



An exponential expression for gas heat capacity, enthalpy, and entropy



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ABSTRACT

Gas heat capacity, C_p , is a fundamental extensive thermodynamic property depending on molecular transitional, vibrational and rotational energy. Empirical four-parameter polynomials approximate the sigmoidal C_p trends for temperatures up to 1500 K and adding parameters extends the range. However, the fitted parameters have no physical significance and diverge beyond their range at high temperature. Here we propose an exponential expression for C_p whose fitted parameters relate to the shape of the C_p versus T curve and to molecular properties: $C_p = C_p^0 + C_p^\infty [1 + \ln(\mathcal{T})(1 + T_i/T)] \exp(-T_i/T)$. It accounts for more than 99% of the variance with a deviation of $\sim 1\%$ from 298 K to 6000 K for linear C_1 – C_7 hydrocarbons and N_2 , H_2O , O_2 , C_2H_4 , H_2 , CO , and CO_2 . We also provide an integrated form for enthalpy and an approximation to calculate entropy variations. This model replaces empirical polynomials with an expression whose constants are meaningful.

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1. Introduction

Heat capacity (C_p) is a critical property in thermodynamics spanning diverse fields related to states and phase transitions [1,2], heat transfer [3], spin measurements [4,5] or materials characterization [6,7]. The Dulong-Petit law [8] accounts for heat capacity of metals. Neglecting vibrational and rotational energies, heat capacity for ideal monoatomic gases is related to translational kinetic energy only [9] (3 degrees of freedom) and the molar

isobaric heat capacities are thus equal to $5/2 R$. Theories for polyatomic gases poorly accounts for the variation of isobaric heat capacity with temperature. Textbooks [10,11] and specialized literature [12] report polynomial expressions that depend uniquely on the temperature (T). However, these expressions are valid over limited temperature ranges and deviate considerably for plasma applications [13] and adiabatic flames that can exceed 5000 K [14] (Fig. 1). NASA proposed a two range 5-term polynomial model [12] (200–1000 K and 1000–6000 K) to address the high temperature limitations (a total of 10 fitted parameters).

Our model characterizes C_p at very high temperatures whereas standard polynomials deviate beyond the specified temperature ranges (Reid et al. [10] and Yaws et al. [11]). The NASA 5-parameter model [12] deviates much less from the experimental C_p than the other polynomial models.

Models that approximate thermodynamic properties must meet several criteria [15,16]: all predicted values should be physically valid, and accurate over a wide range ($\sim 1\%$ average absolute deviation, AAD), the function should be integratable (to calculate changes in enthalpy, ΔH and entropy, ΔS), parsimonious (minimum number of parameters), and suitable for extrapolation. Among the non-polynomial models [17–19], Yuan and Mok [20] (1968) proposed a 4-parameter exponential expression:

$$C_p(T) = A + B \exp\left(-\frac{C}{T^n}\right) \quad (1)$$

It fits polyatomic experimental data better than 5-parameter polynomials but relies on the exponential integral (Ei) to account

Abbreviations: ΔG , Gibbs free energy variation ($J mol^{-1}$); ΔH , enthalpy variation ($J mol^{-1}$); ΔS , entropy variation ($J mol^{-1} K^{-1}$); ϵ , empirical coefficient defined in Eq. (8); a , b , empirical coefficients defined in Eq. (3) ($J mol^{-1} K^{-1}$); A , B , C , n , empirical coefficients defined in Eq. (1); A_0 , B_1 , C_1 , n_1 , B_2 , C_2 , n_2 , empirical coefficients defined in Eq. (2); AAD, Absolute Average Deviation (%); C_p , heat capacity ($J mol^{-1} K^{-1}$); C_p^0 , empirical coefficient defined in Eq. (5) ($J mol^{-1} K^{-1}$); C_p^∞ , empirical coefficient defined in Eq. (5) ($J mol^{-1} K^{-1}$); D , deviance, sum of the squared differences between predicted and experimental values; Dev_i , deviation (%) between the i th experimental value and the i th predicted value; Ei , exponential integral; f , f_i , y_i , n , parameters defined in Eq. (7); n_A , number of atoms in a molecule; R , gas constant; R^2 , correlation coefficient; Res_i , residue of the fitting for the i th experimental value; S , S° , entropy ($J mol^{-1} K^{-1}$); S_0 , empirical coefficient defined in Eq. (11) ($J mol^{-1} K^{-1}$); S_0° , empirical coefficient defined in Eq. (13) ($J mol^{-1} K^{-1}$); T , temperature (K); \mathcal{T} , dimensionless temperature expressed in Kelvin, $\mathcal{T} = T/(1 K)$; T_i , empirical coefficient linked with $T_{inflexion}$ and defined in Eqs. (3)–(5) (K); $T_{inflexion}$, temperature of inflection of the C_p curve's model (K).

