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Estimation of the Thermodynamic Properties of Unbranched Hydrocarbons

A simple model has been developed to estimate the sensible thermodynamic properties such as Gibbs free energy, enthalpy, heat capacity, and entropy of unbranched hydrocarbons over a wide range of temperatures. The model is based on statistical thermodynamic expressions incorporating translational, rotational, and vibrational motions of the atoms. A relatively small number of parameters are needed to calculate the thermodynamic properties of a wide range of molecules. The calculated results are in good agreement with the available experimental data for unbranched hydrocarbons. The model can be used to make estimates for molecules whose properties have not been measured and is simple enough to be easily programmed as a subroutine for on-line kinetic calculations.

Introduction

The thermochemical properties of hydrocarbons over a wide range of temperatures are needed for calculating the equilibrium composition and modeling the chemical kinetics of complex reacting gas phase systems. A major problem encountered in dealing with such a system is that experimental data for such properties as Gibbs free energy, heat capacity, enthalpy, and entropy for many species is lacking. In addition, the data for some species obtained from different sources is inconsistent.

The JANAF Thermochemical Tables (Chase et al., 1985) use statistical thermodynamic expressions to estimate thermodynamic properties for about 50 hydrocarbons in the temperature range 300 to 6000 K based on the detailed knowledge of molecular structure and spectra. The NASA equilibrium data files (Gordon and McBride, 1971) provide polynomial expressions for the properties of approximately 300 hydrocarbons over the temperature range 300 to 5000 K. Polynomials involving seven coefficients have been used to fit the available data for each species for low and high-temperature ranges. The NIST Standard Reference (Domalski et al., 1994) uses the group additivity method (Benson, 1976) to estimate properties of 1521 organic compounds at a temperature of 298.15 K. The American Petroleum Institute (API) Research Project Tables (TRC Thermodynamic Tables, 1991), which are based on a model developed by Scott (1974), provide heat capacities from 0 to 1500 K for about 500 hydrocarbons. They also give the enthalpy and entropy at 298.15 K and 1 bar for normal alkanes up to C₄₀. However, most hydrocarbons listed are C-H compounds; less than 10 species are C-H-O compounds.

As previously mentioned, there are some inconsistencies among these data sources. For example, Fig. 1 shows a comparison of heat capacity of methane obtained from API, JANAF tables, and the NASA correlation. It can be seen that the API and JANAF data differ significantly at high temperatures. In addition, the NASA correlation is limited to temperature range 300 to 5000 K. The disagreement is due to the different models used.

In Benson's group additivity (GA) method, 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 and fairly accurate estimates without requiring substantial molecular structure information. However, it requires a relatively large database compared to the simpler methods, and the data for heat capacities are given in tabular form. A method has been developed by Lay (1995) to improve the accuracy of calculated properties for radicals. Constantinou (1993) has also developed new methods for estimating the enthalpies and entropies of formation of hydrocarbons. Reid (1987) lists several alternative methods, such as Joback's, Yoned's, and Thinh's, for calculating properties based on group additivity. None of these estimation procedures can be used at a temperature above 2000 K, and all use polynomial fits for the heat capacity.

The purpose of this paper is to develop a simple analytic model, with a minimum number of input parameters, which can be used as a subroutine in computational models to determine the sensible thermochemical properties for general unbranched C-H-O species over a wide range of temperatures with engineering accuracy.

Model

For many molecules, under ideal gas condition, the Hamiltonian can be approximately separated with respect to the translational and internal degrees of freedom (Fay, 1965). The total energy of the system is then the summation of translational and internal energies, $E_{\text{tot}} = E_{\text{trans}} + E_{\text{int}}$. We assume that the internal energy is the sum of the rotational (Rot), vibrational (Vib), and electronic (Ele) energies. Figure 2 shows a schematic energy level diagram for a typical diatomic molecule, AB. Associated with each energy mode, there is a corresponding number of degrees of freedom N_i . If the eigenvalue of the Hamiltonian of one mode is ϵ_i , the corresponding energy should be $N_i \epsilon_i$. The total energy then can be expressed as Eq. (1)

$$E_{\text{tot}} = \sum_i N_i \epsilon_i \quad (1)$$

Other properties can also be calculated using the same method.

