circ < \phi < 360^\circ \quad . \quad . \quad . \quad . \quad . \quad (21) \end{aligned}$$

In *cis*-pent-2-ene, owing to steric interference, the rotational potential becomes infinite from 240° to 360°. The form of the potential barrier satisfying these requirements is

$$\begin{aligned} V &= \tfrac{1}{2}(1 - \sin 3\phi)V^0 \text{ cal./mole}; \quad 0^\circ < \phi < 240^\circ \\ V &= \infty; \quad 240^\circ < \phi < 360^\circ \quad . \quad . \quad . \quad . \quad . \quad (22) \end{aligned}$$

Accordingly, the group equation used for evaluating the data for *cis*-pent-2-ene was

cis-pent-2-ene = but-1-ene* + *cis*-but-2-ene − propene + $\boldsymbol{R}\ln 2$
+ [internal rotation contribution calculated from
equation (22) barrier for ethyl group] . . (23)

The *asterisk* on but-1-ene indicates the thermodynamic values not including the contribution from the internal rotation of the ethyl group in but-1-ene. The internal-rotational contributions were calculated by using the classical partition function since the reduced moment of inertia for the rotating group (ethyl or propyl) is several times larger than that of the methyl group. Further examples illustrating this correction, and the four types of barriers to be considered when an ethyl or larger group is bonded to an olefinic group, are discussed in the paper by Kilpatrick, Prosen, Pitzer, and Rossini on mono-olefin hydrocarbons.[27] All other barriers restricting internal rotation were taken to be the same as in the corresponding paraffin or lower olefin hydrocarbons.

It is noteworthy that this approach is being extended to non-hydrocarbons. Pitzer and Barrow [30] have shown that the values for the higher normal thiols, calculated by the above method of group equations starting with the data for ethanethiol, are in good agreement with properties calculated from spectroscopic data. The calculation of rather accurate data

[30] Pitzer and Barrow, *Ind. Eng. Chem.*, 1949, **41**, 2737.

for the non-hydrocarbon species awaits precisely established experimental and spectroscopic data for the lower members in each family of compounds.

Heats of Formation

The methods proposed for the estimation of heats of formation, other than those already described in the preceding parts, are considered here. The well-established methods based on experimental data, *i.e.*, heats of combustion or heats of hydrogenation, will not be discussed.

Kharasch and Sher. Kharasch and Sher[31] proposed an empirical correlation of the heats of combustion of organic compounds based on the electronic concepts of valency theory. With the assumption that whenever an organic substance is burned in oxygen, the heat generated is due to the interdisplacement of the electrons between the carbon and oxygen atoms, it was calculated that energy equivalent to 26·05 kcal. per electron mole was evolved for the methane and carbon dioxide configurations as standards of reference. This led directly to empirical equations of the type:

$$Q = 26{\cdot}05N + w \quad . \quad . \quad . \quad . \quad (24)$$

where Q is the calculated heat of combustion, N the number of electrons, and w an empirical constant to correct for deviations of the electron distribution from that in the reference standard. It was found that, for saturated hydrocarbons and simple aromatics, w was equal to zero, and for aliphatic olefins, 13 kcal. A valuable compilation of all the available information on heats of combustion for organic compounds, with a table of best values for some 1500 substances of all types, was published by Kharasch.[32] Comparison of the calculated values by Kharasch and Sher's method with the observed data established that in most cases the two values agreed within the accuracy of the observed values (*i.e.*, within 1—2%).

