

Article

Heat Capacities and Enthalpies of Normal Alkanes in an Ideal Gas State

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Abstract: The reference literature contains data on the ideal gas-phase heat capacities and enthalpies of substances obtained experimentally. In this brief report, the highly accurate and simple unified analytical dependences of the heat capacity and enthalpy of normal alkanes larger than propane in the ideal gas state on temperature and the number of carbon atoms in a molecule are derived based on the analysis of the structure of chemical groups in the molecules and on the reference values of heat capacity and enthalpy for any two selected normal alkanes at one temperature. The dependences include a single set of coefficients for all normal alkanes and can be applied even to normal alkanes with the number of carbon atoms larger than 20, for which there is no data available. The dependences are thoroughly checked against two different sets of experimental data and two different sets of computational data obtained by low- and high-level theoretical methods: PM6 and G4. The error in calculating the heat capacity and enthalpy in the temperature range 300–1500 K is about 0.1% or less, which is comparable with the error of reference experimental data. Due to the generality of these dependences, one can treat the arising deviations as the indication of possible errors in the sets of reference data used for analysis. Such dependences are useful for estimating the heat capacities and enthalpies of vapors of large n-alkanes with scarce or lacking data. In addition, they can be readily used in computational fluid dynamics applications and provide the accurate interpolation/extrapolation of the tabulated experimental data without using semi-empirical methods of chemical thermodynamics and high-order polynomials.

Keywords: normal alkanes; heat capacity; enthalpy; ideal gas state; analytical dependences

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1. Introduction

The real gas enthalpy $H(T, P)$ is equal to the sum of the ideal gas enthalpy $H^0(T)$ and the residual enthalpy:

$$H_{res}(T, P) = \int_0^P \left[V - T \left(\frac{\partial V}{\partial T} \right)_P \right] dP, \quad (1)$$

$$H^0(T) \gg H_{res}(T, P) \quad (2)$$

where T is the temperature, V is the volume, and P is the pressure. In the case of polyatomic molecules, including heavy normal alkanes C_nH_{2n+2} , the following inequality holds:

and when solving the caloric equation of state $H(T, P)$, an accurate calculation of $H^0(T)$ is necessary. For the theoretical solution of such a problem (from the “first principles”), it is necessary to know the entire spectrum of intramolecular vibrations, inhibited rotations, and anharmonicity parameters, which is a rather complex problem. Therefore, the reference literature contains data on the heat capacities $C_p^0(T)$ and enthalpies $H^0(T)$ of substances obtained experimentally [1,2]. Available experimental data are fitted using

internally consistent correlations within the assigned experimental uncertainty [3]. In many cases, the experimental data on $C_p^0(T)$ and enthalpy $H^0(T)$ are limited with a single or several values of temperature, especially for complex compounds. In such cases, various semiempirical incremental or substitution methods are used to obtain the required data [4]. Thus, to describe the temperature dependence of the ideal gas heat capacity, a group-contribution method [5] is widely used, which is based on a four-parameter polynomial. In computational fluid dynamics (CFD) applications, high-order polynomials for $C_p^0(T)$ approximating the experimental data and the data obtained by the semiempirical methods of chemical thermodynamics are often used [6,7]. Currently, various low through high-level theoretical methods, such as semiempirical PM6 [8], M062X/6-311++G(d,p) density functional [9], CBS-Q//B3 [10], and G4 [11] composite methods for calculating gas-phase heat capacities of various compounds are used. Thus, reported in [12] are the heat capacities $C_p^0(T)$ for the C₁ through C₁₀ normal alkanes for temperatures between 298.15 and 1500 K. A satisfactory agreement with experimental data is obtained.

The purpose of this work was to analyze and process available experimental and computational data in the form of the simple unified analytical dependence of $C_p^0(T)$ and $H^0(T)$ for large n-alkanes, C_nH_{2n+2}, with different numbers of carbon atoms, *n*, in the molecule. Knowledge of this dependence allows accurate estimates of the heat capacities and enthalpies of vapors of large n-alkanes with scarce or lacking data, thus providing the accurate interpolation/extrapolation of available experimental data without applying various semiempirical methods. Furthermore, they can be readily used in CFD applications instead of high-order polynomials with specific sets of coefficients for each compound.

