Prediction of Specific Heat of Organic Liquids

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A theoretical equation is presented for predicting the specific heat at constant volume and constant pressure of organic liquids as a function of temperature from data on the velocity of sound, infrared and Raman spectra. By use of this equation, the average deviation of the calculated from the experimental values of specific heat for 100 organic liquids at 68°F. is ±1.5%.

An alternate correlation for hydrocarbon liquids based on a modified statement of the theory of corresponding states is also presented. Based on it, the average deviation of the calculated from the experimental values for 100 points representing the entire temperature range is ±0.9%.

Heat transfer calculations require, in addition to other physical properties, specific heat data. Reliable experimental data (9) are scanty, particularly for organic liquids other than hydrocarbons, and the data for hydrocarbon liquids are mostly for temperatures below 86°F. Although considerable progress has been made toward an understanding of the liquid state, it is still difficult to derive results of any practical value.

The specific heat of a liquid at its boiling point has been related to that of its vapor by thermodynamic expressions. This method is tedious and its practical value limited.

Chow and Bright (2) have related the specific heat of a liquid with its parachor and molar refraction. The method has little theoretical foundation and is applicable only to homologous series of liquids.

The problem of predicting the specific heat of a liquid is solved here by consideration of a simplified model of liquid state and use of data on the velocity of sound, infrared and Raman spectra. The resulting equation is applicable over large intervals of temperature. An alternate method of correlation based on a modified statement of the theory of corresponding states has been applied to hydrocarbon liquids.

PART I

The prediction of the specific heat of a liquid is somewhat complicated in view of the fact that the liquid state is not so well understood as are the gaseous and solid states. Attempts have been made to predict liquid properties by use of models approximating the liquid to a highly compressed gas or a quasicrystalline solid.

Owing to the large intermolecular forces existing in the liquid state, only a small fraction of the total energy is transferred by individual molecules over relatively long distances. Rather, the greatest part of the energy transfer takes place by the action of neighboring molecules, much in the same way that mechanical motion is transferred from point to point along a vibrating network of spheres connected by springs. The success obtained by using such a model for the prediction of thermal conductivity of liquids (7) suggests that the translational motion of a molecule in the liquid state may be considered as a harmonic oscillation about a mean position. In this way the liquid behaves as a quasicrystalline solid.

The different types of motion of a molecule may be classified into an *acoustical branch* and several *optical branches*. The acoustical branch consists of all vibrations in which the molecule moves essentially as a whole. The optical branches consist of the motion of atoms, or groups of atoms, with respect to each other.

The internal energy of a molecule is present in kinetic and potential forms that result from the motion and attractive forces of the molecules, atoms, and component groups (5).

A nonlinear molecule consisting of n number of atoms possesses $3n$ degrees of freedom, or independent modes of motion.

CONTRIBUTION TO SPECIFIC HEAT OF ACOUSTICAL BRANCH

Translational Motion

A nonlinear molecule possesses three degrees of freedom for translation. The contribution to the specific heat of these degrees of freedom will be evaluated by assuming that the translational motion is actually a harmonic oscillation about a mean position.

The vibration of the molecules will have a broad distribution of frequencies which are determined by the velocity of sound in the medium. The contribution to heat capacity at constant volume can be evaluated by means of a Debye function (5).

$$C_{v_t} = 9R\left(\frac{kT}{h\nu_m}\right)^3$$

$$\cdot \int_0^{h\nu_m/kT} \frac{U^4 e^u \, du}{(e^u - 1)^2} = 3Rf_D \quad (1)$$

where $\nu_m = U_s(3N_0\rho/4\pi M)^{1/3}$. The Debye function f_D has been evaluated (5) as a function of $h\nu_m/kT$. As compared with the solid, however, there can be no transverse waves in the liquid and U_s is simply the velocity of sound in the liquid.

For liquids at temperatures of 300°K. and higher $f_D \sim 1$ and $C_{v_t} \sim 3R$, or R for each degree of freedom.

External Rotation

In the liquid state, with the exception of molecules of very small moments of inertia, the frequency of rotation characteristic of the isolated molecule is less than the frequency of collision with other molecules. Free rotation is so restricted that infrared and Raman spectra do not show bands corresponding to external rotational motion. As a result the rotation may be considered as a torsional motion and its contribution to the heat capacity evaluated by treating it as a harmonic oscillation having a certain fundamental frequency.