Rossini. The status of the data and calculations for the heats of formation of simple organic molecules has been the subject of two reviews by Rossini[33] since the work of Kharasch. It was stressed that practically none of the data before 1937 on organic compounds can be used in thermodynamic calculations where errors in ΔH^0_f of several kcal./mole are significant. Dewar[34] shows that the assumption that heats of formation are additive functions of bond energies carries the following implication. The heat of formation (ΔH^0_f) of a compound may be expressed by the equation:

$$\Delta H^0_f = \Delta E_0 + \Delta E_z + \int_0^T C_p \mathrm{d}T - \int_0^T C_p' \mathrm{d}T \quad . \quad . \quad (25)$$

where ΔE_0, ΔE_z, and C_p are the total bonding energy and zero-point energy, and specific heat of the molecule respectively, and C_p' is the sum of the specific heats of the atoms from which it is formed. If ΔH^0_f is an additive function of the bonds, it follows that all the terms in the above equation

[31] Kharasch and Sher, *J. Phys. Chem.*, 1925, **29**, 625.

[32] Kharasch, *J. Res. Nat. Bur. Stand.*, 1929, **2**, 359.

[33] Rossini, *Ind. Eng. Chem.*, 1937, **29**, 1424; *Chem. Rev.*, 1940, **27**, 1.

[34] Dewar, *Trans. Faraday Soc.*, 1946, **42**, 767.

must be additive. The expression for the heat of formation may thus be written :

$$\Delta H^0_f = \sum \Delta E^*_0 + \sum \Delta E^*_z + \sum \int_0^T C^*_p \mathrm{d}T - \int_0^T C_p' \mathrm{d}T \quad . \quad (26)$$

in which ΔE^*_0, ΔE^*_z, and C^*_p are contributions of the individual bonds to the whole. Not only the bonding energies, but also the specific heat and zero-point energy of a molecule, must be divisible into contributions by individual bonds. The success of Pauling's bond energies in predicting heats of formation for a wide range of unconjugated molecules is in accord with the above conclusions. Rossini [33] notes that the use of tables of bond energies to reproduce heats of formation within narrow experimental limits is not possible largely owing to deviations from additivity in the above points, and because an indisputable value for the energy of formation of gaseous monatomic carbon has not yet been established.

More recently the thermodynamic properties of hydrocarbons have been examined by Cottrell [35] to determine the effect of internal kinetic energy on the additivity of bond energies, resonance, and steric strain. The chemical binding energy for typical hydrocarbons was calculated by subtracting the zero-point vibrational energy and the heat content relative to the molecule at 0 ° K from the total energy of the molecule. It is shown that this may be divided into " binding-energy terms " per bond. The latter are demonstrated to be additive, and, like the conventional bond energies, can be used for estimating the resonance energy and steric strain in polyatomic systems.

An empirical approach of estimation is recommended by Rossini [33] based on inspection of the heat of formation data for a related series of molecules. For normal paraffins, ΔH^0_f is found to be a linear function of the number of carbon atoms for molecules above *n*-pentane. Thus for a molecule (Y–R), the heat of formation can be represented simply by

$$\Delta H^0_f = A + Bn + \Delta \quad . \quad . \quad . \quad . \quad (27)$$

where A is constant characteristic of the end-group Y, and B, n, and Δ are respectively a universal constant, the number of carbon atoms, and the deviation from linearity. For $N \geqslant 5$, the last term is equal to zero. Hence, to know the heats of formation for all the members of a homologous series of molecules, Y–R, it would only be necessary to have the experimental values for not more than six of the lower members, *i.e.*, up to $R = C_5H_{11}$ in this case. The deviation Δ is attributed to interactions of the " near neighbour " atoms not directly attached to each other, as well as deviations from linearity in the zero-point energies for the various members of the series.

Heat Capacity

Several publications concerned specifically with the calculations of the specific heats of organic vapours are of interest in addition to the procedures covered under the comprehensive methods.

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[35] Cottrell, *J.*, 1948, 1448.

