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A GRAPHICAL METHOD OF ESTIMATING HEAT CAPACITIES OF HYDROCARBONS

BY

PU-YING LIU

A

THESIS

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I. INTRODUCTION

Heat capacity arises because the individual particles comprising a substance are able to move and thus take up kinetic energy and usually also potential energy as the temperature rises. In many substances electrons do not absorb energy until very high temperatures are reached. Thus most heat capacity effects are interpreted in terms of the motion of the atoms neglecting electronic transitions.

The total internal energy of a material is, therefore, equal to the sum of the energies due to translational and rotational motion of the molecules and to the vibrational motion of the atoms making up the molecules.

The equipartition principle states that each translational and rotational degree of freedom contributes R/2 cal/(g-mole) (°C) to the heat capacity at constant volume, while the maximum vibrational contribution for each degree of freedom is R cal/(g-mole) (°C). The translational and rotational contributions are fully effective at all except very low temperatures, while the extent of the vibrational contribution depends upon the temperature even to rather high values. Since there is a total of 3N degrees of freedom, the molal heat capacity for non-linear molecules is given by:

$$C_v = 3R + (3N-6)RF \qquad (1)$$

or at low pressures by:

$$C_p = 4R + (3N-6)RF \tag{2}$$

where N = the number of atoms in the molecule

R = gas constant

F = the fraction of the maximum vibrational contribution that is effective

In this equation the only term which varies with temperature is F. Since it is the effective vibrational factor, it may be related with the nature of chemical bonds of the molecules. Similar molecules might be expected to have similar F factors.

The objective of this investigation is to search for the relationship among the F factors of hydrocarbons, and use this relationship to develop a graphical method of determining heat capacities of the hydrocarbons.

II. LITERATURE REVIEW

A. Approximation Methods of Estimating Heat Capacity

Although direct experimental measurement is the primary source of heat capacity values, theoretical calculations based upon the detailed properties of atoms, molecules, or crystals contribute reliable heat capacity values in favorable cases.

1. Dulong and Petit's Rule

In 1819 Dulong and Petit announced the empirical rule that the heat capacity per gram atom is the same for all solid elements.[1] Boltzmann had shown that the rule of Dulong and Petit could be directly deduced from the classical kinetic theory[1] and that the constant of Dulong and Petit should be equal to 3R or approximately 5.96 cal/degree.

Later measurements showed that the Dulong and Petit's constant was merely a high temperature limiting value, approached by different elements at different temperatures. It fails for all solids if the temperature is sufficiently low.

2. Einstein's Theory of Heat Capacities of Solids

An important advance in heat capacity theory was made in 1907, when Einstein applied quantum theory to atomic vibrations. Einstein's basic assumption was that the atoms of a solid vibrate individually and harmonically about their equilibrium positions with a single frequency ν, which is characteristic of the solid.[2] His heat capacity equation is

$$C_v = \frac{3Rx^2e^x}{(e^x - 1)^2} \qquad (3)$$

where $x = \frac{h\nu}{kT}$,

k = Boltzmann's constant,

T = absolute temperature,

h = Planck's constant and,

R = gas constant.

This equation shows C_v to be a function of temperature, and it can readily be shown that (a) C_v approaches zero when T approaches zero, and (b) C_v approaches the classical value of 3R when T becomes large compared to $h\nu/kT$. For intermediate temperatures, Einstein's equation predicts approximately the correct variation of atomic heat, but at low temperatures it yields values that are too low.

3. Debye's Theory of Heat Capacities of Solids

A further advance in theory was made by Debye in 1912. He proposed that a crystal be treated like a giant molecule possessing many different vibrational frequencies ranging almost continuously from zero up to a maximum value, ν_m[3]. He further assumed that the velocity of the different frequencies of vibrations were equal (no dispersion), and were not affected by temperature. In reality, the velocity is dependent on the frequency and some dispersion inevitably results. Debye also assumed that the maximum frequency of the transverse vibrations is equal to the maximum frequency of the longitudinal vibrations, which again is not true. In spite of these assumptions, the Debye theory approximates the experimental data for all solids with remarkable accuracy. Debye's equation is

$$C_v = 3R\left(\frac{T}{\theta}\right)^3 \int_0^{\frac{\theta}{T}} \frac{e^x x^4 dx}{(e^x - 1)^2} \qquad (4)$$

where $\frac{\theta}{T} = \frac{h\nu_m}{kT}$, and

ν_m = maximum frequency possible.

Other variables are the same as those defined in Einstein's equation.

In this equation, as T → ∞, the heat capacity approaches 3R as predicted from the Einstein theory. But as T → 0 the Debye expression for C_V approaches zero much less rapidly than does the Einstein prediction. It is in this respect that Debye's theory is superior for describing heat capacity for actual crystals.

4. Heat Capacities of Monatomic Ideal Gases

In 1867 Naumann predicted that a monatomic ideal gas would possess no thermal energy except that of translation. From elementary kinetic theory, the heat capacity at constant volume will be 3R/2 cal/mole·deg.[1] This prediction has been abundantly verified by measurements on various monatomic gases over wide temperature ranges.

B. The Principle of the Equipartition of Energy

For polyatomic molecules, the energy is not only associated with translational, but also with rotational and vibrational motions. It has been shown that the kinetic energy and the potential energy residing in any degree of freedom is RT/2. This is called the principle of equipartition of energy as developed from classical statistical mechanics by Maxwell and Boltzmann.[4] For vibration the total energy per degree of freedom is RT, RT/2 for the kinetic energy and RT/2 for potential energy. Since translation and rotation involve no potential energy, they contribute RT/2 to the internal energy for each degree of freedom.

C. Boltzmann Distribution Law

For a discussion of the properties of substances it is necessary to know the distribution of molecules among their various quantum states.

The number of molecules in a given quantum state equals the probability that a molecule is there multiplied by the total number of molecules of the system. The probability that a molecule has energy ϵ_i is proportional to $e^{-\epsilon_i/kT}$. Thus, at equilibrium:

$$\frac{N_i}{N_j} = \frac{e^{-\epsilon_i/kT}}{e^{-\epsilon_j/kT}} . \qquad (5)$$

In the case where the energy levels are degenerate, this equation becomes:

$$\frac{N_i}{N_j} = \frac{g_i\, e^{-\epsilon_i/kT}}{g_j\, e^{-\epsilon_j/kT}} \qquad (6)$$

where N_i, N_j = the total number of molecules with energy ϵ_i and ϵ_j respectively,

g_i, g_j = degeneracies of i th and j th energy levels,

k = Boltzmann's constant and,

T = absolute temperature.