The fundamental frequency of the torsional oscillation cannot be observed as such, but, being of the same order of magnitude as the frequencies of translational motion, it can be evaluated from the velocity of sound in the liquid. For this reason this contribution was included in the acoustical branch of energy transfer.

The contribution to the heat capacity at constant volume should be evaluated by means of an Einstein function (5).

$$C_{v_r} = 3R \frac{u^2 e^u}{(e^u - 1)^2} = 3Rf_E \quad (2)$$

where $u = h\nu/kT$. The Einstein function f_E has been evaluated (5) as a function of u.

On the basis of the considered model of liquid state, calculation of u would require use of velocity of sound and X-ray diffraction data.

The Einstein and Debye functions, however, yield the same result to a close approximation, and, to avoid use of X-ray diffraction data, the Debye function will be used to evaluate the contribution to the heat capacity due to the external rotation also. Hence

$$C_{v_r} = 3Rf_D \qquad (4)$$

The total contribution to heat capacity at constant volume of the acoustical branch is

$$C_{v(t+r)} = (6R)f_D \qquad (5)$$

CONTRIBUTION TO SPECIFIC HEAT OF OPTICAL BRANCHES

It is well known that the internal motions of polyatomic molecules take place in the liquid and solid state without appreciable change. The observed characteristic vibrations are substantially independent of temperature and of the molecule in which they occur.

The constancy of group frequencies in different molecules was at first established by observation and later explained theoretically on the basis of the constancy of bond force constants. The observation of the characteristic frequencies has led to the concept that for every bond in a molecule there exist a vibration in which the bond is stretched and another one of much smaller frequency in which it is bent.

Hence, to a good approximation, generalized average values of the stretching and bending frequencies may be assigned to a given bond. The contribution to the specific heat of the internal rotating, stretching, and bending vibrations can be evaluated by treating the motions as harmonic oscillations having the assigned fundamental frequencies.

This general procedure for organic vapors was developed by Bennewitz and Rossner (1), modified by Dobratz (3), and extended by Stull and Mayfield (8). In Table 1 are given the two characteristic fundamental frequencies of various bonds expressed in wave numbers as given by Herzberg. Additional frequencies were obtained from the values of Stull and Mayfield (8). Most values were checked with experimental data and slight changes made. As was previously mentioned, the values of the frequencies are also applicable to liquids.

Internal Rotation

The internal rotation contributions to the specific heat in large molecules are difficult to evaluate. These contributions result from the rotation of groups of atoms about single bonds. As the complexity of the molecule increases, the contributions change. Internal rotation about a multiple bond is highly restrained and the rotation is treated as a harmonic oscillator.

The large intermolecular forces in liquids possibly restrict internal rotation

TABLE 1

Bond	Stretching, ω_ν, cm.$^{-1}$	Bending, ω_δ, cm.$^{-1}$
>C—H	2,960	
—C(H,H,H)		1,450
C(H,H)		1,000
>C(H,H)		1,450
>C—H	3,020	
≡C(H)		1,100
≡C—H	3,300	700
C—C	900	370
C=C	1,650	
C≡C	2,050	
C—C≡C		600
C—C≡C		300
C≡C≡C		350
C—O	1,030	205
C=O	1,700	390
C—N	900	370
C=N	1,620	845
—C≡N	2,250	
C—S	650	330
C=S	1,550	530
>C—F	1,100	530
>C—Cl	650	330
>C—Br	560	280
>C—I	500	260
O—H	3,400	1,150
>N—H	3,350	1,320
N—O	1,030	205
N=O	1,700	390
N—N	990	390
S—H	2,570	1,050
S—S	500	260

to a greater extent. As an approximation all internal rotations will be treated as harmonic oscillations and their contributions evaluated by Debye functions.

$$C_{v_{r'}} = n_{r'}Rf_D \qquad (6)$$

where

n_r' = number of single bonds about which internal rotation of groups can take place, e.g., C—C.

