Estimation of the Thermodynamic Properties of Branched Hydrocarbons

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A simple model has been developed to estimate the sensible thermodynamic properties such as Gibbs free energy, enthalpy, heat capacity, and entropy of hydrocarbons over a wide range of temperatures with special attention to the branched molecules. The model is based on statistical thermodynamic expressions incorporating translational, rotational and vibrational motions of the atoms. A method to determine the number of degrees of freedom for different motion modes (bending and torsion) has been established. Branched rotational groups, such as CH_3 and OH, have been considered. A modification of the characteristic temperatures for different motion mode has been made which improves the agreement with the exact values for simple cases. The properties of branched alkanes up to 2,3,4,-trimthylpentane have been calculated and the results are in good agreement with the experimental data. A relatively small number of parameters are needed in this model to estimate the sensible thermodynamic properties of a wide range of species. The model may also be used to estimate the properties of molecules and their isomers, which have not been measured, and is simple enough to be easily programmed as a subroutine for on-line kinetic calculations. [S0195-0738(00)00902-X]

Introduction

The physical and thermodynamic properties of hydrocarbons and organic chemical compounds are of special interest to engineers in the chemical, combustion processing, biochemistry, and petroleum refining industries. A major problem encountered in the detailed modeling of such a process is that data for such properties as Gibbs free energy, heat capacity, enthalpy, and entropy for many species is lacking. All the calorimetric experimental data is at lower temperatures ($T<550$ K). Data for higher temperature based on statistical mechanical expressions is available for simple molecules.

To do detailed calculations, all of the possible species should be considered. Unfortunately, since data (experimental or estimated) for many of them, especially complex molecules, is not available, they have been omitted. Also, due to incorrect thermochemical properties of many species, there exist significant discrepancies between combustion model predictions and experimental results. Therefore, it is very important to develop accurate methods for calculating the thermochemical properties of general hydrocarbons over a wide temperature range.

The thermodynamic properties of large molecules at high temperature can only be estimated. Many researches have been done in this area. The JANAF thermochemical tables [1] use statistical thermodynamic expressions to estimate thermodynamic properties for about 50 hydrocarbons in the temperature range 300 K to 6000 K based on the detailed knowledge of molecular structure and spectra. Unfortunately, they do not cover branched hydrocarbons. The NASA equilibrium data files [2] provide estimated values of these properties for about 300 hydrocarbons, however, only a small amount of them are the branched molecules. The NIST standard reference [3] uses the group additivity method [4] to estimate properties of 1521 organic compounds at a temperature of 298.15 K. Although they provided data for many large molecules and their isomers, the theoretical models they used are uncertain; for example, the same properties are assigned to some molecules and their isomers. The American Petroleum Institute Research Project [5], which is based on a model developed by Scott [6], provides heat capacities from 0 to 1500 K for about 500 hydrocarbons. It also gives the enthalpy and entropy at 298.15 K and 1 bar for normal alkanes and some of their isomers up to C_{40}. However, very few hydrocarbons listed are oxygenated hydrocarbons.

Different models have been used to estimate the properties of species. In Benson's group additivity (GA) method [4], the properties are estimated as the sum of the contributions of groups of polyvalent atoms. This is more accurate than the zero-order method (properties estimated from atomic contributions alone) and the first-order method (properties estimated from chemical bond additivity). The advantage is that it can give quick estimates without requiring substantial molecular structure information. However, it requires a relatively large database compared to the simpler methods. Reid [7] lists several alternative methods, such as Joback's, Yoned's and Thinh's, for calculating properties based on group additivity. They are simpler than GA approach, but none of these estimation procedures can be used at the temperature above 2000 K. Leonidas [8] uses the ABC approach to estimate the standard entropy and enthalpies of formation of acyclic hydrocarbons. The ABC method is based on the contributions of atoms and bonds in the properties of conjugate forms of a molecular structure. It is simpler than the GA approach, but only properties at standard temperature have been covered. Lay and Bozzelli [9] use hydrogen atom bond increments (HBI) approach to estimate the thermodynamic properties of hydrocarbon radical species. He et al. [10] developed a simple model to estimate the sensible thermodynamic properties of hydrocarbons over a wide temperature range, but only unbranched molecules are covered.