2. Heat capacity

An increase in the number *n* by one at an initial value of $n \geq 2$ (i.e., starting with ethane) corresponds to the addition of one CH₂ group to the molecule. For $n \geq 4$, only CH₂ groups can be the nearest neighbors of the added group since the edge CH₃ groups already have such neighbors. In this case, the C_{n+1}H_{2n+4} molecule differs from the C_nH_{2n+2} molecule structurally in that the number of CH₂ groups in it that are not adjacent to the edge groups is larger by one. Therefore, it can be assumed that, up to interaction with more distant neighbors, the addition of the CH₂ group at $n \geq 4$ leads to an increase in the heat capacity $f(T)$ on the isotherm, which does not depend on *n*:

$$f(T) = C_{p,n+1}^0(T) - C_{p,n}^0(T), \quad n \geq 4 \quad (3)$$

and, accordingly, to the linear dependence of the specific heat and enthalpy on *n* for $n \geq 4$. Choosing $n = 5$ in Equation (3) for definiteness, one has:

$$f(T) = C_{p,6}^0(T) - C_{p,5}^0(T) \quad (4)$$

In this case, from the above linear dependence of the specific heat on *n*, one obtains a simple unified analytical dependence for $C_{p,n}^0(T)$ valid for all normal alkanes with $n \geq 4$:

$$C_{p,n}^0(T) = C_{p,5}^0(T) + f(T)(n - 5), \quad n \geq 4 \quad (5)$$

Let us now check the accuracy of simple Equation (5) using the data of [1], where the measured values of $C_{p,n}^0(T)$ are listed for the widest range of normal alkanes from $n = 1$ to $n = 20$. Instead of [1], any other reference data can be used, e.g., [2] (see Appendix A), and [12] (see Appendix B).

Table 1 shows the measured values of $C_{p,5}^0(T)$ and $C_{p,6}^0(T)$ [1] as well as the calculated values of function $f(T)$ in Equation (4) for the temperature range from 300 to 1500 K. Table 2 illustrates the accuracy of Equation (5) for normal alkanes with $n = 4, 10$, and 20. The error, ΔC_p^0 , is estimated as $\Delta C_p^0 = [(C_{p,calc}^0 - C_{p,exp}^0)/C_{p,exp}^0] \cdot 100\%$, where $C_{p,calc}^0$ and $C_{p,exp}^0$ are the calculated and measured values of heat capacity. As seen, excellent agreement is obtained, as the error is less than 0.1%, which is comparable with

the error of reference data in [1]. Thus, the unified dependence of Equation (5) can be used for obtaining accurate estimates of the heat capacities of vapors of the various n-alkanes, and even those with scarce or lacking data.

Table 1. Function $f(T)$ in Equation (4).

| T, K | $C_{P,5}^0$ | $C_{P,6}^0$ | $f(T)$ |
|--------|-------------|-------------|--------------|
| | cal/(mol·K) | cal/(mol·K) | cal/(mol·K) |
| | [1] | [1] | Equation (4) |
| 300 | 28.87 | 34.37 | 5.50 |
| 400 | 36.53 | 43.47 | 6.94 |
| 500 | 43.58 | 51.83 | 8.25 |
| 700 | 54.83 | 65.10 | 10.27 |
| 900 | 63.18 | 74.93 | 11.75 |
| 1100 | 69.48 | 82.32 | 12.84 |
| 1300 | 74.24 | 87.89 | 13.65 |
| 1500 | 77.83 | 92.10 | 14.27 |

Table 2. Accuracy of Equation (5) for $C_p^0(T)$ of $n\text{-C}_4\text{H}_{10}$, $n\text{-C}_{10}\text{H}_{22}$, $n\text{-C}_{20}\text{H}_{42}$.

