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Heats of Formation and Thermodynamic Functions for C_2H, C_3H, and C_4H From 300 K to 6000 K

Antony F. Saturno

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Antony F. Saturno
Langley Research Center
Hampton, Virginia

National Aeronautics
and Space Administration

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SUMMARY

Values for the heat of formation and the thermodynamic functions of C_2H have previously been based on data acquired in 1959 and have been considered uncertain. More recently published data are reviewed and analyzed and are shown to provide a reasonably certain basis for values of both the heat of formation (129 kcal/mol) and the thermodynamic functions of C_2H. In addition, the heats of formation of C_3H and C_4H are derived and are calculated to be 139 and 166 kcal/mol.

The procedure for computing thermodynamic data from partition functions is reviewed. Working expressions for approximate partition functions, free-energy function, and heat capacity for a linear polyatomic species are also presented.

INTRODUCTION

Entry into the atmospheres of the outer planets is accompanied by intense radiative heating of the entry probe. To some degree, this thermal radiation is absorbed by the cooler gases being evolved from the ablative heat shield. Calculation of this radiant heat transfer requires knowledge of both the composition and the absorption properties of the ablated gases. In particular, the calculation of the equilibrium composition of such gases requires that the heat of formation and the thermodynamic functions of enthalpy $(H^o - H^o_o)/T$ and free energy $(G^o - H^o_o)/T$ of the constituent gases be known.

This report is specifically concerned with the carbon-rich species C_2H, C_3H, and C_4H and their thermochemical properties. It should be pointed out that these properties, especially the heats of formation, strongly affect the composition of the gas mixtures; in fact, to assume the absence of any one species is to assign it an extremely high positive heat of formation. Furthermore, the overall radiant heat transfer is dependent upon this composition, which eventually enters into the weight requirements of the shield itself.

HEATS OF FORMATION

General Theory

Bond dissociation energy D_o and subsequently the heat of formation ΔH^o_{fo} of a particular species (free radical or ion) are often obtained by the determination of appearance potentials (AP) (or threshold energies) of the ion or radical formed by either a photon or electron impact procedure in a known process or processes. Typical examples of these determinations are as follows:

1. Heat of formation of R_1 via electron impact:

$$e^- + R_1\text{-}R_2 \rightarrow R_1^+ + R_2 + 2e^- \qquad \Delta E \equiv AP(R_1^+)$$

$$e^- + R_1 \rightarrow R_1^+ + 2e^- \qquad \Delta E \equiv IP(R_1)$$

The net reaction is

$$R_1\text{-}R_2 \rightarrow R_1 + R_2 \qquad \Delta E \equiv D_o(R_1\text{-}R_2)$$

with

$$D_o(R_1\text{-}R_2) = AP(R_1^+) - IP(R_1)$$

$$= \Delta H^o_{fo}(R_1) + \Delta H^o_{fo}(R_2) - \Delta H^o_{fo}(R_1\text{-}R_2)$$

Note that we also require $\Delta H^o_{fo}(R_2)$ and $\Delta H^o_{fo}(R_1\text{-}R_2)$ to be known.

2. Heat of formation of R_1 via photon impact:

$$h\nu + R_1\text{-}R_2 \rightarrow R_1 + R_2 \qquad \Delta E = D_o(R_1\text{-}R_2) = h\nu$$

$$h\nu' + R_1\text{-}R_2 \rightarrow R_1^+ + R_2 + e^- \qquad \Delta E = h\nu'$$

The net reaction is

$$R_1 \rightarrow R_1^+ + e^- \qquad \Delta E = IP(R_1) = h\nu' - h\nu$$

with

$$h\nu' - h\nu = \Delta H^o_{fo}(R_1^+) - \Delta H^o_{fo}(R_1)$$

In this reaction, $\Delta H^o_{fo}(R_1^+)$ should be known.

Ethynyl Radical C_2H

Although the existence of C_2H has been reported by several laboratories, its heat of formation has remained uncertain (refs. 1 to 5). After reviewing the literature, Tsang et al. (ref. 6) adopted a value of 116 kcal/mol; a value of 114 kcal/mol is listed in the JANAF tables (ref. 7). From 1971 to the present, a series of experiments all lead to values of the heat of formation ΔH^o_{fo} of C_2H in the range 124 to 129 kcal/mol. (An average of the reported values is 127 ± 3 kcal/mol.) These experiments include the following: the determination of the equilibrium constants for the reaction of graphite at high temperatures with hydrogen, methane, and acetylene in an integral furnace mass spectrometer (Wyatt and Stafford, ref. 8); electron-impact studies on $CH_3C{\equiv}CH$ in a sector field mass spectrometer (Sharma and Franklin, ref. 9); photon-impact studies on cyanoacetylene, C_2HCN (Okabe and Dibeler, ref. 10); and photodissociation ionization of C_2H_2 using the supersonic molecular-beam method (Ono and Ng, ref. 11). It would appear the uncertainty in the heat of formation of C_2H is no longer warranted. Discussions and summaries of these experiments follow.

Experiment of Wyatt and Stafford.- Intensities were measured with a furnace mass spectrometer for H^+, C^+, $C_2{}^+$, C_2H^+, and $C_2H_2{}^+$ at various temperatures using hydrogen, acetylene, or methane as inlet gases. The sensitivity factor used to convert ion intensity to pressure was chosen to minimize the difference between calculated and experimental pressures of both C and C_3. To help confirm equilibrium, the heat of formation of acetylene was calculated from the intensity of H^+ and $C_2H_2{}^+$. For various runs the values found for C_2H_2 were within ±3 kcal/mol of the accepted value of 54 kcal/mol. In addition, there was no observed dependence of the heat of formation of C_2H on the inlet gas nor on the reaction chosen from $2C(s) + H(g) \rightarrow C_2H(g)$, $C_2 + C_2H_2 \rightarrow 2C_2H$, or $2C(s) + C_2H_2 \rightarrow 2C_2H$. Analysis of the pressure data using the third law method for the various equilibria produces a value of $\Delta H^o_{fo}(C_2H) = 129 \pm 3$ kcal/mol. (An example of a representative calculation is given in appendix A.) This value, essentially a directly determined one as opposed to the remaining indirect determinations described below, is recommended for use in all applications.

Experiment of Sharma and Franklin.- In a sector field mass spectrometer the appearance potential for the onset of CH_3^+ from methylacetylene HC_2CH_3 was measured, that is, $CH_3C{\equiv}CH + e^- \rightarrow CH_3^+ + C_2H + 2e^-$, from which the heat of formation of C_2H was calculated. It should be noted that this method tends to give low rather than high values of heat of formation. For the reaction studied the appearance potential observed was 346 kcal. With the heats of formation of CH_3^+ and $CH_3C{\equiv}CH$ at 260 and 44.3 kcal/mol (ref. 12), the heat of formation of C_2H at 300 K is calculated to be 130 kcal/mol.

Photon-impact experiments of Okabe and Dibeler.- The basis for these experiments is that by the absorption of light in the vacuum ultraviolet, some polyatomic molecules undergo dissociation to produce fluorescing excited states, and the measurement of threshold energies of incident photons required to produce the excited species provides information on bond dissociation energies and, subsequently, on heats of formation. In this experiment, the bond dissociation energy of cyanoacetylene $D_o(C_2H\text{-}CN)$ and the appearance potential of C_2H^+ from C_2HCN make it possible to derive the heat of formation of C_2H as $\Delta H^o_{fo}(C_2H) = 127 \pm 1$ kcal/mol. (See appendix B.) It should be pointed out that the derivation in essence requires the ionization energy of $C_2H \rightarrow C_2H^+ + e^-$ and the threshold energy for the process $C_2H_2 + h\nu \rightarrow C_2H^+ + H + e^-$.