Stretching and Bending Vibrations

These vibrations are essentially harmonic oscillations and their contribution is evaluated by Einstein functions using the fundamental bond frequencies assigned from spectroscopic data. For a given bond two characteristic fundamental frequencies, one stretching and one bending, are used, each representing one degree of freedom. The total contribution due to stretching and bending vibrations is obtained by summing up the atomic contributions.

$$C_{v(r+b)} = \sum_i q_i f_{Ev_i} + \sum_i q_i f_{E\delta_i} \qquad (7)$$

where

f_{Ev_i} = contribution to the heat capacity from the stretching vibrations of bond i

$f_{E\delta_i}$ = contribution to the heat capacity from the bending vibrations of bond i

$\sum q_i$ = total number of bonds in the molecule

In addition to the considered contributions there are

$$3n - 6 - n_{r'} - 2\sum q_i$$

degrees of freedom to be accounted for. Assuming that the remaining degrees of freedom make the same contribution to the heat capacity that the known bending vibrations do, their contribution is added to that of the bending vibrations as follows

$$\left[\frac{3n - 6 - n_{r'} - \sum q_i}{\sum q_i}\right] \sum_i q_i f_{E\delta_i}$$

The contribution to heat capacity at constant volume of the optical branches is

$$C_{v(r'+r+\delta)} = n_{r'}Rf_D + \sum_i q_i f_{Ev_i}$$
$$+ \left[\frac{3n - 6 - n_{r'} - \sum q_i}{\sum q_i}\right]$$
$$\sum_i q_i f_{E\delta_i} \qquad (8)$$

The complete expression for the heat capacity of a liquid at constant volume becomes

$$C_v = (6 + n_{r'})Rf_D + \sum_i q_i f_{Ev_i}$$
$$+ \left[\frac{3n - 6 - n_{r'} - \sum q_i}{\sum u_i}\right]$$
$$\sum_i q_i f_{E\delta_i} \qquad (9)$$

PREDICTION OF SPECIFIC HEAT OF LIQUIDS

Equation (9) was used to predict the specific heat at constant volume of a number of liquids. Since very few values of the specific heat at constant volume for liquids are available, and further since the specific heat at constant pressure is more useful, the ratio of the specific heats at constant pressure and constant volume was used as a check of Equation (9).

The velocity of sound in a liquid can be expressed in terms of the adiabatic and isothermal compressibility

$$K_{ad} = \frac{1}{U_s^2 \rho} \qquad (10)$$

$$K_{is} = \frac{C_p/C_v}{U_s^2 \rho} \qquad (11)$$

Given the coefficient of thermal expansion, β, of a liquid the following thermodynamic relation may be used:

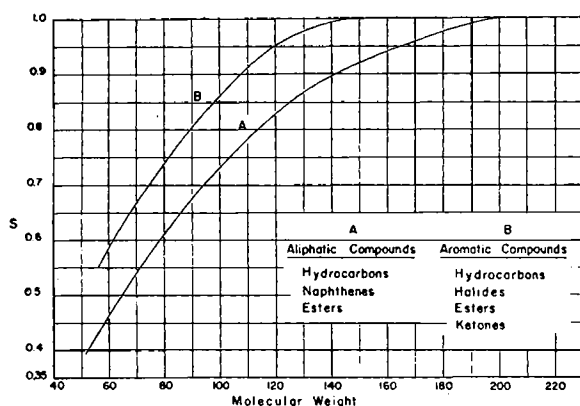$$C_p - C_v = \frac{T\beta^2}{K_{is}\rho} \qquad (12)$$

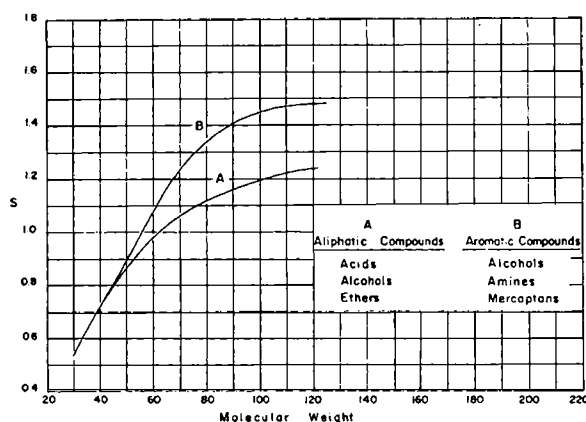Fig. 1. Correction factor, S, vs. molecular weight.

Fig. 2. Correction factor, S, vs. molecular weight.

TABLE 2. COMPARISON OF SOME EXPERIMENTAL VALUES OF SPECIFIC HEAT WITH VALUES CALCULATED BY THEORETICAL EQUATION AT 68°F.