The expression for N_i/N_j is called the Boltzmann distribution law[5] in honor of Boltzmann, who was a pioneer investigator of such relationships.

With this law, the thermodynamic properties of any system can be calculated as long as its molecular parameters are known.

D. Partition Function

The Boltzmann distribution law can take another form as follows:

$$\frac{N_i}{N} = \frac{g_i e^{-\epsilon_i/kT}}{\sum_l g_l e^{-\epsilon_l/kT}} \tag{7}$$

where N = the total number of molecules in the system. The expression $\sum_l g_l e^{-\epsilon_l/kT}$ is very important in statistical mechanics. It is called the partition function and usually denoted by the symbol Q, ie.,

$$Q \equiv \sum_l g_l e^{-\epsilon_l/kT} .$$

The terms in the summation for Q indicate how the molecules are partitioned among the various energy states.

The relationship between the internal energy and the partition function for one mole of gas is given by the expression:[6]

$$E = RT^2 \left(\frac{\partial \ln Q}{\partial T} \right)_v . \qquad (8)$$

The heat capacity contribution follows directly by differentiation:

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = R \left(T^2 \frac{\partial^2 \ln Q}{\partial T^2} + 2T \frac{\partial \ln Q}{\partial T} \right) \qquad (9)$$

E. Contribution of Three Kinds of Motions of Molecules to Heat Capacity

For polyatomic molecules there are three kinds of motion possessed by a molecule, translational, rotational and vibrational. Each kind of motion has its independent contribution to heat capacity, each of which can be calculated from its partition function.

1. Translational Contribution to Heat Capacity

The translational energy levels for a molecule in a three-dimensional box are given by:[3]

$$\epsilon_n = \frac{n^2 h^2}{8m V^{2/3}} \qquad (10)$$

where n = the translational quantum number,

m = the mass of a molecule,

V = the volume of the box and,

h = Planck's constant.

The degeneracy of each level is unity, $g_n = 1$; therefore the translational partition function Q becomes:

$$Q_T = \Sigma \exp \left(\frac{- n^2h^2/8mV^{2/3}}{kT} \right). \tag{11}$$

The energy levels are so closely packed together that they can be taken to be continuous and the summation can be replaced by an integration. The result is:

$$Q_T = \frac{(2\pi mkT)^{3/2} V}{h^3} . \tag{12}$$

From the translational partition function, the translational contributions to internal energy and heat capacity of one mole of gas can be obtained as follows:

$$E = RT^2 \left(\frac{\partial \ln Q_T}{\partial T} \right)_v = \frac{3}{2} RT \tag{13}$$

$$C_v = \left(\frac{\partial E}{\partial T} \right)_v = \frac{3}{2} R. \tag{14}$$

2. Rotational Contribution to Heat Capacity

For linear molecules, the allowable rotational energy levels are given by an expression of the form:

$$\epsilon_r = \frac{J(J+1)h^2}{8\pi^2 I} . \tag{15}$$

In this equation J is known as the rotational quantum number and I is the moment of inertia of the molecule about its center of gravity. The degeneracy of the rotational energy levels is equal to 2J + 1. Hence the rotational partition function for a linear molecule will be:

$$Q_r = \frac{8\pi^2 IkT}{\sigma h^2} \tag{16}$$

where σ = symmetry number of the molecule.

By a similar procedure, the rotational partition function of non-linear polyatomic molecules can be obtained.[4] It is:

$$Q_r = \frac{8\pi^2}{\sigma h^3} (8\pi^3 ABC)^{1/2} (kT)^{3/2} \tag{17}$$

where A, B and C are the three principal moments of inertia of the molecule. Then the internal energy and heat capacity due to rotation will be $3RT/2$ and $3R/2$ respectively for non-linear molecules, RT and R for linear molecules.

3. Vibrational Contribution to Heat Capacity

In general, the vibrational energy of a molecule lies in several modes of vibration each of which constitutes a single degree of freedom. Since the energy levels of the harmonic oscillator (one degree of freedom) are:

$$\epsilon_v = (v + 1/2) h\nu \tag{18}$$

the partition function for each vibrational degree of freedom will be:[6]

$$Q_v = \frac{e^{-x/2}}{1 - e^{-x}} \tag{19}$$

where $x = \frac{h\nu}{KT}$, and

ν = the fundamental frequency of the vibration.

For one mole of gas, the internal energy and heat capacity contributed by the vibration of one degree of freedom are as follows:

$$E = RT\left(\frac{x}{2} + \frac{x}{e^x - 1}\right) \tag{20}$$

$$C_v = \frac{Rx^2e^x}{(e^x-1)^2} \tag{21}$$

The value of the expression $\frac{x^2e^x}{(e^x-1)^2}$ is, in general, less than one. It approaches one when the temperature is sufficiently high.[4] To simplify the form of the equation of heat capacity, replace the expression $\frac{x^2e^x}{(e^x-1)^2}$ by F, so that the heat capacity becomes:

$$C_v = RF \tag{22}$$

As there are (3N-5) vibrations for a linear molecule and (3N-6) for a non-linear molecule, the heat capacities for these two kinds of gases are given by the following expressions:

For linear molecules:

$$C_v = (3N-5)RF. \tag{23}$$

For non-linear molecules:

$$C_v = (3N-6)RF \tag{24}$$

F. Heat Capacities of Gases

Translational and rotational contributions are fully effective at all except very low temperatures. The extent of the vibrational contribution depends upon the temperature even to rather high values. However the electronic contribution is negligible even at high temperatures. Hence the total heat capacity of a gas is given by the sum of the contributions due to translation, rotation, and vibration.

