

TEMPERATURE DEPENDENCE OF HEATS OF VAPORIZATION
OF SATURATED HYDROCARBONS C5—C8;
EXPERIMENTAL DATA AND AN ESTIMATION METHOD*

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Received January 2nd, 1978

Heats of vaporization of a group of 10 alkanes C6—C8 and 2 cycloalkanes were measured in a temperature range of 25—80°C. By combining the obtained results with selected literature data, a set of very accurate values of heats of vaporization as functions of temperature was made up for 22 saturated C5—C8 hydrocarbons. This set was employed for the verification of the proposed estimation method for the determination of heat of vaporization which is based on the principle of combination of a contribution method with constant entropy-of-vaporization rules. In this way it is then possible to estimate heats of vaporization of C4—C9 alkanes with an error lower than 0.5%.

Hydrocarbons are the commonest organic substances which are of great importance for both chemical technology and research. However, their heats of vaporization as functions of temperature have not been systematically experimentally studied yet. Certainly, the fact has also contributed to it that the accurate values of saturated vapour pressures determined within the framework of the API projects¹ make it possible to calculate heat of vaporization of a number of hydrocarbons with an accuracy of 0.5—1%. The values with a lower error can be, however, obtained only in the direct experimental way. Therefore the aim of this work is to contribute to the extension of knowledge of the temperature dependence of heats of vaporization of hydrocarbons. For the measurements, a group of 12 saturated C6—C8 hydrocarbons was chosen. So we partly reassumed the older works that had dealt mostly with isomeric pentanes and hexanes, partly some literature data were verified for the substances where the values reported by different authors differ. Thus, the new results combined with the older calorimetric data made it possible to form a set of very accurate values of heats of vaporization as a function of temperature for saturated C5—C8 hydrocarbons. These data were exploited in the second part of the work to verify the applicability of the proposed estimation method which is based on the combination of a contribution method and the constant entropy rules.

* Part XIII in the series Enthalpy Data of Liquids; Part XII: This Journal 43, 2973 (1978)

The values of heats of vaporization determined calorimetrically are known for a number of hydrocarbons at 25°C thanks to the excellent work by Osborne and Ginnings². For several hydrocarbons (2-methylbutane, hexane isomers, n-heptane, 2,2,3-trimethylbutane and three cyclohexanes) the heats of vaporization were determined at several temperatures by Waddington and coworkers³⁻⁷. Heats of vaporization of several hydrocarbons were measured in a wide temperature range by Sage and coworkers⁸⁻¹¹. However, their data, in the cases when comparison is possible (n-heptane, cyclohexane), differ strongly from the values given by the other authors (as much as 1% at the temperature of normal boiling point) and therefore it is possible to assume that they are subject to a considerable systematic error. The Lemons and Felsing data¹² for the temperature dependence of heats of vaporization of isomeric hexanes are unsuitable to consider; their experimental accuracy with an error approximately 1% is insufficient and the comparison with data of the other authors⁷ implies a considerable systematic error.

The following compounds were chosen for measuring: two isomeric hexanes (n-hexane, 3-methylpentane), four isomeric heptanes (n-heptane, 2-methylhexane, 3-methylhexane, 2,3-dimethylpentane), four isomeric octanes (n-octane, 2-methylheptane, 3-methylheptane, 2,2,4-trimethylpentane), cyclohexane and methylcyclohexane. In addition to the above-mentioned viewpoints the selection of hydrocarbons for measuring was influenced by the accessibility of pure substances, too.

EXPERIMENTAL

Preparation and Purity of Substances

n-Hexane was prepared by the Wurtz reaction of propyl iodide with sodium. The raw product was rectified from sodium on a forty-plate bubble-cup column and a 68.7–68.8°C fraction was taken.

n-Heptane, A.R. grade (Loba-Chemie, Vienna), was distilled on a hundred-plate packed column. By combining the chromatographic and mass-spectroscopic analysis it was found out that after the distillation n-heptane contained some admixtures of isomers (in the main 3-methylhexane and 2,3-dimethylpentane) below 0.5%.

n-Octane (Laborchema, Apolda) was twice distilled on a hundred-plate packed column and the middle runnings were always taken. By a combined chromatographic and mass-spectroscopic analysis it was found that n-octane after twice distillation contained some impurities (2-methylheptane, 3-methylheptane) about 0.7%. The contamination with isomers in the given amounts has a minimum effects on the values of heats of vaporization of n-heptane and n-octane and this can be neglected with respect to the experimental error.

Cyclohexane, A.R. grade (Reanal, Budapest), was twice distilled on a twenty-plate column. The formaldehyde test for benzene was negative.