Liquid	$C_{p_{exp.}}$, B.t.u./ (lb.)(°F.)	S	$C_{p_{obs.}}$, B.t.u./ (lb.)(°F.)	% Dev.
n-Hexane	0.534	0.655	0.534	0
n-Dodecane	0.521	0.957	0.521	0
Pentene-1	0.524	0.524	0.523	−0.2
2-Methyl pentane	0.533	0.655	0.523	−1.9
2,2,3—Trimethyl butane	0.497	0.732	0.510	+2.6
2-Methyl butadiene	0.530	0.652	0.533	+0.6
Ethyl cyclohexane	0.446	0.795	0.452	+1.3
1, 2, 4-Trimethyl benzene	0.420	0.952	0.418	−0.5
n-Propyl acetate	0.459	0.742	0.451	−1.7
Ethyl n-butyrate	0.457	0.807	0.456	−0.2
Ethyl benzoate	0.387	1.000	0.389	+0.5
Acetone	0.517	0.568	0.513	−0.8
o-Methyl cyclohexanone	0.439	0.920	0.445	+1.4
n-Propyl alcohol	0.563	0.985	0.566	+0.5
Benzyl alcohol	0.481	1.470	0.469	−2.5
Caproic acid	0.533	1.235	0.530	−0.6
Aniline	0.496	1.430	0.487	−1.8
Phenetole	0.446	1.240	0.453	+1.6
Chlorobenzene	0.318	0.925	0.319	+0.3
Iodobenzene	0.186	1.000	0.183	−1.6

Substituting Equation (11) in (12) and dividing by C_v results in

$$C_p/C_v = 1 + \frac{T\beta^2 U_s^{\,2}}{C_p} \quad (13)$$

Hence the ratio of the specific heats can be calculated independently from the velocity of sound and used to check that calculated from Equation (9). The procedure was as follows

1. C_v was calculated from Equation (9) and, given C_p, the ratio C_p/C_v was determined.

2. Given C_p, β, and U_s, the ratio C_p/C_v was calculated from Equation (13).

3. Next the ratio $\mathbf{R}$ of the C_p/C_v values calculated from Equations (9) and (13) was taken.

If Equation (9) is correct, the ratio $\mathbf{R}$ would be unity. The results showed that the ratio varied a maximum of ±25% from unity.

This deviation probably results from the fact that (1) in the calculation of the contribution to the heat capacity of the remaining degrees of freedom, the arbitrary assumption was made that their contribution is the same as that of the bending vibrations and evaluated by the ratio

$$\frac{3n - 6 - n_{r'} - \sum q_i}{\sum q_i}$$

or (2) that all internal rotations are possible and contribute to the same extent to the specific heat.

Next the calculated C_v from Equation (9) was adjusted in such a way as to make $\mathbf{R}$ equal to unity. The adjustment was made by multiplying the term by an appropriate factor S. This factor will correct the contribution to the specific heat of the remaining degrees of freedom. Further, as a good approximation, the Debye factor f_D was taken as 1.0 in these calculations.

As expected, it was found that this correction factor was a simple function of molecular weight, or actually molecular mass. Plots of S as a function of molecular weight are given in Figures 1 and 2.

Procedure for Calculating the Specific Heat of a Liquid

The final equation for calculating the specific heat at constant volume of a liquid is

$$C_v = (6 + n_{r'})R + \sum_i q_i f_{Ev_i}$$

$$+ \left[\frac{3n - 6 - n_{r'} - \sum q_i}{\sum q_i} \right] S$$

$$\cdot \sum_i q_i f_{Eb_i} \quad (14)$$

The specific heat at constant pressure of a liquid may be evaluated as follows:

1. Calculate the specific heat at constant volume, C_v, from Equation (14).

2. Calculate the ratio C_p/C_v as a function of C_p from Equation (13).

3. Substitute C_v from Equation (14) in Equation (13) and solve for C_p.

An example follows.

Calculation of Specific Heat at Constant Volume and Constant Pressure for Ethyl Butyrate at 68°F.