Photon-impact/supersonic molecular-beam experiment of Ono and Ng.- A source of uncertainty in the photon-impact determination of the heat of formation of C_2H lies in the determination of the threshold energy (or appearance potential) for the photodissociation process $HC{\equiv}CH + h\nu \rightarrow C_2H^+ + H + e^-$, which is used to determine the heat of formation of C_2H^+. This result coupled with an independent determination of the ionization energy of C_2H produces a value of the heat of formation of C_2H. The authors state that the best estimate of ionization energy of C_2H is 11.51 eV (from ref. 13). The latest photon-impact value for the appearance potential of C_2H^+ from C_2H_2 is 17.36 eV (from ref. 14), which leads to a value of the heat of formation of C_2H equal to 137 kcal/mol when coupled with the ionization energy of C_2H of 11.51 eV.

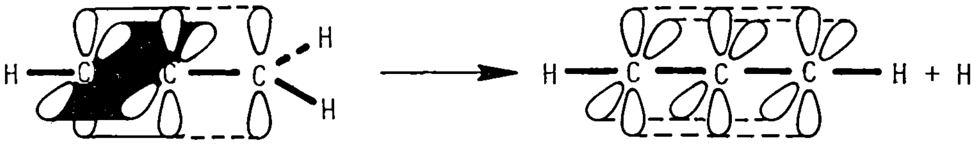
This experiment seeks to repeat the photon-impact determination of the appearance potential of C_2H^+ from C_2H_2 because the previously measured value of 17.36 eV is probably too high by 0.50 eV due to hot-band effects in the photoionization energy curves for C_2H^+. The use of the supersonic molecular-beam method reduces the rotational and vibrational temperatures of C_2H_2 and thereby eliminates these effects. The remeasured photoionization energy curve for C_2H^+ yields a threshold energy (or appearance potential) of 16.79 eV, which produces a value of 124 kcal/mol for the heat of formation of C_2H. In appendix C we summarize and compare the results of both sets of experiments.

The C_3H Molecule

Our objective in this and the following section is the estimation of the heats of formation of the low-molecular-weight, carbon-rich fragments C_3H and C_4H. The estimates are made by the method of Cowperthwaite and Bauer (ref. 15). (See appendix D.) This empirical procedure produces an estimate by (1) assigning to each species a formal electronic configuration; (2) selecting a path for dissociation which, when followed, generates the species under consideration in going from one molecule of known structure to another; and (3) estimating the bond dissociation energies from known simple dissociations corrected for nonlocalized electron interactions. Thus, experimental values which link two states are divided into unit steps on the basis of empirically assigned parameters. For example, $C_3H_3 \rightarrow C_3H_2 + H$ and $C_3H_2 \rightarrow C_3H + H$. Thus, the first estimated bond dissociation energy $D_o(C_3H_2\text{-}H)$ together with the known heats of formation of C_3H_3 and H give $\Delta H^o_{fo}(C_3H_2)$, and the second estimated bond dissociation energy $D_o(C_3H\text{-}H)$ together with the heat of formation of C_3H_2 determined in step 1 determines the heat of formation of C_3H. The following illustrates this procedure:

Step 1: $C_3H_3 \rightarrow C_3H_2 + H$

that is,



Thus, we have ruptured an ethylenic C-H bond (D_o = 104 kcal/mol) and produced a stabilization energy γ as a result of the interaction of three pπ electrons on three centers, that is,

$$D_o(C_3H_2\text{-}H) \approx 104 - \gamma = 104 - 23.1 = 80.9 \text{ kcal/mol}$$

Thus,

$$D_o(C_3H_2\text{-}H) = \Delta H^o_{fo}(C_3H_2) + \Delta H^o_{fo}(H) - \Delta H^o_{fo}(C_3H_3)$$

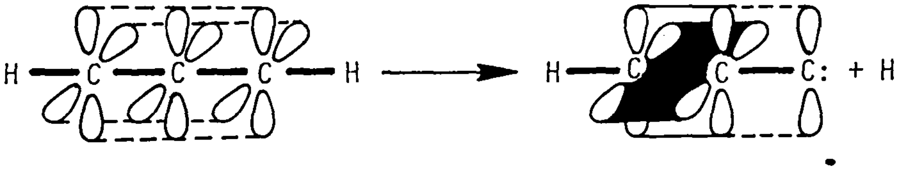
$$80.9 = \Delta H^o_{fo}(C_3H_2) + \Delta H^o_{fo}(H) - \Delta H^o_{fo}(C_3H_3)$$

$$= \Delta H^o_{fo}(C_3H_2) + 51.6 - 77.3$$

$$\Delta H^o_{fo}(C_3H_2) = 106.6 \text{ kcal/mol}$$

Step 2: $C_3H_2 \rightarrow C_3H + H$

that is,



Thus, we have a ruptured acetylenic C-H bond followed by formation of a pπ-pπ ethylenic bond β coupled with loss of the stabilization energy γ resulting from the interaction of three pπ electrons on three centers. This results in

$$D_o(C_3H\text{-}H) \approx D_o(C_2H\text{-}H) - \beta + \gamma = D_o(C_2H\text{-}H) - 65 + 23.1$$

We note at this point the dependence of $\Delta H^o_{fo}(C_3H)$ on $\Delta H^o_{fo}(C_2H)$. It has entered into our calculation of the bond dissociation energy of acetylene, that is,

$$C_2H_2 \rightarrow C_2H + H$$

and

$$D_o(C_2H\text{-}H) = \Delta H^o_{fo}(C_2H) + \Delta H^o_{fo}(H) - \Delta H^o_{fo}(C_2H_2)$$

$$= 129 + 51.6 - 54.3 = 126.3 \text{ kcal/mol}$$

Thus,

$$D_o(C_3H\text{-}H) = 126.3 + 23.1 - 65 = 84.4 \text{ kcal/mol}$$

$$84.4 = \Delta H^o_{fo}(C_3H) + \Delta H^o_{fo}(H) - \Delta H^o_{fo}(C_3H_2)$$

$$\Delta H^o_{fo}(C_3H) = 84.4 + 106.6 - 51.6 = 139.4 \text{ kcal/mol}$$

The C_4H Molecule

The estimated heat of formation for C_4H is obtained by considering the bond dissociation energy for diacetylene

$$H\text{-}C{\equiv}C\text{-}C{\equiv}C\text{-}H \rightarrow H\text{-}C{\equiv}C\text{-}C{=}C{:} + H$$

Thus, we have ruptured an acetylenic C-H bond ($D_o = 126.3$ kcal/mol), corrected for extra delocalization energy $g/2$, and produced stabilization energy γ by the interaction of three pπ electrons on three centers, that is,

$$D_o(HC_4\text{-}H) = 126.3 + g/2 - \gamma = 126.3 + 3.3 - 23.1 = 106.5 \text{ kcal/mol}$$

Thus,

$$D_o(HC_4\text{-}H) = \Delta H^o_{fo}(C_4H) + \Delta H^o_{fo}(H) - \Delta H^o_{fo}(C_4H_2)$$

$$106.5 = \Delta H^o_{fo}(C_4H) + 51.6 - 111.3$$

$$\Delta H^o_{fo}(C_4H) = 166.2 \text{ kcal/mol}$$

THERMODYNAMIC FUNCTIONS

The basic equations to be used in computing the thermodynamic functions for a linear polyatomic molecule are given below in working form. Their derivation may be found in any standard text on statistical thermodynamics and spectroscopy (e.g., ref. 16).

The translation and rotation contribution is the following:

$$-\left(G^o - H^o_o\right)/T = 2.98747 \ln M + 4.967912 \ln T - 1.987165 \ln \left(B\sigma/T\right)$$

$$+ 0.953038(B/T) + 0.0457074(B/T)^2 - 8.005805$$

$$\left(H^{\circ} - H^{\circ}_{o}\right)/T = 6.955077 - 0.953038(B/T) - 0.0914148(B/T)^{2}$$

$$Cp^{\circ} = 6.955077 + 0.0914148(B/T)^{2}$$

Note that the rotational constant $B = B_e - (\alpha_e/2)$ when spectroscopic constants are available, or $B = 2.799076 \times 10^{-39}/I$ when calculated from a molecular model (where I is in gram-centimeters squared).