| T, K | $C_{P,4}^0$ | $C_{P,4}^0$ | $\Delta C_{P,4}^0$ | % | $C_{P,10}^0$ | $C_{P,10}^0$ | $\Delta C_{P,10}^0$ | % | $C_{P,20}^0$ | $C_{P,20}^0$ | $\Delta C_{P,20}^0$ | % |
|--------|--------------|-------------|--------------------|---|--------------|--------------|---------------------|---|--------------|--------------|---------------------|---|
| | cal/(mol·K) | cal/(mol·K) | | | cal/(mol·K) | cal/(mol·K) | | | cal/(mol·K) | cal/(mol·K) | | |
| | Equation (5) | [1] | | | Equation (5) | [1] | | | Equation (5) | [1] | | |
| 300 | 23.37 | 23.40 | -0.13 | | 56.37 | 56.34 | 0.05 | | 111.37 | 111.28 | 0.08 | |
| 400 | 29.59 | 29.60 | -0.03 | | 71.23 | 71.24 | 0.01 | | 140.63 | 140.65 | -0.01 | |
| 500 | 35.33 | 35.34 | -0.03 | | 84.83 | 84.81 | 0.02 | | 167.33 | 167.27 | 0.04 | |
| 700 | 44.56 | 44.55 | 0.02 | | 106.18 | 106.21 | -0.03 | | 208.88 | 208.97 | -0.04 | |
| 900 | 51.43 | 51.44 | -0.02 | | 121.93 | 121.92 | 0 | | 239.43 | 239.38 | 0.02 | |
| 1100 | 56.64 | 56.64 | 0 | | 133.68 | 133.7 | -0.02 | | 262.08 | 262.0 | 0.03 | |
| 1300 | 60.59 | 60.58 | 0.02 | | 142.49 | 142.5 | -0.01 | | 278.99 | 279.1 | -0.04 | |
| 1500 | 63.56 | 63.57 | -0.02 | | 149.18 | 149.2 | -0.01 | | 291.88 | 291.9 | -0.01 | |

As could be expected, application of Equation (5) to propane ($n = 3$) provides a slightly worse accuracy than for n-alkanes with $n \geq 4$, especially at low temperatures $T < 500$ K (Table 3), since the difference between the heat capacity of propane and that of n-butane is not related to the difference in the number of CH_2 groups that would not be adjacent with an edge CH_3 group. Nevertheless, at $T \geq 500$ K, the error is also at the level of 0.1% on average.

Table 3. Accuracy of Equation (5) for $C_p^0(T)$ of C_3H_8 .

| T, K | $C_{P,3}^0$ | | $\Delta C_{P,3}^0, \%$ |
|--------|---------------|-------|------------------------|
| | cal/(mol·K) | | |
| | Equations (5) | [1] | |
| 300 | 17.87 | 17.66 | 1.2 |
| 400 | 22.65 | 22.54 | 0.5 |
| 500 | 27.08 | 27.04 | 0.1 |
| 700 | 34.29 | 34.20 | 0 |
| 900 | 39.68 | 39.61 | 0.3 |
| 1100 | 43.80 | 43.75 | 0.1 |
| 1300 | 46.94 | 46.89 | 0.1 |
| 1500 | 49.29 | 49.26 | 0.1 |

3. Enthalpy

Integration of Equation (5) gives:

$$H_n^0(T) = H_n^0(T_1) + \int_{T_1}^T C_{p,5}^0(T) dT + (n-5) \int_{T_1}^T f(T) dT, \quad n \geq 4 \quad (6)$$

where $T_1 = 300$ K. The dependence of the first term in Equation (6), $H_n^0(T_1)$, on n can be expressed through the corresponding measured data [1] for any two alkanes with $n \geq 4$, for example, $H_5^0(T_1) = 5682$ cal/mol (n -pentane) and $H_{20}^0(T_1) = 20730$ cal/mol (eicosane). In the linear approximation in n one obtains:

$$H_n^0(T_1) = H_5^0(T_1) + (n-5) \frac{H_{20}^0(T_1) - H_5^0(T_1)}{15} = 5682 + 1003(n-5) \text{ cal/mol}, \quad n \geq 4 \quad (7)$$

