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# A NEW CORRELATION FOR SPECIFIC HEAT OF NORMAL ALKANES (C1-C30) AS A FUNCTION OF TEMPERATURE AND CARBON NUMBER

Ahmed Abdul Hussain Ayash

Lecturer, Materials Engineering Department, Mustansiriyah University, Baghdad, Iraq.

**Abstract:** the paper is about establishing a reliable correlation that can predict specific heat ($C_p$) of a series of normal alkanes over a wide range of temperatures. High quality experimental measurements reported in the relevant literature were used to verify the accuracy of the developed correlation, including data of heavy *n*-alkanes up to (*n*-$C_{30}H_{62}$). For a fair assessment, all the experimental data used were selected such that are measured at constant pressure. The developed correlation, for the first time, considers the effect of both temperature and carbon number for gas and liquid phase of normal alkanes, ranging from C1 to C30. Interestingly, the results showed that the correlation predicts closely the experimental data with an average relative error (AARE) not exceeding 3.63% for 97 data points.

**Keywords**: *General Correlation; n-alkanes; Specific Heat; Carbon Number.*

## 1. Introduction

The importance of the specific heat in chemical process design makes it one of the most measured transport properties. In gas and liquid phase chemical reactions, the heat capacity is required to determine the energy (heat) necessary to bring the chemical reactants up to reaction temperature. Additionally, the specific heat is a crucial property that uses heavily in design calculations many heat transfer equipment such heat exchanger, evaporators and humidifier. Knowledge of heat capacities is also required for evaluating the effect of temperature on phase and reaction equilibrium. Variations in heat capacities serve as a sensitive indicator of phase transitions and are an important tool for understanding changes in the structure of liquid solutions.

In petrochemical technology, n-alkanes are raw material and the end product of many processes. The processes involving n-alkanes are performed in the liquid and vapor phases.

A small variation in the process parameters (pressure and temperature) causes changes in the caloric properties (specific heat at constant pressure, enthalpy, entropy and heat of evaporation).

* *Corresponding Authors*: ahmedayash@uomustansiriyah.edu.iq

These changes can be one to two orders of magnitude, and that may affect immediately the economic performance of the process [1]. So, knowing the variations of the caloric properties, in particular the specific heat, can help to assess and improve the processing units of n-alkanes.

The determination of the specific heat of n-alkane is studied in Kuznetsov and Gorbachev [1]. However, the study is rather limited to a narrow section of n-alkane ($C_5$-$C_{11}$). Further, the developed correlations in the this study can only determine the $C_p$ values of the liquid and vapor branches of the boundary curve from the normal boiling point to $0.98T_c$. Perry and Green [2] also reported $C_p$ for pure compounds as a polynomial equation (first degree for some compounds and higher order for others). The authors give the temperature range, which starts from 273 K, the coefficients and the uncertainty of these equations. While the equations cover a good range of pure compounds, only few compounds of n-alkane are considered in this reference.

Different than the above studies, a study of two parts made by Palczewska-Tuliňska et al. [3, 4] compiled a massive data of specific heat of organic compounds in the condensed phase. The authors present data of 480 compounds (usually one or two sets of experimental data), giving altogether 610 data sets selected from about 350 literature references. Similarly, a good amount of data of n-alkanes specific heat values is reported in [5] and [6].

Here, a new correlation for estimating the specific heat of a wide range of n-alkanes is developed and compared to the data reported in [3-6]. As far as the author knows, a little amount of work has established a single correlation that can predict, comprehensively, $C_p$ values for a wide spectrum of organic compounds. It is believed that such correlation will be a useful, fast and reliable tool that helps design calculations of n-alkanes processing units.