Methylcyclohexane used was a product supplied by VUOS Pardubice-Rybitví that was prepared by catalytic hydrogenation of toluene (A.R. grade) followed by rectification. By the chromatographic analysis it was found that the methylcyclohexane used contained below 0.1% impurities.

Further the densities (g cm^{-3}) and refractive indexes at 25°C are listed for the above-mentioned substances and compared with the literature values (given in parentheses): In case of cyclohexane

the data source^{13,14} was used, for the other substances the given data were found in the literature¹⁵. n-Hexane $d = 0.65477$ (0.65481), $n_D = 1.3723$ (1.37226); n-heptane $d = 0.67956$ (0.67951), $n_D = 1.3852$ (1.38511); n-octane $d = 0.69853$ (0.69849), $n_D = 1.3950$ (1.39505); cyclohexane $d = 0.77391$ (0.77386), $n_D = 1.4236$ (1.42356); methylcyclohexane $d = 0.76510$ (0.76501), $n_D = 1.42205$ (1.42058).

The samples of 2-methylpentane, 2-methylhexane, 3-methylhexane, 2,3-dimethylpentane, 2-methylheptane, 4-methylheptane and 2,2,4-trimethylpentane were prepared in Laboratory of Synthetic Fuels, Prague Institute of Chemical Technology, where they are produced for the use as chromatographic standards. Their purity was checked by mass spectroscopy and in all the samples the content of impurities was below 0.3%. The classical physico-chemical methods to verify the purity were not applied here because the substances were available in small amounts and in the literature there are not in some cases accurate values for comparison.

Except for the latter substances given all others were stored in the presence of molecular sieves for water of the Nalsit A4 type.

Apparatus

Heats of vaporization of the group of hydrocarbons selected were measured by using the calorimeter whose construction and control principles as well as the procedure are described in the literature¹⁶ in detail. The values determined in the apparatus are subject to error below 0.15% at saturated vapour pressures up to 150 kPa and when measuring up to 200 kPa, the accuracy is 0.2%. The heats of vaporization were determined for all the hydrocarbons studied at temperatures of 25, 40, 60 and 80°C. Three to four experiments were carried out for all the substances at each temperature.

RESULTS

The measured values of heats of vaporization $\Delta H_{v,exp}$ are given lucidly in Table I and compared with literature values. The comparison of the newly measured values of heats of vaporization of n-hexane and cyclohexane with the literature shows again the probable systematic error in the measurements of Sage and coworkers. The agreement with the results of Osborne and coworkers and Waddington and coworkers is very good.

Data Set for Temperature Dependence of Heats of Vaporization of Hydrocarbons

To obtain a set of representative data on the dependence of heats of vaporization of C5—C8 hydrocarbons on temperature a critical analysis was carried out of the literature and newly determined values of heats of vaporization and their mutual consistence was compared. On the basis of this analysis the data were selected that were considered to be the most accurate; in some cases the data of several authors were combined to cover a wider temperature range and to reduce the possibility of the occurrence of systematic errors. In this way sorted-out data were correlated by the Thiesen relation

$$\Delta H_v = K(1 - T_r)^\alpha, \quad (1)$$

TABLE I
Heats of Vaporization ΔH_v (kJ/mol) for Set of Hydrocarbons

| $t, ^\circ\text{C}$ | $\Delta H_{v,\text{exp}}$ | $\Delta H_{v,\text{lit}}$ | $t, ^\circ\text{C}$ | $\Delta H_{v,\text{exp}}$ | $\Delta H_{v,\text{lit}}$ |
|---------------------|---------------------------|--|------------------------|---------------------------|--|
| n-Hexane | | | 3-Methylpentane | | |
| 25 | 31.55 | 31.55 ² | 25 | 30.26 | 30.27 ² 30.19 ^{1,7} |
| 40 | 30.68 | 30.71 ⁶ 30.54 ⁸ | 40 | 29.46 | 29.44 ⁷ |
| 60 | 29.46 | 29.63 ⁶ 29.28 ⁸ | 60 | 28.25 | 28.28 ⁷ |
| 80 | 28.16 | 27.98 ⁸ | 80 | 27.02 | |
| n-Heptane | | | 2-Methylhexane | | |
| 25 | 36.58 | 36.54 ² | 25 | 34.85 | |
| 40 | 35.63 | | 40 | 33.93 | |
| 60 | 34.35 | 33.36 ⁵ | 60 | 32.68 | |
| 80 | 33.07 | 33.02 ⁵ | 80 | 31.28 | |
| 3-Methylhexane | | | 2,3-Dimethylpentane | | |
| 25 | 35.05 | | 25 | 34.25 | 34.23 ² |
| 40 | 34.18 | | 40 | 33.43 | |
| 60 | 32.92 | | 60 | 32.23 | |
| 80 | 31.67 | | 80 | 31.07 | |
| n-Octane | | | 2-Methylheptane | | |
| 25 | 41.47 | 41.48 ² 41.48 ¹⁸ 41.50 ¹⁷ | 25 | 39.66 | 39.67 ² |
| 40 | 40.48 | 40.45 ¹¹ | 40 | 38.70 | |
| 60 | 39.10 | 39.02 ¹¹ | 60 | 37.32 | |
| 80 | 37.79 | 37.54 ¹¹ | 80 | 35.99 | |
| 4-Methylheptane | | | 2,2,4-Trimethylpentane | | |
| 25 | 39.71 | 39.68 ² | 25 | 35.13 | 35.12 ² |
| 40 | 38.74 | | 40 | 34.34 | |
| 60 | 37.37 | | 60 | 33.16 | |
| 80 | 36.05 | | 80 | 31.95 | |