Table 4 illustrates the accuracy of calculating $H_n^0(T_1)$ by Equation (7) using examples of n -butane, n -pentane, n -hexane, n -heptane, n -decane, n -pentadecane, and eicosane. The error, ΔH_n^0 , is estimated as $\Delta H_n^0 = [(\Delta H_{n,calc}^0 - \Delta H_{n,exp}^0) / \Delta H_{n,exp}^0] \cdot 100\%$, where $\Delta H_{n,calc}^0$ and $\Delta H_{n,exp}^0$ are the calculated and measured values of enthalpy. As seen, Equation (7) predicts with excellent accuracy the values of $H_n^0(T_1)$ for normal alkanes with $4 \leq n \leq 20$.

Table 4. Accuracy of Equation (7) for calculating $H_n^0(T_1)$ with $n = 4-7, 10, 15$, and 20 ($T_1 = 300$ K).

| n | $H_n^0(T_1)$, cal/mol | | $\Delta H_n^0(T_1)$, % |
|-----|------------------------|--------|-------------------------|
| | Equation (7) | [1] | |
| 4 | 4679 | 4689 | -0.2 |
| 5 | 5682 | 5682 | 0 |
| 6 | 6685 | 6687 | 0 |
| 7 | 7688 | 7689 | 0 |
| 10 | 10,697 | 10,696 | 0 |
| 15 | 15,712 | 15,714 | 0 |
| 20 | 20,727 | 20,730 | 0 |

To apply Equation (6) for calculating $H_n^0(T)$ at temperatures other than $T_1 = 300$ K, one has to take integral of $C_{p,n}^0(T)$ in Equation (5). For this purpose, let us approximate the tabulated data [1] for the specific heats of n -pentane, $C_{p,5}^0(T)$, and n -hexane, $C_{p,6}^0(T)$, entering Equations (5) and (4) by the third-order polynomials in temperature in the range of 298.16–1500 K:

$$C_{p,5}^0(T) = -0.96411 + 11.681\tau - 0.62063\tau^2 + 0.01282\tau^3 \text{ cal/(mol} \cdot \text{K)} \quad (8)$$

$$C_{p,6}^0(T) = -1.12013 + 13.92285\tau - 0.74752\tau^2 + 0.0156\tau^3 \text{ cal/(mol} \cdot \text{K)} \quad (9)$$

where the temperature is expressed in 100 K ($\tau = T/100$). Table 5 illustrates the accuracy of approximations (8) and (9). The approximation error is on the level of 0.1% on average.

Table 5. Accuracy of Equations (8) and (9) for $C_p^0(T)$ of n -C₅H₁₂ and n -C₆H₁₄.

| T , K | $C_{p,5}^0$ | $C_{p,5}^0$ | $\Delta C_{p,5}^0$, % | $C_{p,6}^0$ | $C_{p,6}^0$ | $\Delta C_{p,6}^0$, % |
|---------|--------------|-------------|------------------------|--------------|-------------|------------------------|
| | cal/(mol·K) | cal/(mol·K) | | cal/(mol·K) | cal/(mol·K) | |
| | Equation (8) | [1] | | Equation (9) | [1] | |
| 300 | 28.87 | 28.87 | 0 | 34.34 | 34.37 | -0.1 |
| 400 | 36.65 | 36.53 | 0.3 | 43.61 | 43.47 | 0.3 |
| 500 | 43.53 | 43.58 | -0.1 | 51.76 | 51.83 | -0.1 |
| 700 | 54.79 | 54.83 | -0.1 | 65.06 | 65.10 | 0.1 |
| 900 | 63.24 | 63.18 | 0.1 | 75.01 | 74.93 | 0.1 |
| 1100 | 69.49 | 69.48 | 0 | 82.34 | 82.32 | 0 |
| 1300 | 74.17 | 74.24 | -0.1 | 87.82 | 87.89 | -0.1 |
| 1500 | 77.88 | 77.83 | 0.1 | 92.18 | 92.10 | 0.1 |

Substituting Equations (8) and (9) in Equation (4), one obtains:

$$f(T) = -0.15602 + 2.24185\tau - 0.12689\tau^2 + 0.00278\tau^3 \text{ cal}/(\text{mol} \cdot \text{K}) \quad (10)$$