Mol. wt. = 116.16
$\beta = 6.57 \times 10^{-4}$ 1/°F.
$U_s = 3874$ ft./sec.*
$T = 528°R.$

Formula:
$$CH_3 \cdot CH_2 \cdot CH_2 \cdot CO_2 \cdot C_2H_5.$$

Bond	q_{iv}	$q_{i\delta}$	ω_v†	ω_δ†	f_{Ev}‡	$f_{E\delta}$‡	$q_i f_{Ev_i}$	$q_i f_{E\delta_i}$
⟩C—H	12		2960		0.0002		0	
⟩C⟨^H_H		6		1450		0.0829		0.498
⋯C⟨^H_H		6		1000		0.3610		2.167
C—C	4	4	900	370	0.482	1.522	1.928	6.088
C—O	2	2	1030	205	0.329	1.829	0.658	3.658
C=O	1	1	1700	390	0.033	1.476	0.033	1.476
							2.619	13.887

*The velocity of sound in the liquid may be obtained from reference 6 or estimated by the method given in reference 7.

†Frequencies were read from Table 1.

‡The contributions to the heat capacity of the stretching and bending vibrations are calculated as follows: $u = 2.585\omega/T$ for C—C bending

$u = 2.585 \times 370/528 = 1.816$

Read $f_{E\delta}$ from Figure 3.

$f_{E\delta}/R = 0.7652$ at $u = 1.816$

$f_{E\delta} = 1.987 \times 0.7652 = 1.522$ B.t.u./(lb. mole)(°F.)

Number of atoms in molecule, $n = 20$
Number of bonds about which internal rotation is possible, $n_r' = 4$ (C—C).
Total number of bonds in molecule, $\sum q_i = 19$

$$\left[\frac{3n - 6 - n_{r'} - \sum q_i}{\sum q_i} \right]$$

$$= \left[\frac{(3)(20) - 6 - 4 - 19}{19} \right] = 1.630$$

Read S factor from Figure 1.

$S = 0.807$ at $M = 116.16$

$C_v = (6 + 4) 1.9872 + 2.62 + 1.630 \times$

0.807×13.89 (14)

$C_v = 40.782$ B.t.u./(lb. mole)(°F.)

$C_v = 0.351$ B.t.u./(lb.)(°F.)

Use Equation (13).

$$C_p/C_v = 1 + \frac{T\beta^2 U_s^2}{32.174 \times 778.16 \times C_p}$$

$$C_p/C_v = 1 + \frac{528 \times (6.57 \times 10^{-4})^2 \times (3874)^2}{32.174 \times 778.16 \times C_p}$$

$$C_p/C_v = 1 + \frac{0.1368}{C_p}$$

$$C_p = 0.351 + \frac{0.0480}{C_p}$$

Solve for C_p.

   Answer $C_v = 0.351$ (B.t.u./(lb.)(°F.)
        $C_p = 0.456$ (B.t.u./(lb.)(°F.)

The observed value of the specific heat at constant pressure is 0.457 B.t.u./(lb.)(°F.)

The curves of Figures 1 and 2 cover a large range of molecular weights and chemical types of organic compounds. This method of calculation was used to predict the specific heat at constant pressure at 68°F. for 100 liquids. A sample of the results is given in Table 2. The average deviation of the calculated from the observed values of the specific heat for the 100 liquids was found to be ±1.5%. The maximum deviation was ±4.0%. *It must be emphasized that this method must not be used with the first one or two members of the series, or small molecules, since the generalized frequencies apply mainly to the higher members.*

Variations of Specific Heat with Temperature

The specific heat of a liquid at a temperature other than 68°F. may be calculated also by use of Equations (13) and (14). The method of calculation is the same. Results for seven liquids for which reliable values of the specific heat are available (9) are given in Table 3.

It will be noted that the agreement between the calculated and observed values is good. The agreement is better at the higher temperatures than at the lower. In these calculations the factor S was taken to be the same as at 68°F.

TABLE 3. VARIATION OF SPECIFIC HEAT WITH TEMPERATURE

Low Temperatures

T, °F.	$C_{pobs.}$, B.t.u./(lb.)(°F.)	$C_{pcalc.}$, B.t.u./(lb.)(°F.)	% Dev.
	n-Heptane		
—94	0.481	0.460	—4.3
14	0.504	0.505	+0.2
50	0.518	0.520	—0.4
	1,2-Dimethyl transcyclohexane		
—94	0.365	0.359	—1.6
14	0.411	0.418	+1.7
50	0.430	0.435	+1.2
	Ethyl acetate		
—94	0.435	0.402	—7.6
14	0.445	0.434	—2.5
50	0.454	0.443	—2.4
	2,2-Dimethyl pentane		
—94	0.430	0.459	+6.7
14	0.485	0.502	+3.5
50	0.507	0.514	+1.4
	High Temperatures *p*-Xylene		
68	0.406	0.406	0
194	0.460	0.463	+0.7
266	0.495	0.489	—1.2
	Benzene		
68	0.412	0.399	—3.1
122	0.433	0.419	—3.2
149	0.446	0.428	—4.0
	Iodobenzene		
68	0.1857	0.1830	—1.45
86	0.1866	0.1851	—0.81
113	0.1884	0.1898	+0.74