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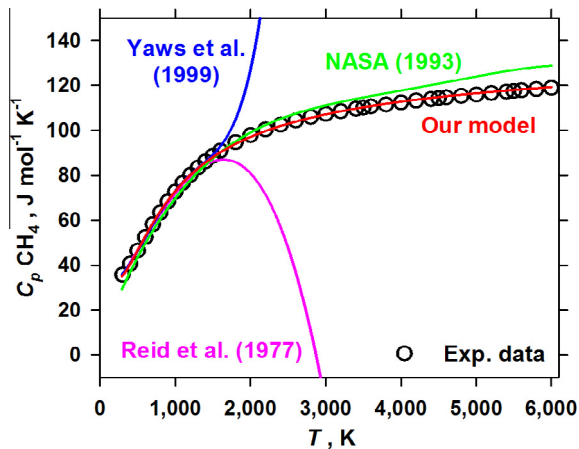


Fig. 1. Experimental methane heat capacity compared to model predictions from 298 K to 6000 K.

for ΔH and ΔS as a function of the temperature. The model accounts for over 99.5% of the experimental C_p , even up to 6000 K (SI Table 1) but it tends toward a finite asymptote while the experimental values continue to increase. Furthermore, there is no coherent relationship between the 4 constants and molecular properties. Thinh et al. [21] expanded the exponential model to a 7-parameter group additive correlation:

$$C_p^*(T) = A_0 + B_1 \exp\left(-\frac{C_1}{T^{n_1}}\right) - B_2 \exp\left(-\frac{C_2}{T^{n_2}}\right) \quad (2)$$

The number of parameters increases with the complexity of the molecule and can reach dozens of terms. Group additive correlations are often the most accurate [10,22] but also the most complex to handle [21,23–25]. Thinh et al. further developed additive models to calculate enthalpy, entropy and Gibbs free energy [26,27]. These correlations are accurate but cumbersome to implement because of the large number of parameters (not parsimonious). They are necessary for applications for which experimental heat capacity is nonexistent, sparse (as for polycyclic aromatic hydrocarbons) or for computed assisted engineering and modeling. (The thermodynamic package Factsage™ relies on up to 16 parameters to approximate gas C_p between 298.15 K and 6000 K). Textbooks and handbooks [10,11] thus still report 4 to 5-term polynomials applicable over a narrower temperature-range that have no physical meaning.

2. Mathematical formulation of the C_p model

To reduce the empiricism of the polynomial models and account for the increase in C_p above 3000 K, we modified the Yuan and Mok model with an expression that, contrary to Thinh et al. correlations, maintains its simplicity and can be integrated to calculate ΔH .