TABLE I
(Continued)

| $t, ^\circ\text{C}$ | $\Delta H_{v,\text{exp}}$ | $\Delta H_{v,\text{lit}}$ | $t, ^\circ\text{C}$ | $\Delta H_{v,\text{exp}}$ | $\Delta H_{v,\text{lit}}$ |
|---------------------|---------------------------|---|---------------------|---------------------------|---|
| Cyclohexane | | | Methylcyclohexane | | |
| 25 | 33.02 | 33.03 ² 32.90 ⁹ 33.00 ¹⁷ | 25 | 35.38 | 35.35 ² 35.36 ¹⁷ |
| 40 | 32.25 | 32.23 ¹⁹ 32.19 ¹⁰ | 40 | 34.58 | |
| 60 | 31.19 | 31.14 ¹⁹ 31.05 ¹⁰ | 60 | 33.49 | |
| 65 | 30.95 | | | | |
| 75 | 30.37 | | | | |
| 80 | 30.08 | 30.09 ¹⁹ 29.89 ¹⁰ | 80 | 32.47 | |

where K and α are constants and T_r denotes the reduced temperature. Table II gives the survey of substances which were included into the set. In the second, third and fourth columns of the table the values are given of constants K (kJ/mol) and α of the Thiesen correlation relation and the standard deviations δ_s of values of heats of vaporization, calculated in this way, from the experimental values in kJ/mol. In the next columns we give the corresponding temperature ranges in $^\circ\text{C}$, the number of temperatures at which the heat of vaporization was measured and the references. Besides our measurements (denoted by capital letter M) we used especially the data of Waddington and coworkers and for temperature of 25°C , the data of Osborne and Ginnings. On the basis of errors in measurements reported by the authors (about 0.15%), the mutual correspondence of the data of different authors and low values of standard deviations of single correlations it is to be assumed justifiably that it is possible, in terms of the constants given, to determine heat of vaporization in the respective temperature ranges with an accuracy of 0.2%.

Estimation Method

Contribution methods enable to calculate thermodynamic quantities on the basis of knowledge of the compound structural formula. This method is, for its simplicity, very attractive and an effort was therefore exerted to apply it to the estimation of heat of vaporization, too, despite it is not a quantity which would exhibit in general the

additive character. A number of authors tried to express the contributions, from experimentally determined heats of vaporization, for individual groups of atoms in molecule²⁰⁻²² or for characteristic interactions among them²³⁻²⁶. A method of correlating the physico-chemical properties with the degree of branching and the shape of molecule applied to hydrocarbons Greenshield and Rossini²⁷. The calculations were mostly carried out at a temperature of 25°C.

The rules of constant entropy, $\Delta S_v = \Delta H_v/T = \text{const.}$, are also used for estimating heat of vaporization. Usually the rules differ each from other in the choice of state variable (hereafter the term reference level will be used more often) at constant value of which the entropies of vaporization are compared. The best-known rules are (in parentheses the respective reference levels are given): the Trouton rule²⁷ (constant

TABLE II
Constants of Correlation Relation $\Delta H_v = K(1 - T_r)^\alpha$ for Set of Hydrocarbons