TABLE 4. COMPARISON OF SOME EXPERIMENTAL VALUES OF SPECIFIC HEAT WITH VALUES CALCULATED BY CORRELATION BASED ON THEORY OF CORRESPONDING STATES

T_r	$C_{pexp.}$, B.t.u./(lb.)(°F.)	$C_{pcalc.}$, B.t.u./(lb.)(°F.)	% Dev.
	n-Pentane		
0.345	0.468	0.465	—0.6
0.456	0.485	0.485	0
0.605	0.536	0.536	0
	n-Nonane		
0.384	0.489	0.488	—0.2
0.500	0.523	0.525	+0.4
	2,3-Dimethyl butane		
0.375	0.428	0.432	+0.9
0.599	0.525	0.527	+0.4
	2,2,4-Trimethyl pentane		
0.364	0.403	0.394	—2.2
0.469	0.452	0.454	+0.4
0.542	0.489	0.496	+1.4
	Benzene		
0.511	0.409	0.407	—0.5
0.569	0.431	0.431	0
0.600	0.444	0.445	+0.2
	Ethyl benzene		
0.294	0.354	0.354	0
0.495	0.424	0.414	—2.3
	Pentene-1		
0.350	0.443	0.446	+0.7
0.461	0.464	0.464	0
0.626	0.526	0.525	—0.2
	2 Methyl butene-2		
0.350	0.451	0.446	—1.1
0.498	0.474	0.476	+0.4
0.638	0.522	0.531	+1.7

Fig. 3.   Einstein function vs. u.

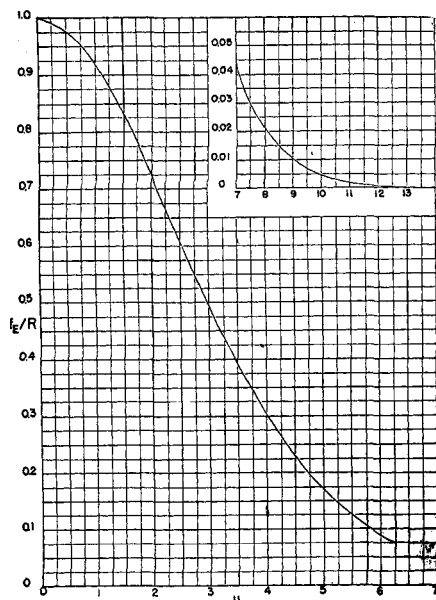Fig. 4.   Branch contribution to C_p vs. T_r.

Fig. 5.   Branch contribution to C_p vs. T_r.

The results show that the correction factor S is independent of temperature.

SUMMARY

An equation for predicting the specific heat of liquids at constant volume and pressure from molecular structure is proposed. The different types of motion of a molecule were classified into an acoustical branch and several optical branches. The contribution to the specific heat of the optical branches is evaluated by means of generalized frequencies assigned from spectroscopic data. The contribution to the specific heat of the acoustical branches is evaluated on the basis of a simplified model of liquid state and data on the velocity of sound in liquids. The total specific heat is evaluated by summing all contributions.

The equation has been tested on 100 organic liquids of all chemical types at 68°F. The average deviation of the calculated from the observed values of specific heat at constant pressure is ±1.5%. The equation has also been tested on seven liquids over wide temperature ranges.

PART II

An alternate correlation of specific-heat data for liquids based on a modified statement of the theory of corresponding states is possible. This method of correlation was applied successfully to thermal conductivity data (7). Essentially, at the same reduced temperature T_r, it involves consideration of corresponding behavior between the same members of two different series to the same other members of their respective series. The reduced pressure is omitted from the correlation since at 1 atm. the effect of differences in P_r on specific heat is very small.

DEVELOPMENT OF CORRELATION

The correlation was limited to hydrocarbons, as reliable data of specific heat as a function of temperature over a large temperature range, for other types of compounds, are not available. The specific-heat data on hydrocarbons were obtained from reference 9.