For non-linear molecules:

$$C_v = \frac{3}{2} R + \frac{3}{2} R + (3N-6) R \cdot F \tag{25}$$

At low pressure the gases act as ideal gases. Thus the heat capacity at constant pressure will be:

$$C_p = C_v + R \tag{26}$$

or $$C_p = 4R + (3N-6) R \cdot F. \qquad (2\ \ )$$

Similarly for linear molecules:

$$C_p = \frac{7}{2} R + (3N-5) R \cdot F. \tag{27}$$

III. EXPERIMENTAL

In the review of the literature on heat capacities of gases, it is found that the heat capacity at constant pressure for linear molecules can be expressed as:

$$C_p = \frac{7}{2} R + (3N-5) R \cdot F \qquad (27)$$

while for non-linear molecules:

$$C_p = 4R + (3N-6) R \cdot F \qquad (2)$$

On the other hand, for most substances, the heat capacities due to direct measurements can be formulated as:

$$C_p = a + bT + cT^2 \qquad (28)$$

The terms, a, b and c, are constants which can be found in literature reports[7] for various gases. By comparing equation (27), (2) and (28), it is readily found that:

$$F = \frac{(a + bT + cT^2) - \frac{7}{2} R}{(3N-5)R} \qquad (29)$$

and

$$F = \frac{(a + bT + cT^2) - 4R}{(3N-6)R} \qquad (30)$$

for linear and non-linear molecules respectively.

The temperature range over which data for equation (2) were valid was approximately 300°-1500°K. This range was used in this investigation and is a range of temperature often encountered in industry. The calculated values of the vibrational factors, F, for all hydrocarbons studied, were obtained at increments of $50^{o}K$ using an IBM 1620 computer (Appendix 1). The data are graphically illustrated in Figures 1-3 for three kinds of hydrocarbons. It is apparent that F increases as T increases and that the slope of the curve in the low temperature range is greater than that in high temperature range.

If the curve of methane is used as a standard, it is found that all other curves will approximately coincide with this standard by an appropriate shifting of the temperature axis. The values of the temperature shifts for all hydrocarbons are shown in Table I.

Plots of ΔT_s, the temperature shifts, against N, the number of atoms in a molecule, produced three curves, each of which represents a family of hydrocarbons. In the alkyne family, acetylene is far off the curve. It is the only exception in this study.

It is also found that in plots of ΔT_s against the molecular weights of the hydrocarbons, the alkanes and alkenes can be represented by a single curve. That is, the curves for these two families of hydrocarbons become the same. Since the curve for alkynes is still far removed, this correlation is not of much greater value than ΔT_s versus number of atoms.

For convenience, the standard Vibrational Factor-Temperature curve and three Temperature Shift-Atom Number curves were

TABLE I

Temperature Shifts For Hydrocarbons

Substance	Temperature Shift (^{o}K)
CH_4	0
C_2H_6	155
C_3H_8	225
n-C_4H_{10}	265
n-C_5H_{12}	290
n-C_6H_{14}	304
n-C_7H_{16}	315
n-C_8H_{18}	327
C_2H_4	155
C_3H_6	220
1-C_4H_8	265
1-C_5H_{10}	295
1-C_6H_{12}	312
1-C_7H_{14}	322
1-C_8H_{16}	330
C_2H_2	308
C_3H_4	290
1-C_4H_6	315
1-C_5H_8	335
1-C_6H_{10}	350
1-C_7H_{12}	360
1-C_8H_{14}	367

placed on the same diagram (Figure 4). These four curves can be represented by equations which were found by the least square method (Appendix 2) as follows:

1. Standard Vibrational Factor - Temperature Curve

$$F = a_o + a_1T + a_2T^2 + a_3T^3 \tag{31}$$

where

$a_o = -0.24954394$

$a_1 = 0.9624508 \times 10^{-3}$

$a_2 = -0.16980579 \times 10^{-6}$

$a_3 = -0.27122797 \times 10^{-10}$

2. Temperature Shift-Atom Number curve for Alkanes:

$$\Delta T_s = b_o + b_1N + b_2N^2 + b_3N^3 + b_4N^4 + b_5N^5 + b_6N^6 \tag{32}$$