## 2. Correlation Development

As discussed, a wider and more comprehensive temperature ranges were covered compared to those developed in Kuznetsov and Gorbachev [1] and Perry and Green [2]. As a main difference than these studies, the effect of carbon number was taken into account to reduce the error as less as possible. The correlation is developed based on precise experimental data of $C_p$ values of n-alkanes from methane ($CH_4$) to n-triacontane ($C_{30}H_{62}$) reported in [3-6]. The functional relationship between n-alkanes heat capacity of the above hydrocarbons and the temperature and the number of hydrocarbon atoms of each component) is expressed as:

$$C_p = (A_1 * C^{A2} * T^{A3})^{A4} * (B_1 + B_2 T) + D_1 + D_2 * (C/T) + D_3 * (C/T)^2 + D_4 * (C/T)^3 + D_5 C \qquad (1)$$

where $C_p$ is the heat capacity of n-alkane, kJ/kg.K, T the temperature, K, C number of carbon atoms of the n-alkane component and $A_1$, $A_2$, …… $D_5$ constants and are listed in Table 1.

Table 1. Constants proposed in Eq.1

| Constant | Value |
|---|---|
| $A_1$ | ß |
| $A_2$ | 0.3540 |
| $A_3$ | -0.0514 |
| $A_4$ | 0.8951 |
| $B_1$ | 8.6968 |
| $B_2$ | 0.0280 |
| $D_1$ | -8.5629 |
| $D_2$ | 127.9441 |
| $D_3$ | -1301.4800 |
| $D_4$ | 4852.7900 |
| $D_5$ | 0.0372 |

Temperature range application of the proposed formula (Eq.1) is shown in Table (2) for heat capacity prediction.

Table 2. Permitted temperature range of Eq.1.

| Component | Formula | Temperature Range, $^oC$ | |
|---|---|---|---|
| | | Minimum | Maximum |
| Methane | $CH_4$ | -260 | -165 |
| Ethane | $C_2H_6$ | -200 | -90 |
| Propane | $C_3H_8$ | -175 | -50 |
| n-Butane | $C_4H_{10}$ | -150 | -25 |
| n-Pentane | $C_5H_{12}$ | -100 | 25 |
| n-Hexane | $C_6H_{14}$ | -75 | 50 |
| n-Heptane | $C_7H_{16}$ | -50 | 75 |
| n-Octane | $C_8H_{18}$ | 0 | 125 |
| n-Nonan | $C_9H_{20}$ | 25 | 150 |
| n-Decan | $C_{10}H_{22}$ | 25 | 150 |
| n-Undecane | $C_{11}H_{24}$ | 25 | 150 |
| n-Dodecane | $C_{12}H_{26}$ | 25 | 150 |
| n-Tridecane | $C_{13}H_{28}$ | 25 | 150 |
| n-Tetradecane | $C_{14}H_{30}$ | 25 | 150 |
| n-Pentadecane | $C_{15}H_{32}$ | 25 | 150 |
| n-Hexadecane | $C_{16}H_{34}$ | 25 | 150 |
| n-Heptadecane | $C_{17}H_{36}$ | 25 | 150 |
| n-Octadecane | $C_{18}H_{38}$ | 25 | 150 |

| | | | |
|---|---|---|---|
| n-Nondecane | $C_{19}H_{40}$ | 25 | 150 |
| n-Eicosane | $C_{20}H_{42}$ | 25 | 150 |
| n-Heneicosane | C21H44 | 25 | 150 |
| n-Docosane | C22H46 | 0 | 125 |
| n-Trikosane | C23H48 | 0 | 125 |
| n-Tetracosane | C24H50 | 0 | 125 |
| n-Pentacosane | C25H52 | 0 | 125 |
| n-Hexeikosane | C26H54 | 0 | 125 |
| n-Heptacosane | C27H56 | 0 | 125 |
| n-Octacosane | C28H58 | 0 | 125 |
| n-Nonacosane | C29H60 | 0 | 125 |
| n-Triacontane | C30H62 | 0 | 125 |

Throughout the analysis of the results the following basic definitions have been used [7]:

$$\text{Absolute Error(AE)} = C_{p\,exp} - C_{p\,cal} \quad (2)$$

$$\text{Absolute Relative Error (ARE)} = \left| C_{p\,exp} - C_{p\,cal} \right| / \left| C_{p\,exp} \right| \quad (3)$$

$$\text{Average of Absolute Relative Errors (AARE)} = \sum (\text{ARE}) / \text{M} \quad (4)$$

where M is the number of data points in a given set of data and the average of absolute relative error = 3.63 % of 97 data points. Table (3) also demonstrates the percentage error between measured and calculated values of the heat capacity.