As a first step the specific heat of normal aliphatic hydrocarbons was plotted as a function of reduced temperature with the number of carbon atoms as a parameter. Smooth curves were drawn through the points and it was noted that a family of parallel curves was obtained. This set of curves is shown in Figure 4. The differ-
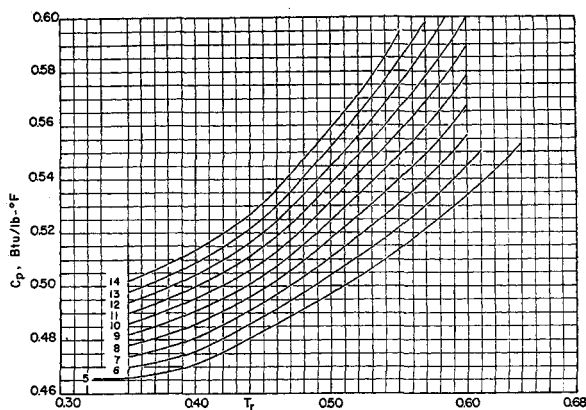
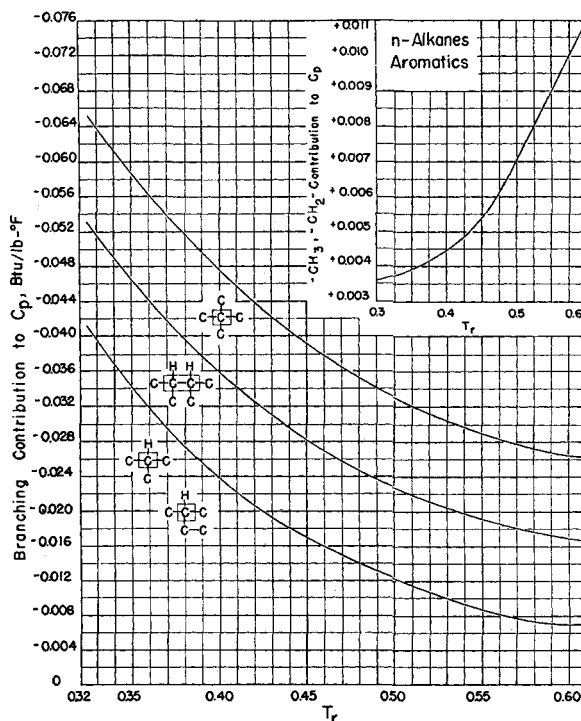ence in specific heat between one curve and another at a given reduced temperature represents the contribution of a —CH_2— group. This difference was found to be independent of chain length, and its variation with reduced temperature is shown in the insert of Figure 5.

Next the effect of branching in the chain was determined by taking the difference in specific heat between a branched alkane and the normal alkane with the same number of carbon atoms at the same reduced temperature. This contribution was found to be independent of chain length, and its variation with reduced temperature for three main types

of branching is shown in Figure 5. The contribution for two types of branching in the same molecule may be taken as the sum of the component contributions.

For the olefinic compounds the procedure for determining the effect of the double bond was the same as that for the effect of branching. It was found that the contribution of one or two double bonds in the molecule is -0.020 B.t.u. (lb.)(°F.) at all temperatures. The few
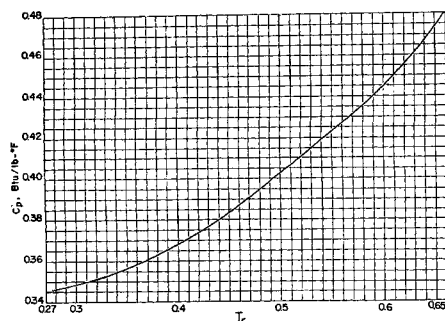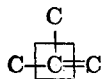

Fig. 6. C_p vs. T_r for benzene.

available data show that the effect of one branched group

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      C
      |
 C----C====C
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in an olefinic hydrocarbon is negligible.

The aromatic hydrocarbons were treated the same way as the normal aliphatic hydrocarbons, and their behavior was found to be similar. In Figure 6 is shown the specific heat of benzene as a function of reduced temperature. The curve has been extrapolated by use of the data of p-xylene. The effect of adding one or more —CH₂ or —CH₃— groups to the benzene ring is shown in the insert of Figure 5, which applies also to the aliphatic hydrocarbons.