Bennewitz and Rossner. The rigorous evaluation of the individual degrees of vibrational freedom requires extensive spectroscopic data and is tedious. Mecke [36] noted the invariancy of the frequencies associated with the stretching and deformation modes of the characteristic bonds in organic molecules. Bennewitz and Rossner [37] extended the use of these generalised frequencies to the calculation of heat-capacity data, using the tables of Einstein functions. It was found that the experimental specific heats for non-linear molecules containing carbon, hydrogen, and oxygen could be expressed by

$$(C_p)_{P=0} = 4R + \sum_i q_i E_{\nu_i} + (3n - 6 - \sum_i q_i) \sum_i q_i E_{\delta_i} / \sum_i q_i \quad . \qquad (28)$$

where $\sum q_i$ and n are respectively the number of valency bonds and the total number of carbon atoms in the molecule, and E_{ν_i}, E_{δ_i} are the Einstein functions for a given bond with characteristic stretching and deformation frequencies ν_i and δ_i respectively. Bennewitz and Rossner compiled tables of data for ready use of this method for compounds containing carbon, hydrogen, and oxygen atoms for which no experimental data existed. Numerical values of ν for the bonds in question were taken from Raman data, while the values of δ were determined empirically from the experimental heat-capacity data. The values of the Einstein functions are tabulated at 40°-intervals over the temperature range 290—690° K. The above equation was found to reproduce experimental data within 5% in the temperature region of 400° K if these data were used.

These data were recalculated by Fugassi and Rudi [38] to fit the power series equation

$$(C_v)_{P=0} = a + bT + cT^2 \quad . \quad . \quad . \quad . \qquad (29)$$

to simplify the computation of heat capacities over a temperature range. On the assumption that the organic vapours obey Berthelot's equation of state, these data can be converted into C_p data by the expression

$$(C_p)_{P=P} = (C_v)_{P=0} + R\left[1 + \frac{81}{23} \times \frac{P}{P_c} \times \left(\frac{T_c}{T}\right)^3\right] \quad . \qquad (30)$$

where the critical data can be estimated when necessary, as a first approximation, by the simple relations, $T_c = 1{\cdot}5T_b$ and $\log P_c = 3(T_c/T_b) - 1$, T_b being the normal boiling point.

Dobratz. Some of the errors of the estimates at lower temperatures by Bennewitz and Rossner's method can be attributed to the fact that the molecules were treated as rigid rotators. Dobratz [39] proposed a modified form of Bennewitz and Rossner's equation to take into account internal rotation in these molecules, *i.e.*:

$$(C_p)_{P=0} = 4R + \frac{aR}{2} + \sum q_i C_{v_i} + (3n - 6 - a - \sum q_i) \sum q_i C_{\delta_i} / \sum q_i \quad . \qquad (31)$$

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[36] Mecke, *Z. phys., Chem.*, 1932, **16**, *B*, 409, 421.

[37] Bennewitz and Rossner, *ibid.*, 1938, **39**, *B*, 126.

[38] Fugassi and Rudi, *Ind. Eng. Chem.*, 1938, **30**, 1029.

[39] Dobratz, *ibid.*, 1941, **33**, 759.

where *a* equals the number of bonds permitting free rotation, *i.e.*, C–C or similar. This equation reproduces the data for propane and *n*-butane to within 5% of the experimental values, whereas the simple Bennewitz and Rossner equation gives deviations up to 15% at the lower temperatures. The work of Stull and Mayfield [40] extended Dobratz's method up to 15C0° K, and reassigned certain characteristic frequencies in the light of more recent data. A useful table of solutions to the Einstein functions for one degree of freedom is found in this paper.[40]

Comparison of Comprehensive Estimation Methods

The work of Parks and Huffman [1] demonstrated the additive nature of the thermodynamic data for organic compounds, and served to stimulate interest and activity in this field. The increments tabulated for structural modifications are based on early data (1932) and are not recommended except for the most tentative estimates. The increments for entropy and free energy are tabulated for the liquid state, and only at 25° C. The work of Pitzer [19] demonstrated theoretically that the method of group increments can be applied to achieve quite accurate estimates for the higher members of the normal and branched-chain aliphatic hydrocarbons.