where

$b_o = -537.9203$

$b_1 = 152.53113$

$b_2 = -9.585085$

$b_3 = .327194 \times 10^{-1}$

$b_4 = .23516294 \times 10^{-1}$

$b_5 = 0.10194573 \times 10^{-2}$

$b_6 = .13497531 \times 10^{-4}$

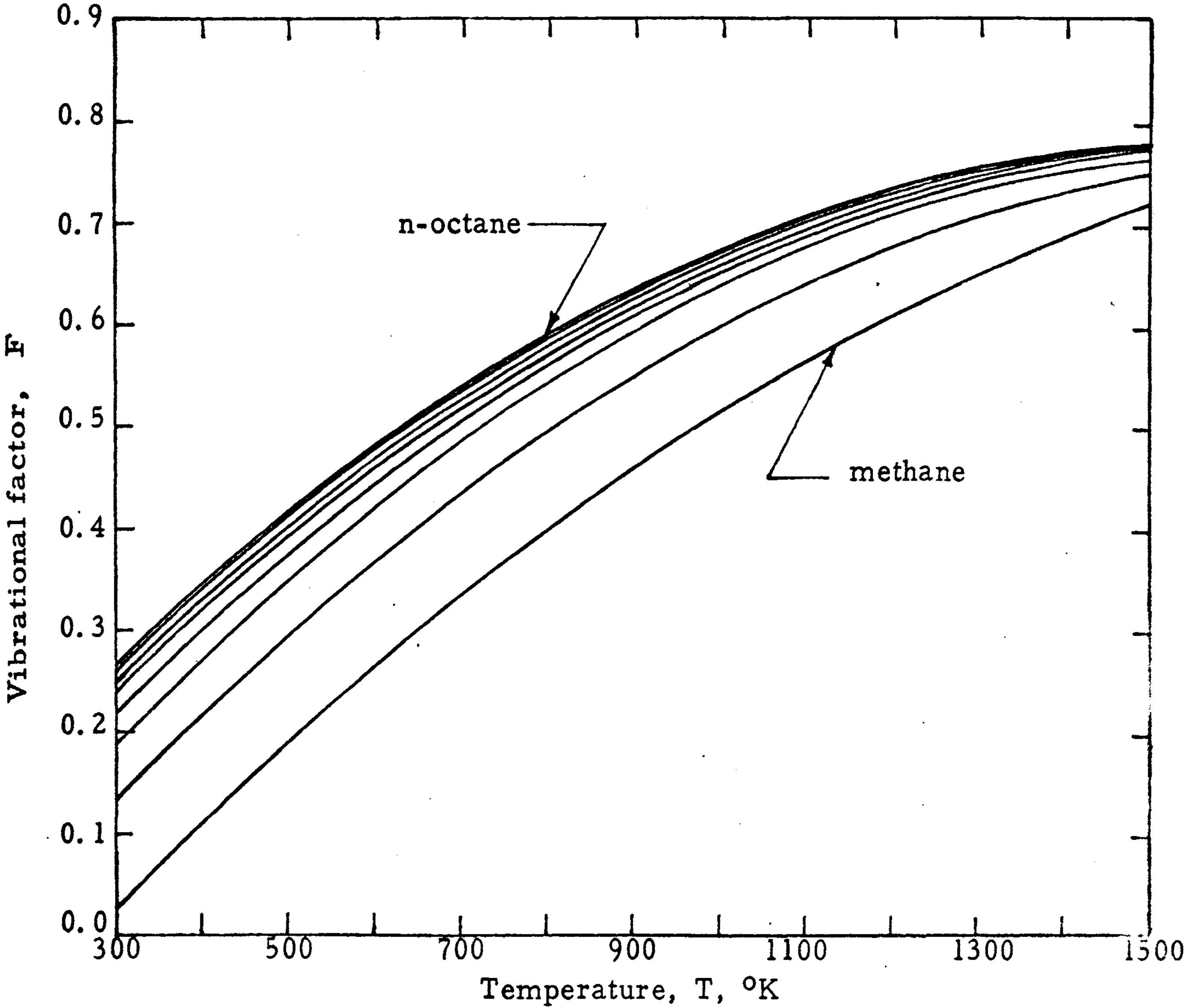

Figure 1. Vibrational factors for alkanes (methane through n-Octane) as a function of temperature in ideal gaseous state.

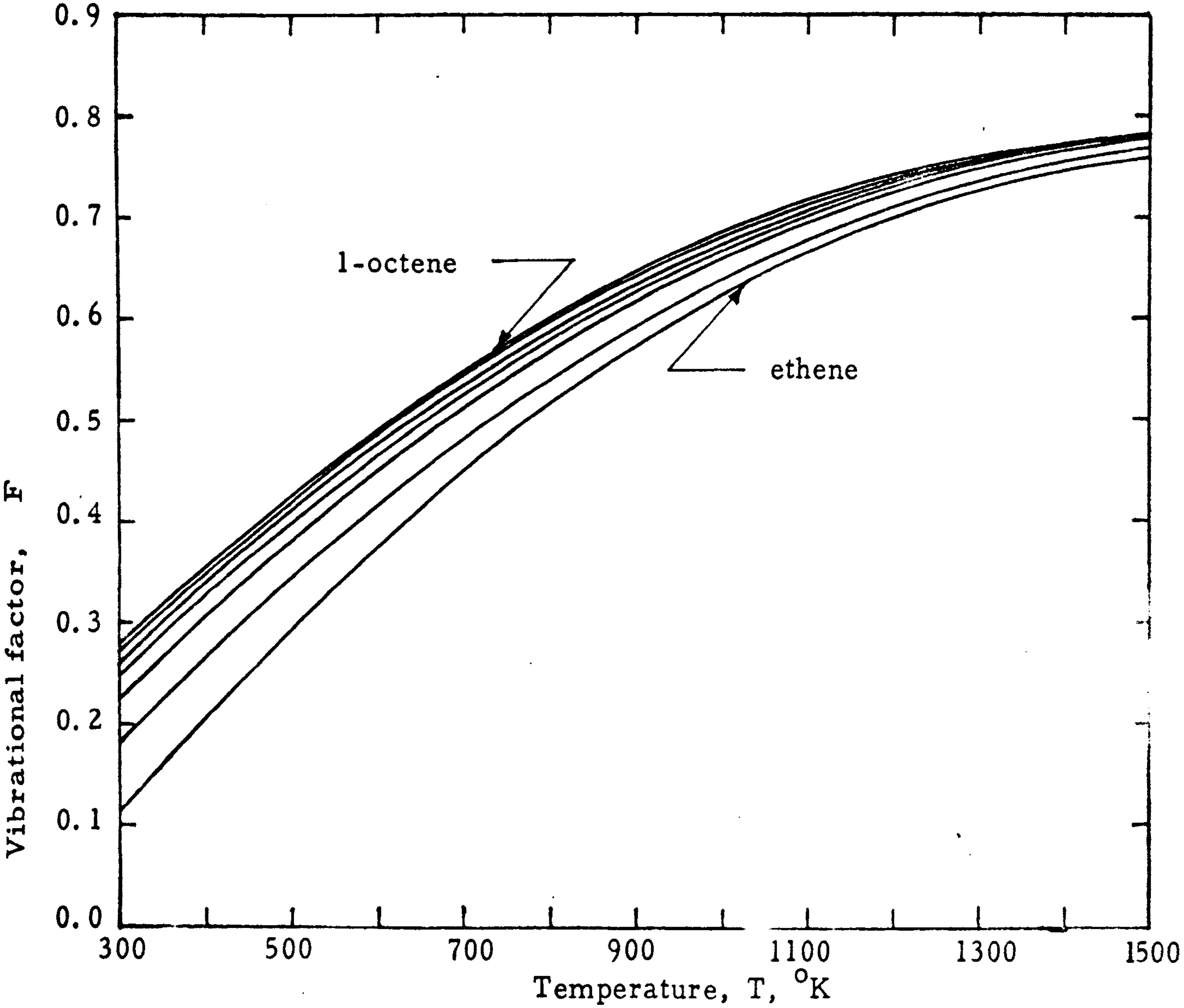

Figure 2. Vibrational factors for alkenes (ethene through 1-octene) as a function of temperature in ideal gaseous state.