The purpose of this paper is to develop an analytic model with a minimum number of input parameters to determine thermochemical properties for branched hydrocarbons over a wide range of temperatures. Instead of using approximate rotational characteristic temperatures, as He et al. [10] did, the rotational characteristic temperatures are calculated from the exact moment of inertia of molecules. Also, the restricted rotation function $f(a)$ is calculated using a polynomial formula instead of an integral. This can speed on-line calculations. The result of this work can be used as a subroutine in computational models.

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Model

The physical model is based on statistical thermodynamics expressions for ideal gases. The energy of the system is the summation of translational and internal components, written as $E_{tot} = E_{trans} + E_{int}$. We assume that the internal contribution is the sum of the rotational(Rot), vibrational(Vib), and electronic(Ele) energies. Associated with each mode i, there is a corresponding number of degrees of freedom N_i. If the eigenvalues of the separated Hamiltonian of one mode is ε_i, the corresponding energy should be $N_i\varepsilon_i$. The total energy then can be expressed as

$$E_{tot} = \sum_i N_i \varepsilon_i \tag{1}$$

Other properties, such as Gibbs free energy, can also be calculated using the same method

$$\mu_{tot} = \sum_i N_i \mu_i \tag{2}$$

The total number of degrees of freedom of a species containing n atoms is $3n$. There are three translational degrees of freedom, and three rotational degrees of freedom for nonlinear molecules. Therefore, the number of vibrational degrees of freedom is $3n-6$. These may further be decomposed into two parts: the contributions from heavy particles and from hydrogen atoms. Each part has stretching, bending, and torsional degrees of freedom. The heavy particle stretching mode may be further divided into three modes associated with single, double, and triple bonds in the molecule.

Table 1 summarizes the degrees of freedom for different modes of branched chains, along with their symbols and values used in this model. In this table, the total number of heavy particles X in the molecule is equal to the sum of carbon atoms EC, nitrogen atoms EN, and oxygen atoms EO. EH is the number of hydrogen atoms. HRR is the number of hydrogen restricted rotor groups in the molecule, e.g., CH_3 or OH. A simple relationship between X and number of bonds for acyclic molecules is given by (3). Also, for the molecules with two terminal H-rotors, the number of branches BR can be calculated using Eq. (4). Accordingly, the number of heavy particles L in the principal chain can be calculated by Eq. (5).

$$B1+B2+B3 = X-1 \tag{3}$$

$$BR = HRR-2 \tag{4}$$

$$L = X-BR \tag{5}$$

For example, $HO-HC=C(CH_3)-CH_3$ is a simple branched molecule with $X=EO+EC+EN=5$, $B1=3$, $B2=1$, $B3=0$, $OH=1$, $CH_3=2$, $HRR=CH_3+OH=3$. Using formulas (3) to (5), we can get $BR=1$ and $L=4$. Out of its 39 total degrees of freedom ($N_{tot}=3*n=3*13$), three are translational and three are rotational. Among the 33 left, there are three for heavy particle stretching associated with single bonds ($B1=3$), one for heavy particle stretching associated with double bonds ($B2=1$), four for heavy particle bending ($L-2+2BR=4$), one for torsion out of plane ($L-3=1$), eight for hydrogen stretching ($EH=8$), three for hydrogen torsion ($HRR=3$), and 13 for hydrogen bending ($2EH-HRR=13$).

The thermodynamic properties are based on the calculation of the partition function for each mode i. The sensible Gibbs free energy μ_i can be calculated knowing partition function Q_i using the equation

$$\frac{\mu_i(T)}{RT} = -\ln Q_i \tag{6}$$

where partition function is defined as

$$Q_i = \sum_j e^{-\varepsilon_{ij}/kT} \tag{7}$$

Here ε_{ij} is the discrete energy of level j of mode i, and k is Boltzmann's constant.