The total number of degrees of freedom of a species containing n atoms is $3n$. There are 3 translational degrees of freedom, 2 rotational degrees of freedom for linear molecules, and 3 rotational degrees of freedom for nonlinear molecules. Therefore, the number of vibrational degrees of freedom is $3n - 5$ for linear molecules and $3n - 6$ for nonlinear molecules. These may be further divided into stretching, bending, and tor-

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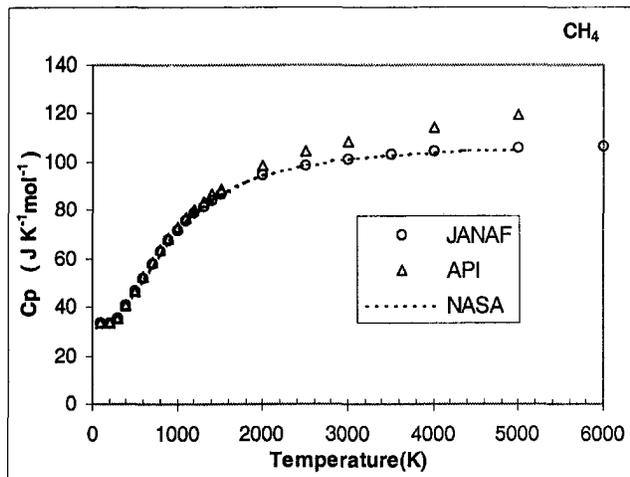


Fig. 1 Heat capacity of methane

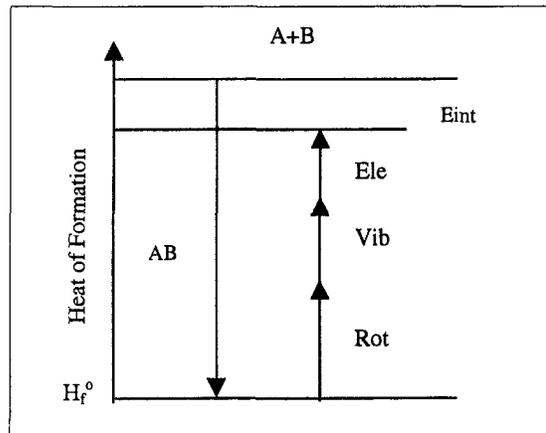


Fig. 2 Internal energy level distribution of AB

sional degrees of freedom for heavy particles (carbon, oxygen, or nitrogen) and hydrogen atoms. Finally, the heavy particle stretching mode may be 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 unbranched chain molecules, along with their symbols and values used in this model. There are 3 degrees of freedom for translation (TRANS = 3). The number of rotational degrees of freedom (ROT) is 2 for linear molecules and 3 for staggered molecules or axial hydrogen rotors. B1, B2, and B3 denote the number of single, double, and triple bonds between heavy particles in the molecule. The total number of heavy particles in the molecule is $X = EC + EN + EO$, where EC, EN, and

EO denote the number of carbon, nitrogen, and oxygen atoms, respectively. EH is the number of hydrogen atoms. For acyclic molecules, the relationship between X and number of bonds is $B1 + B2 + B3 = X - 1$.

For example, ethylene (C_2H_4) is an axial rotor with $n = EC + EN + EO + EH = 6$. It has a total of 18 degrees of freedom ($N_{tot} = 3 * n$); three are translational, two are free heavy particle rotations, and one is a free hydrogen rotation (HFR = 1). The remaining 12 are vibrational degrees of freedom contributed by both heavy particles (carbon) and hydrogen atoms. Of these, 1 is a carbon double-bond stretching ($XSTR = STR2 = B2 = 1$) and 11 are hydrogen vibrations: 1 restricted rotation (HRR = 1), 4 stretching vibrations (HSTR = EH = 4), and 6 bending vibrations ($HBND = 2EH - HFR - HRR = 6$).