The vibration contribution (per normal mode) is the following:

$$-(G^{\circ} - H^{\circ}_{o})/T = -1.987165 \ln(1 - e^{-u})$$

$$(H^{\circ} - H^{\circ}_{o})/T = 1.987165ue^{-u}/(1 - e^{-u})$$

$$Cp^{\circ} = 1.987165u^{2}e^{-u}/(1 - e^{-u})^{2}$$

where $u = 1.438790(\omega_e - 2\omega_e x_e)/T$ when spectroscopic constants are available, or $u = 1.438790\omega/T$ where ω is the fundamental wave number of a harmonic oscillator.

Finally, the electronic contribution is as follows:

$$-\left(G^{\circ} - H^{\circ}_{o}\right)/T = 1.987165 \ln \sum_{i} g_{ei} \exp\left(-\omega_i\right)$$

$$\left(H^{\circ} - H^{\circ}_{o}\right)/T = 1.987165 \sum_{i} \omega_i g_{ei} \exp(-\omega_i) \Big/ \sum_{i} g_{ei} \exp\left(-\omega_i\right)$$

$$Cp^{\circ} = 1.987165\left\{\frac{\sum_{i} \omega_i^{2} g_{ei} \exp(-\omega_i)}{\sum_{i} g_{ei} \exp(-\omega_i)} - \left[\frac{\sum_{i} \omega_i g_{ei} \exp(-\omega_i)}{\sum_{i} g_{ei} \exp(-\omega_i)}\right]^{2}\right\}$$

where $\omega_i = 1.438790T_{ei}/T$ with T_{ei} in cm^{-1} and where $g_{ei} = (2S + 1)$ for Σ-states, $2(2S + 1)$ for Π-states, and so forth.

SPECTROSCOPIC DATA AND THERMODYNAMIC FUNCTIONS

Calculation of thermodynamic functions requires as input electronic excitation energies, rotational constants, and normal-mode vibrational frequencies, and where possible, parameters describing the coupling of rotational and vibrational motion are included (refs. 16 and 17). Such data are available for stable species but less so for unstable or transient molecules. In such cases data are generally derived from analogous compounds. The present JANAF table entry for C_2H is derived from the data for HCN (ref. 18) (compare $H\text{-}C{\equiv}C\cdot$ with $H\text{-}C{\equiv}N\cdot$). More recent spectroscopic data on the normal-mode frequencies of C_2H have been obtained by Jacox (ref. 19) and are incorporated in the following table:

Species	Normal-mode frequencies, cm^{-1}, for degeneracies of -			Rotational constant, B, cm^{-1}
	1	2	1	
H-C-N	2089	712	3312	
H-C-C*	1920	640	3220	1.475
H-C-C†	1848		3612	1.460

*From reference 18.
†From reference 19.

This table presents the normal-mode frequencies of both HCN and C_2H as derived by Plooster and Reed (ref. 18) and as determined by Jacox (ref. 19). Included also are the rotational constants. The table below presents the ground and lowest lying first excited electronic states and their degeneracies.

State	T_{ei}, cm^{-1}	g_{ei}
$X^2\Sigma^+$	0	2
$A^2\Pi$	[a]3500	4

[a] From reference 20.

Tables I(a) and I(b) present the calculated thermodynamic functions for C_2H. The values in table I(b) are recommended since they are computed using directly observed data on the higher normal-mode frequencies of C_2H, whereas the JANAF table values make use of what must be termed hypothetical normal-mode frequencies which have been derived from the corresponding HCN frequencies.

Since no data are available for either C_3H or C_4H, tables of their thermodynamic functions must perforce be empirical. Tables II, III, and IV present the thermodynamic functions recommended by Duff and Bauer (ref. 21) for C_2H, C_3H, and C_4H. These authors expressed the thermodynamic functions in the following polynomial form:

$$\frac{H_T^o - H_o^o}{RT} = a + bT + cT^2 + dT^3 + eT^4$$

and

$$\frac{G_T^o - H_o^o}{RT} = a(1 - \ln T) - bT - \frac{c}{2}T^2 - \frac{d}{3}T^3 - \frac{e}{4}T^4 - k$$

The parameters a to e were evaluated for the enthalpy function with the method of least squares. The magnitude of k is computed for each temperature from the known values of the free energy. The value of k was the average k over a set of equally spaced temperature points. On the average, the polynomial fits reproduce tabulated values of the enthalpy function to 0.1 percent and free-energy function to

0.01 percent. This was done for a total of 57 C/H species. A further refinement and expansion of the data set has been made by G. S. Bahn for about 180 C/H and C/H/O species; the set is tabulated in reference 22. This work is viewed as an improvement over that of Duff and Bauer and is recommended as the data of choice for C_3H and C_4H.

APPLICATION OF THE PRESENT WORK

The present study has been applied to the analysis of heat shield mass loss for a Jupiter probe (ref. 23). The gases which are emitted from the heat shield by ablation absorb and thereby block a portion of the shock layer radiation. Calculations of the net radiant flux reaching the probe surface, therefore, require the determination of the density distribution of the various component species of the ablation layer.

The higher values of the heats of formation of C_2H, C_3H, and C_4H as compared with the values formerly used cause a decrease in the predicted number density of these species within the ablation layer. Conservation of elemental mass thus forces a corresponding increase in the density of other carbon-containing species, the most important of which are diatomic (C_2) and triatomic (C_3) carbon. These species possess absorption bands which are instrumental in blocking shock layer radiation. In addition, there is a marked change in the chemical makeup of the ablation species, a result of which is that the sublimation enthalpy for the phenolic-carbon ablator is increased. Thus, less mass is lost for a given heat input. This is particularly important for the Jupiter probe, for which the mass loss during entry represents about one-fourth the total probe mass. The calculation reported in reference 23 with the revised values of the relevant thermodynamic variables produced a reduction of 9 percent in the calculated mass loss rate over that of the "standard model as of August 1981."

CONCLUDING REMARKS

In this study we have examined the recent literature for the purpose of reviewing and updating the thermodynamic data for C_2H, with primary focus on the standard heat of formation. The recent literature indeed provides a basis for an accurate and reasonably certain value of this quantity. We also updated the heats of formation of both C_3H and C_4H. The set of values for the standard heats of formation of C_2H, C_3H, and C_4H are 129, 139, and 166 kcal/mol. It may be noted that previous values for these species were 112, 124, and 150 kcal/mol.

We have also presented a review and summary of the procedure for computing thermodynamic data from partition functions. Working expressions applicable to a linear polyatomic species are displayed.

Finally, the results of this study were applied to an analysis of heat shield mass loss for a Jupiter probe. The revised values of the relevant thermodynamic variables produced a 9-percent reduction in the calculation of mass loss rate compared with the previous values used.

Langley Research Center
National Aeronautics and Space Administration
Hampton, VA 23665
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APPENDIX A

REPRESENTATIVE CALCULATION OF HEAT OF FORMATION OF C_2H FROM EQUILIBRIUM PRESSURE DATA

A representative calculation of heat of formation for C_2H from equilibrium pressure data is given below. The reaction involved is $2C(s) + H(g) \rightarrow C_2H(g)$ at $T = 2233$ K. The equilibrium pressures used are 0.12×10^{-8} atm (1 atm = 101.3 kPa) for C_2H and 570×10^{-8} atm for H. Other values necessary for the calculations are given in the following table:

Species	$(G^o - H^o_{298})/T$ from -		$\Delta H^o_{f,298}$, kcal/mol
	JANAF[a]	Duff and Bauer[b]	
C_2H	-62.106	-63.157	52.10
H	-33.090	-33.091	0
C(s)	-5.964	-6.001	

[a] Reference 7.
[b] Reference 21.