Statistical mechanics provides expression for calculating the partition functions for different motion modes. Equations (8) and (9) are the examples of the translational and rotational partition functions

$$Q_{trans} = \left(\frac{T}{\theta_{trans}}\right)^{5/2} W^{3/2} g_o \tag{8}$$

$$Q_{rot} = \frac{1}{\sigma}\left(\frac{\pi T^3}{\theta_A \theta_B \theta_C}\right) \tag{9}$$

where W is the molecular weight, g_o is the ground state electronic degeneracy, σ is the symmetry number for external rotations of the whole molecule. Associated with different modes, there exist characteristic frequencies; but in calculating the thermodynamic properties, it is more convenient to introduce the characteristic temperatures. The characteristic temperature θ_i(K) is related to its

Table 1 Number of degrees of freedom for different modes

Modes Description	Symbol	Value
Translation	TRANS	3
Rotation	ROT	3
Vibration	VIB	XVIB+HVIB
Heavy Particle Vibration	XVIB	XSTR+XBND+XTOR
Heavy Particle Stretching	XSTR	X-1
associated with Single Bond associated with Double Bond associated with Triple Bond	STR1 STR2 STR3	B1 B2 B3
Heavy Particle Bending	XBND	L-2+2BR
Heavy Particle Internal Rotation	XTOR	L-3
Hydrogen Vibration	HVIB	HSTR+HBND+HRR
Hydrogen Stretching	HSTR	EH
Hydrogen Bending	HBND	2EH-HRR
Hydrogen Internal Rotation	HRR	$CH_3+CH_2+NH_2+OH+CH+NH$

Table 2 Examples of product of moment of inertia

Formula	Molecules	$I_A I_B I_C$ (kgm^2)
C_5H_{12}	3-methylbutane	6.8916E-133
C_6H_{14}	3-methylpentane	3.0277E-132
	3-ethylbutane	2.8762E-132
	2,2-dimethylpropane	1.2733E-133
C_8H_{18}	2-methylheptane	3.0850E-131
	3-methylheptane	2.9778E-131
	3,3-Dimethylhexane	1.0852E-131
	2,2,4-trimethylpentane	3.9766E-132
	2,2,3-trimethylbutane	6.2780E-133

corresponding frequency $\omega_i(\text{cm}^{-1})$ by $\theta_i = c_2\omega_i$. The characteristic rotational temperature is defined by $\theta_A = \hbar^2/2I_A k$, in which I_A is the moment of inertia along the principal axis A.

Although the principal axes A, B, and C of most branched molecules are not apparent, the quantity of interest for the calculation of thermodynamic functions is the product $\theta_A\theta_B\theta_C$, which equals $(\hbar^2/2k)^3 I_A I_B I_C$. It can be shown that the determinant of the inertia tensor is invariant under a rotation of the axes. Therefore, we can choose any arbitrary coordinate system (x,y,z) for our convenience. The mass center of the molecule can be found easily by

$$\bar{x} = \frac{\sum_i m_i x_i}{W}, \quad \bar{y} = \frac{\sum_i m_i y_i}{W}, \quad \bar{z} = \frac{\sum_i m_i z_i}{W} \tag{10}$$

The inertia tensor in this coordinate system is then

$$\bar{I} = \begin{vmatrix} I_{xx} & -I_{xy} & -I_{xz} \\ -I_{xy} & I_{yy} & -I_{yz} \\ -I_{xz} & -I_{yz} & I_{zz} \end{vmatrix} \tag{11}$$

Where the elements are defined as

$$I_{xx} = \sum_i m_i((y_i-\bar{y})^2 + (z_i-\bar{z})^2)$$

$$I_{xy} = \sum_i m_i(x_i-\bar{x})(y_i-\bar{y})$$

et al.

Therefore

$$I_A I_B I_C = \text{Det}|\bar{I}| = I_{xx}I_{yy}I_{zz} - 2I_{xy}I_{yz}I_{xz} - I_{xx}I_{yz}^2 - I_{yy}I_{zx}^2 - I_{zz}I_{xy}^2 \tag{12}$$

Table 2 shows values of product $I_A I_B I_C$ for several branched molecules calculated from known bond distances and angles.