Table 1 Number of degrees of freedom for different modes ($X = EC + EN + EO > 1$)

Modes Description	Symbol	Value
Translation	TRANS	3
Rotation about Center of Mass	ROT	LXR or SXR or AHR
Linear Chain Rotor	LXR	2
Staggered Chain Rotor	SXR	3
Axial Hydrogen Rotor	AHR	3
Hydrogen Free Rotation	HFR	0 or 1
Vibration	VIB	XVIB+HVIB
Heavy Particle	XVIB	XSTR+XBND
Stretching	XSTR	$X-1=B1+B2+B3$
Single Bond	STR1	B1
Double Bond	STR2	B2
Triple Bond	STR3	B3
Bending	XBND	LXB or SXB+XTOR
Linear Chain Bend	LXB	$2(X-2)$
Staggered Chain Bend	SXB	$X-2$
Staggered Chain Torsion	XTOR	$X-3$
Hydrogen	HVIB	HSTR+HBND+HRR
Hydrogen Stretching	HSTR	EH
Hydrogen Bending	HBND	$2EH-HFR-HRR$
Hydrogen Restricted Rotation	HRR	$CH_3+CH_2+NH_2+OH+CH+NH$

Table 2 Dimensionless standard Gibbs free energies, characteristic temperatures, and characteristic frequencies for different modes ($X = EC + EN + EO > 1$)

MODES	EQUATIONS	CHARACTERISTIC		
		TEMPERATURE		FREQUENCY
		Symbol	Value (K)	Value (cm ⁻¹)
TRANS	$\frac{\mu_{TRANS}}{RT} = -\frac{5}{2} \ln \frac{T}{\theta_{TRANS}} - \frac{3}{2} \ln W$	θ_{TRANS}	4.31	3
LXR	$\frac{\mu_{LXR}}{RT} = -\ln \frac{T}{\theta_{LXR}} + \ln \sigma$	θ_{LXR}	14/(X(X ² -1))	10/(X(X ² -1))
SXR	$\frac{\mu_{SXR}}{RT} = -\ln \frac{T}{\theta_{PROT}} - \frac{1}{2} \ln \frac{\pi T}{\theta_{AROT}} + \ln \sigma$	θ_{AROT}	4/X	3/X
		θ_{PROT}	13/(X(X ² -1))	9/(X(X ² -1))
AHR	$\frac{\mu_{AHR}}{RT} = -\ln \frac{T}{\theta_{LXR}} - \frac{1}{2} \ln \frac{\pi T}{\theta_{HFR}} + \ln \sigma$	θ_{HFR}	25/HAR*	17/HAR
STR1	$\frac{\mu_{STR1}}{RT} = B1 \ln(1 - e^{-\frac{\theta_{STR1}}{T}})$	θ_{STR1}	1400	1000
STR2	$\frac{\mu_{STR2}}{RT} = B2 \ln(1 - e^{-\frac{\theta_{STR2}}{T}})$	θ_{STR2}	2400	1600
STR3	$\frac{\mu_{STR3}}{RT} = B3 \ln(1 - e^{-\frac{\theta_{STR3}}{T}})$	θ_{STR3}	3200	2200
LXB	$\frac{\mu_{LXB}}{RT} = 2 \sum_{i=1}^{X-2} \ln(1 - e^{-\frac{i}{X-2}(\frac{\theta_{LXB}}{T})})$	θ_{LXB}	1000	700
SXB	$\frac{\mu_{SXB}}{RT} = \sum_{i=1}^{X-2} \ln(1 - e^{-\frac{i}{X-2}(\frac{\theta_{SXB}}{T})})$	θ_{SXB}	1000	700
XTOR	$\frac{\mu_{XTOR}}{RT} = \sum_{i=1}^{X-3} \ln(1 - e^{-\frac{i}{X-3}(\frac{\theta_{XTOR}}{T})})$	θ_{XTOR}	500	350
HSTR	$\frac{\mu_{HSTR}}{RT} = HSTR \ln(1 - e^{-\frac{\theta_{HSTR}}{T}})$	θ_{HSTR}	4200	3000
HBND	$\frac{\mu_{HBND}}{RT} = HBND \ln(1 - e^{-\frac{\theta_{HBND}}{T}})$	θ_{HBND}	2000	1400
HRR	$\frac{\mu_{HRR}}{RT} = -\frac{1}{2} \ln \frac{\pi T}{\theta_{HROT}} + \ln \sigma_{RB}^{**} - \ln f(\frac{\theta_{RB}}{T})$	θ_{RB}	Table 3	

*: HAR is defined as the number of hydrogen atoms in rotor

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

The thermodynamic properties are based on the calculation of the partition function for each mode. The statistical mechanical expression for Q_i for different modes is given by Eq. (2).