For the reaction $2C(s) + H = C_2H$,

$$\Delta H^o_{298,rx} = -RT \ln K_p - T\left[\Delta\left(G^o - H^o_{298}\right)/T\right]_{rx}$$

$$= \Delta H^o_{f,298}(C_2H) - \Delta H^o_{f,298}(H) - 2\Delta H^o_{f,298}(C(s))$$

With values from reference 7, $\Delta H^o_{f,298}(C_2H) = 128$ kcal/mol, and with values from reference 21, $\Delta H^o_{f,298}(C_2H) = 130$ kcal/mol.

APPENDIX B

PHOTON-IMPACT DETERMINATION OF HEAT OF FORMATION OF C_2H

Determination of the heat of formation of C_2H with the photon-impact method involves the use of several energy values. The threshold energy for formation of excited state for $C_2HCN + h\nu \rightarrow C_2H + CN^*$ is 9.41 eV. The excitation energy for $CN^* \rightarrow CN$ is -3.20 eV (ref. 24). Therefore, the derived bond dissociation energy for $C_2HCN \rightarrow C_2H + CN$ is 6.21 eV. If the threshold energy for $C_2HCN + h\nu \rightarrow C_2H^+ + CN + e^-$ is 18.19 eV, then the derived threshold ionization of $C_2H \rightarrow C_2H^+ + e^-$ is 18.19 - 6.21 = 11.98 eV. Threshold energy for $C_2H_2 + h\nu \rightarrow C_2H^+ + H + e^-$ from reference 14 is 17.36 eV; thus, derived threshold energy for $C_2H_2 \rightarrow C_2H + H$ is 5.38 eV. Therefore, the heat of formation of C_2H derived with the photon-impact method is

$$\Delta H^o_{fo}(C_2H) = 5.38 + \Delta H^o_{fo}(C_2H_2) - \Delta H^o_{fo}(H)$$

$$= 5.50 \text{ eV} = 127 \text{ kcal/mol}$$

APPENDIX C

HEATS OF FORMATION FROM PHOTON-IMPACT EXPERIMENTS

Consider the processes for the appearance potential of C_2H^+ from $C_2H_2 + h\nu \rightarrow C_2H^+ + H + e^-$ (designated $AP(C_2H^+)$) and for the ionization of C_2H from $C_2H \rightarrow C_2H^+ + e^-$ (designated $IE(C_2H)$). These two processes together give

$$\Delta H^o_{fo}(C_2H) = AP(C_2H^+) - IE(C_2H) + \Delta H^o_{fo}(C_2H_2) - \Delta H^o_{fo}(H)$$

$$= AP(C_2H^+) - IE(C_2H) + 0.12 \text{ eV}$$

From the experiment of Okabe and Dibeler (ref. 10),

$$AP(C_2H^+) = 17.36 \text{ eV}$$

and

$$IE(C_2H) = 11.98 \text{ eV}$$

Therefore,

$$\Delta H^o_{fo}(C_2H) = 17.36 - 11.98 + 0.12 = 5.50 \text{ eV}$$

$$= 127 \text{ kcal/mol}$$

From the experiment of Ono and Ng (ref. 11),

$$AP(C_2H^+) = 16.79 \text{ eV}$$

and

$$IE(C_2H) = 11.51 \text{ eV}$$

resulting in

$$\Delta H^o_{fo}(C_2H) = 16.79 - 11.51 + 0.12 = 5.40 \text{ eV}$$

$$= 124 \text{ kcal/mol}$$

APPENDIX D

METHOD OF COWPERTHWAITE AND BAUER

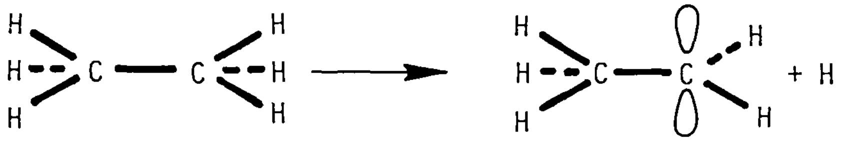
This empirical procedure from reference 15 produces an estimate of experimentally inaccessible bond dissociation energies by the method of generating a set of energy parameters which are used to describe the energy changes accompanying bond dissociation. Consider, for example, the following processes (with measured bond dissociation energies):

$C_2H_6 \rightarrow C_2H_5 + H$ $\qquad D_o(C_2H_5\text{-}H) = 98$ kcal/mol

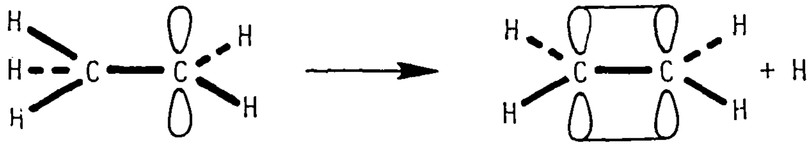
and

$C_2H_5 \rightarrow C_2H_4 + H$ $\qquad D_o(C_2H_4\text{-}H) = 36.2$ kcal/mol

Proceeding according to Cowperthwaite and Bauer, we assign an electronic structure to each species, that is,



and



which we describe energetically as rupture of a saturated C-H bond (98 kcal/mol) stabilized by formation of a $p\pi$ ethylenic pi bond α. Thus, the observed $D_o(C_2H_4\text{-}H)$ is given by

$$D_o(C_2H_4\text{-}H) = 36.2 \text{ kcal} = 98 - \alpha$$

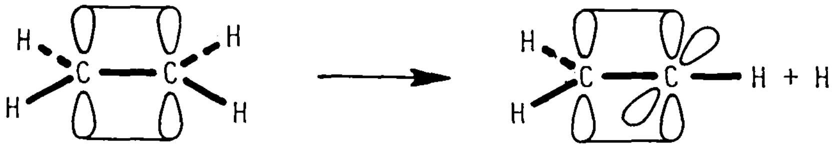
and $\alpha = 61.8$ kcal/mol is the stabilization energy resulting from formation of an ethylenic pi bond.

Consider the following:

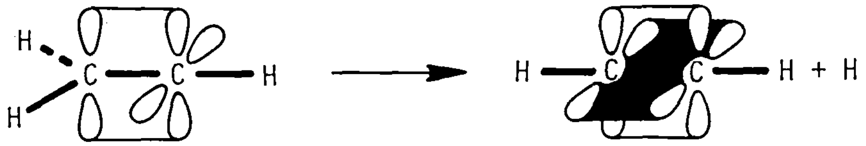
$C_2H_4 \rightarrow C_2H_3 + H$ $\qquad D_o(C_2H_3\text{-}H) = 104$ kcal/mol and

$C_2H_3 \rightarrow C_2H_2 + H$ $\qquad$ $D_o(C_2H_2\text{-}H) = 39$ kcal/mol

the electronic structures of which are



and



Rupture of C_2H_2-H is accompanied by formation of an acetylenic pi bond β, that is,

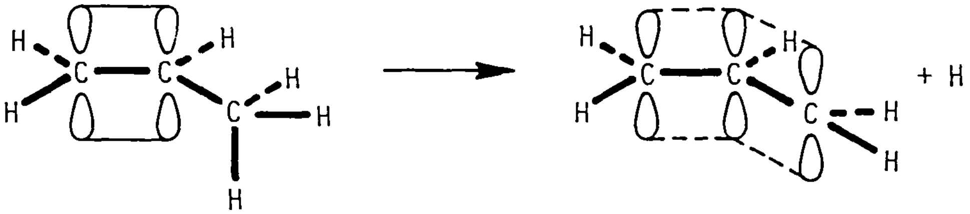
$$39 = 104 - \beta$$

So $\beta = 65$ kcal/mol is the stabilization energy accompanying formation of an acetylenic pi bond.

