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Molar Group Contributions to the Heat of Combustion

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16. Abstract

Experimental results for the gross heat of combustion of over 140 commercial and developmental polymers and small molecules of known chemical structure were used to derive additive molar group contributions. Predicted gross heats of combustion were within 2.5 percent of the values measured by oxygen bomb calorimetry.

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EXECUTIVE SUMMARY

Experimental results for the gross heat of combustion of over 140 commercial and developmental polymers and small molecules of known chemical structure were used to derive additive molar group contributions to the heat of combustion. The materials examined contained carbon, hydrogen, oxygen, nitrogen, phosphorous, sulfur, chlorine, fluorine, and silicon in linear, branched and cyclic structures. Values for the molar group contributions are summed and divided by the molecular weight of the molecule or polymer repeat unit to yield the gross heat of combustion as determined by oxygen bomb calorimetry. This new method provides an accurate single step method for calculating the heat of combustion. The average relative error of the calculated gross heats of combustion is 2.5 percent.

INTRODUCTION

Several approaches have been taken to calculate the heat of combustion based on the molecular structure of a material [1-3]. Oxygen consumption is a commonly used method for calculating the heat of combustion from known chemical structures [4] and for measuring heat release rates in flaming combustion tests [5 and 6]. Another method for obtaining the heat of combustion is by using the heats of formation of the products and the reactants [7-9]. These different methods have been examined by the author [10 and 11] and found to agree to within ±5%.

Heats of combustion calculated from oxygen consumption rely on the empirical observation that a wide range of organic compounds, including polymers, have approximately the same heat of complete combustion per gram of diatomic oxygen consumed

$$E = \Delta h_c \left[\frac{n_p M_p}{n_{O_2} M_{O_2}} \right] = \frac{\Delta h_c}{r_o} = 13.1 \pm 0.7\ kJ/g\text{–}O_2 \tag{1}$$

where Δh_c is the net heat of complete combustion of the sample with all products in their gaseous state, n_p and M_p are the number of moles and molecular weight of the molecule or polymer repeat unit, respectively, n_{O_2} is the number of moles of O_2 consumed in the balanced thermochemical equation, and M_{O_2} = 32 g/mol is the molecular weight of diatomic oxygen. In equation 1, the quantity $r_o = [n_{O_2} M_{O_2} / n_p M_p]$ is the stoichiometric oxygen-to-fuel mass ratio. This calculation was performed for polymers in several studies [5, 10, and 11] to determine E from known atomic compositions and measured heats of combustion. Inverting equation 1 shows that the net heat of complete combustion of a polymer is simply calculated if the atomic composition of the polymer is known so that the balanced thermochemical reaction equation can be written.

$$\Delta h_c = E \left[\frac{n_{O_2} M_{O_2}}{n_p M_p} \right] = E r_o \tag{2}$$

The additivity of molar group contributions to the physical and chemical properties of materials is the basis of an empirical methodology for relating chemical structure to properties [1-3]. The early work in this area focused on calculating heats of combustion from the individual atoms comprising small molecules. However, performing calculations for large (polymer) molecules based on the interactions of the individual atoms can prove to be very difficult. A simpler approach to correlating polymer chemical structure with properties is to group the atomic contributions into characteristic structural elements (e.g., $–CH_3$), determine the value of the group contribution to the property of interest parametrically, and add these group contributions according to their mole fraction in the polymer repeat unit. This method has been used to relate the chemical structure of polymers to their thermal, chemical, optical, and mechanical properties, as well as flammability, with excellent results [1-3].

Other methods involve compiling structural group contributions and correction factors for their adjacent bonds [12]. This method for deriving the heat of combustion is very accurate but difficult to perform and is only applicable to linear hydrocarbon molecules. A simpler, more accurate method has been developed for calculating the heat of combustion under standard conditions using molar group additivity.

The calculation of the heat of the combustion can also be carried out using the principle of molar additivity of the heats of formation of the combustion products and reactants [13]. The concept is derived from the fact that enthalpy (H) is a state function and therefore its change in any process is independent of the path from reactants to products. Thus, the overall enthalpy of a reaction is simply the sum of the enthalpies of the component reactions. In practice, the heat of combustion of the reaction can be calculated by subtracting the heat of formation of the products from the heat of formation of the reactants

$$\Delta h_c = \sum_i n_p \Delta h^o{}_{f,p} - \sum_i n_r \Delta h^o{}_{f,r} \tag{3}$$

where p and r denote products and reactants, respectively, in the standard state at temperature, 298 K. For polymeric reactants the molar heat of formation can be estimated from the tabulated molar contributions of the chemical groups which constitute the monomer or repeat unit.