| Substance | K | α | δ_s | Range of $t, ^\circ\text{C}$ | Number of temperatures | Reference ^a |
|------------------------------|-------|----------|------------|------------------------------|------------------------|------------------------|
| Pentane | 38.58 | 0.375 | 0.007 | 25-80 | 5 | 2, 9 |
| 2-Methylbutane | 36.36 | 0.365 | 0.003 | 6-28 | 3 | 2, 4 |
| n-Hexane | 43.97 | 0.375 | 0.008 | 25-80 | 6 | M, 2, 6 |
| 2-Methylpentane | 42.04 | 0.373 | 0.002 | 25-80 | 3 | 2, 7 |
| 3-Methylpentane | 42.03 | 0.367 | 0.004 | 25-80 | 8 | M, 2, 7 |
| 2,2-Dimethylbutane | 39.07 | 0.366 | 0.004 | 23-50 | 3 | 2, 6 |
| 2,3-Dimethylbutane | 39.85 | 0.346 | 0.007 | 23-60 | 5 | 2, 7 |
| n-Heptane | 50.11 | 0.393 | 0.007 | 25-80 | 8 | M, 2, 5 |
| 2-Methylhexane | 48.42 | 0.398 | 0.006 | 25-80 | 4 | M |
| 3-Methylhexane | 47.99 | 0.386 | 0.009 | 25-80 | 4 | M |
| 2,3-Dimethylpentane | 46.28 | 0.372 | 0.001 | 25-80 | 4 | M |
| 2,2,3-Trimethylbutane | 43.72 | 0.377 | 0.000 | 40-80 | 2 | 5 |
| n-Octane | 56.24 | 0.411 | 0.017 | 25-80 | 4 | M |
| 2-Methylheptane | 54.30 | 0.413 | 0.014 | 25-80 | 4 | M |
| 4-Methylheptane | 54.29 | 0.414 | 0.015 | 25-80 | 4 | M |
| 2,2,4-Trimethylpentane | 47.33 | 0.375 | 0.006 | 25-80 | 4 | M |
| Cyclopentane | 39.21 | 0.364 | 0.001 | 25-50 | 3 | 3 |
| Methylcyclopentane | 43.12 | 0.378 | 0.002 | 25-72 | 4 | 2, 3 |
| 1,3-cis-Dimethylcyclopentane | 46.61 | 0.420 | 0.001 | 50-91 | 3 | 3 |
| Cyclohexane | 40.40 | 0.383 | 0.004 | 25-80 | 6 | M |
| Methylcyclohexane | 46.90 | 0.384 | 0.017 | 25-80 | 4 | M |

^a Capital letter M denotes the present data of authors given in this work.

pressure, usually $P = 101.325$ kPa), the Hildebrand rule²⁸ (constant molar volume of the vapour phase V^g), the Pitzer rule²⁹ (constant molar volume ratio of the vapour and liquid phases V^g/V^l) and the Guggenheim rule³⁰ (constant reduced temperature T_r). The rules mentioned are of empirical or semi-empirical character and were discussed and tested by several authors^{31–33}. The Hildebrand rule^{34,35} is usually considered to be the best one. Some authors tried, when using this rule, to deduce even the degree of structural arrangement in the liquid and the degree of restrictions of intermolecular rotations^{34,36} from changes of the entropy of vaporization with the shape and character of molecule.

Considering the fact that the entropy of vaporization, on choosing suitably the reference level, changes with the composition and the structure of molecule essentially less than heat of vaporization, it is possible to combine the principle of the contribution method with the rules of constant entropy of vaporization and to try to express the entropy of vaporization or better its difference from some empirically determined constant in dependence on the structural formula of molecule. It can be assumed with justification that such a procedure will yield better results than the direct application of the contribution method for the estimation of heat of vaporization. That was also proved in the Novák work³⁷ who estimated entropies of vaporization of hydrocarbons at normal boiling point with an accuracy of 0.5%.

When deriving such an estimation method it is necessary to pay attention above all to these aspects: 1) It is necessary to choose as a reference level such a state variable at constant value of which the entropy of vaporization changes with the size and structure of molecule in a reproducible way and in a small range. 2) It is necessary to find a minimum number of parameters expressing the molecule structure which would make it possible to describe the dependence of entropy of vaporization on composition and spatial arrangement of molecule with sufficient accuracy. 3) If we wish to estimate heat of vaporization as a function of temperature it is necessary to develop a suitable procedure enabling to express the dependence of individual contributions of entropy of vaporization on temperature or other state variable or to convert reliably the value of heat or entropy of vaporization from the temperature corresponding to the given value of the reference level chosen to another temperature.

To be able to test the possibilities of the estimation method based on the principle outlined we decided to exploit for this purpose the set of data on the temperature dependence of heats of vaporization of hydrocarbons and to propose a contribution method enabling the calculation of entropy of vaporization (heat of vaporization) of hydrocarbons as a function of temperature.