Consider the following:

$H_2C{=}CHCH_3 \rightarrow H_2C{=}CH\text{-}CH_2 + H$ $\qquad$ $D_o(H_2C{=}CHCH_2\text{-}H) = 78$ kcal/mol

The electronic structure is



APPENDIX D

Rupture of a saturated C-H bond on the methyl radical (98 kcal/mol) corrected for extra delocalization energy a followed by stabilization energy γ resulting from interaction of three pπ electrons on three centers gives

$$78 = 98 + a - \gamma$$

Since a = 3.1 kcal/mol (see below), γ = 23.1 kcal/mol.

The parameters for extra delocalization energy a and g are obtained as differences in hydrogenation energies as follows:

For a,

$H_2 + H_2C{=}CH_2 \rightarrow H_3C{-}CH_3$ $\Delta E = -31.04$ kcal/mol

and

$H_2 + H_2C{=}CHCH_3 \rightarrow H_3C{-}CH_2{-}CH_3$ $\Delta E = -27.95$ kcal/mol

$a = -27.95 - (-31.04) = 3.1$ kcal/mol

For g,

$H{-}C{\equiv}C{-}C{\equiv}C{-}H + 4H_2 \rightarrow H_3C{-}CH_2{-}CH_2{-}CH_3$ $\Delta E = -135$ kcal/mol

and

$2HC{\equiv}CH + 4H_2 \rightarrow 2CH_3{-}CH_3$ $\Delta E = -141.6$ kcal/mol

$g = -135 - (-141.6) = 6.6$ kcal/mol

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TABLE I.- CALCULATED THERMODYNAMIC FUNCTIONS FOR C_2H

(a) Taken from JANAF, reference 7

T,K	CP	S	-(G-H298)/T	H-H298
3.0000E+02	8.8848E+00	4.9608E+01	4.9553E+01	1.6421E+01
4.0000E+02	9.6546E+00	5.2276E+01	4.9912E+01	9.4557E+02
5.0000E+02	1.0234E+01	5.4495E+01	5.0613E+01	1.9411E+03
6.0000E+02	1.0716E+01	5.6404E+01	5.1422E+01	2.9891E+03
7.0000E+02	1.1141E+01	5.8089E+01	5.2257E+01	4.0824E+03
8.0000E+02	1.1523E+01	5.9602E+01	5.3082E+01	5.2159E+03
9.0000E+02	1.1867E+01	6.0979E+01	5.3884E+01	6.3857E+03
1.0000E+03	1.2176E+01	6.2246E+01	5.4658E+01	7.5881E+03
1.1000E+03	1.2453E+01	6.3419E+01	5.5401E+01	8.8197E+03
1.2000E+03	1.2701E+01	6.4514E+01	5.6116E+01	1.0078E+04
1.3000E+03	1.2925E+01	6.5539E+01	5.6802E+01	1.1359E+04
1.4000E+03	1.3129E+01	6.6505E+01	5.7461E+01	1.2662E+04
1.5000E+03	1.3317E+01	6.7417E+01	5.8094E+01	1.3984E+04
1.6000E+03	1.3492E+01	6.8282E+01	5.8704E+01	1.5325E+04
1.7000E+03	1.3656E+01	6.9105E+01	5.9292E+01	1.6683E+04
1.8000E+03	1.3813E+01	6.9890E+01	5.9859E+01	1.8056E+04
1.9000E+03	1.3964E+01	7.0641E+01	6.0407E+01	1.9445E+04
2.0000E+03	1.4109E+01	7.1361E+01	6.0937E+01	2.0849E+04
2.1000E+03	1.4250E+01	7.2053E+01	6.1450E+01	2.2267E+04
2.2000E+03	1.4386E+01	7.2719E+01	6.1947E+01	2.3698E+04
2.3000E+03	1.4519E+01	7.3361E+01	6.2429E+01	2.5144E+04
2.4000E+03	1.4648E+01	7.3982E+01	6.2898E+01	2.6602E+04
2.5000E+03	1.4773E+01	7.4583E+01	6.3353E+01	2.8073E+04
2.6000E+03	1.4893E+01	7.5164E+01	6.3796E+01	2.9557E+04
2.7000E+03	1.5008E+01	7.5729E+01	6.4228E+01	3.1052E+04
2.8000E+03	1.5119E+01	7.6276E+01	6.4649E+01	3.2558E+04
2.9000E+03	1.5224E+01	7.6809E+01	6.5059E+01	3.4075E+04
3.0000E+03	1.5324E+01	7.7327E+01	6.5459E+01	3.5603E+04
3.1000E+03	1.5418E+01	7.7831E+01	6.5850E+01	3.7140E+04
3.2000E+03	1.5506E+01	7.8322E+01	6.6232E+01	3.8686E+04
3.3000E+03	1.5589E+01	7.8800E+01	6.6606E+01	4.0241E+04
3.4000E+03	1.5665E+01	7.9267E+01	6.6971E+01	4.1804E+04
3.5000E+03	1.5736E+01	7.9722E+01	6.7329E+01	4.3374E+04
3.6000E+03	1.5801E+01	8.0166E+01	6.7680E+01	4.4951E+04
3.7000E+03	1.5861E+01	8.0600E+01	6.8023E+01	4.6534E+04
3.8000E+03	1.5915E+01	8.1023E+01	6.8360E+01	4.8123E+04
3.9000E+03	1.5963E+01	8.1437E+01	6.8690E+01	4.9716E+04
4.0000E+03	1.6007E+01	8.1842E+01	6.9013E+01	5.1315E+04
4.1000E+03	1.6046E+01	8.2238E+01	6.9331E+01	5.2918E+04
4.2000E+03	1.6080E+01	8.2625E+01	6.9643E+01	5.4524E+04
4.3000E+03	1.6110E+01	8.3004E+01	6.9949E+01	5.6134E+04
4.4000E+03	1.6136E+01	8.3374E+01	7.0250E+01	5.7746E+04
4.5000E+03	1.6158E+01	8.3737E+01	7.0546E+01	5.9361E+04
4.6000E+03	1.6177E+01	8.4093E+01	7.0837E+01	6.0978E+04
4.7000E+03	1.6192E+01	8.4441E+01	7.1122E+01	6.2596E+04
4.8000E+03	1.6203E+01	8.4782E+01	7.1403E+01	6.4216E+04
4.9000E+03	1.6212E+01	8.5116E+01	7.1680E+01	6.5837E+04
5.0000E+03	1.6219E+01	8.5443E+01	7.1952E+01	6.7458E+04
5.1000E+03	1.6223E+01	8.5765E+01	7.2220E+01	6.9080E+04
5.2000E+03	1.6224E+01	8.6080E+01	7.2483E+01	7.0703E+04
5.3000E+03	1.6224E+01	8.6389E+01	7.2743E+01	7.2325E+04
5.4000E+03	1.6221E+01	8.6692E+01	7.2998E+01	7.3947E+04
5.5000E+03	1.6217E+01	8.6990E+01	7.3250E+01	7.5569E+04
5.6000E+03	1.6212E+01	8.7282E+01	7.3498E+01	7.7191E+04
5.7000E+03	1.6205E+01	8.7569E+01	7.3742E+01	7.8811E+04
5.8000E+03	1.6196E+01	8.7850E+01	7.3983E+01	8.0432E+04
5.9000E+03	1.6187E+01	8.8127E+01	7.4220E+01	8.2051E+04
6.0000E+03	1.6177E+01	8.8399E+01	7.4454E+01	8.3669E+04