EXPERIMENTAL

MATERIALS.

Polymer samples were unfilled, natural, or virgin-grade resins obtained from Aldrich Chemical Company, Scientific Polymer Products, or directly from manufacturers. The oxygen gas used for testing was dry, >99.99% purity grade obtained from Matheson Gas Products.

METHODS.

The gross heat of combustion was measured in an oxygen bomb calorimeter (Model 1341, Plain Jacket Oxygen Bomb Calorimeter, Parr Instrument Co., Moline, Illinois) according to a standard procedure ASTM D 2382-88 [14], with corrections for the heat of solution of any acid gases that may have been formed [15]. The average standard error for this technique is 0.51 kJ/mol.

There are no direct methods for measuring the net heat of combustion—which is the gross heat of combustion minus the latent heat of vaporization of the water produced during the reaction. The net or lower heat of combustion is relevant to flaming combustion, where water is in the gaseous state at flame temperatures of ≈ 1000 K. As a result, the latent heat of water at 298 K is subtracted from the gross heat of combustion because this amount of heat is required to maintain the combustion product water in the gaseous state. The gross heat of combustion measured by the procedure stated above is corrected for the heat of vaporization of the water formed during the combustion to give the net heat of combustion, Δh_c in kJ/g, using the relation [16]

$$\Delta h_c = Q_c - 21.96 w_H \tag{4}$$

where Q_c is the gross heat of combustion in kJ/g, w_H is the weight fraction of hydrogen in the sample.

THEORY.

An empirical approach was taken to derive values for the structural group contributions to the heat of combustion. The molar heat of complete combustion ΔH_c is a thermodynamic property and should be calculable from the molar group contributions of the structural components. Assume that there is a molar heat of combustion, $\boldsymbol{H}$, with units of kJ/mol, in which each chemical group i in the polymer contributes according to its mole fraction, n_i, in the repeat unit,

$$\boldsymbol{H} = \sum_i n_i H_i \tag{5}$$

with H_i, the molar heat of combustion of component i. Since,

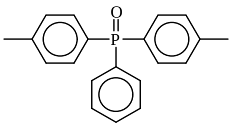
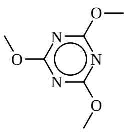
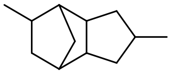
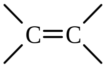
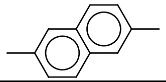
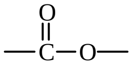
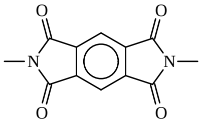
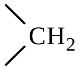
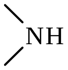
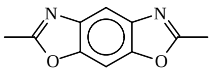
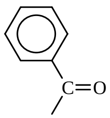
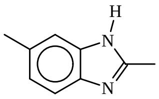
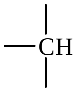
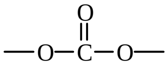
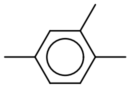
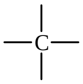
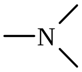
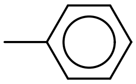
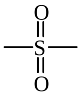
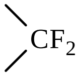
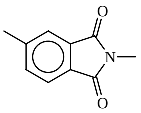
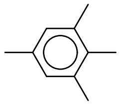
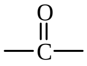
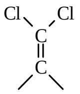
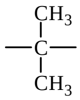
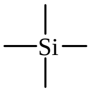
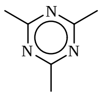
$$n_i = \frac{N_i}{\sum_i N_i} \quad \text{and} \quad \boldsymbol{M} = \sum_i n_i M_i = \frac{\sum_i N_i M_i}{\sum_i N_i} \tag{6}$$

where N_i and M_i are the number of moles and molar mass, respectively, of group i in the polymer having repeat unit of molar mass $\boldsymbol{M}$, the heat of combustion can be expressed on a mass basis.

$$\Delta h_c = \frac{\boldsymbol{H}}{\boldsymbol{M}} = \frac{\sum_i n_i H_i}{\sum_i n_i M_i} = \frac{\sum_i N_i H_i}{\sum_i N_i M_i} \tag{7}$$

In practice, the largest chemical groups listed in the table 1 are used to calculate the heat of combustion of the molecule. The sum of the molar group contributions is divided by the molecular weight of the molecule or polymer repeat unit to yield the specific heat of combustion.