Both the Einstein model and the Debye model [11] have been used to estimate the vibrational properties. The Einstein model treats the vibrations as independent oscillators, and the vibrational partition function is given by

$$Q_{\text{vib}}^{\text{Eins}} = (1 - e^{-\theta_{\text{vib}}/T})^{-N_{\text{vib}}} \tag{13}$$

where N_{vib} is the number of Einstein oscilators with characteristic temperature θ_{vib}. The Debye model treats vibrations as wave oscillators and the vibrational partition function is then

$$Q_{\text{vib}}^{\text{Deby}} = \sum_{j=1}^{N_{\text{vib}}} (1 - e^{-j\theta_{\text{vib}}/N_{\text{vib}}T})^{-1} \tag{14}$$

where N_{vib} is the number of atoms in the chain, and θ_{vib} is the characteristic temperature of the highest mode.

This work uses the Einstein model for heavy particle stretching modes and the Debye model for heavy particle bending and torsional modes. For hydrogen vibrations, the Einstein model has been used.

Knowing the partition function for different modes, the Gibbs free energy can be calculated using Eq. (6). Table 3 summarizes the dimensionless standard Gibbs free energies derived from corresponding partition function for molecules with X greater than 2. Note that in this table, Eins(N,θ) is the Einstein dimensionless

Table 3 Dimensionless standard Gibbs free energies, characteristic temperatures, and characteristic frequencies for different modes

MODES i	$\frac{\mu_i}{RT}$	CHARACTERISTIC TEMPERATURE		CHARACTERISTIC FREQUENCY
		Symbol	Value (K)	Value (cm^{-1})
TRANS	$-\frac{5}{2}\ln\frac{T}{\theta_{TRANS}} - \frac{3}{2}\ln W - \ln g_o$	θ_{TRANS}	4.31	3
ROT	$-\frac{1}{2}\ln\frac{\pi T^3}{\theta_A\theta_B\theta_C} + \ln\sigma$	$\theta_A\theta_B\theta_C$	$\frac{(h^2/8\pi^2 k)^3}{I_A I_B I_C}$	
STR1	$Eins\ (B1, \theta_{STR\,1})$	θ_{STR1}	1400	1000
STR2	$Eins\ (B2, \theta_{STR\,2})$	θ_{STR2}	2400	1600
STR3	$Eins\ (B3, \theta_{STR\,3})$	θ_{STR3}	3200	2200
XBND	$Deby\ (L-2+2BR, \theta_{XBND})$	θ_{XBND}	1000	700
XTOR	$Deby\ (L-3, \theta_{XTOR})$	θ_{XTOR}	500	350
HSTR	$Eins\ (HSTR, \theta_{HSTR})$	θ_{HSTR}	4200	3000
HBND	$Eins\ (HBND, \theta_{HBND})$	θ_{HBND}	2000	1400
HRR	$-\frac{1}{2}\ln\frac{\pi T}{\theta_{HRR}} + \ln\sigma_{RB}^* - \ln f(\frac{\theta_{RB}}{T})$	θ_{HRR} θ_{RB}	$27/\sigma_{RB}$ Table 4	$18/\sigma_{RB}$

*σ_{RB} is the symmetry number of rotational potential.

Table 4 Characteristic rotational barrier temperatures, θ_{RB} (K)

	$-CH_3$	$-CH_2$	NH_2	XH
A_3C-	1500	0	1000	500
A_2C-	500	1000	500	500
A_2N-	1000	1000	1000	500
AO–	500	500	500	500
≡C–	0	0	0	0
=N–	0	0	0	0

Table 5 Coefficients of sixth-order polynomial approximation

	Value		Value
C_1	4.9898E-01	C_4	2.0240E-03
C_2	7.3809E-02	C_5	- 1.4460E-04
C_3	- 2.2039E-02	C_6	2.9846E-04

Gibbs free energy function and Deby(N,θ) is the Debye dimensionless Gibbs free energy function. These two functions are given by

$$\text{Eins}(N,\theta) = -\ln Q_{\text{vib}}^{\text{Eins}} = N\ln(1-e^{-\theta/T}) \tag{15}$$

$$\text{Deby}(N,\theta) = -\ln Q_{\text{vib}}^{\text{Deby}} = \sum_{j=1}^{N} \ln(1-e^{-j\theta/NT}) \tag{16}$$

Table 3 also shows the symbols and values of characteristic temperatures for the different modes used by the model as well as the corresponding frequencies. In this table, the characteristic temperatures have been estimated from measured wave numbers.