$$Q_i = \sum_j e^{-\epsilon_{ij}/kT} \quad (2)$$

where ϵ_{ij} is the discrete energy of level j of mode i , and k is Boltzmann's constant. The sensible Gibbs free energy μ_i for motion i can be calculated from Eq. (2) using

$$\frac{\mu_i(T)}{RT} = -\ln Q_i \quad (3)$$

Table 2 summarizes the expressions for the dimensionless standard Gibbs free energies for the various modes derived from the corresponding partition functions (Fay, 1965). In this table, θ_i denotes the characteristic temperature of mode i , W the molecular weight, and σ the symmetry number for free rotation about the center-of-mass. HAR is the number of hydrogen atoms in a hydrogen rotor. σ_{RB} is the symmetry number of rotational potential, which is equal to the number of identical minimum in the potential. The characteristic temperatures were first estimated from measured wave numbers ω_i using the relation $\theta_i = c_2\omega_i$, where $c_2 = 1.4387$ cm-K is the second radiation constant, and then adjusted to give the best fit to experimental data. The symmetry number σ is defined as the number of indistinguishable positions into which the molecule may be carried under rigid rotation. For a more detailed discussion, see Herzberg (1951).

For heavy atom vibrations, we use the Einstein model for stretching modes and the Debye model for bending and torsional modes. For hydrogen vibrations, we use the Einstein model for stretching and bending modes and a sinusoidal potential for restricted rotations.

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

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

$$\rightarrow 1: a \ll 1 \quad (4)$$

$$\rightarrow 1/\sqrt{\pi a}: a \gg 1$$

where $a = \theta_{RB}/T$, $\theta_{RB} = D_{RB}/R$, and D_{RB} is the height of rotational barriers. Figure 3 shows the characteristics of the function $f(a)$ and its first two derivatives: $f'(a)$ and $f''(a)$. For a more complete discussion of restricted rotation, see Münster (1969).

Table 2 also shows the symbols and values for the characteristic temperatures and corresponding frequencies used in the model. For the rotational modes of staggered molecules, two characteristic temperatures were assigned: θ_{AROT} for the rotation parallel to the axis of the molecule and θ_{PROT} for the rotation perpendicular to the axis. For axial hydrogen rotors, a characteristic temperature, θ_{LXR} , was assigned for the two equal heavy particle rotations and a temperature, θ_{HFR} , for the hydrogen rotation about the axis.

Table 3 shows the characteristic rotational barrier temperatures for various hydrogen rotors.

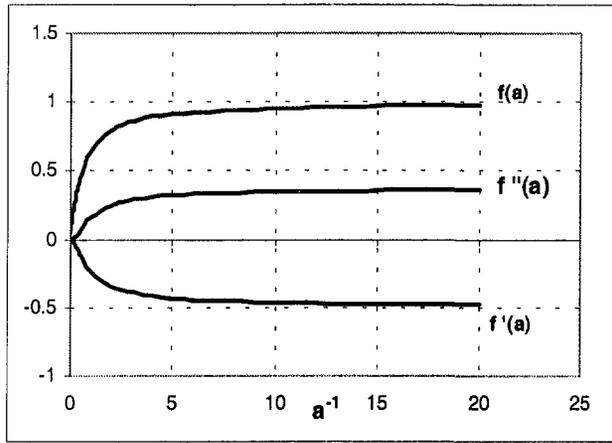


Fig. 3 Characteristics of $f(a)$, $f'(a)$, and $f''(a)$

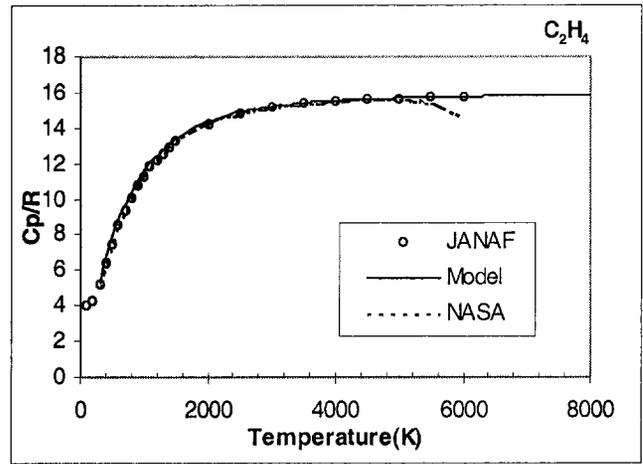


Fig. 5 Dimensionless heat capacity of ethylene

Table 3 Characteristic rotational barrier temperatures, θ_{RB} (K)