TABLE I.- Concluded

(b) Calculated with data from Jacox and Carrick et al., references 19 and 20

T,K	CP	S	-(G-H298)/T	H-H298
3.0000E+02	8.8900E+00	4.9629E+01	4.9574E+01	1.6431E+01
4.0000E+02	9.6741E+00	5.2300E+01	4.9933E+01	9.4675E+02
5.0000E+02	1.0276E+01	5.4526E+01	5.0635E+01	1.9452E+03
6.0000E+02	1.0798E+01	5.6446E+01	5.1447E+01	2.9993E+03
7.0000E+02	1.1294E+01	5.8148E+01	5.2285E+01	4.1040E+03
8.0000E+02	1.1785E+01	5.9688E+01	5.3116E+01	5.2580E+03
9.0000E+02	1.2269E+01	6.1104E+01	5.3926E+01	6.4607E+03
1.0000E+03	1.2736E+01	6.2421E+01	5.4710E+01	7.7112E+03
1.1000E+03	1.3176E+01	6.3656E+01	5.5468E+01	9.0071E+03
1.2000E+03	1.3577E+01	6.4820E+01	5.6199E+01	1.0345E+04
1.3000E+03	1.3933E+01	6.5921E+01	5.6905E+01	1.1721E+04
1.4000E+03	1.4242E+01	6.6965E+01	5.7587E+01	1.3130E+04
1.5000E+03	1.4505E+01	6.7957E+01	5.8245E+01	1.4568E+04
1.6000E+03	1.4724E+01	6.8900E+01	5.8882E+01	1.6030E+04
1.7000E+03	1.4903E+01	6.9799E+01	5.9498E+01	1.7511E+04
1.8000E+03	1.5048E+01	7.0655E+01	6.0094E+01	1.9009E+04
1.9000E+03	1.5162E+01	7.1472E+01	6.0672E+01	2.0520E+04
2.0000E+03	1.5250E+01	7.2252E+01	6.1231E+01	2.2041E+04
2.1000E+03	1.5317E+01	7.2997E+01	6.1774E+01	2.3569E+04
2.2000E+03	1.5366E+01	7.3711E+01	6.2300E+01	2.5104E+04
2.3000E+03	1.5401E+01	7.4395E+01	6.2812E+01	2.6642E+04
2.4000E+03	1.5425E+01	7.5051E+01	6.3308E+01	2.8183E+04
2.5000E+03	1.5438E+01	7.5681E+01	6.3790E+01	2.9727E+04
2.6000E+03	1.5445E+01	7.6287E+01	6.4259E+01	3.1271E+04
2.7000E+03	1.5446E+01	7.6870E+01	6.4716E+01	3.2815E+04
2.8000E+03	1.5442E+01	7.7431E+01	6.5160E+01	3.4360E+04
2.9000E+03	1.5435E+01	7.7973E+01	6.5592E+01	3.5904E+04
3.0000E+03	1.5425E+01	7.8496E+01	6.6014E+01	3.7447E+04
3.1000E+03	1.5414E+01	7.9002E+01	6.6425E+01	3.8989E+04
3.2000E+03	1.5401E+01	7.9491E+01	6.6825E+01	4.0530E+04
3.3000E+03	1.5387E+01	7.9965E+01	6.7216E+01	4.2069E+04
3.4000E+03	1.5372E+01	8.0424E+01	6.7598E+01	4.3607E+04
3.5000E+03	1.5358E+01	8.0869E+01	6.7971E+01	4.5143E+04
3.6000E+03	1.5343E+01	8.1302E+01	6.8335E+01	4.6678E+04
3.7000E+03	1.5328E+01	8.1722E+01	6.8691E+01	4.8212E+04
3.8000E+03	1.5313E+01	8.2130E+01	6.9040E+01	4.9744E+04
3.9000E+03	1.5299E+01	8.2528E+01	6.9381E+01	5.1275E+04
4.0000E+03	1.5285E+01	8.2915E+01	6.9714E+01	5.2804E+04
4.1000E+03	1.5271E+01	8.3292E+01	7.0041E+01	5.4332E+04
4.2000E+03	1.5258E+01	8.3660E+01	7.0361E+01	5.5858E+04
4.3000E+03	1.5245E+01	8.4019E+01	7.0674E+01	5.7383E+04
4.4000E+03	1.5233E+01	8.4369E+01	7.0981E+01	5.8907E+04
4.5000E+03	1.5221E+01	8.4712E+01	7.1283E+01	6.0430E+04
4.6000E+03	1.5210E+01	8.5046E+01	7.1578E+01	6.1951E+04
4.7000E+03	1.5199E+01	8.5373E+01	7.1868E+01	6.3472E+04
4.8000E+03	1.5188E+01	8.5693E+01	7.2153E+01	6.4991E+04
4.9000E+03	1.5178E+01	8.6006E+01	7.2433E+01	6.6509E+04
5.0000E+03	1.5168E+01	8.6312E+01	7.2707E+01	6.8027E+04
5.1000E+03	1.5159E+01	8.6613E+01	7.2977E+01	6.9543E+04
5.2000E+03	1.5150E+01	8.6907E+01	7.3242E+01	7.1058E+04
5.3000E+03	1.5142E+01	8.7195E+01	7.3502E+01	7.2573E+04
5.4000E+03	1.5134E+01	8.7478E+01	7.3759E+01	7.4087E+04
5.5000E+03	1.5126E+01	8.7756E+01	7.4011E+01	7.5600E+04
5.6000E+03	1.5119E+01	8.8029E+01	7.4259E+01	7.7112E+04
5.7000E+03	1.5112E+01	8.8296E+01	7.4502E+01	7.8624E+04
5.8000E+03	1.5105E+01	8.8559E+01	7.4743E+01	8.0134E+04
5.9000E+03	1.5098E+01	8.8817E+01	7.4979E+01	8.1645E+04
6.0000E+03	1.5092E+01	8.9071E+01	7.5212E+01	8.3154E+04