Now, the second and third terms in Equation (6) can be derived based on Equations (8) and (10), respectively:

$$\int_{T_1}^T C_{P,5}^0(T) dT = 100 \int_{\tau_1}^{\tau} C_{P,5}^0(\tau) d\tau = -96.411(\tau - \tau_1) + 584.1(\tau^2 - \tau_1^2) - 20.688(\tau^3 - \tau_1^3) + 0.3205(\tau^4 - \tau_1^4) \quad (11)$$

$$\int_{T_1}^T f(\tau) dT = 100 \int_{\tau_1}^{\tau} f(\tau) d\tau = -15.602(\tau - \tau_1) + 112.09(\tau^2 - \tau_1^2) - 4.2297(\tau^3 - \tau_1^3) + 0.0695 \cdot 10^{-4}(\tau^4 - \tau_1^4) \quad (12)$$

Substituting Equations (7), (11), and (12) into the sum of Equation (6), one finally obtains:

$$H_n^0(T) = -96.411(\tau - \tau_1) + 584.1(\tau^2 - \tau_1^2) - 20.688(\tau^3 - \tau_1^3) + 0.3205(\tau^4 - \tau_1^4) + (n-5)[-15.602(\tau - \tau_1) + 112.09(\tau^2 - \tau_1^2) - 4.2297(\tau^3 - \tau_1^3) + 0.0695 \cdot 10^{-4}(\tau^4 - \tau_1^4) + 1003] + 5682 \text{ cal/mol}, \quad (13)$$

$$\tau = T/100, \quad n \geq 4, \quad 2.9816 \leq \tau \leq 15$$

Formula (13) provides the unified analytical dependence of the enthalpies of all normal alkanes in the ideal gas state on temperature and the number of carbon atoms in an alkane molecule $n \geq 4$ with an error less than 0.1%, which is comparable with the error of reference data in [1] (Table 6).

Table 6. Accuracy of Equation (13) for calculating $H_n^0(T)$ with $n = 4, 10$, and 20 .

| T, K | H_4^0 , cal/mol | | | H_{10}^0 , cal/mol | | | H_{20}^0 , cal/mol | | |
|------|-------------------|--------|------------------|----------------------|---------|---------------------|----------------------|---------|---------------------|
| | Equation (13) | [1] | ΔH_4^0 % | Equation (13) | [1] | ΔH_{10}^0 % | Equation (13) | [1] | ΔH_{20}^0 % |
| 300 | 4679 | 4689 | -0.02 | 10,697 | 10,696 | 0 | 20,727 | 20,730 | 0.01 |
| 400 | 7337 | 7340 | 0 | 17,103 | 17,030 | 0.4 | 33,380 | 33,332 | 0.17 |
| 500 | 10,593 | 10,595 | 0 | 24,924 | 24,905 | 0.08 | 48,810 | 48,772 | 0.08 |
| 700 | 18,618 | 18,620 | 0 | 44,111 | 44,072 | 0.09 | 86,599 | 86,506 | 0.1 |
| 900 | 28,252 | 28,251 | 0 | 67,017 | 66,996 | 0.03 | 131,627 | 131,580 | 0.08 |
| 1100 | 39,091 | 39,083 | 0.02 | 92,663 | 92,620 | 0.05 | 181,949 | 181,850 | 0.05 |
| 1300 | 50,826 | 50,843 | -0.03 | 120,320 | 120,320 | 0 | 236,143 | 236,220 | 0.03 |
| 1500 | 63,248 | 63,270 | -0.03 | 149,522 | 149,500 | 0.01 | 293,311 | 293,240 | 0.02 |

For the sake of completeness, we also present here the unified analytical dependence for $C_{P,n}^0(T)$, which can be readily obtained by substituting Equations (8) and (10) in Equation (5):

$$C_{P,n}^0(T) = -0.18401 + 0.47175\tau + 0.01382\tau^2 - 0.00108\tau^3 + n(-0.15602 + 2.24185\tau - 0.12689\tau^2 + 0.00278\tau^3) \quad (14)$$

$$\tau = T/100, \quad n \geq 4, \quad 2.9816 \leq \tau \leq 15$$

Table 7 illustrates the accuracy of approximation (14). Comparison with Table 2 indicates that the accuracy of Equation (14) is slightly worse than that of Equation (5), but it is still on the level of 0.1% on average.