	-CH ₃	-CH ₂	NH ₂	XH
A ₃ C-	1500	0	1000	500
A ₂ C-	500	1000	500	500
A ₂ N-	1000	1000	1000	500
AO-	500	500	500	500
≡C-	0	0	0	0
=N-	0	0	0	0

Note: Double Bond: for A₂C=CH₂, θ_{RB} =30000 K

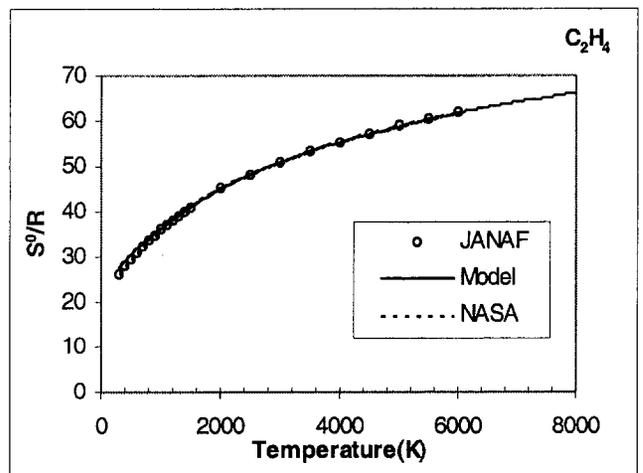


Fig. 6 Dimensionless entropy of ethylene

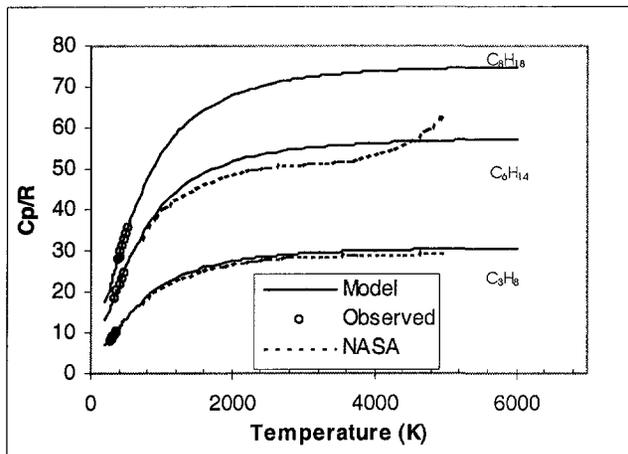


Fig. 4 Dimensionless heat capacity of three alkanes

Once the degrees of freedom for the different modes (translational, rotational, vibrational) have been determined and the corresponding characteristic temperatures θ_i have been assigned, the sensible Gibbs free energy can be calculated from the equations in Table 2 using the summation

$$\mu(T) = \sum_i \mu_i(N_i, \theta_i, T, W, \sigma, \sigma_{RB} \dots) \quad (5)$$

Other properties such as the sensible enthalpy, heat capacity, and entropy can be calculated using Eqs. (6) to (8)

$$H(T) = -RT^2 \frac{d}{dT} \left(\frac{\mu(T)}{RT} \right) \quad (6)$$

$$C_p(T) = \frac{d}{dT} H(T) \quad (7)$$

$$S(T) = \frac{H(T) - \mu(T)}{T} \quad (8)$$

The electronic contribution was not listed in Table 2. The partition function for the electronic motion is expressed as

$$Q_{\text{ele}} = \sum_i g_i e^{-\epsilon_i/T} = \sum_e g_i e^{-\theta_e/T} \quad (9)$$

which is the direct summation of the discrete energies for all the electronic states. Here, ϵ_i is the i th electronic energy level and g_i is the quantum weight of the i th electronic state. The electronic energies of molecules are generally much higher than those for atomic motions. An electronic term of unit statistical weight lying at 30000 cm^{-1} or above contributes a negligible amount to the thermodynamic functions at temperatures below 6000 K. We add electronic contributions when the low-lying levels are known. In other cases, we estimate thermodynamic functions only for ground electronic state.

The electronic contribution can be derived from Eq. (9) and the corresponding thermodynamic properties are given by Eqs.