As a first step the suitability of different reference levels was tested at several values (sections) of the state variable chosen for the given set of C5—C8 hydrocarbons. For the levels of constant T , T_r , P , P_r , V^g , V_r^g , V^g/V^l the entropies of vaporization of individual substances were calculated and for aliphatic hydrocarbons in addition the differences between the entropy of vaporization of normal and branched

isomer. The degree of constancy of entropy of vaporization was investigated as well as the reproducibility of its changes with the molecule structure and with a change of the state variables chosen. The following conclusions can be drawn from the obtained results:

TABLE III

Variations of Values ΔS_v (%) for Reference Levels Given

| Reference level | T | T_r | P | P_r | V^g | V_r | V^g/V^l |
|---------------------|-----|-------|-----|-------|-------|-------|-----------|
| All the set | 55 | 20 | 5 | 11 | 4 | 9 | 10 |
| Normal hydrocarbons | 50 | 15 | 4 | 8 | 0.4 | 7 | 7 |

TABLE IV

Entropies of Vaporization ΔS_v ($\text{J mol}^{-1} \text{K}^{-1}$) of Normal Aliphatic Hydrocarbons at Different Reference Levels^a.

| Reference level | n-Pentane | n-Hexane | n-Heptane | n-Octane |
|--|------------------|------------------|-------------------|----------|
| $T = 40^\circ\text{C}$ | 81.58 (16.28) | 97.96 (15.86) | 113.82 (15.46) | 129.28 |
| $T_r = 0.63$ | 89.81 (4.93) | 94.74 (4.87) | 99.61 (4.69) | 104.30 |
| $P = 53.33 \text{ kPa}$ | 91.95 (1.31) | 93.26 (1.23) | 94.49 (0.86) | 95.35 |
| $P_r = 0.002$ | 88.89 (2.94) | 91.83 (2.30) | 94.13 (2.22) | 96.35 |
| $V^g = 45 \text{ dm}^3 \text{ mol}^{-1}$ | 92.18 (-0.09) | 92.09 (-0.03) | 92.06 (-0.33) | 91.73 |
| $V_r = 190$ | 95.63 (2.95) | 98.58 (2.26) | 100.84 (2.00) | 102.84 |
| $V^g/V^l = 600$ | 97.26 (3.12) | 100.38 (2.41) | 102.79 (1.98) | 104.77 |

^a Differences between entropies of vaporization are given in parentheses.

The degree of validity of the constant entropy rules for hydrocarbons is expressed in Table III where per cent variances are given for values of entropy of vaporization for the whole set of substances studied and for normal hydrocarbons when using different reference levels. Table IV gives the values of entropies of vaporization of normal aliphatic hydrocarbons for one section of the levels used together with the differences Δ ($\text{J mol}^{-1} \text{K}^{-1}$) between the entropies of vaporization of substances differing in number of carbons. The Hildebrand rule can be considered as the best one, somewhat worse results yields the Trouton rule. The reference levels issuing from the theorem of corresponding states did not prove to be very good, however, the entropies of vaporization at constant value of reduced temperature exhibit well reproducible dependence on the length and the degree of branching of molecule (Table V).

The entropy of vaporization decreases for aliphatic hydrocarbons with the degree of branching of molecule. With increasing length of the main chain the decrease of

TABLE V
Values of Molar Entropies of Vaporization ΔS_v ($\text{J mol}^{-1} \text{K}^{-1}$) at Constant Reduced Temperature $T_r = 0.63$

| Substance | $t, ^\circ\text{C}$ | ΔS_v | $\Delta S_v^i - \Delta S_v^n$ |
|------------------------------|---------------------|--------------|-------------------------------|
| n-Pentane | 22.7 | 89.82 | |
| 2-Methylbutane | 16.9 | 87.21 | -2.61 |
| n-Hexane | 46.5 | 94.74 | |
| 2-Methylpentane | 40.2 | 92.58 | -2.16 |
| 3-Methylpentane | 44.6 | 91.83 | -2.91 |
| 2,2-Dimethylbutane | 34.7 | 88.19 | -6.56 |
| 2,3-Dimethylbutane | 41.8 | 89.70 | -5.05 |
| n-Heptane | 67.2 | 99.62 | |
| 2-Methylhexane | 60.9 | 97.57 | -2.05 |
| 3-Methylhexane | 64.0 | 96.97 | -2.65 |
| 2,3-Dimethylpentane | 65.3 | 94.39 | -5.23 |
| 2,2,3-Trimethylbutane | 61.4 | 89.82 | -9.8 |
| n-Octane | 85.2 | 104.31 | |
| 2-Methylheptane | 79.4 | 102.15 | -2.16 |
| 4-Methylheptane | 80.5 | 101.73 | -2.58 |
| 2,2,4-Trimethylpentane | 69.5 | 95.15 | -9.16 |
| Cyclopentane | 49.2 | 84.72 | |
| Methylcyclopentane | 62.5 | 88.23 | |
| 1,3-cis-Dimethylcyclopentane | 74.5 | 88.29 | |
| Cyclohexane | 75.5 | 85.08 | |
| Methylcyclohexane | 87.3 | 88.83 | |

entropy of vaporization somewhat reduces owing to the branching. The data obtained on the entropy of vaporization of cycloparaffins are rather fragmentary (small number of substances studied) and therefore it is difficult to draw conclusions concerning the dependence of entropy of vaporization on the manner of cyclic arrangement and branching of molecule.