Table 7. Accuracy of Equation (14 for $C_p^0(T)$ of n -C₄H₁₀, n -C₁₀H₂₂, and n -C₂₀H₄₂.

| T, K | $C_{P,4}^0$ cal/(mol·K) | | $\Delta C_{P,4}^0$ % | $C_{P,10}^0$ cal/(mol·K) | | $\Delta C_{P,10}^0$ % | $C_{P,20}^0$ cal/(mol·K) | | $\Delta C_{P,20}^0$ % |
|------|----------------------------|-------|-------------------------|-----------------------------|--------|--------------------------|-----------------------------|--------|--------------------------|
| | Equation (14) | [1] | | Equation (14) | [1] | | Equation (14) | [1] | |
| | 300 | 23.34 | | 23.40 | -0.26 | | 56.35 | 56.34 | |
| 400 | 29.69 | 29.60 | 0.3 | 71.45 | 71.24 | 0.3 | 141.04 | 140.65 | 0.3 |
| 500 | 35.30 | 35.34 | -0.1 | 84.67 | 84.81 | -0.16 | 166.95 | 167.27 | -0.2 |
| 700 | 44.52 | 44.55 | 0.07 | 106.15 | 106.21 | -0.1 | 208.88 | 208.97 | -0.04 |
| 900 | 51.47 | 51.44 | 0 | 122.09 | 121.92 | 0.1 | 239.78 | 239.38 | 0.17 |
| 1100 | 56.64 | 56.64 | 0 | 133.75 | 133.7 | 0 | 262.26 | 262.0 | 0.1 |
| 1300 | 60.52 | 60.58 | -0.1 | 142.42 | 142.5 | -0.1 | 278.94 | 279.1 | -0.06 |
| 1500 | 63.57 | 63.57 | 0 | 149.40 | 149.2 | 0.1 | 292.44 | 291.9 | 0.18 |

4. Conclusions

Based on the analysis of the number of repeating groups in saturated linear hydrocarbons and tabulated reference data, the simple unified analytical dependences of heat capacity and enthalpy in the ideal gas state on temperature and on the number of carbon atoms n in a molecule are derived. The dependences include a single set of coefficients for all normal alkanes and can be applied even to normal alkanes with the number of carbon atoms $n > 20$, for which there is no data available. The dependences are thoroughly checked against two different sets of experimental data and two different sets of computational data obtained by low- and high-level theoretical methods: PM6 and G4. In all the cases, the error in calculating $C_p^0(T)$ and $H^0(T)$ in the temperature range of 300 to 1500 K at $n \geq 4$ is about 0.1% or less, which is comparable with the error of reference experimental data. Based on the generality of these dependences, one can treat the arising deviations as the indication of possible errors in the sets of reference data used for analysis. Knowledge of these dependences allows accurate estimates of the heat capacities and enthalpies of vapors of n-alkanes with scarce or lacking data, thus providing the accurate interpolation/extrapolation of available experimental data without applying various semiempirical methods. Moreover, they can be readily used in CFD applications instead of high-order polynomials with different sets of coefficients for each compound. The approach suggested herein can be also applied to alkane isomers and other compounds exhibiting structural isomerism.

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Appendix A

Here, we check the validity of the approach using the reference data of [2]. Table A1 shows the measured values of $C_{p,5}^0(T)$ and $C_{p,6}^0(T)$ [2] as well as the calculated values of function $f(T)$ in Equation (4) for the temperature range from 300 to 1500 K. Table A2 illustrates the accuracy of Equation (5) for normal alkanes with $n = 4, 10$, and 20. The error, ΔC_p^0 , is estimated as $\Delta C_p^0 = [(C_{p,calc}^0 - C_{p,exp}^0)/C_{p,exp}^0] \cdot 100\%$, where $C_{p,calc}^0$ and $C_{p,exp}^0$ are the calculated and measured values of heat capacity. As seen, excellent agreement was obtained, as the error was also less than 0.1%, which is comparable with the error of reference data in [2].