## 3. Results

Having established the correlation, now it can be examined by comparing its perditions against a range of experimental data. Table 3 shows the intended comparison and the error determined using Eq. 4.

Table 3. Comparisons of experimental and calculated values of specific heat

| Carbon number | T, K | measured mass heat capacity | Calculated mass heat capacity | %Error |
|---|---|---|---|---|
| 1 | 108.15 | 3.448188 | 3.258301 | 5.5 |
| | 98.15 | 3.385719 | 3.147037 | 7.0 |
| | 73.15 | 3.344568 | 2.982978 | 10.8 |
| | 48.15 | 3.460527 | 3.133786 | 9.4 |
| 2 | 183.15 | 2.345099 | 2.65536 | 13.2 |
| | 173.15 | 2.285442 | 2.543226 | 11.3 |
| | 148.15 | 2.173334 | 2.297046 | 5.7 |
| | 123.15 | 2.106288 | 2.118945 | 0.6 |
| | 98.15 | 2.084189 | 2.048087 | 1.7 |

| | | | | |
|---|---|---|---|---|
| | 73.15 | 2.119168 | 2.156335 | 1.8 |
| 3 | 223.15 | 2.129367 | 2.368448 | 11.2 |
| | 198.15 | 1.979083 | 2.139044 | 8.1 |
| | 173.15 | 1.849663 | 1.94816 | 5.3 |
| | 148.15 | 1.738067 | 1.810458 | 4.2 |
| | 123.15 | 1.645046 | 1.74812 | 6.3 |
| | 98.15 | 1.575667 | 1.794648 | 13.9 |
| 4 | 248.15 | 2.072113 | 2.196883 | 6.0 |
| | 223.15 | 1.922821 | 1.999971 | 4.0 |
| | 198.15 | 1.782404 | 1.834586 | 2.9 |
| | 173.15 | 1.649517 | 1.710283 | 3.7 |
| | 148.15 | 1.524545 | 1.640139 | 7.6 |
| | 123.15 | 1.409845 | 1.641468 | 16.4 |
| 5 | 298.15 | 2.268426 | 2.351039 | 3.6 |
| | 273.15 | 2.121976 | 2.151946 | 1.4 |
| | 248.15 | 1.983001 | 1.973618 | 0.5 |
| | 223.15 | 1.849292 | 1.821002 | 1.5 |
| | 198.15 | 1.719965 | 1.700468 | 1.1 |
| | 173.15 | 1.595152 | 1.620094 | 1.6 |
| 6 | 323.15 | 2.312609 | 2.356544 | 1.9 |
| | 298.15 | 2.172867 | 2.172015 | 0.0 |
| | 273.15 | 2.037789 | 2.005029 | 1.6 |
| | 248.15 | 1.90573 | 1.859145 | 2.4 |
| | 223.15 | 1.77594 | 1.738721 | 2.1 |
| | 198.15 | 1.648351 | 1.648967 | 0.0 |
| 7 | 348.15 | 2.392138 | 2.403986 | 0.5 |
| | 323.15 | 2.259291 | 2.229415 | 1.3 |
| | 298.15 | 2.129853 | 2.069725 | 2.8 |
| | 273.15 | 2.002407 | 1.927519 | 3.7 |
| | 248.15 | 1.876235 | 1.805858 | 3.8 |
| | 223.15 | 1.751132 | 1.708224 | 2.5 |
| 8 | 273.15 | 1.982651 | 1.891775 | 4.6 |
| | 298.15 | 2.11249 | 2.015073 | 4.6 |
| | 323.15 | 2.24199 | 2.155208 | 3.9 |
| | 348.15 | 2.371964 | 2.30998 | 2.6 |
| | 373.15 | 2.503829 | 2.477453 | 1.1 |
| | 398.15 | 2.640014 | 2.655954 | 0.6 |
| 9 | 323.15 | 2.212228 | 2.115513 | 4.4 |
| | 348.15 | 2.331455 | 2.254441 | 3.3 |
| | 373.15 | 2.451796 | 2.40575 | 1.9 |
| | 398.15 | 2.574537 | 2.567973 | 0.3 |
| | 423.15 | 2.701916 | 2.739815 | 1.4 |
| | 298.15 | 2.076671 | 1.985157 | 4.4 |
| 10 | 323.15 | 2.192400 | 2.098561 | 4.3 |
| | 348.15 | 2.307886 | 2.224976 | 3.6 |
| | 373.15 | 2.423569 | 2.363167 | 2.5 |
| | 398.15 | 2.540235 | 2.511928 | 1.1 |
| | 423.15 | 2.659212 | 2.670136 | 0.4 |
| | 298.15 | 2.07122 | 1.991535 | 3.8 |
| 11 | 323.15 | 2.184853 | 2.096525 | 4.0 |
| | 348.15 | 2.297853 | 2.21327 | 3.7 |