We fit Eq. (1) to the C_p of linear hydrocarbons (C_1 – C_7), O_2 , H_2O , H_2 , CO_2 , CO , N_2 , and ethylene (gas). All data we retrieved from the literature [28–30] and are either purely experimental [28,30] or interpolated [29]. With an exponential value of $n = 1$, we accounted for more than 99.6% of the variance in the data, which is as good as the fitting reported by Yuan and Mok [20]. Consequently, we integrated these expressions numerically to generate enthalpy as a function of temperature and fit the enthalpy with

$$H^*(T) = aT + bT \ln(T) \exp(-T_i/T) \quad (3)$$

This expression accounts for more than 99% of the variance in the integrated C_p where a , b and T_i are fitted parameters. Differentiating $H^*(T)$ gives:

$$C_p(T) = \frac{dH^*}{dT} = a + b \left[1 + \ln(T) \left(1 + \frac{T_i}{T} \right) \right] \exp\left(-\frac{T_i}{T}\right) \quad (4)$$

where the upper and lower bounds are $\lim_{T \rightarrow 0K} C_p(T) = a = C_p^0$ and $\lim_{T \rightarrow \infty K} C_p(T) = \lim_{T \rightarrow \infty K} b \ln(T) = \lim_{T \rightarrow \infty K} C_p^\infty \ln(T) = +\infty$. Physically, the parameters C_p^0 ($=a$) and C_p^∞ ($=b$), both in $J \text{ mol}^{-1} \text{ K}^{-1}$, are thus respectively the limit of C_p at low temperature and the growing rate of C_p at high temperature, while T_i , in K, is a temperature related with the inflection point of the sigmoid and thus with the transition between low and high C_p values. The inflection of a curve is mathematically defined as the point where the second derivative is null while its third derivative is different than zero. It happens for the C_p model in $T_{\text{inflection}} = T_i (0.353 + 0.234/T_i^{0.384})$ where $T_{\text{inflection}}$ and T_i are both in K (R^2 above 0.999). This expression comes from the resolution of the non-linear equation $(d^2C_p/dT^2)=0$ (Fig. 2).

Replacing a and b with these limiting factors gives:

$$C_p(T) = C_p^0 + C_p^\infty \left[1 + \ln(T) \left(1 + \frac{T_i}{T} \right) \right] \exp\left(-\frac{T_i}{T}\right) \quad (5)$$

$$\Delta H_{T_1 \rightarrow T_2} = \left[C_p^0 T + C_p^\infty T \ln(T) \exp\left(-\frac{T_i}{T}\right) \right]_{T_1}^{T_2} \quad (6)$$

3. Methods

Models were fitted to experimental data based on a Marquardt–Levenberg algorithm [31] to minimize the sum of the squared differences (deviance D) between the experimental data and the predicted values:

$$D = \sum_{i=1}^n (f_i - y_i)^2 \quad (7)$$

where n and y_i are the number and the values of experimental data and f_i values predicted by the model.

$$\text{Res}_i = f_i - y_i \quad (8)$$

The deviation Dev_i between a prediction and an experimental value, in %, is calculated from the residues Res_i :

$$\text{Dev}_i = 100 \text{Res}_i / y_i = 100(f_i - y_i) / y_i \quad (9)$$

The average absolute deviation, AAD, is the average of the absolute values of Dev_i , it is a measure of the average deviation a user can expect from the fitted expression:

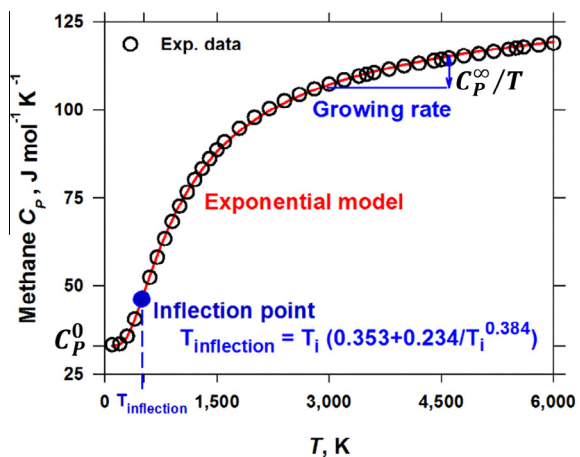


Fig. 2. Methane model parameters deduced from experimental data: $C_p^0 \sim 8/2 R$, C_p^∞ accounts for the growing rate of C_p at high temperature, and T_i relates to the inflection point of the curve $T_{\text{inflection}}$.

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