(10) to (12). These values should be added to Eqs. (6) to (8), respectively.

$$\frac{H_{\text{ele}}(T)}{RT} = \frac{\Sigma_2}{\Sigma_1} \quad (10)$$

$$\frac{Cp_{\text{ele}}(T)}{R} = \frac{(\Sigma_1 \Sigma_3 - \Sigma_2^2)}{\Sigma_1^2} \quad (11)$$

$$\frac{S_{\text{ele}}(T)}{R} = \frac{\Sigma_2}{\Sigma_1} + \ln(\Sigma_1) \quad (12)$$

where Σ_1 , Σ_2 , Σ_3 are defined by

$$\Sigma_1 = \sum g_i e^{-c_2 \epsilon_i / T} \quad (13)$$

$$\Sigma_2 = \sum g_i \frac{c_2 \epsilon_i}{T} e^{-c_2 \epsilon_i / T} \quad (14)$$

$$\Sigma_3 = \sum g_i \left(\frac{c_2 \epsilon_i}{T} \right)^2 e^{-c_2 \epsilon_i / T} \quad (15)$$

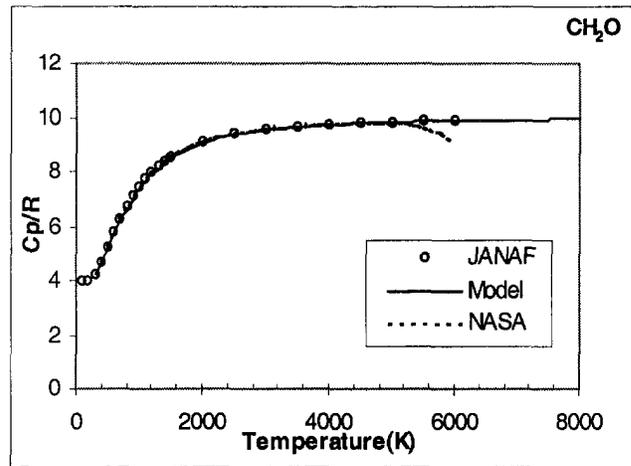


Fig. 7 Dimensionless heat capacity of formaldehyde

Results and Discussion

The model has been used to calculate the properties of over 20 typical hydrocarbons. Figure 4 shows a typical comparison of the dimensionless heat capacity of 3 alkanes with the NASA power law fits and the experimental observations. The observed data is from API and is all at low temperatures where the model gives good agreement with both the NASA correlations and the observations. At high temperatures, where there are no experimental data, the NASA correlations for hexane do not approach the correct asymptotic values and exhibit unrealistic behavior. We were unable to obtain a NASA correlation for octane.

Figures 5 and 6 show the calculated values of the dimensionless heat capacity and entropy of ethylene (C_2H_4) between 300 to 8000 K. The results are compared with values from the JANAF tables. Also shown are the NASA correlations, which are valid from 300 to 5000 K. Figures 7 and 8 show the calculated values of the dimensionless heat capacity and entropy of formaldehyde (CH_2O) between 300 to 8000 K.

Similar data for five alkanes are shown in tabular form in Table 4. In cases where all the data are available, the model calculations are comparable in accuracy with the NASA correlations. At high temperatures, where no experimental data are

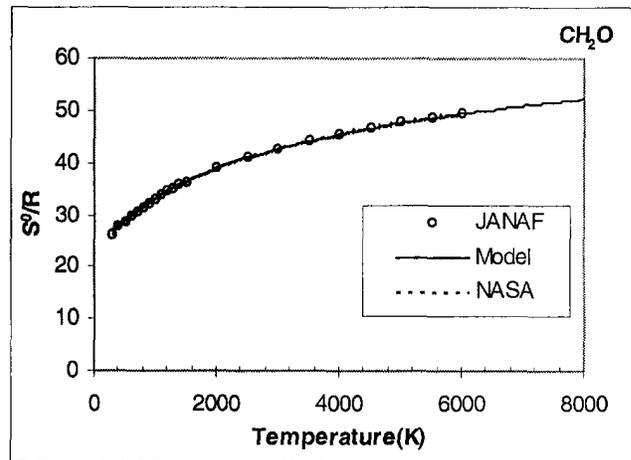


Fig. 8 Dimensionless entropy of formaldehyde

Table 4 Comparison of calculated dimensionless heat capacities for five alkanes with experimental data and the NASA correlations