This approach was extended by Franklin [21] and by Souders *et al.*[24] to tabulate group increments for quite specific structural units of the saturated and unsaturated aliphatic and aromatic hydrocarbons. These two methods give quite comparable and good estimates for hydrocarbons. The basic difference is in the data estimated, the former leading to values of ΔH^0_f and ΔG^0_f, but not heat capacities, and the latter to values of ΔH^0_f and ΔS^0_f and heat capacities. The tabulations of Souders *et al.* are for hydrocarbons only, while a limited extension of the method to non-hydrocarbon groups is given in Franklin's work.

The approach of Anderson *et al.*[20] and of Van Krevelin and Chermin [25] was to tabulate the group increments to permit a ready estimate of the thermodynamic data in the form of a temperature-dependent equation. The data compiled by Anderson *et al.* have been used in part by Van Krevelin and Chermin for some of the non-hydrocarbon groups. For the hydrocarbons, Van Krevelin and Chermin's method is probably superior to that of Anderson *et al.*, being based on more recent data, and being able to distinguish between isomeric compounds. Franklin's extension [21] to non-hydrocarbons groups is more limited in nature than either of the above two methods. These methods give good approximations, but the results should be regarded as an order of magnitude rather than best values or exact quantitative data.

The work of Bremner and Thomas [26] is of interest mainly for the extension of the method of group equations to estimate the data for alicyclic and aromatic compounds from aliphatic values. Rossini, Pitzer, *et al.*[27] developed and applied the method of group equations to calculate rather accurate data for the statistical thermodynamic functions of hydrocarbons of all types. Many of the data for the higher hydrocarbons in the tables of the

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[40] Stull and Mayfield, *Ind. Eng. Chem.*, 1943, **35**, 639; Stull, *ibid.*, p. 1301.

American Petroleum Institute and National Bureau of Standards [2] were evaluated by their method. When precise data for the non-hydrocarbons become available, this method will provide the means for obtaining the best values for higher homologues in these series.

A brief summary of the comparison of these methods has been compiled in Table 4. The comprehensive nature and type of data that may be estimated from the numerical tabulations are indicated. The remarks on each method are based on the method with the assumption that the data presented by these authors at the time of publication are being used. In practice, each approach should be capable of giving almost comparable estimates providing the latest data are used to formulate the group increments or equations.

Applications of the Thermodynamic Method

In the field of organic chemical reactions, the application of thermodynamics has proved useful for the prediction of reaction equilibria, and the evaluation of the thermodynamic feasibility of novel processes. In the former case, where precisely determined thermodynamic data are available, the reaction equilibrium can frequently be predicted more accurately than could be established by direct measurements. In the latter case, estimates of the required thermodynamic functions, by the preceding methods, are of sufficient accuracy to predict the free-energy changes for novel processes over a temperature range for use as a guide to the experimental investigation.

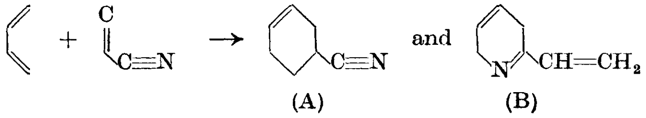
The thermodynamic criterion for reaction equilibrium and spontaneous processes can be summarised in terms of the free-energy change, ΔG^0, as follows. If ΔG^0 is negative, the reaction is promising; if ΔG^0 is greater than zero but less than $+ 10$ kcal., it is of questionable value, but warrants investigation; and if ΔG^0 is larger than $+ 10$ kcal, the reaction is predicted to be not feasible except under unusual conditions. It should be recalled that such considerations predict only the possible equilibrium yields, *i.e.*

$$\Delta G^0 = - RT \ln K \quad . \quad . \quad . \quad . \quad (32)$$

and throw no light on the actual products and yields. The latter are ultimately dependent on the relative rates and energies of activation in the chemical processes.

Some recent applications of the thermodynamic approach to chemical problems have been selected to illustrate these points.