The expression of entropy of vaporization by a contribution method is advantageous in the group of aliphatic hydrocarbons; a common treatment with cycloparaffins is not suitable if an accuracy better than 1% is to be reached. At a chosen value of the reference level it is the most advantageous to express the entropy of vaporization of normal hydrocarbons and to correlate the differences between the values ΔS_v^0 for branched and straight isomers with the parameters accounting for the branching of molecule.

From the point of view of the constancy of entropy of vaporization it is the most advantageous to use the reference level of constant molar volume of the vapour phase, V^g , for suggesting the estimation method. A substantial disadvantage is, however, the necessity of knowing the saturated vapour pressures. The respective temperature can be then determined only by solving numerically an equation of state together with the Antoine equation and consequently the method is not very convenient. Therefore it is more advantageous to use the level of constant reduced temperature T_r where the constant entropy rule is satisfied badly, however, as it has been said, the deviations are well reproducible.

On the basis of the given results of the study on entropy of vaporization of the hydrocarbons studied the following procedure was suggested for expressing the heat of vaporization of aliphatic C5–C8 hydrocarbons:

1) As a reference level the reduced temperature $T_r = 0.63$ was chosen. This numerical value was selected above all for the reason that the corresponding temperatures are for all substances within the range in which the experimental values of heats of vaporization are known or their moderate extrapolation is sufficient. The entropy of vaporization of normal hydrocarbons ΔS_v^0 ($\text{J mol}^{-1} \text{K}^{-1}$) can be expressed by the relation

$$\Delta S_v^0 = 90 + 4.8(N - 5), \quad T_r = 0.63, \quad (2)$$

where N denotes the number of carbons in molecule.

2) The branching and shape of molecule were expressed in terms of the number of quaternary and tertiary carbons (C_4 , C_3), the difference between the number of carbons distant over three bonds for branched and normal hydrocarbon $\Delta P = P^i - P^n$ and the difference of the Wiener numbers between the respective branched and straight molecule $\Delta W = W^i - W^n$ (the index i refers to the branched isomer, the index n denotes the normal hydrocarbon). More detailed information on the calculation of the quantities ΔP and ΔW is given *e.g.* in ref.²⁷. The difference between the entropy

of vaporization of the branched and straight isomer $\Delta S_v^i - \Delta S_v^n$ was then expressed by the equation

$$\Delta S_v^i - \Delta S_v^n = -2.3371C_3 - 6.8197C_4 - 0.38623 \Delta P - 0.02698 \Delta W/N^{0.5},$$

$$T_r = 0.63 \quad (3)$$

where the numerical values of constants were determined by the least-square method. Standard deviation of the correlation mentioned is $0.17 \text{ (J mol}^{-1} \text{ K}^{-1}\text{)}$. It was proved during the processing that the main effect have the parameters C_3 and C_4 ; ΔP and ΔW have only marginal importance. The quantity $N^{0.5}$ serves to reduce the importance of the difference of the Wiener numbers ΔW .

3) Eqs (2) and (3) enable to determine heat of vaporization at one value of reduced temperature. To express heat of vaporization at another temperature the Thiesen relation (1) was employed. One constant can be eliminated on the basis of knowledge of the heat of vaporization at the chosen reference level. The remaining constant is then determined by the following empirical procedure: In Table II a relatively regular increase of the constant α with the chain length is obvious for normal hydrocarbons. For these substances fixed values of the constant were chosen (n-pentane $\alpha = 0.37$,

TABLE VI

Values of Constants of the Thiesen Correlation Relation Determined by Contribution Method

| Substance | K | α | $\bar{\delta}$ |
|------------------------|-------|----------|----------------|
| n-Pentane | 38.47 | 0.370 | 0.24 |
| 2-Methylbutane | 36.55 | 0.364 | 0.37 |
| n-Hexane | 44.22 | 0.380 | 0.05 |
| 2-Methylpentane | 42.05 | 0.374 | 0.01 |
| 3-Methylpentane | 42.52 | 0.375 | 0.28 |
| 2,2-Dimethylbutane | 38.95 | 0.364 | 0.07 |
| 2,3-Dimethylbutane | 40.87 | 0.370 | 0.13 |
| n-Heptane | 49.95 | 0.390 | 0.04 |
| 2-Methylhexane | 47.62 | 0.383 | 0.23 |
| 3-Methylhexane | 47.91 | 0.384 | 0.04 |
| 2,3-Dimethylpentane | 46.55 | 0.380 | 0.11 |
| 2,2,3-Trimethylbutane | 43.45 | 0.370 | 0.08 |
| n-Octane | 56.24 | 0.410 | 0.08 |
| 2-Methylheptane | 53.72 | 0.402 | 0.14 |
| 4-Methylheptane | 53.69 | 0.402 | 0.14 |
| 2,2,4-Trimethylpentane | 47.97 | 0.385 | 0.37 |