| | | | | |
|---|---|---|---|---|
| | 373.15 | 2.410486 | 2.340951 | 2.9 |
| | 398.15 | 2.523263 | 2.478653 | 1.8 |
| | 423.15 | 2.637045 | 2.625461 | 0.4 |
| | 298.15 | 2.053181 | 2.004819 | 2.4 |
| 12 | 323.15 | 2.165522 | 2.104056 | 2.8 |
| | 348.15 | 2.276869 | 2.213579 | 2.8 |
| | 373.15 | 2.38738 | 2.333002 | 2.3 |
| | 398.15 | 2.497394 | 2.461728 | 1.4 |
| | 423.15 | 2.607492 | 2.599068 | 0.3 |
| | 323.15 | 2.212228 | 2.115513 | 4.4 |
| 13 | 298.15 | 2.108 | 2.02169 | 4.1 |
| | 323.15 | 2.169247 | 2.117433 | 2.4 |
| | 348.15 | 2.278918 | 2.221844 | 2.5 |
| | 373.15 | 2.387518 | 2.33497 | 2.2 |
| | 398.15 | 2.495279 | 2.456538 | 1.6 |
| | 423.15 | 2.495279 | 2.586102 | 3.6 |
| 14 | 298.15 | 2.062767 | 2.039904 | 1.1 |
| | 323.15 | 2.172266 | 2.134053 | 1.8 |
| | 348.15 | 2.280501 | 2.235166 | 2.0 |
| | 373.15 | 2.387492 | 2.343699 | 1.8 |
| | 398.15 | 2.493389 | 2.459703 | 1.4 |
| | 423.15 | 2.598485 | 2.58298 | 0.6 |
| 15 | 298.15 | 2.050444 | 2.057974 | 0.4 |
| | 323.15 | 2.15942 | 2.152095 | 0.3 |
| | 348.15 | 2.266979 | 2.251454 | 0.7 |
| | 373.15 | 2.373113 | 2.356874 | 0.7 |
| | 398.15 | 2.477927 | 2.468714 | 0.4 |
| | 423.15 | 2.581648 | 2.587022 | 0.2 |
| 16 | 298.15 | 2.056703 | 2.07496 | 0.9 |
| | 323.15 | 2.164799 | 2.17031 | 0.3 |
| | 348.15 | 2.271439 | 2.26921 | 0.1 |
| | 373.15 | 2.376587 | 2.372791 | 0.2 |
| | 398.15 | 2.480314 | 2.48169 | 0.1 |
| | 423.15 | 2.582802 | 2.596193 | 0.5 |
| 17 | 298.15 | 2.036724 | 2.090331 | 2.6 |
| | 323.15 | 2.14472 | 2.187869 | 2.0 |
| | 348.15 | 2.251089 | 2.287372 | 1.6 |
| | 373.15 | 2.355777 | 2.390197 | 1.5 |
| | 398.15 | 2.458827 | 2.497221 | 1.6 |
| | 423.15 | 2.560369 | 2.608943 | 1.9 |
| 18 | 298.15 | 2.030981 | 2.103861 | 3.6 |
| | 323.15 | 2.13858 | 2.204261 | 3.1 |
| | 348.15 | 2.244482 | 2.305205 | 2.7 |
| | 373.15 | 2.348619 | 2.408179 | 2.5 |
| | 398.15 | 2.451011 | 2.514243 | 2.6 |
| | 423.15 | 2.551758 | 2.624085 | 2.8 |
| 19 | 298.15 | 2.023473 | 2.115559 | 4.6 |
| | 323.15 | 2.130751 | 2.219218 | 4.2 |
| | 348.15 | 2.236256 | 2.32223 | 3.8 |
| | 373.15 | 2.339912 | 2.426087 | 3.7 |
| | 398.15 | 2.441722 | 2.531968 | 3.7 |
| | 423.15 | 2.541765 | 2.640713 | 3.9 |