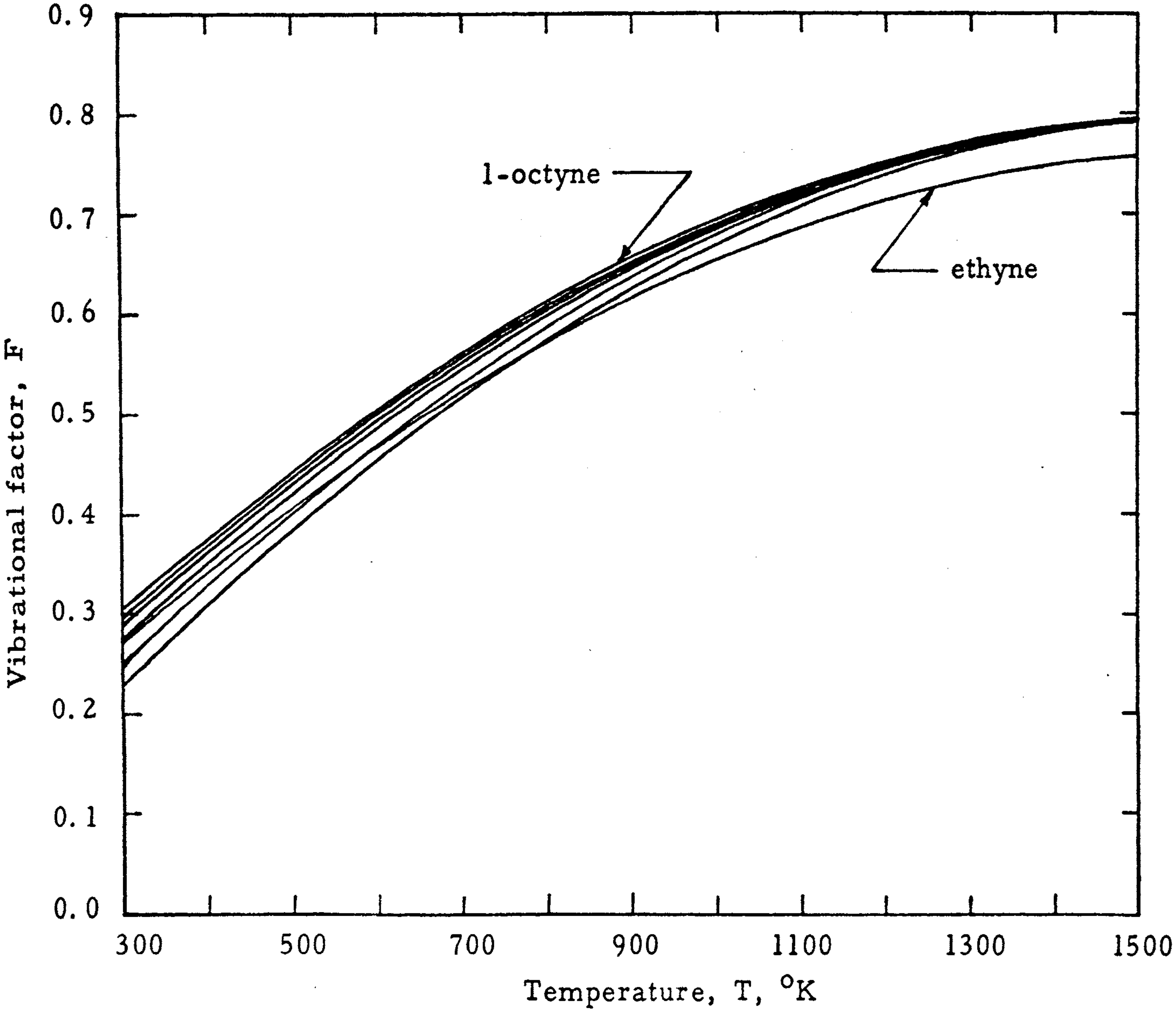

Figure 3. Vibrational factors for alkynes (ethyne through 1-octyne) as a function of temperature in ideal gaseous state.

