


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:

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

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:

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

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 CH_2 group to the molecule. For $n \geq 4$, only CH_2 groups can be the nearest neighbors of the added group since the edge CH_3 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 CH_2 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 CH_2 group at $n \geq 4$ leads to an increase in the heat capacity $f(T)$ on the isotherm, which does not depend on n :

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

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 $n \geq 4$:

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

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 $\Delta C_p^0 = \left[(C_{p,calc}^0 - C_{p,exp}^0) / C_{p,exp}^0 \right] \cdot 100\%$, 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	$C_{P,5}^0$ cal/(mol·K)	$C_{P,6}^0$ cal/(mol·K)	$f(T)$ 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 -C₄H₁₀, n -C₁₀H₂₂, n -C₂₀H₄₂.

T, K	$C_{P,4}^0$ cal/(mol·K)	$C_{P,4}^0$ cal/(mol·K)	$\Delta C_{P,4}^0$ %	$C_{P,10}^0$ cal/(mol·K)	$C_{P,10}^0$ cal/(mol·K)	$\Delta C_{P,10}^0$ %	$C_{P,20}^0$ cal/(mol·K)	$C_{P,20}^0$ cal/(mol·K)	$\Delta C_{P,20}^0$ %
	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 CH₂ groups that would not be adjacent with an edge CH₃ 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 C₃H₈.

T, K	$C_{P,3}^0$ cal/(mol·K)		$\Delta C_{P,3}^0$ %
	Equation (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:

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

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:

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

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 $\Delta H_n^0 = \left[(\Delta H_{n,calc}^0 - \Delta H_{n,exp}^0) / \Delta H_{n,exp}^0 \right] \cdot 100\%$, 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	$C_{p,5}^0$ cal/(mol·K)	$C_{p,5}^0$ cal/(mol·K)	$\Delta C_{p,5}^0$, %	$C_{p,6}^0$ cal/(mol·K)	$C_{p,6}^0$ cal/(mol·K)	$\Delta C_{p,6}^0$, %
	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:

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

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:

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

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

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	$H_4^0, \text{ cal/mol}$		$\Delta H_4^0 \%$	$H_{10}^0, \text{ cal/mol}$		$\Delta H_{10}^0 \%$	$H_{20}^0, \text{ cal/mol}$		$\Delta H_{20}^0 \%$
	Equation (13)	[1]		Equation (13)	[1]		Equation (13)	[1]	
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):

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

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

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 $n\text{-C}_4\text{H}_{10}$, $n\text{-C}_{10}\text{H}_{22}$, and $n\text{-C}_{20}\text{H}_{42}$.

T, K	$C_{P,4}^0$		$\Delta C_{P,4}^0$ %	$C_{P,10}^0$		$\Delta C_{P,10}^0$ %	$C_{P,20}^0$		$\Delta C_{P,20}^0$ %
	cal/(mol·K)			cal/(mol·K)			cal/(mol·K)		
	Equation (14)	[1]		Equation (14)	[1]		Equation (14)	[1]	
300	23.34	23.40	−0.26	56.35	56.34	0	111.38	111.28	0.09
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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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

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 $n\text{-C}_5\text{H}_{12}$ and $n\text{-C}_6\text{H}_{14}$ [2].

T, K	$C_{p,5}^0/\text{J}/(\text{mol} \cdot \text{K})$	$C_{p,6}^0/\text{J}/(\text{mol} \cdot \text{K})$
	[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 $n\text{-C}_7\text{H}_{16}$ and $n\text{-C}_{10}\text{H}_{22}$ [2].