TABLE 1. STRUCTURAL GROUPS AND THEIR MOLAR CONTRIBUTIONS TO THE GROSS HEAT OF COMBUSTION

Structural Group, *i*	H_i (kJ/mol)	Structural Group, *i*	H_i (kJ/mol)	Structural Group, *i*	H_i (kJ/mol)
	9845*		939	$-\mathrm{CF_3}$	213
	4955*		781	$-\mathrm{H}$	190
	4889	$-\mathrm{CH_3}$	775	 $-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{O}-$	112
	4343*		670		77
	3964*	$-\mathrm{C{\equiv}N}$	548	$-\mathrm{NO_2}$	0
	3725*	$-\mathrm{CH_2}\text{-}\mathrm{O}-$	522*	$-\mathrm{Cl}$	-43
	3444*	 $-\overset{\vert}{\underset{\vert}{\mathrm{C}}}\mathrm{H}$	518	 $-\mathrm{O}-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-\mathrm{O}-$	-78*
	3186	 $-\overset{\vert}{\underset{\vert}{\mathrm{C}}}-$	431		-100
	3130	 $-\overset{\mathrm{O}}{\overset{\Vert}{\underset{\underset{\mathrm{O}}{\Vert}}{\mathrm{S}}}}-$	338	$-\mathrm{OH}$	-108
	2871		328	$-\mathrm{O}-$	-132
	2746	$-\mathrm{S}-$	311	$-\mathrm{F}$	-230
	2653	 $-\overset{\mathrm{O}}{\overset{\Vert}{\mathrm{C}}}-$	259		NA
 $-\overset{\mathrm{CH_3}}{\overset{\vert}{\underset{\underset{\mathrm{CH_3}}{\vert}}{\mathrm{C}}}}-$	2294	 $-\overset{\vert}{\underset{\vert}{\mathrm{Si}}}-$	219		NA

RESULTS

Measured heat of combustion values for 66 polymers [10 and 11] and 78 small molecules [16 and 17] with known chemical structure have been used to generate the additive molar group contributions shown in table 1. The molar group contributions were obtained by treating the H_i as adjustable parameters in the linear system of equations for materials with known chemical structures and measured Δh_c. The optimization calculation continued until the sum of the squares of the relative error between the measured Δh_c and calculated values was a minimum. The calculation converged rapidly to the unique H_i, listed in table 1, which were independent of initial estimates. Molar group contributions derived from a single material are marked with an asterisk (*) to indicate that these are not average values. Measured and calculated heats of combustion for the 66 polymers and 78 small molecules are plotted against one another in figure 1.