Table A1. Data for $C_p^0(T)$ of n-C₅H₁₂ and n-C₆H₁₄ [2].

| <i>T</i> , K | $C_{p,5}^0$ | $C_{p,6}^0$ |
|--------------|-------------|-------------|
| | J/(mol·K) | J/(mol·K) |
| | [2] | [2] |
| 300 | 120.62 | 143.26 |
| 400 | 152.55 | 181.54 |
| 500 | 182.59 | 217.28 |
| 700 | 231.38 | 274.05 |
| 900 | 266.94 | 315.06 |
| 1100 | 293.72 | 345.18 |
| 1300 | 313.80 | 368.19 |
| 1500 | 330.54 | 389.11 |

Table A2. Accuracy of Equation (5) for $C_p^0(T)$ of n-C₇H₁₆ and n-C₁₀H₂₂ [2].

| <i>T</i> , K | $f(T)$ | $C_{p,7}^0$ | $C_{p,7}^0$ | $\Delta C_{p,7}^0$, % | $C_{p,10}^0$ | $C_{p,10}^0$ | $\Delta C_{p,10}^0$ |
|--------------|--------------|--------------|-------------|------------------------|--------------|--------------|---------------------|
| | J/(mol·K) | J/(mol·K) | J/(mol·K) | | J/(mol·K) | J/(mol·K) | |
| | Equation (4) | Equation (5) | [2] | | Equation (5) | [2] | |
| 300 | 22.64 | 165.90 | 165.98 | −0.05 | 233.82 | 234.18 | −0.15 |
| 400 | 28.99 | 210.53 | 210.66 | −0.06 | 297.50 | 297.98 | −0.16 |
| 500 | 34.69 | 251.97 | 252.09 | −0.05 | 356.04 | 356.43 | −0.11 |
| 700 | 42.67 | 316.72 | 317.15 | −0.13 | 444.73 | 446.43 | −0.38 |
| 900 | 48.12 | 363.18 | 363.59 | −0.11 | 507.54 | 508.36 | −0.16 |
| 1100 | 51.46 | 396.64 | 397.06 | −0.10 | 551.02 | 551.87 | −0.15 |
| 1300 | 54.39 | 422.58 | 422.58 | 0 | 585.75 | 585.76 | 0 |
| 1500 | 58.57 | 447.68 | 443.50 | 0.9 | 623.39 | 610.86 | 2.05 |

Appendix B

Here, we check the validity of the approach using the calculated data reported in [12]. Table A3 shows the values of $C_{p,5}^0(T)$ and $C_{p,6}^0(T)$ obtained by PM6 [8] and G4 [11] methods, as well as the corresponding values of function $f(T)$ in Equation (4) for the temperature range from 300 to 1500 K. Table A4 illustrates the accuracy of Equation (5) for normal alkanes with $n = 4, 8$, and 10. The error, ΔC_p^0 , is estimated as $\Delta C_p^0 = [(C_{p,calc}^0 - C_{p,PM6}^0)/C_{p,PM6}^0] \cdot 100\%$ or $\Delta C_p^0 = [(C_{p,calc}^0 - C_{p,G4}^0)/C_{p,G4}^0] \cdot 100\%$ where $C_{p,calc}^0$, $C_{p,PM6}^0$, and $C_{p,G4}^0$ are the values of heat capacity calculated based on Equation (5) and using PM6 or G4 methods, respectively. As seen, excellent agreement was obtained, as the error was less than 0.1%.