The Diels–Alder reaction, in which a stable six-membered ring is formed by the 1 : 4-addition of an unsaturated linkage to a diene, is a well-known process of wide synthetical application. With acrylonitrile, in which both the C=C and C≡N dienophilic groups are present, two competing processes can be foreseen, *i.e.*,



(33)

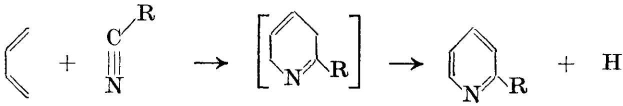
namic properties of

Method	Compounds	Data	Remarks
Parks and Huffman [1] (empirical)	All types *	ΔS^0_{298}, $\Delta G^0_{f,298}$	Demonstrated additive nature of thermodynamic properties
Pitzer [19] (theoretical)	Branched and *n*-aliphatics	Statistical thermodynamic functions	Developed to give accurate estimates for higher hydrocarbons
Anderson *et al.*[20] (group increments)	All types	ΔH^0_{298}, S^0_{298} $C^0_p = a + bT + cT^2$	Useful approach for good approximations but not best values
Franklin [41] (group increments)	All types	$(G^0 - H^0)$, $(H^0 - H^0_0)$, ΔH^0_f, ΔG^0_f	Improves on Anderson *et al.* for hydrocarbons, but not for non-hydrocarbons
Souders *et al.*[24] (group increments)	Hydrocarbons	C^0_p, ΔH^0_f, ΔS^0	Compares with Franklin for accuracy: C^0_p data on Fahrenheit temperature scale
Van Krevelin and Chermin [25] (group increments)	All types	$\Delta G^0 = A + 10^{-2}BT$	Compares with Franklin for hydrocarbons and Anderson *et al.* for non-hydrocarbons
Bremner and Thomas [26] (group equations)	Hydrocarbons	ΔG^0_f, S^0	Estimates aromatic data from aliphatic data
Rossini, Pitzer, *et al.* (group equations)	Hydrocarbons	Statistical thermodynamic functions and ΔH^0	Used to compile the best values for hydrocarbons in the A.P.I.–N.B.S. tables

* Hydrocarbons and organic compounds containing N, O, S, and halogens.

Thus 4-cyano*cyclo*hexene (A) and 3 : 6-dihydro-2-vinylpyridine (B) would be predicted as products if acrylonitrile adds to the diene by virtue of the vinyl and cyano-groups respectively. The theoretical and experimental aspects of these processes were investigated by Janz and Duncan.[41] The thermodynamic free-energy changes at 700° K for the formation of cyano*cyclo*hexene and dihydrovinylpyridine were predicted to be — 21 and — 14 kcal./mole, *i.e.*, both reactions are highly probable. From a consideration of the kinetic data for related high-temperature Diels–Alder associations it was possible to predict that the formation of cyano*cyclo*hexane is 5800 times as rapid as that of dihydrovinylpyridine. The experimental study of the homogeneous gas-phase reactions established that only cyano*cyclo*hexene is formed in this temperature range. The work was extended to some experiments using heterogeneous catalysts, in view of the favourable free-energy changes for both processes. It is noteworthy that on using a chromia–alumina surface, both cyano*cyclo*hexene and dihydrovinylpyridine were obtained. Over this surface, acrylonitrile reacts by the C=C and C≡N bonds as predicted from thermodynamic considerations.

The fundamental steps in the catalytic ring closure of open-chain hydrocarbons have been discussed by Taylor and Turkevich,[42] using the thermodynamic approach as a guide to evaluate the following high-temperature processes for *n*-hexane : formation of (1) a paraffin and olefin, (2) a higher paraffin and hydrogen, (3) a higher paraffin and a lower paraffin, (4) carbon and hydrogen, (5) olefin and hydrogen, (6) *cyclo*paraffin and hydrogen, (7) *cyclo*olefin and hydrogen, and (8) an aromatic compound and hydrogen. The main conclusions drawn from the thermodynamic considerations were that one should operate above 300° C for aromatisation, should use catalysts that activate the carbon–hydrogen bond, and should avoid all substances that rupture the carbon–carbon bond. More recently, the ring closure of the nitriles–dienes reaction leading to pyridine-like products, *i.e.*, reaction (34) has been treated thermodynamically by Janz, McCulloch, and Timpane[43] as a guide in studying the value of catalysts. The results of these calculations are summarised in Fig. 1, giving the temperature dependence of ΔG^0 for each step and the overall process. It is concluded that at all temperatures up to 1000° K, the dihydro-intermediate is unstable relative to the pyridinic product, and that catalysts promoting cyclisation reactions, *i.e.*, activating the carbon–hydrogen bond, should be investigated. A subsequent report by Janz and McCulloch[44] shows that the rate is appreciably increased by such surfaces, *i.e.*, Al_2O_3 and Cr_2O_3–Al_2O_3 catalysts.