The function $f(a)$ associated with hindered rotation is defined by

$$f(a) = \frac{2}{\pi}\int_0^{\pi/2} e^{-a\sin^2 x}dx \tag{17}$$

where $a = D_{\text{ROT}}/RT$.

The function $f(a)$ can be approximated by the polynomial expression (18), which gives values for all the thermodynamic properties with an accuracy better than one percent for the range $0<a<10$.

$$f(a) = \frac{1}{1+\sum_{i=1}^{N} c_i a^i} \tag{18}$$

Table 4 lists characteristic rotational barrier temperatures. Table 5 lists the coefficients used for sixth-order ($N=6$) polynomial estimation.

The electronic contribution from the excited states was omitted in Table 3. If the excited electronic energies are known, they can be included using the expressions in He et al. [10].

Based on Table 1, the degrees of freedom N_i for different modes (translational, rotational, and vibrational) can be determined. Using the corresponding characteristic temperatures θ_i listed in Table 3, we can get the total sensible Gibbs free energy from Eq. (2).

Other properties such as sensible enthalpy, heat capacity, and entropy can be calculated using Eqs. (19) to (21)

$$H(T) = -RT^2\frac{d}{dT}(\mu(T)/RT) \tag{19}$$

$$Cp(T) = \frac{d}{dT}H(T) \tag{20}$$

$$S(T) = \frac{H(T)-\mu(T)}{T} \tag{21}$$

Results and Discussion

The model has been used to calculate the properties of several hydrocarbons. Figure 1 compares the dimensionless heat capacity of three normal alkanes (BR=0) with available experimental data. The dotted lines show the classical limits for the model. The observed data is from API and is all at low temperatures. The model agrees with experimental results to better than 1 percent.