T, K	$f(T)/(\text{mol}\cdot\text{K})$	$C_{p,7}^0/(\text{mol}\cdot\text{K})$	$C_{p,7}^0/(\text{mol}\cdot\text{K})$	$\Delta C_{p,7}^0, \%$	$C_{p,10}^0/(\text{mol}\cdot\text{K})$	$C_{p,10}^0/(\text{mol}\cdot\text{K})$	$\Delta C_{p,10}^0$
	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 $\Delta C_p^0 = \left[(C_{p,calc}^0 - C_{p,PM6}^0) / C_{p,PM6}^0 \right] \cdot 100\%$ or $\Delta C_p^0 = \left[(C_{p,calc}^0 - C_{p,G4}^0) / C_{p,G4}^0 \right] \cdot 100\%$ 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	$C_{p,5}^0/\text{cal}/(\text{mol}\cdot\text{K})$		$C_{p,6}^0/\text{cal}/(\text{mol}\cdot\text{K})$		$f(T)/\text{cal}/(\text{mol}\cdot\text{K})$	
	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 $n\text{-C}_4\text{H}_{10}$, $n\text{-C}_8\text{H}_{18}$, $n\text{-C}_{10}\text{H}_{22}$ [12].

T, K	$C_{p,4}^0/\text{cal}/(\text{mol}\cdot\text{K})$	$C_{p,4}^0/\text{cal}/(\text{mol}\cdot\text{K})$	$\Delta C_{p,4}^0, \%$	$C_{p,8}^0/\text{cal}/(\text{mol}\cdot\text{K})$	$C_{p,8}^0/\text{cal}/(\text{mol}\cdot\text{K})$	$\Delta C_{p,8}^0, \%$	$C_{p,10}^0/\text{cal}/(\text{mol}\cdot\text{K})$	$C_{p,10}^0/\text{cal}/(\text{mol}\cdot\text{K})$	$\Delta C_{p,10}^0, \%$
	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

References

- Vargaftik, N.B. *Handbook of Thermophysical Properties of Gases and Liquids*, 1st ed.; State Publisher of Physical and Mathematical Literature: Moscow, Russia, 1963; (Translation: Vargaftik, N.B. *Handbook of Physical Properties of Liquids and Gases: Pure Substances and Mixtures*; Hemisphere Pub. Corp.: Washington, DC, USA, 1975).
- Available online: <https://webbook.nist.gov/chemistry/> (accessed on 20 April 2021).

3. Scott, D.W. Correlation of the chemical thermodynamic properties of alkane hydrocarbons. *J. Chem. Phys.* **1974**, *60*, 3144–3165. [[CrossRef](#)]
4. Reid, R.C.; Prausnitz, J.M.; Sherwood, T.K. *The Properties of Gases and Liquids*, 3rd ed.; McGraw-Hill: New York, NY, USA, 1977.
5. Joback, K.G.; Reid, R.C. Estimation of pure-component properties from group-contributions. *Chem. Eng. Commun.* **1987**, *57*, 233–243. [[CrossRef](#)]
6. McBride, B.J. *Coefficients for Calculating Thermodynamic and Transport Properties of Individual Species*; NASA Technical Memorandum 4513; National Aeronautics and Space Administration: Washington, DC, USA, 1993.
7. McBride, B.J.; Zehe, M.J.; Gordon, S. *NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species*; Technical Paper 2002-211556; NASA Center for Aerospace Information: Nanover, MD, USA, 2002.
8. Stewart, J.J.P. Optimization of parameters for semiempirical methods. V. Modification of NDDO approximations and application to 70 elements. *J. Molec. Model.* **2007**, *13*, 1173–1213. [[CrossRef](#)] [[PubMed](#)]
9. Zhao, Y.; Truhlar, D.G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: Two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008**, *120*, 215–241. [[CrossRef](#)]
10. Montgomery, J.A.; Frisch, M.J.; Ochterski, J.W.; Petersson, G.A. A complete basis set model chemistry. VII. Use of the minimum population localization method. *J. Chem. Phys.* **2000**, *112*, 6532–6542. [[CrossRef](#)]
11. Curtiss, L.A.; Redfern, P.C.; Raghavachari, K. Gaussian-4 theory. *J. Chem. Phys.* **2007**, *126*, 084108. [[CrossRef](#)] [[PubMed](#)]
12. Rayne, S.; Forest, K. Gas phase constant pressure heat capacities ($C_{p,gas}$) for the C₁ through C₁₀ straight chain alkanes, isobutane, hydrogen atom, hydroxyl and methyl radicals, and water between 298.15 and 1500 K: A comparison of theoretical values against experimental data. *Nat. Prec.* **2010**. [[CrossRef](#)]