Procedure for Calculating Specific Heat

1. Normal saturated aliphatic hydrocarbons: Figure 4.
2. Branched saturated aliphatic hydrocarbons: Figures 4 and 5.
3. Normal and branched olefinic hydrocarbons: Figure 4, also

Contribution to C_p

One or two double bonds -0.020 B.t.u./(lb.)(°F.) at all T_r

```
      C
      |
 C----C====C              O
```
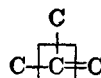
4. Aromatic hydrocarbons: Figures 5 (insert) and 6.

The method of calculation will be illustrated by a few examples.

a. Estimate the specific heat of n-decane at 75°F.

$T_c = 1,100.4$°R.

$T_r = 535/1,110.4 = 0.482$

Estimated $C_p = 0.523$ B.t.u./(lb.)(°F.): Figure 4

Observed $C_p = 0.523$ B.t.u./(lb.)(°F.)

b. Estimate the specific heat of 3-ethyl pentane at 70°F.

$T_c = 973.4$°R.

$T_r = 530/973.4 = 0.544$

Number of carbon atoms in molecule = 7

C_p, n-heptane at $T_r = 0.544$, = 0.528 B.t.u./(lb.)(°F.): Figure 4

```
       H
       |
Type of branching A, C---C---C
       |
       C---C
```

Effect of branching, at $T_r = 0.544$, = -0.010 B.t.u./(lb.)(°F.): Figure 5

Estimated $C_p = 0.428 - 0.010 = 0.518$ B.t.u./(lb.)(°F.)

Observed $C_p = 0.519$ B.t.u./(lb.)(°F.)

c. Estimate the specific heat of transpentene-2 at -163.0°F.

$T_c = 848.5$°R.

$T_r = 297/848.5 = 0.350$

C_p, n-pentane at $T_r = 0.350$, = 0.466 B.t.u./(lb.)(°F.): Figure 4

Effect of double bond = -0.20 B.t.u./(lb.) (°F.)

Estimated $C_p = 0.466 - 0.020 = 0.446$ B.t.u./(lb.)(°F.)

Observed $C_p = 0.444$ B.t.u./(lb.)(°F.)

d. Estimate the specific heat of p-xylene at 257°F.

$T_c = 1,108.8$°R.

$T_r = 707/1,108.8 = 0.638$

Number of —CH₃ groups on ring = 2

Contribution of each —CH₃ group, at $T_r = 0.638 = 0.0125$ B.t.u./(lb.)(°F.) (Insert Figure 5)

C_p, benzene at $T_r = 0.638$, = 0.466 B.t.u./(lb.)(°F.): Figure 6

Estimated $C_p = 0.466 + 2 \times 0.0125 = 0.491$ B.t.u./(lb.)(°F.)

Observed $C_p = 0.486$ B.t.u./(lb.)(°F.)

Figures 4 to 6 were constructed from 400 individual points picked at random from a total of over 1,000 points. The accuracy of the correlation was tested on 32 liquids, or a total of 100 points selected in such a way as to cover the entire range of temperatures. A sample of the results is shown in Table 4.

The average deviation of the calculated from the observed values of specific heat at constant pressure for the 100 points was found to be $\pm 0.9\%$. The maximum deviation was $\pm 2.7\%$. Propane and butane show somewhat higher deviations. There are no data on ethane.

SUMMARY

A correlation, based on a semiempirical application of the theory of corresponding states, for predicting the specific heat of

hydrocarbons at constant pressure as a function of temperature has been developed. Contributions to the specific heat of chain length, different types of branching, and unsaturation were evaluated. The correlation was tested on a total of 100 points selected to cover the entire range of temperatures. The average deviation of the calculated from the observed values of specific heat was found to be $\pm 0.9\%$. The method of calculation is simple and rapid.

NOTATION

C_p = specific heat at constant pressure
C_v = specific heat a constant volume
f_D = Debye function
f_E = Einstein function
h = Planck's constant
K_{ad} = adiabatic compressibility
K_{is} = isothermal compressibility
k = Boltzmann's constant
M = molecular weight
n = number, number of atoms in molecule
N_0 = Avogadro's number
P = pressure
q = bond
R = gas constant
$\mathbf{R}$ = ratio
S = factor
T = absolute temperature
U_s = velocity of sound in liquid
u = $h\nu/kT$

Greek Symbols

β = coefficient of thermal expansion
δ = bending
ν = stretching
ν = frequency
ρ = density
ω = wave number

Subscripts

c = critical
m = maximum
r = external rotation
r = reduced
r' = internal rotation

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