n-hexane $\alpha = 0.38$, n-heptane $\alpha = 0.39$, n-octane $\alpha = 0.41$). In this way the temperature dependence of heat of vaporization of normal hydrocarbons is determined. From Table II it also follows that within the framework of a group of isomers, the value of both K and α decreases simultaneously with the degree of branching. The ratio $(\alpha^i - \alpha^n)/(K^i - K^n)$ is equal on the average $3 \cdot 10^{-3}$ mol/kJ. Therefore, to evaluate the constants K and α the following approximate procedure was used: In the first approximation, the value of the constant α is chosen to be identical with that for normal hydrocarbon and from the heat of vaporization at a reference level the constant K^i is calculated. In the next step a new value of the constant α^i is calculated from the relation

$$\alpha^i = \alpha^n + 3 \cdot 10^{-3}(K^i - K^n) \quad (4)$$

and the whole procedure is repeated until the values of α^i determined in two consecutive steps differ less than by 10^{-3} (in the second and next steps, in Eq. (4) the values of α^i and K^i from the preceding approximation are inserted instead of the values α^n and K^n).

Table VI gives the constants of temperature dependence K and α determined in the described way by means of the contribution method together with mean per cent deviations in calculated values of heats of vaporization from the experimental ones in the temperature range which corresponds to the experiment for individual substances. The proposed contribution method describes the temperature dependence of heats of vaporization for most substances studied with an accuracy comparable with the experimental error.

DISCUSSION

The first part of this work deals with the experimental determination of heats of vaporization of hydrocarbons as a function of temperature. The substances are treated for which saturated vapour pressures are known with good accuracy and whose P-V-T behaviour of the vapor phase can be estimated on the whole reliably unless the experimental values are known directly. On the basis of these input data, it is therefore possible to determine easily heat of vaporization of hydrocarbons indirectly by calculating with the use of the Clapeyron equation. Therefore it is necessary to consider whether it is useful to determine the heats of vaporization of hydrocarbons by direct calorimetric measurement.

In this connection a very often discussed question arises whether the computation methods for determining heat of vaporization can approach, as to their accuracy, the direct experimental determination and to what extent may a simple computation procedure replace the complicated calorimetric experiment. The determination of heat of vaporization from the Clapeyron equation is generally considered as the most

accurate calculation method. However, its successful application is conditioned above all by a good quality of the data on the temperature dependence of saturated vapour pressures since any inaccuracy in vapour pressures is usually by derivative still accentuated. The method is not very suitable for calculating in the region of low vapour pressures which can undergo considerable errors and also in the region of higher pressures above normal boiling point, where the temperature dependence of saturated vapour pressures is steep. When using this method it is as well necessary to know or estimate the P-V-T behaviour of the liquid and above all of the gas phase; this is typical especially at higher temperatures about the temperature of normal boiling point. Considering that the difference between molar volumes of the gas and liquid phases at the normal boiling point is approximately $25 \text{ dm}^3/\text{mol}$ then the assumption of an ideal behaviour would cause an error about 4–5% and neglecting the volume of the liquid phase corresponds to an error about 0.4%. The ten per cent error in the second virial coefficient, by which even relatively accurate data on P-V-T behaviour are usually subjected, causes uncertainty about 0.4%. It follows from the facts mentioned that the calculation of heat of vaporization with an error about 1% requires good knowledge of saturated vapour pressures and P-V-T behaviour.

For the case of hydrocarbons, it is possible to reach with that method even better results than for other organic substances with regard to the exceptionally good knowledge of input quantities. Despite these good results of the computation method the experimental determination has, however, even in this case its importance providing that it yields the results which are subjected, in comparison with calculation, to a lower error. The accurate knowledge is necessary especially in those cases where heat of vaporization is employed for numerically less stable procedures (estimation of P-V-T behaviour from the vapour pressure and calorimetric data, determination of temperature derivative of ΔH_v , etc.).

The method suggested was applied successfully to the group of aliphatic hydrocarbons. The application of the contribution method to the entropy of vaporization at a constant value of the state variable chosen proved to be substantially more advantageous in comparison with the hitherto familiar procedures where authors used the contribution method for direct expression of heat of vaporization at a constant temperature. The use of the Thiesen relation with the approximate adjustment of constants enabled to express on the whole reliably the temperature dependence of heat of vaporization.

The contribution method was derived for hydrocarbons C5–C8, however, it can be used for aliphatic hydrocarbons with four and nine carbons, too. It is to be expected that the values calculated by such an extrapolation will undergo larger errors; it is possible to assume that they will not exceed 0.5%.