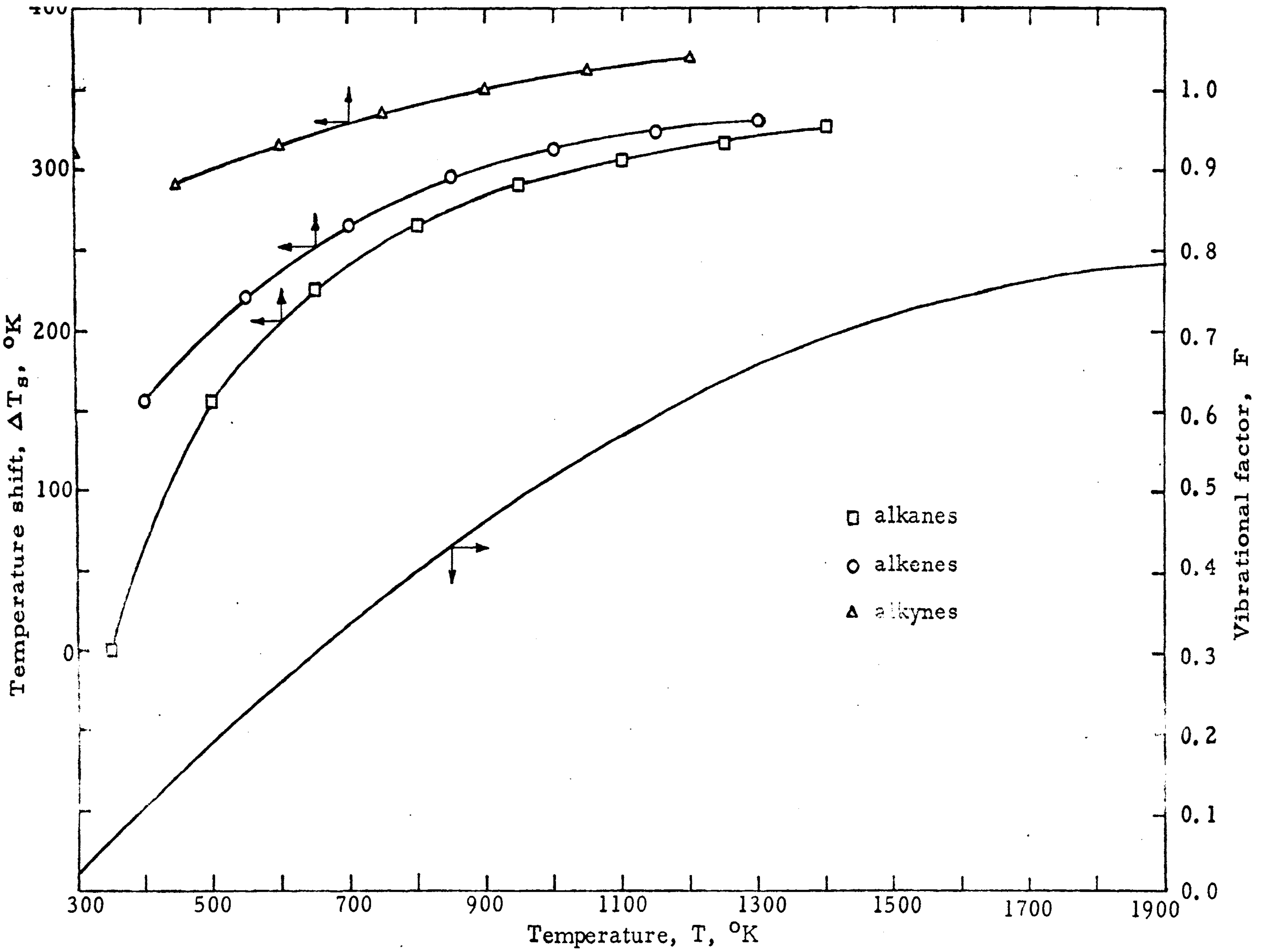

Figure 4. Standard vibrational factor-temperature curve and temperature shift - atom number curves for hydrocarbon gases.

3. Temperature Shift-Atom Number Curve for Alkenes:

$$\Delta T_s = c_o + c_1 N + c_2 N^2 + c_3 N^3 + c_4 N^4 \qquad (33)$$

where

$c_o = -44.781258$

$c_1 = 41.959716$

$c_2 = -1.526562$

$c_3 = .12638149 \times 10^{-1}$

$c_4 = .2179645 \times 10^{-3}$

4. Temperature Shift-Atom Number curve for Alkynes:

$$\Delta T_s = d_o + d_1 N + d_2 N^2 \qquad (34)$$

where

$d_o = 215.47516$

$d_1 = 12.45551$

$d_2 = -.25298128$

Use of the chart to find the heat capacity of a gas at a specified temperature is very simple. First, determine the temperature shift for the gas from the Temperature Shift-Atom Number curve and then add it to the temperature for which the heat capacity is desired. Second, read off the value of the vibrational factor from the Vibrational Factor-Temperature curve. Finally substitute the F value into the heat capacity equation

$$C_p = 4R + (3N-6)R \cdot F \qquad (2)$$

The heat capacities of all hydrocarbons have been checked from $300^{\circ}K$ through $1500^{\circ}K$ by a computer program. (Appendix 3) It is found that the deviations in the temperature range over $400^{\circ}K$ are less than 2% of the values obtained from the empirical equation, $C_p = a + bT + cT^2$. In the range of 300°-$400^{\circ}K$, some are greater than 5% but the average in this range of temperature is less than 4%. Therefore the method developed in this research is a good approximation method of estimating heat capacities of hydrocarbons.

IV. DISCUSSION

As mentioned in the Experimental Section, for each gas the slope of the vibrational factor-temperature curve in the temperature range of 300°-400°K is much greater than that in the high temperature range. For this reason it is found, after shifting, that the vibrational factor-temperature curve in the range of 300°-400°K is not close to the standard as is the part in the high temperature range. Since the F factor in equation (2) is obtained from the standard curve, the deviation of heat capacity in the range of 300°-400°K is greater than that in the higher temperature range.

In this investigation the only linear molecule is acetylene. The temperature shift for this molecule is found to be much higher than that for propyne, the next hydrocarbon in the family of alkynes. This causes the data point for acetylene to be far removed from the ΔT_s-N curve for alkynes (Fig. 4). A quantitative interpretation would be possible if the frequency for each mode of vibration was known. In general, for complex organic compounds this is impossible. But for the present case some characteristic stretching and bending frequencies of particular bonds or groups have been obtained through the analysis of molecular spectra[8]:

TABLE II

Characteristic Frequencies of Chemical Bonds and Groups

Bond	Stretching Frequency (cm^{-1})
C-H	2800-3300
C-C	800-1200
C≡C	2100

Group	Characteristic Bending Frequency (cm^{-1})
H-C-H	1300-1400
C-C-H	800-1200
C-C-C	300-400

The data in Table II show that the frequencies of bending vibrations are much less than those for stretching vibrations of C-H and C≡C. The high value of the temperature shift for acetylene might be due to the lesser modes (reduced degrees of freedom) of bending vibrations.

Alkanes and alkenes having the same number of carbon atoms have very similar values of ΔT_s whereas alkynes possessing the same number of carbon atoms have a much higher value. This can not be interpreted quantitatively either, because only a few frequencies for the vibrations are known. However, plots of the free energy of formation of the hydrocarbons against the number of atoms seem to reflect a similar phenomenon (Fig. 5). The curve for the alkynes is further removed from that of the alkenes than the curve of alkenes is removed from the alkanes. Although these plots show a similar displacement to these of ΔT_s-N, there is no apparent interpretation or correlation.

In the empirical equation of heat capacity $C_p = a + bT + cT^2$, all the constants a, b and c are characteristic of each gas. In calculating the heat capacity of a mixture of gases the three constants for each component of the mixture are required. However in the method developed in this thesis, the heat capacity of a gas is a function of two terms only, the number of atoms in a molecule and the temperature shift of the gas, both of which are easy to find. The number of atoms is obtained directly from the molecular formula and the temperature shift comes from a graph supplied from this work.

The temperature shift for a hydrocarbon series can also be calculated from the empirical equation that is supplied. The lesser amount of required data and its reduction to equation form is the major advantage of this method in determining the heat capacities of gases. It can also be extended to gaseous mixtures in a similar fashion.