Table A3. Function $f(T)$ in Equation (4) [12].

| T, K | $C_{P,5}^0$ | | $C_{P,6}^0$ | | $f(T)$ | |
|--------|-------------|-------|-------------|-------|-------------|-------|
| | cal/(mol·K) | | cal/(mol·K) | | cal/(mol·K) | |
| | G4 | PM6 | G4 | PM6 | G4 | PM6 |
| 300 | 26.67 | 27.34 | 31.56 | 32.30 | 4.89 | 4.96 |
| 400 | 34.52 | 35.90 | 40.97 | 42.54 | 6.45 | 6.64 |
| 500 | 42.06 | 44.04 | 49.99 | 52.26 | 7.93 | 8.22 |
| 700 | 54.43 | 57.14 | 64.74 | 67.83 | 10.31 | 10.69 |
| 900 | 63.67 | 66.63 | 75.70 | 79.07 | 12.03 | 12.44 |
| 1100 | 70.63 | 73.53 | 83.93 | 87.22 | 13.30 | 13.69 |
| 1300 | 75.90 | 78.57 | 90.14 | 93.15 | 14.24 | 14.58 |
| 1500 | 79.91 | 82.28 | 94.84 | 97.52 | 14.93 | 15.24 |

Table A4. Accuracy of Equation (5) for $C_p^0(T)$ of n -C₄H₁₀, n -C₈H₁₈, n -C₁₀H₂₂ [12].

| T, K | $C_{P,4}^0$ | $C_{P,4}^0$ | $\Delta C_{P,4}^0$ | % | $C_{P,8}^0$ | $C_{P,8}^0$ | $\Delta C_{P,10}^0$ | % | $C_{P,10}^0$ | $C_{P,10}^0$ | $\Delta C_{P,20}^0$ | % | |
|--------|--------------|-------------|--------------------|---|--------------|-------------|---------------------|---|--------------|--------------|---------------------|---|-------------|
| | cal/(mol·K) | cal/(mol·K) | | | cal/(mol·K) | cal/(mol·K) | | | cal/(mol·K) | cal/(mol·K) | | | cal/(mol·K) |
| | Equation (5) | G4 | | | Equation (5) | G4 | | | Equation (5) | PM6 | | | |
| 300 | 21.78 | 21.76 | 0.09 | | 41.34 | 41.34 | 0 | | 52.14 | 52.17 | -0.06 | | |
| 400 | 28.07 | 28.05 | 0.07 | | 53.87 | 53.89 | -0.04 | | 69.10 | 69.13 | -0.04 | | |
| 500 | 34.13 | 34.12 | 0.03 | | 65.85 | 65.87 | -0.03 | | 85.14 | 85.13 | 0.01 | | |
| 700 | 44.12 | 44.14 | -0.05 | | 85.36 | 85.33 | 0.04 | | 110.59 | 110.60 | -0.01 | | |
| 900 | 51.64 | 51.67 | -0.06 | | 99.76 | 99.70 | 0.06 | | 128.83 | 128.84 | -0.01 | | |
| 1100 | 57.33 | 57.39 | -0.1 | | 110.53 | 110.44 | 0.08 | | 141.98 | 141.98 | 0 | | |
| 1300 | 61.66 | 61.72 | -0.1 | | 118.62 | 118.52 | 0.08 | | 151.47 | 151.51 | -0.02 | | |
| 1500 | 64.98 | 65.02 | -0.06 | | 124.70 | 124.63 | 0.06 | | 158.48 | 158.51 | -0.02 | | |

Nomenclature

| | |
|----------------|---|
| C_p^0 | ideal gas heat capacity |
| $C_{p,calc}^0$ | calculated heat capacity |
| $C_{p,exp}^0$ | measured heat capacity |
| $C_{p,G4}^0$ | heat capacity calculated by G4 method |
| ΔC_p^0 | error in the estimation of C_p^0 |
| $C_{p,PM6}^0$ | heat capacity calculated by PM6 method |
| f | function in Equation (3) |
| H | real gas enthalpy |
| H^0 | ideal gas enthalpy |
| H_{res} | residual enthalpy |
| $H_{n,calc}^0$ | calculated ideal gas enthalpy |
| $H_{n,exp}^0$ | measured ideal gas enthalpy |
| ΔH_n^0 | error in the estimation of H^0 |
| n | numbers of carbon atoms in n-alkane molecules |
| P | pressure |
| T | temperature |
| T_1 | reference temperature |
| V | volume |
| τ | reduced temperature |

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