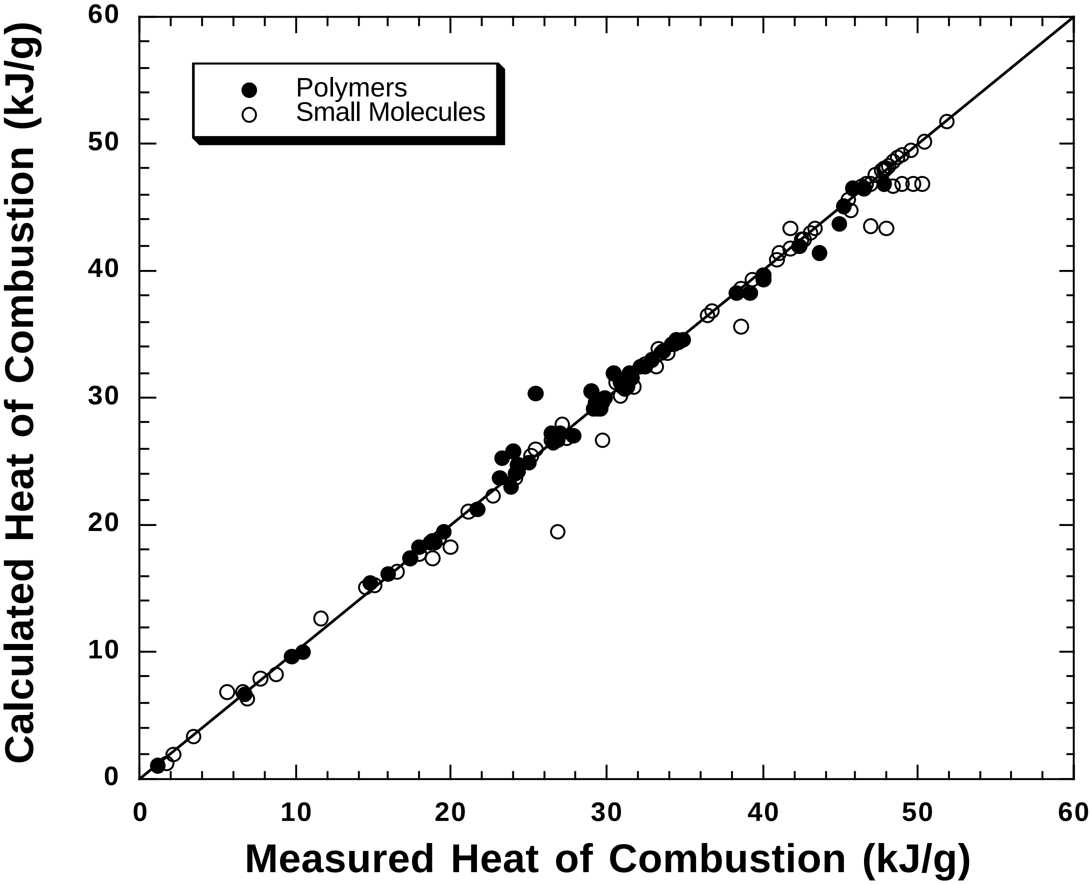
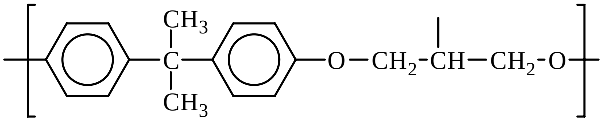


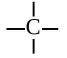
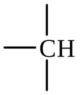
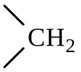
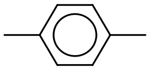
FIGURE 1. PLOT OF THE CALCULATED VERSUS THE MEASURED HEAT OF COMBUSTION FOR 66 POLYMERS AND 78 SMALL MOLECULES

Table 2 shows an example of the thermochemical calculation of the heat of combustion from additive molar group contributions for a ring-opening polymerization of the diglycidyl ether of bisphenol-A (BPA epoxy). This polymer has the repeat unit structure:



The polymer repeat unit is comprised of six basic chemical groups and the heat of combustion is calculated from the associated N_i, M_i, and H_i as follows.

TABLE 2. CALCULATION OF HEAT OF COMBUSTION OF BISPHENOL-A EPOXY

Structural Group, i	N_i	M_i (g/mole)	Group Value, H_i (kJ/mole)	$N_i M_i$ (g)	$N_i H_i$ (kJ)
	1	12.011	431	12.011	431
	1	13.0189	518	13.0189	518
	2	14.0268	670	28.5036	1340
$-CH_3$	2	15.0347	775	30.0694	1550
	2	76.0976	2653	152.1952	5306
—O—	2	15.9994	-132	31.9988	-264
			Total:	267.7969	8881

The molar heat of combustion, obtained by summing the group contributions according to their mole fraction is then divided by the molar mass of the repeat unit to give the heat of combustion in units of kJ/g. The predicted value of 33.16 kJ/g compares well with the measured value of 32.50 kJ/g for this particular polymer.

$$\Delta H_c = \frac{\sum_i N_i H_i}{\sum_i N_i M_i} = \frac{8881\ kJ}{267.797\ g} = 33.16\ kJ/g$$

Molecules that can be described by several different group combinations should use the largest groups listed for calculating the heat of combustion.

Since the molar group contributions are derived from experimental data they should correlate well with measured heats of combustion. In fact, calculated and measured heats of combustion for over 140 compounds differ by only ±2.5% on average.

CONCLUSION

Additive molar contributions to the gross heat of complete combustion for 37 structural groups have been determined from data for 66 polymers and 78 small molecules with known chemical structure. The group contribution method improves upon previous techniques by providing a direct, single step method for calculating the heat of combustion of chemical compounds.

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