The proposed contribution method was limited to a smaller number of simple compounds, it enabled to express quite accurately the entropy of vaporization

in dependence on structural parameters of molecule and on temperature. However, the chief object of the procedure derived should be to provide a basis for application of the method to derivatives of aliphatic hydrocarbons. Considering that the estimation of heat of vaporization for these substances is essentially more difficult than for hydrocarbons, the application of the contribution method would be in these cases of considerable importance. The necessary condition for the determination of corresponding contributions is, however, good knowledge of the temperature dependence of heat of vaporization for some substances of the group of compounds considered.

REFERENCES

1. Wilhoit R. C., Zwolinski B. J.: *Handbook of Vapor Pressures and Heats of Vaporization of Hydrocarbons and Related Compounds*. API, Texas 1971.
2. Osborne N. S., Ginnings D. C.: *J. Res. Nat. Bur. Stand., Sect A* 39, 453 (1947).
3. McCulloch J. P., Pennington R. E., Smith J. C., Hossenlopp I. A., Waddington G.: *J. Amer. Chem. Soc.* 81, 5880 (1959).
4. Scott D. W., McCullough J. P., Williamson K. D., Waddington G.: *J. Amer. Chem. Soc.* 73, 1707 (1951).
5. Waddington G., Todd S. S., Huffman H. M.: *J. Amer. Chem. Soc.* 69, 22 (1947).
6. Waddington G., Douslin D. R.: *J. Amer. Chem. Soc.* 69, 2275 (1947).
7. Waddington G., Smith J. C., Scott D. W., Huffman H. M.: *J. Amer. Chem. Soc.* 71, 3902 (1949).
8. Huisman J., Sage B. H.: *J. Chem. Eng. Data* 9, 223 (1964).
9. Kozicki W., Sage B. H.: *J. Chem. Eng. Data* 5, 331 (1960).
10. Kozicki W., Sage B. H.: *Chem. Eng. Sci.* 15, 270 (1961).
11. McKay R. A., Sage B. H.: *J. Chem. Eng. Data* 5, 23 (1960).
12. Lemons J. F., Felsing W. A.: *J. Amer. Chem. Soc.* 65, 46 (1943).
13. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*, Vol. 1. Elsevier, Amsterdam 1950.
14. Timmermans J.: *Physico-Chemical Constants of Pure Organic Compounds*, Vol. 2. Elsevier, Amsterdam 1965.
15. *Selected Values of Physical and Thermodynamic Properties of Hydrocarbons and Related Compounds*. API Res. Proj. 44, Carnegie Press, Pittsburgh 1953.
16. Majer V., Svoboda V., Hýnek V., Pick J.: *This Journal* 43, 1313 (1978).
17. Wadsö I.: *Acta Chem. Scand.* 20, 536 (1966).
18. Morawetz E.: *Chem. Scripta* 1, 103 (1971).
19. Svoboda V., Veselý F., Holub R., Pick J.: *This Journal* 38, 3539 (1973).
20. Wadsö I.: *Acta Chem. Scand.* 20, 544 (1966).
21. Morawetz E.: *J. Chem. Thermodyn.* 4, 139 (1972).
22. Morawetz E.: *J. Chem. Thermodyn.* 4, 145 (1972).
23. Laidler K. J.: *Can. J. Chem.* 34, 626 (1956).
24. Lovering E. G., Laidler K. J.: *Can. J. Chem.* 38, 2367 (1960).
25. Lovering E. G., Nor O. M.: *Can. J. Chem.* 40, 199 (1962).
26. McCurdy K. G., Laidler K. J.: *Can. J. Chem.* 41, 1867 (1963).
27. Greenshields J. B., Rossini S. D.: *J. Phys. Chem.* 62, 271 (1958).
28. Hildebrand J. H.: *J. Amer. Chem. Soc.* 37, 970 (1915).

29. Pitzer K. S.: J. Chem. Phys. 7, 583 (1939).
30. Guggenheim E. A.: J. Chem. Phys. 13, 253 (1945).
31. Hildebrand J. H., Prausnitz J. M., Scott R. L.: *Regular and Related Solutions*. Van Nostrand, Reinhold Company, New York 1970.
32. Reid R. C., Sherwood T. K.: *The Properties of Gases and Liquids*. McGraw-Hill, New York 1966.
33. Thomas L. H.: J. Chem. Soc. 1959, 2132.
34. Halford R. S.: J. Chem. Phys. 8, 496 (1940).
35. Hermesen R. W., Prausnitz J. M.: J. Chem. Phys. 34, 108 (1961).
36. Staveley L. A. K., Tupman W. I.: J. Chem. Soc. 1950, 3597.
37. Novák J. P.: Chem. Prům. 14/39, 546 (1964).

Translated by J. Linek.