(34)

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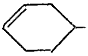
[41] Janz and Duncan, *Nature*, 1953, **171**, 933 ; *J. Amer. Chem. Soc.*, 1953, **75**, 5389.
[42] Taylor and Turkevich, *Trans. Faraday Soc.*, 1939, **35**, 921.
[43] Janz, McCulloch, and Timpane, *Ind. Eng. Chem.*, 1953, **45**, 1343.
[44] Janz and McCulloch, *J. Amer. Chem. Soc.*, in the press.

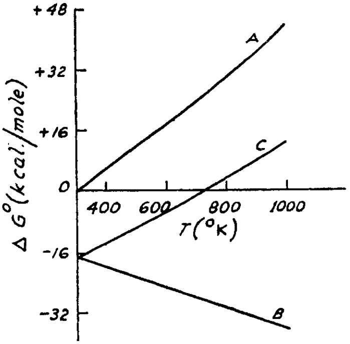
The kinetics of the dimerisation of butadiene and of the dissociation of vinyl*cyclo*hexene :

2(CH$_2$=CH—CH=CH$_2$) → -CH=CH$_2$ . . (35)

have been re-examined by Duncan and Janz [45] in the light of thermodynamic equilibrium calculations. The data for vinyl*cyclo*hexene and the activated complex were approximated by the estimation methods. A comparison of the equilibrium free-energy change predicted by the thermodynamic method and from the experimental rate equation is shown in Fig. 2. The

FIG. 1

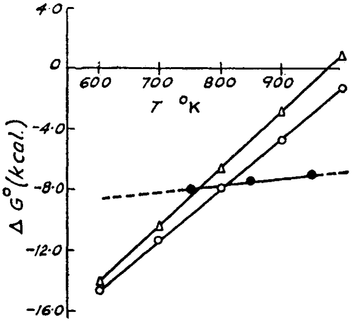
Temperature dependence of free-energy change for the two-step formation of phenylpyridine.



A. *Cyclisation to dihydrophenylpyridine*
B. *Dehydrogenation to phenylpyridine*
C. *Overall reaction*

FIG. 2

Temperature dependence of free-energy change for the equilibrium :
2(CH$_2$=CH—CH=CH$_2$) $\rightleftharpoons$ C$_8$H$_{12}$



● *Data from experimental rate equations*
○ *Thermodynamic calculation*
△ *Data from experimental rate equation for the dimerisation and calculated equation for depolymerisation*

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[45] Duncan and Janz, *J. Chem. Phys.*, 1952, **20**, 1644.

lack of agreement between these two methods was resolved if the dissociation of vinyl*cyclo*hexene was given by the expression:

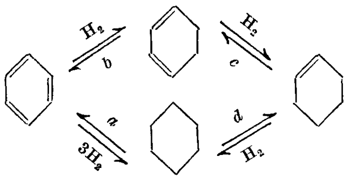
$$k_d = 5{\cdot}02 \times 10^{15} \exp(-61{,}800/\boldsymbol{R}T) \text{ sec.}^{-1}$$

rather than the experimental rate equation:

$$k_d = 2{\cdot}35 \times 10^{8} \exp(-36{,}000/\boldsymbol{R}T) \text{ sec.}^{-1}$$

reported by Doumani *et al.*[46] As seen by the criterion of thermodynamic methods, the experimental energy of activation and frequency factor seem too low for the homogeneous thermal dissociation of vinyl*cyclo*hexene. It is suggested that the low values may possibly be accounted for by a catalysis or wall effect being present but not reported in the experimental study.