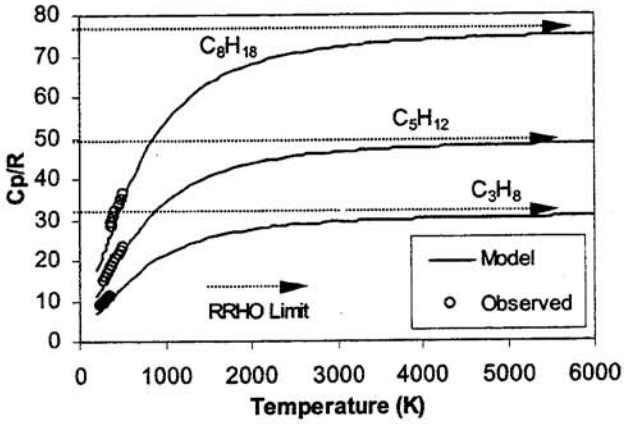

Fig. 1 Dimensionless heat capacity of three hydrocarbons

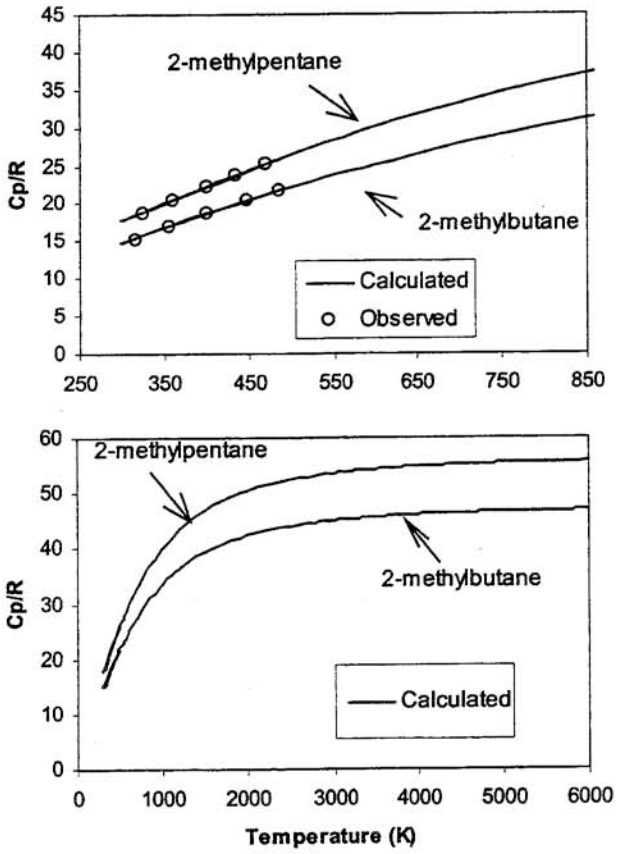

Fig. 2 Dimensionless heat capacity of two branched hydrocarbons

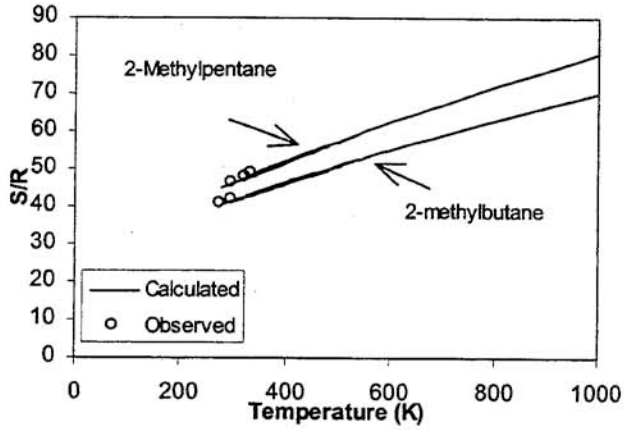

Fig. 3 Dimensionless entropy of two branched hydrocarbons

Figure 2 compares the dimensionless heat capacity of 2-methylbutane and 2-methylpentane with the experimental data. These two molecules have one branch structure (BR=1). To facilitate the comparison with experimental data, both high and low temperature ranges are shown.

Figure 3 compares the dimensionless entropy of 2-methylbutane and 2-methylpentane with their experimental data.

Figures 4 and 5 show the dimensionless heat capacity of other branched hydrocarbons having two and three branches, respectively.