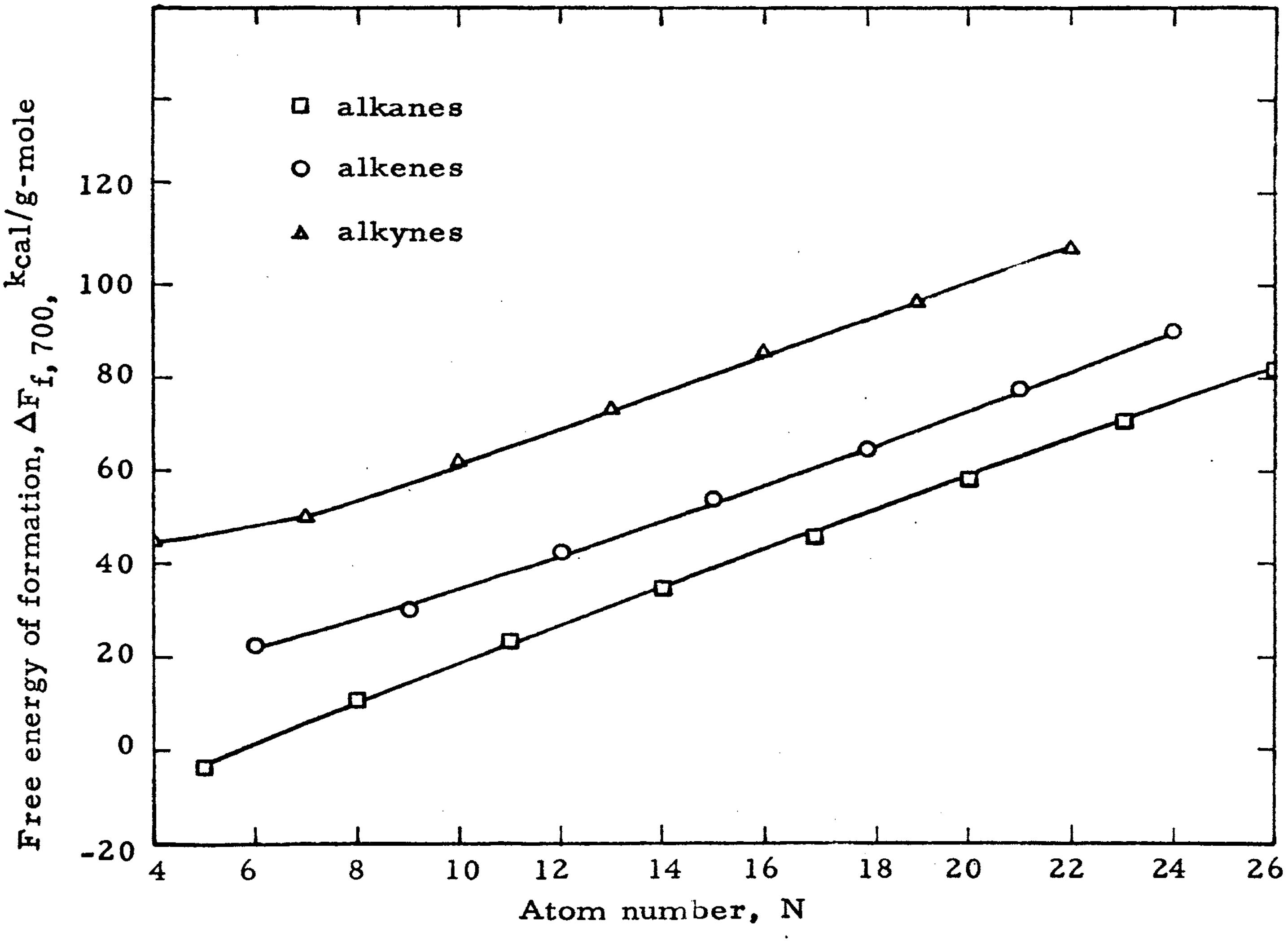

Figure 5. Free energy of formation at 700°K of hydrocarbons as a function of atom number.

V. RECOMMENDATIONS

In this investigation only three series of hydrocarbons were studied. The results are very satisfactory. It might be possible to extend this approach to other series of substances, such as alcohols, aldehydes and ketones. Perhaps it would be necessary to find another parameter to relate the temperature shifts of a new series of gases, although the vibrational factor-temperature curves found by this method might be adequate.

Since alcohols, aldehydes and ketones are also the main organic compounds used in industry, the extension of this method to these new organic gases could prove valuable.

VI. CONCLUSIONS AND SUMMARY

Twenty two gases of three hydrocarbon series were studied in this investigation. All the hydrocarbons were similar to some degree. It is found that the vibrational factor-temperature curves for each of these gases approximately coincide if appropriate shifts are made on the temperature axis. If the methane curve is used as a standard, each of the other hydrocarbons has a positive temperature shift for coincidence. Plots of the temperature shifts of the hydrocarbons against the number of atoms in a molecule produce three curves, each representing a family of hydrocarbons. From these curves the required temperature shift can be found; then the vibrational factor can be obtained from the standard vibrational factor-temperature curve. Substituting the vibrational factor and the number of atoms into equation (2), the heat capacity of a gas at the specified temperature can be readily calculated.

The values of heat capacities of these hydrocarbons, excepting acetylene, were checked from 300° through 1500°K. The deviation from the values calculated from the empirical equation $C_p = a + bT + cT^2$ for all gases is found to be less than 2% at temperatures over 400°K. In the range 300°-400°K, the average of the deviations for each gas is less than 4%. Therefore the method developed in this study is a good approximation method of estimating heat capacities of hydrocarbons. As mentioned in the discussion, the method is particularly convenient for calculations involving a large number of gases as the amount of heat capacity data is significantly reduced.

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VIII. APPENDICES

APPENDIX 1

Program For the Calculation of Vibrational Factors of Hydrocarbons

```
      DIMENSION A(22),B(22),C(22),P(22)
      READ 15,(A(I),B(I),C(I),P(I),I=1,22),R
      DO 121 I=1,22
      PUNCH 32,A(I),B(I),C(I),P(I),R
      PUNCH 21
      T=300.0
      DO 22 K=1,25
      CP=A(I)+B(I)*T+C(I)*T*T
      F=(CP-4.*R)/((3.*P(I)-6.)*R)
      PUNCH 23,T,CP,F
   22 T=T+50.0
  121 CONTINUE
   15 FORMAT(4E18.8)
   21 FORMAT(/10X,1HT,9X,2HCP,10X,1HF)
   32 FORMAT(/3E15.5)
   23 FORMAT(F13.1,F11.3,F12.6)
      STOP
      END
```