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|---|---|---|---|---|
| 20 | 298.15 | 2.041783 | 2.125618 | 4.1 |
| | 323.15 | 2.148717 | 2.232665 | 3.9 |
| | 348.15 | 2.253806 | 2.338165 | 3.7 |
| | 373.15 | 2.356954 | 2.443476 | 3.7 |
| | 398.15 | 2.458146 | 2.549818 | 3.7 |
| | 423.15 | 2.557441 | 2.658135 | 3.9 |
| 21 | 298.15 | 2.203569 | 2.134379 | 3.1 |
| | 323.15 | 2.303779 | 2.244678 | 2.6 |
| | 348.15 | 2.403317 | 2.352883 | 2.1 |
| | 373.15 | 2.501993 | 2.460061 | 1.7 |
| | 398.15 | 2.599696 | 2.56738 | 1.2 |
| | 423.15 | 2.696386 | 2.675837 | 0.7 |
| 22 | 273.15 | 2.106355 | 2.027906 | 3.7 |
| | 298.15 | 2.206826 | 2.142295 | 2.9 |
| | 323.15 | 2.306872 | 2.25545 | 2.2 |
| | 348.15 | 2.406204 | 2.366383 | 1.7 |
| | 373.15 | 2.504626 | 2.475688 | 1.2 |
| | 398.15 | 2.602019 | 2.584376 | 0.7 |
| 23 | 273.15 | 2.119711 | 2.03516 | 4.0 |
| | 298.15 | 2.21964 | 2.149917 | 3.1 |
| | 323.15 | 2.319168 | 2.265277 | 2.3 |
| | 348.15 | 2.417991 | 2.378765 | 1.6 |
| | 373.15 | 2.515902 | 2.490306 | 1.0 |
| | 398.15 | 2.612769 | 2.600638 | 0.5 |
| 24 | 273.15 | 2.13054 | 2.044571 | 4.0 |
| | 298.15 | 2.230115 | 2.157871 | 3.2 |
| | 323.15 | 2.329294 | 2.274531 | 2.4 |
| | 348.15 | 2.427763 | 2.390212 | 1.5 |
| | 373.15 | 2.525308 | 2.503951 | 0.8 |
| | 398.15 | 2.621788 | 2.616085 | 0.2 |
| 25 | 273.15 | 2.07152 | 2.057175 | 0.7 |
| | 298.15 | 2.173417 | 2.166847 | 0.3 |
| | 323.15 | 2.274566 | 2.283651 | 0.4 |
| | 348.15 | 2.374705 | 2.400975 | 1.1 |
| | 373.15 | 2.473653 | 2.516729 | 1.7 |
| | 398.15 | 2.571294 | 2.630707 | 2.3 |
| 26 | 273.15 | 2.146705 | 2.074058 | 3.4 |
| | 298.15 | 2.245739 | 2.177589 | 3.0 |
| | 323.15 | 2.344375 | 2.293131 | 2.2 |
| | 348.15 | 2.442289 | 2.411361 | 1.3 |
| | 373.15 | 2.539252 | 2.528806 | 0.4 |
| | 273.15 | 2.146705 | 2.074058 | 3.4 |
| 27 | 273.15 | 2.161466 | 2.096349 | 3.0 |
| | 298.15 | 2.259956 | 2.190883 | 3.1 |
| | 323.15 | 2.358089 | 2.303511 | 2.3 |
| | 348.15 | 2.455526 | 2.421726 | 1.4 |
| | 373.15 | 2.552029 | 2.540396 | 0.5 |
| | 398.15 | 2.647434 | 2.657742 | 0.4 |