Species	T (K)	OBS	Model	Error	NASA	Error	Species	T (K)	OBS	Model	Error
Propane C_3H_8	272.43	8.1480	8.2036	0.68%	8.1922	0.54%	Heptane C_7H_{16}	357.01	23.0347	22.9961	-0.17%
	300.42	8.8475	8.7825	-0.74%	8.9041	0.64%		466.1	28.6865	28.6583	-0.10%
	1000		21.4325		21.0015			1000		47.3212	
	2000		27.4864		26.7437			2000		59.8210	
	5000		30.3527		29.5434		5000		65.6802		
Pentane C_5H_{12}	298.15	14.4439	14.2975	-1.01%	14.4201	-0.16%	Octane C_8H_{18}	386.65	27.9970	28.0175	0.07%
	523.15	22.7428	22.6461	-0.43%	22.7131	-0.13%		473.15	33.0700	33.0675	-0.01%
	1000		34.3713		33.8670			1000		53.7954	
	2000		43.6523		42.6661			2000		67.9051	
	5000		48.0162		57.0383		5000		74.5122		
Hexane C_6H_{14}	333.85	18.7972	18.7015	-0.51%	18.8461	0.26%	T (K) Temperature in K OBS Observed data from API Error Relative error calculated by comparing Model or NASA with observed data				
	469.9	24.8918	24.8091	-0.33%	24.8932	0.01%					
	1000		40.8467		39.8554						
	2000		51.7367		48.6351						
	5000		56.8483		63.5436						

Table 5 Parameters used in sample calculation

	C ₂ H ₄	CH ₂ O	n-C ₈ H ₁₈
W	28	30	114
σ	4	2	18
σ_{RB}	2	0	3
TRANS	3	3	3
ROT	3	3	3
STR1	0	0	7
STR2	1	1	0
STR3	0	0	0
XBND	0	0	6
XTOR	0	0	5
HSTR	4	2	18
HBND	6	3	34
HRR	1	0	2

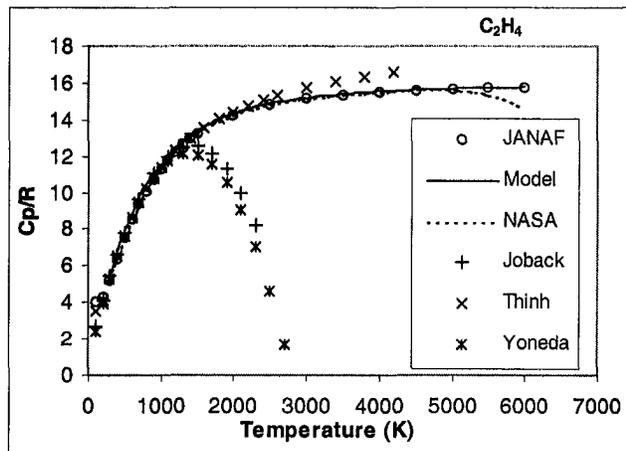


Fig. 9 Dimensionless heat capacity of ethylene

available, the NASA correlations for pentane and hexane are unrealistic, as noted in the foregoing. Table 5 summarizes the parameters the model used to estimate the thermodynamic properties of these sample molecules.

Figure 9 compares the dimensionless heat capacity of C₂H₄ calculated by the model with the results of those methods listed by Reid (1987). None of these estimation procedures, except the procedure of Thinh, can be used outside the range of 280 to 1100 K. Thinh's form is valid from 200 to 1500 K.

At high temperature, the model results are in good agreement with both the JANAF data and the NASA correlations. There exist small errors at low temperatures because the properties become quite sensitive to the thermodynamic temperature when it is below the characteristic heavy particle bending and torsional vibrational temperature. Providing the exact characteristic temperatures for the species when they are known can reduce this error. As more detailed spectra data for polyatomic molecules become available, the accuracy of the model can be improved by performing a least-squares regression to adjust the characteristic temperatures listed in Table 2.

In summary, a simple model has been developed which requires a minimum number of parameters to estimate the sensible thermochemical properties of unbranched hydrocarbons. The results of the model are in good agreement with existing experimental data and the model can be used to estimate properties of molecules for which no measurements or detailed calculations exist. It can easily be programmed as a subroutine for on-line use in chemical kinetic calculations.

Acknowledgments

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