Table 6 compares the dimensionless entropy of other branched

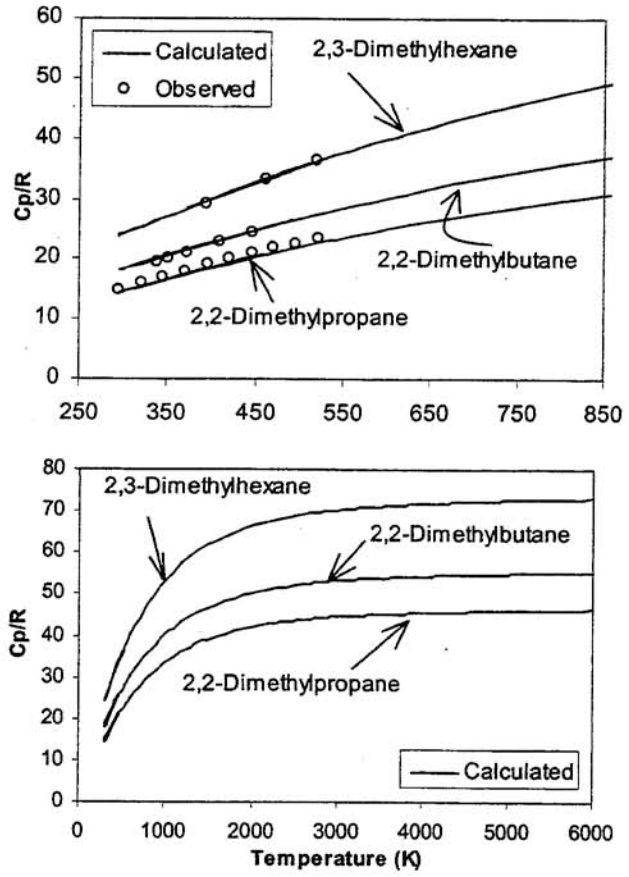

Fig. 4 Dimensionless heat capacity of three branched hydrocarbons

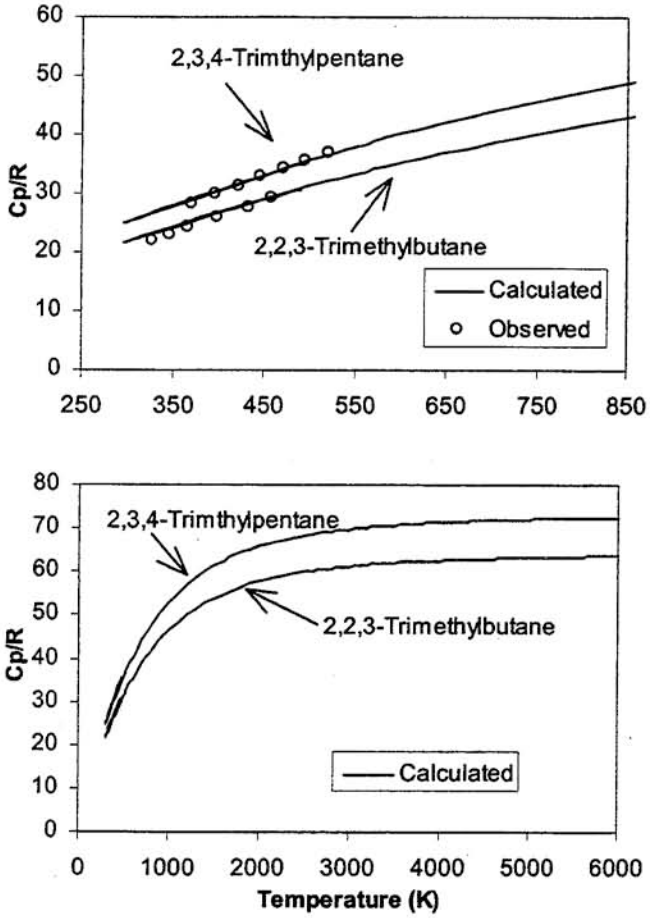

Fig. 5 Dimensionless heat capacity of two branched hydrocarbons

Table 6 Comparison of observed and calculated values of dimensionless entropy $S°/R$

T (K)	Calculated	Observed	Error
3-Methylpentane			
298.15	45.8633	46.0447	-0.39%
323.8	47.3683	47.4789	-0.23%
336.5	48.1012	48.1885	-0.18%
2,2-Dimethylbutane			
296.05	42.7968	42.9599	-0.38%
298.15	42.9249	43.0857	-0.37%
322.65	44.4001	44.4847	-0.19%
2,3-Dimethylhexane			
298.15	44.2820	43.9966	0.65%
313.12	45.1875	44.8470	0.76%
331.14	46.2607	45.8384	0.92%
2,2,3-Trimethylbutane			
298.15	45.5040	46.1051	-1.30%
313.83	46.6261	47.1467	-1.10%
353.95	49.4223	49.7283	-0.62%
2,2,4-Trimethylbutane			
298.15	50.7228	50.9031	-0.37%

hydrocarbons with their experimental data. The relative error is calculated by comparing the model calculation and the observed data from API.

For the branched species shown, the model agrees very well with experimental data. The errors are within 5 percent. Largest error appears at lowest temperatures. This is because the properties become very sensitive to the thermodynamic temperature when it is below the characteristic temperature. As more detailed spectral data for polyatomic molecules become available, the accuracy of the model can be improved by performing the least-squares regression to adjust the characteristic temperatures in Table 3.

In summary, a simple model has been developed which requires a relative small number of parameters to estimate the thermochemical properties of branched hydrocarbons. The results of this model are in good agreement with existing data and it may be used with reasonable confidence to estimate properties of branched molecules for which no measurements exist. It can easily be programmed as a subroutine for on-line use in chemical kinetic calculations.

Acknowledgments

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Nomenclature

c_2 = second radiation constant
h = Planck's constant
k = Boltzmann's constant
$\hbar$ = Planck's constant ($\hbar \equiv h/2\pi$)
W = molecular weight
σ = symmetry no.
θ_i = characteristic temperature of motion mode i
D_{ROT} = rotational barrier height
X = total no. of heavy particles in molecule
EH = no. of hydrogen atoms in molecule
EC = no. of carbon atoms in molecule
EN = no. of nitrogen atoms in molecule
EO = no. of oxygen atoms in molecule
B1 = no. of single bonds in molecule
B2 = no. of double bonds in molecule
B3 = no. triple bonds in molecule
BR = no. of branches
L = length of principal chain
I = moment of inertia

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