The thermodynamics of the hydrogenation of benzene have been discussed by Janz.[47] In addition to the overall hydrogenation to *cyclo*hexane, the process is considered in three steps:



. . . . (36)

Comparison of the equilibrium data for the overall process predicted from precisely established thermodynamic data and experimental results, as in Fig. 3, shows that the agreement leaves little to be desired. This serves

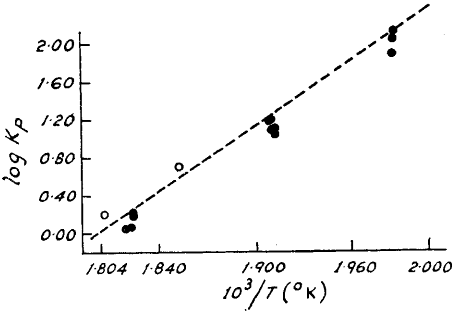


FIG. 3

Comparison of experimental data and thermodynamic values for the benzene–cyclohexane hydrogenation reaction at equilibrium.

○ *Burrows and Lucarni* ● *Zharkov and Frost*
--- *Values predicted thermodynamically*

to emphasise the point that well-established thermodynamic data may be used to predict reaction equilibria as accurately as, and frequently better than, the best directly measured experimental values. For the step-wise

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[46] Doumani, Deering, and McKinnis, *Ind. Eng. Chem.*, 1947, **39**, 89.
[47] Janz, *J. Chem. Phys.*, 1954, **22**, 751.

processes, some of the data for *cyclo*hexadiene (*b*) and *cyclo*hexene (*c*) were estimated by the semi-empirical methods owing to the lack of experimental values. These calculations established that over the temperature range up to 1000° K, *cyclo*hexadiene is thermodynamically unstable relative to the other three compounds. It follows, from the very unfavourable equilibria predicted thermodynamically, at moderately high temperatures, that one could not expect to isolate *cyclo*hexadiene as an intermediate in the hydrogenation of benzene. No report of *cyclo*hexadiene, even in trace amounts, in this process is known.

The thermodynamic approach has been applied to predict reaction equilibria for the reactions of cyanogen and hydrogen cyanide with ethane and methane,[48] the vapour-phase hydration of ethylene,[49] the catalytic alkylation of benzene with ethylene,[50] various organic syntheses,[51] the reaction of benzene and ethyl ether,[52] direct cyanogenation of benzene by cyanogen,[53] and dehydrogenation, isomerisation, alkylation, and cyclisation reactions of hydrocarbons.[54] It should be recalled that the free-energy changes and equilibrium constants calculated from any but the most precise data are of interest only for predicting the driving forces, *i.e.*, the thermodynamic feasibility, of the processes considered. The degree to which such results may be applied more quantitatively will be dependent on the limitations imposed by the approximation methods and data, and on the experience or skill with which these methods are used. Application of the thermodynamic approach to the many problems of interest in the field of organic compounds will become increasingly easier as accurate experimental data for the simpler members of the various types of organic compounds are established.

[48] Thompson, *Trans. Faraday Soc.*, 1941, **37**, 344.

[49] Bliss and Dodge, *Ind. Eng. Chem.*, 1937, **29**, 19.

[50] Pardee and Dodge, *ibid.*, 1943, **35**, 274.

[51] Nyholm, *Austral. Chem. Inst. J. and Proc.*, 1947, **14**, 135.

[52] Given and Hammick, *J.*, 1947, 928.

[53] Janz, *J. Amer. Chem. Soc.*, 1952, **74**, 4529.

[54] Rossini, " Physical Chemistry of Hydrocarbons ", Vol. II, Academic Press, Inc., New York, 1950.