TABLE II.- EMPIRICAL THERMODYNAMIC FUNCTIONS FOR C_2H

RUN

T,K	CP	S	-(G-H298)/T	H-H298
3.0000E+02	8.7113E+00	5.0836E+01	5.0782E+01	1.6103E-02
4.0000E+02	9.4086E+00	5.3440E+01	5.1133E+01	9.2287E-01
5.0000E+02	1.0018E+01	5.5606E+01	5.1816E+01	1.8949E+00
6.0000E+02	1.0552E+01	5.7481E+01	5.2608E+01	2.9240E+00
7.0000E+02	1.1019E+01	5.9143E+01	5.3425E+01	4.0031E+00
8.0000E+02	1.1428E+01	6.0642E+01	5.4235E+01	5.1259E+00
9.0000E+02	1.1788E+01	6.2009E+01	5.5024E+01	6.2870E+00
1.0000E+03	1.2105E+01	6.3268E+01	5.5786E+01	7.4820E+00
1.1000E+03	1.2387E+01	6.4435E+01	5.6520E+01	8.7069E+00
1.2000E+03	1.2638E+01	6.5524E+01	5.7225E+01	9.9584E+00
1.3000E+03	1.2863E+01	6.6545E+01	5.7903E+01	1.1234E+01
1.4000E+03	1.3065E+01	6.7506E+01	5.8555E+01	1.2530E+01
1.5000E+03	1.3248E+01	6.8413E+01	5.9183E+01	1.3846E+01
1.6000E+03	1.3412E+01	6.9274E+01	5.9787E+01	1.5179E+01
1.7000E+03	1.3559E+01	7.0091E+01	6.0369E+01	1.6528E+01
1.8000E+03	1.3689E+01	7.0870E+01	6.0931E+01	1.7890E+01
1.9000E+03	1.3801E+01	7.1613E+01	6.1474E+01	1.9265E+01
2.0000E+03	1.3893E+01	7.2324E+01	6.1999E+01	2.0650E+01
2.1000E+03	1.4015E+01	7.3000E+01	6.2506E+01	2.2037E+01
2.2000E+03	1.4112E+01	7.3655E+01	6.2998E+01	2.3444E+01
2.3000E+03	1.4200E+01	7.4284E+01	6.3475E+01	2.4859E+01
2.4000E+03	1.4278E+01	7.4890E+01	6.3938E+01	2.6283E+01
2.5000E+03	1.4349E+01	7.5474E+01	6.4388E+01	2.7715E+01
2.6000E+03	1.4414E+01	7.6038E+01	6.4826E+01	2.9153E+01
2.7000E+03	1.4472E+01	7.6583E+01	6.5251E+01	3.0597E+01
2.8000E+03	1.4526E+01	7.7111E+01	6.5665E+01	3.2047E+01
2.9000E+03	1.4575E+01	7.7621E+01	6.6069E+01	3.3502E+01
3.0000E+03	1.4621E+01	7.8116E+01	6.6462E+01	3.4962E+01
3.1000E+03	1.4663E+01	7.8596E+01	6.6846E+01	3.6426E+01
3.2000E+03	1.4704E+01	7.9062E+01	6.7220E+01	3.7895E+01
3.3000E+03	1.4742E+01	7.9515E+01	6.7586E+01	3.9367E+01
3.4000E+03	1.4779E+01	7.9956E+01	6.7943E+01	4.0843E+01
3.5000E+03	1.4814E+01	8.0385E+01	6.8293E+01	4.2323E+01
3.6000E+03	1.4848E+01	8.0803E+01	6.8634E+01	4.3806E+01
3.7000E+03	1.4882E+01	8.1210E+01	6.8969E+01	4.5292E+01
3.8000E+03	1.4914E+01	8.1607E+01	6.9296E+01	4.6782E+01
3.9000E+03	1.4946E+01	8.1995E+01	6.9617E+01	4.8275E+01
4.0000E+03	1.4977E+01	8.2374E+01	6.9931E+01	4.9771E+01
4.1000E+03	1.5006E+01	8.2744E+01	7.0239E+01	5.1270E+01
4.2000E+03	1.5035E+01	8.3106E+01	7.0541E+01	5.2773E+01
4.3000E+03	1.5062E+01	8.3460E+01	7.0838E+01	5.4277E+01
4.4000E+03	1.5087E+01	8.3807E+01	7.1128E+01	5.5785E+01
4.5000E+03	1.5110E+01	8.4146E+01	7.1414E+01	5.7295E+01
4.6000E+03	1.5130E+01	8.4478E+01	7.1694E+01	5.8807E+01
4.7000E+03	1.5147E+01	8.4804E+01	7.1970E+01	6.0321E+01
4.8000E+03	1.5160E+01	8.5123E+01	7.2241E+01	6.1836E+01
4.9000E+03	1.5168E+01	8.5436E+01	7.2507E+01	6.3352E+01
5.0000E+03	1.5170E+01	8.5742E+01	7.2768E+01	6.4869E+01
5.1000E+03	1.5166E+01	8.6043E+01	7.3026E+01	6.6386E+01
5.2000E+03	1.5155E+01	8.6337E+01	7.3279E+01	6.7902E+01
5.3000E+03	1.5136E+01	8.6625E+01	7.3528E+01	6.9417E+01
5.4000E+03	1.5107E+01	8.6908E+01	7.3773E+01	7.0929E+01
5.5000E+03	1.5067E+01	8.7185E+01	7.4014E+01	7.2438E+01
5.6000E+03	1.5016E+01	8.7456E+01	7.4252E+01	7.3942E+01
5.7000E+03	1.4952E+01	8.7721E+01	7.4486E+01	7.5441E+01
5.8000E+03	1.4873E+01	8.7981E+01	7.4716E+01	7.6932E+01
5.9000E+03	1.4778E+01	8.8234E+01	7.4943E+01	7.8415E+01
6.0000E+03	1.4666E+01	8.8482E+01	7.5167E+01	7.9887E+01

TABLE III.- EMPIRICAL THERMODYNAMIC FUNCTIONS FOR C_3H

RUN

T,K	CP	S	-(G-H298)/T	H-H298
3.0000E+02	1.0623E+01	5.5324E+01	5.5259E+01	1.9627E-02
4.0000E+02	1.2028E+01	5.8578E+01	5.5693E+01	1.1540E+00
5.0000E+02	1.3229E+01	6.1394E+01	5.6557E+01	2.4184E+00
6.0000E+02	1.4251E+01	6.3899E+01	5.7576E+01	3.7937E+00
7.0000E+02	1.5119E+01	6.6163E+01	5.8643E+01	5.2635E+00
8.0000E+02	1.5853E+01	6.8231E+01	5.9714E+01	6.8131E+00
9.0000E+02	1.6474E+01	7.0135E+01	6.0768E+01	8.4303E+00
1.0000E+03	1.6999E+01	7.1899E+01	6.1794E+01	1.0105E+01
1.1000E+03	1.7445E+01	7.3540E+01	6.2788E+01	1.1827E+01
1.2000E+03	1.7827E+01	7.5075E+01	6.3749E+01	1.3592E+01
1.3000E+03	1.8157E+01	7.6515E+01	6.4676E+01	1.5391E+01
1.4000E+03	1.8448E+01	7.7872E+01	6.5570E+01	1.7222E+01
1.5000E+03	1.8709E+01	7.9153E+01	6.6434E+01	1.9080E+01
1.6000E+03	1.8948E+01	8.0369E+01	6.7267E+01	2.0963E+01
1.7000E+03	1.9171E+01	8.1524E+01	6.8072E+01	2.2869E+01
1.8000E+03	1.9383E+01	8.2626E+01	6.8850E+01	2.4797E+01
1.9000E+03	1.9587E+01	8.3679E+01	6.9603E+01	2.6745E+01
2.0000E+03	1.9784E+01	8.4689E+01	7.0332E+01	2.8714E+01
2.1000E+03	1.9865E+01	8.5641E+01	7.1038E+01	3.0667E+01
2.2000E+03	2.0007E+01	8.6569E+01	7.1723E+01	3.2660E+01
2.3000E+03	2.0130E+01	8.7461E+01	7.2388E+01	3.4667E+01
2.4000E+03	2.0237E+01	8.8320E+01	7.3034E+01	3.6686E+01
2.5000E+03	2.0329E+01	8.9148E+01	7.3662E+01	3.8714E+01
2.6000E+03	2.0408E+01	8.9947E+01	7.4274E+01	4.0751E+01
2.7000E+03	2.0475E+01	9.0719E+01	7.4868E+01	4.2795E+01
2.8000E+03	2.0533E+01	9.1464E+01	7.5448E+01	4.4846E+01
2.9000E+03	2.0583E+01	9.2186E+01	7.6013E+01	4.6902E+01
3.0000E+03	2.0626E+01	9.2884E+01	7.6563E+01	4.8962E+01
3.1000E+03	2.0663E+01	9.3561E+01	7.7101E+01	5.1027E+01
3.2000E+03	2.0695E+01	9.4218E+01	7.7626E+01	5.3095E+01
3.3000E+03	2.0724E+01	9.4855E+01	7.8138E+01	5.5166E+01
3.4000E+03	2.0751E+01	9.5474E+01	7.8639E+01	5.7240E+01
3.5000E+03	2.0776E+01	9.6076E+01	7.9129E+01	5.9316E+01
3.6000E+03	2.0800E+01	9.6662E+01	7.9608E+01	6.1395E+01
3.7000E+03	2.0823E+01	9.7232E+01	8.0076E+01	6.3476E+01
3.8000E+03	2.0846E+01	9.7787E+01	8.0535E+01	6.5559E+01
3.9000E+03	2.0870E+01	9.8329E+01	8.0984E+01	6.7645E+01
4.0000E+03	2.0895E+01	9.8858E+01	8.1425E+01	6.9733E+01
4.1000E+03	2.0921E+01	9.9374E+01	8.1856E+01	7.1824E+01
4.2000E+03	2.0947E+01	9.9879E+01	8.2279E+01	7.3917E+01
4.3000E+03	2.0975E+01	1.0037E+02	8.2694E+01	7.6014E+01
4.4000E+03	2.1003E+01	1.0085E+02	8.3102E+01	7.8112E+01
4.5000E+03	2.1031E+01	1.0133E+02	8.3501E+01	8.0214E+01
4.6000E+03	2.1060E+01	1.0179E+02	8.3894E+01	8.2319E+01
4.7000E+03	2.1089E+01	1.0224E+02	8.4279E+01	8.4426E+01
4.8000E+03	2.1116E+01	1.0269E+02	8.4658E+01	8.6536E+01
4.9000E+03	2.1142E+01	1.0312E+02	8.5031E+01	8.8649E+01
5.0000E+03	2.1166E+01	1.0355E+02	8.5397E+01	9.0765E+01
5.1000E+03	2.1186E+01	1.0397E+02	8.5757E+01	9.2882E+01
5.2000E+03	2.1202E+01	1.0438E+02	8.6111E+01	9.5002E+01
5.3000E+03	2.1212E+01	1.0478E+02	8.6460E+01	9.7123E+01
5.4000E+03	2.1216E+01	1.0518E+02	8.6803E+01	9.9244E+01
5.5000E+03	2.1212E+01	1.0557E+02	8.7140E+01	1.0137E+02
5.6000E+03	2.1198E+01	1.0595E+02	8.7473E+01	1.0349E+02
5.7000E+03	2.1173E+01	1.0633E+02	8.7800E+01	1.0560E+02
5.8000E+03	2.1135E+01	1.0670E+02	8.8123E+01	1.0772E+02
5.9000E+03	2.1083E+01	1.0706E+02	8.8441E+01	1.0983E+02
6.0000E+03	2.1015E+01	1.0741E+02	8.8754E+01	1.1194E+02