APPENDIX 2

Program 1. Fitting Equations for Temperature Shift-Atom Number Curves of Hydrocarbons

```
      DIMENSION X(8), Y(8), S(17), B(9), A(9, 10)
      DO 88 LL=1, 3
      READ 100, G, P
      MN=P
      READ 100, (X(I), Y(I), I=1, MN)
      S(1)=P
      E=0. 0
      DO 66 I=1, MN
 66   E=E+Y(I)
      B(1)=E
      DO 105 M=1, 16
      R=0. 0
      DO 110 I=1, MN
110   R=R+X(I)**M
105   S(M+1)=R
      DO 115 N=1, 8
      C=0. 0
      DO 120 I=1, MN
120   C=C+Y(I)*X(I)**N
115   B(N+1)=C
      NN=3
      MM=4
      DO 155 L=1, 7
      DO 199 I=1, NN
      DO 199 J=1, NN
      M=I+J-1
199   A(I, J)=S(M)
      DO 188 I=1, NN
188   A(I, MM)=B(I)
      DO 30 I=1, NN
      TEMP=1. 0/A(I, I)
      NI=I+1
      DO 10 J=NI, MM
 10   A(I, J)=A(I, J)*TEMP
      DO 30 K=1, NN
      IF(I-K)25, 30, 25
 25   DO 20 J=NI, MM
 20   A(K, J)=A(K, J)-A(K, I)*A(I, J)
 30   CONTINUE
```

```
     DO 40 I=1, NN
 40  PUNCH 100, A(I, MM)
     PUNCH 22
     W=G
     DO 33 I=1, MN
     K=MM-2
     U=0. 0
     DO 222 N=1, K
222  U=U+A(N+1, MM)*W**N
     V=U+A(1, MM)
     PUNCH 44, W, V, Y(I)
 33  W=W+3. 0
     NN=NN+1
155  MM=MM+1
 88  CONTINUE
100  FORMAT(4E18. 8)
200  FORMAT(2I10)
 44  FORMAT(F13. 1, F17. 1, F17. 1)
 22  FORMAT(/10X, 1HN, 12X, 9HDT(CALC.), 8X, 9HDT(CURVE))
     STOP
     END
```

Program 2. Fitting Equation For Standard Vibrational Factor-Temperature Curve

```
     DIMENSION X(17), Y(17), S(11), B(6), A(6. 7)
     READ 100, (X(I), Y(I), I=1, 17)
     E=0. 0
     DO 66 I=1, 17
 66  E=E+Y(I)
     B(1)=E
     S(1)=17. 0
     DO 105 M=1, 10
     R=0. 0
     DO 110 I=1, 17
110  R=R+X(I)**M
105  S(M+1)=R
     DO 115 N=1, 5
     C=0. 0
     DO 120 I=1, 17
120  C=C+Y(I)*X(I)**N
115  B(N+1)=C
     DO 155 L=1, 5
```

```
    READ 200 NN,MM
    DO 199 I=1,NN
    DO 199 J=1,NN
    M=I+J-1
199 A(I,J)=S(M)
    DO 188 I=1,NN
188 A(I,MM)=B(I)
    DO 30 I=1,NN
    TEMP=1.0/A(I,I)
    NI=I+1
    DO 10 J=NI,MM
 10 A(I,J)=A(I,J)*TEMP
    DO 30 K=1,NN
    IF(I-K)25,30,25
 25 DO 20 J=NI,MM
 20 A(K,J)=A(K,J)-A(K,I)*A(I,J)
 30 CONTINUE
    DO 40 I=1,NN
 40 PUNCH 100,A(I,MM)
    PUNCH 22
    DO 33 I=1,17
    K=MM-2
    U=0.0
    DO 222 N=1,K
222 U=U+A(N+1,MM)*X(I)**N
    V=U+A(1,MM)
 33 PUNCH 44, X(I), V, Y(I)
155 CONTINUE
 22 FORMAT(/11X,1HT,11X,8HF(CALC.),9X,8HF(CURVE))
100 FORMAT(4E18.8)
200 FORMAT(2I10)
 44 FORMAT(F14.1,F14.3,F18.3)
    STOP
    END
```

APPENDIX 3

Program For the Calculation Of Deviations of Heat Capacities

```
      DIMENSION A(21), B(21), C(21), PN(21), A1(7), B1(5), C1(6), E(5)
      READ 1000, (A(I), B(I), C(I), PN(I), I=1, 21),(A1(I), I=1, 7), (B1(I),
               I=1, 5), (C1(I), I=1, 6), (E(I), I=1, 5), R
      DO 123 I=1, 21
      PUNCH 99
      T=300
      DO 223 N=1, 25
      CP1=A(I)+B(I)*T+C(I)*T*T
      IF(I-8)1, 1, 5
    5 IF(I-15)2, 2, 3
    1 U=0. 0
      DO 1234 M=1, 6
 1234 U=U+A1(M+1)*PN(I)**M
      DT=A1(1)+U
      GO TO 4
    2 U=0. 0
      DO 323 L=1, 4
  323 U=U+B1(L+1)*PN(I)**L
      DT=B1(1)+U
      GO TO 4
    3 U=0. 0
      DO 2234 J=1, 5
 2234 U=U+C1(J+1)* PN(I)**J
      DT=C1(1)+U
    4 TDT=T+DT
      S=0. 0
      DO 3234 K=1, 4
 3234 S=S+E(K+1)*TDT**K
      F=S+E(1)
      CP2=4. *R+(3. *PN(I)-6. )*R*F
      DCP=CP2-CP1
      DEV=DCP*100. 0 / CP1
      PUNCH 423, T, CP1, CP2, DCP, DEV
  223 T=T+50. 0
  123 CONTINUE
 1000 FORMAT(4E18. 8)
  423 FORMAT(F24. 1, F9.2, F12. 2, F13. 3, F10. 2)
   99 FORMAT(//22X, 45HT CP1(EQU. ) CP2(CURVE) CP2-CP1 DEV.)
      STOP
      END
```

IX. VITA

The author, Pu-ying Liu, was born on December 18, 1936, in Ho-pei, China. He received his primary education in his home town and his secondary education in Taiwan, China. After graduating from high school in 1957, he studied Chemical Engineering in the National Taiwan University. He received a Bachelor of Science Degree in Chemical Engineering in June, 1961. Following graduation he was called to the services of the Chinese Army. After one year of military service, he held a teaching position in Kai-Ping high school, Taipei, Taiwan. To pursue advanced studies in chemistry, he left Taiwan for the United States and entered the University of Missouri at Rolla in February, 1964, as a full time graduate student working toward a Master of Science in Chemistry.