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|---|---|---|---|---|
| 28 | 273.15 | 2.160886 | 2.125212 | 1.7 |
| | 298.15 | 2.259368 | 2.207554 | 2.3 |
| | 323.15 | 2.357458 | 2.315369 | 1.8 |
| | 348.15 | 2.45482 | 2.432466 | 0.9 |
| | 373.15 | 2.551215 | 2.551753 | 0.0 |
| | 398.15 | 2.646477 | 2.670404 | 0.9 |
| 29 | 273.15 | 2.163841 | 2.161844 | 0.1 |
| | 298.15 | 2.262352 | 2.228458 | 1.5 |
| | 323.15 | 2.36045 | 2.329318 | 1.3 |
| | 348.15 | 2.457796 | 2.44401 | 0.6 |
| | 373.15 | 2.554151 | 2.56317 | 0.4 |
| | 398.15 | 2.649345 | 2.682729 | 1.3 |
| 30 | 273.15 | 2.033844 | 2.207465 | 8.5 |
| | 298.15 | 2.137444 | 2.254478 | 5.5 |
| | 323.15 | 2.239907 | 2.345996 | 4.7 |
| | 348.15 | 2.341008 | 2.456817 | 4.9 |
| | 373.15 | 2.440587 | 2.574967 | 5.5 |
| | 398.15 | 2.538532 | 2.694928 | 6.2 |

## 4. Conclusions

The proposed correlation is excellent and dependable with average absolute relative error (AARE) of 3.63% for 97 data points. Accordingly, this result suggests that the correlation can be used in various engineering calculations which require a precise value of specific heat for liquid and gas phase components of pure alkanes at a specific temperature range. However, the user of this correlation must take into account two important aspects. First, the unit of temperature is in Kelvin scale. Second, the unit of the obtained specific heat is kJ/kg.k.

## 5. References


1. Kuznetsov M. A. and Gorbachev A. S., (2005) "*Determination of the specific heat of the normal alkanes $C_7$-$C_{11}$*" ,Theoretical foundations of chemical engineering , vol.39,no.4,pp.450-454.
2. Perry, R.H. and D.W. Green, (1997) "*Perry's Chemical Engineer's Handbook*", 7th ed., McGraw-Hill, New York.
3. M.Palczewska-Tulinska, D.Wyrzykowska-Stankiewicz, A.M.Szafranski,J.Cholinski, , (1997) "*Solid and Liquid Heat Capacity Data Collection, Part 2: $C_1$-$C_6$*" ,Dechema, Chem.Technik und Biotechnologie e.V., Frankfurt am Main.
4. M.Palczewska-Tulinska, D.Wyrzykowska-Stankiewicz, A.M.Szafranski, J.Cholinski, (1997). "*Solid and Liquid Heat Capacity Data Collection, Part 1:$C_1$-$C_6$*" ,Dechema, Chem.Technik und Biotechnologie e.V., Frankfurt am Main,
5. Reid R. C., J. M. Prausnitz, and T. K. Sherwood, (1977) "*The Properties of Gases and Liquids*", 3rd ed. (McGraw-Hill, New York).

6. Robert A. Alberty and Catherine A. Gehrig, (1984) "*standard chemical thermodynamic properties of alkane isomer groups*", J. Phys. Chem. Ref. Data, vol. 13, No. 4.
7. S.I. Abu-Eishah, Y.Haddad, A. Solieman et al. (2004) "*A new correlation for the specific heat of metals, metal oxides and metal fluorides as a function of temperature*" , Latin American Applied Research ,34; 257-265