TABLE IV.- EMPIRICAL THERMODYNAMIC FUNCTIONS FOR C_4H

RUN

T,K	CP	S	-(G-H298)/T	H-H298
3.0000E+02	1.5155E+01	6.2790E+01	6.2687E+01	2.7999E-02
4.0000E+02	1.7126E+01	6.7422E+01	6.3306E+01	1.6462E+00
5.0000E+02	1.8647E+01	7.1414E+01	6.4538E+01	3.4382E+00
6.0000E+02	1.9817E+01	7.4922E+01	6.5982E+01	5.3639E+00
7.0000E+02	2.0722E+01	7.8048E+01	6.7487E+01	7.3927E+00
8.0000E+02	2.1438E+01	8.0863E+01	6.8986E+01	9.5020E+00
9.0000E+02	2.2025E+01	8.3423E+01	7.0450E+01	1.1676E+01
1.0000E+03	2.2531E+01	8.5770E+01	7.1866E+01	1.3904E+01
1.1000E+03	2.2991E+01	8.7940E+01	7.3230E+01	1.6181E+01
1.2000E+03	2.3430E+01	8.9959E+01	7.4541E+01	1.8502E+01
1.3000E+03	2.3856E+01	9.1851E+01	7.5800E+01	2.0866E+01
1.4000E+03	2.4268E+01	9.3634E+01	7.7011E+01	2.3273E+01
1.5000E+03	2.4649E+01	9.5322E+01	7.8176E+01	2.5719E+01
1.6000E+03	2.4972E+01	9.6924E+01	7.9298E+01	2.8201E+01
1.7000E+03	2.5196E+01	9.8445E+01	8.0380E+01	3.0710E+01
1.8000E+03	2.5267E+01	9.9888E+01	8.1424E+01	3.3235E+01
1.9000E+03	2.5119E+01	1.0125E+02	8.2432E+01	3.5756E+01
2.0000E+03	2.4672E+01	1.0253E+02	8.3405E+01	3.8248E+01
2.1000E+03	2.5799E+01	1.0380E+02	8.4350E+01	4.0850E+01
2.2000E+03	2.5953E+01	1.0501E+02	8.5262E+01	4.3438E+01
2.3000E+03	2.6084E+01	1.0616E+02	8.6146E+01	4.6040E+01
2.4000E+03	2.6195E+01	1.0728E+02	8.7003E+01	4.8654E+01
2.5000E+03	2.6289E+01	1.0835E+02	8.7836E+01	5.1279E+01
2.6000E+03	2.6367E+01	1.0938E+02	8.8645E+01	5.3912E+01
2.7000E+03	2.6432E+01	1.1038E+02	8.9431E+01	5.6552E+01
2.8000E+03	2.6485E+01	1.1134E+02	9.0196E+01	5.9198E+01
2.9000E+03	2.6529E+01	1.1227E+02	9.0942E+01	6.1848E+01
3.0000E+03	2.6564E+01	1.1317E+02	9.1668E+01	6.4503E+01
3.1000E+03	2.6594E+01	1.1404E+02	9.2375E+01	6.7161E+01
3.2000E+03	2.6618E+01	1.1488E+02	9.3066E+01	6.9822E+01
3.3000E+03	2.6639E+01	1.1570E+02	9.3739E+01	7.2485E+01
3.4000E+03	2.6657E+01	1.1650E+02	9.4397E+01	7.5149E+01
3.5000E+03	2.6674E+01	1.1727E+02	9.5040E+01	7.7816E+01
3.6000E+03	2.6691E+01	1.1802E+02	9.5668E+01	8.0484E+01
3.7000E+03	2.6709E+01	1.1876E+02	9.6282E+01	8.3154E+01
3.8000E+03	2.6727E+01	1.1947E+02	9.6883E+01	8.5826E+01
3.9000E+03	2.6747E+01	1.2016E+02	9.7471E+01	8.8500E+01
4.0000E+03	2.6770E+01	1.2084E+02	9.8047E+01	9.1176E+01
4.1000E+03	2.6795E+01	1.2150E+02	9.8611E+01	9.3854E+01
4.2000E+03	2.6823E+01	1.2215E+02	9.9163E+01	9.6535E+01
4.3000E+03	2.6853E+01	1.2278E+02	9.9705E+01	9.9218E+01
4.4000E+03	2.6886E+01	1.2340E+02	1.0024E+02	1.0191E+02
4.5000E+03	2.6922E+01	1.2400E+02	1.0076E+02	1.0460E+02
4.6000E+03	2.6960E+01	1.2459E+02	1.0127E+02	1.0729E+02
4.7000E+03	2.7000E+01	1.2517E+02	1.0177E+02	1.0999E+02
4.8000E+03	2.7041E+01	1.2574E+02	1.0227E+02	1.1269E+02
4.9000E+03	2.7083E+01	1.2630E+02	1.0275E+02	1.1540E+02
5.0000E+03	2.7124E+01	1.2685E+02	1.0323E+02	1.1811E+02
5.1000E+03	2.7165E+01	1.2739E+02	1.0370E+02	1.2082E+02
5.2000E+03	2.7203E+01	1.2791E+02	1.0416E+02	1.2354E+02
5.3000E+03	2.7237E+01	1.2843E+02	1.0461E+02	1.2626E+02
5.4000E+03	2.7267E+01	1.2894E+02	1.0506E+02	1.2899E+02
5.5000E+03	2.7291E+01	1.2944E+02	1.0549E+02	1.3171E+02
5.6000E+03	2.7307E+01	1.2993E+02	1.0593E+02	1.3444E+02
5.7000E+03	2.7314E+01	1.3042E+02	1.0635E+02	1.3718E+02
5.8000E+03	2.7309E+01	1.3089E+02	1.0677E+02	1.3991E+02
5.9000E+03	2.7291E+01	1.3136E+02	1.0718E+02	1.4264E+02
6.0000E+03	2.7258E+01	1.3182E+02	1.0759E+02	1.4536E+02

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Antony F. Saturno: NASA/ASEE Summer Fellow from State University of New York at Albany.

16. Abstract

A review of the energy level and heat of formation data for the species C_2H, C_3H, and C_4H is given. The procedure for computing thermochemical data from partition functions is also reviewed. Working expressions for approximate partition functions, free-energy function, enthalpy function, and heat capacity for a linear polyatomic species are presented.

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