



NASA Polynomial representation of molecular specific heats

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ABSTRACT

So called NASA polynomials are widely used in plasma and combustion models to represent the specific heat of molecules as a function of temperature. In this work, we compute seven-term NASA polynomials for 464 molecules of which 44 are cations and 9 are anions; polynomials are not currently available for almost 200 of these species. Calculation of the NASA polynomials utilises data provided by the ExoMol database, the HITRAN database, the diatomic partition functions computed by Barklem and Collet, and the JANAF thermodynamic tables. Our results are compared against existing polynomial compilations where available, and for cases where there are multiple datasets the recommended polynomials are identified. As proposed in the original compilation, the seven-term polynomials are fitted separately for the temperature ranges 200 – 1000 K and 1000 – 6000 K. In general, different data sources give good agreement in the lower temperature range but there are significant discrepancies at higher temperatures, which can be attributed to the underlying assumptions made about highly excited rotation-vibration energy levels.

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1. Introduction

The varied ability of a species to absorb heat is characterised by its specific heat. This property is important in many areas of chemistry, physics, and engineering such as combustion, [1–6] plasma modelling, [7–9] and atmospheric processes [10–12]. In these environments the temperature-dependent specific heat at constant pressure, $C_p(T)$, is the key parameter. As discussed below, the NASA polynomial representation can be extended to also represent temperature-dependent entropy, $S^0(T)$, and enthalpy of formation, $\Delta_f H^0$.

Over the years workers at NASA developed a compact representation of $C_p(T)$ in terms of polynomials generally known as NASA polynomials. In particular the NASA Glenn Thermodynamic database [13] provides comprehensive sets of NASA polynomials. Before NASA polynomials, all properties of individual species were stored in tables. McBride and Gordon consolidated and documented the computer codes used in calculating and fitting thermodynamic data into a single FORTRAN IV code, called PAC (Properties and Coefficients) [14,15]. There is a preference for thermodynamic data in the provided functional form, especially in computerised form. Storing the data in polynomial format saves memory storage and allows for the thermodynamic properties to be calculated at any temperature. Additionally, polynomial representation

of the heat capacity allows for the calculation of other thermodynamic quantities through simple integration [13].

Initially, NASA Glenn (then Lewis) Research Centre needed to obtain thermodynamic data for products of rocket combustion [16]. In 1950, Gordon et al. [17] published tables containing thermodynamic functions for 42 substances in the temperature range 300 – 6000 K based on various sources. An efficient solution to obtaining thermodynamic data was introduced in 1961, when Zeleznik and Gordon presented a simultaneous least squares fitting of thermodynamic functions, namely the heat capacity, enthalpy, and entropy to empirical formulas, such that a single set of coefficients to a seven-term polynomial was obtained [18]. Ehlers et al. [19] wrote a computer program PAC1, which provided a means to generate thermodynamic functions from molecular data and a least squares fit of these functions to empirical equations. A set of five temperature coefficients was generated for fixed temperature ranges, as a single polynomial could not be fit for the full temperature range up to 6000 K. Instead, one range was dedicated to temperatures of 298.15 – 1000 K, and one to temperatures of 1000 – 6000 K, meaning the polynomial was ‘pinned’ at 1000 K [16]. A library of NASA coefficients was not published until 1993, when seven-term polynomials were also introduced [20]. These five or seven coefficient polynomial fits are often referred to as NASA polynomials, although we note that the seven-term representations, which we define below and adopt here, are not strictly polynomials.

The latest available report, NASA Glenn Coefficients for Calculating Thermodynamic Properties of Individual Species [13] forms the

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starting point for this work. The work at NASA effectively stopped twenty years ago with this report. Since then, in 2005, Burcat and Ruscic created an extended database named Third Millennium Thermodynamic Database [21]. The most recent compilation comes from ESA (the European Space Agency) who produced relatively accurate NASA polynomials for the Mars-atmosphere [10] and Jupiter-atmosphere [12] molecules in 2005 and 2009, respectively. Despite this, the number of species studied in this database are small. Moreover, although accurate thermodynamic data has been published as part of dedicated studies of key species such as water [22–25], C_2 [26], HCN [27], ammonia [28] and phosphine [28], these results are generally stored in tables rather than the polynomial format. Finally, Colonna and co-workers [29,30] have proposed simplified expressions for the thermodynamic properties of atoms and molecules based on the use of a small number of parameters

In the published NASA Glenn database (2002), [13] NASA polynomial coefficients are available for 1140 gaseous species (including electron gas). Other databases that provide data in NASA polynomial format (Burcat, [21] GRI-MECH, [1,31]) largely give coefficients already published by NASA. However, some new polynomials have been calculated since the last NASA compilation. In particular, Burcat published new NASA polynomials for some species that had been calculated using PAC, including but not limited to cellulose nitrate in 2020, [32] 20 carbon oxonium cations in 2016, [33] and several phosphorus species [34]. Goos and Burcat [35] also introduced a method to include better enthalpies of formation into PAC calculations. The method allows the use of updated enthalpy of formation values without changing the other already available thermodynamic data. A similar database to that of NASA Glenn is IVTANTHERMO, [36] a Russian thermodynamic database based on Gurvich's Thermodynamic Properties of Individual Substances. As of 2018, this database contains more than 3400 substances made of 96 chemical elements [36]. It is said that the characteristic feature of the database is that it does not borrow information, but rather obtains it by critically analysing data available in the literature [36].

There are a number of reasons for re-visiting this problem. Firstly, there are many species for which there are no NASA polynomials available. Secondly, significant improvements in the underlying available data, particularly partition functions, suggests that it is possible to vastly improve the accuracy for many of the polynomials. In particular, the earlier treatments of properties at higher temperatures often relied on simplified assumptions such as straight line extrapolations or the harmonic oscillator approximation, which does not account for molecular dissociation; Vidler and Tennyson considered these issues in detail for water [23].

In this work, we provide new NASA polynomials for 464 molecules of varying size. To do this we use four different data sets as starting points for generating the polynomials: (a) the extensive sets of energy levels and partition functions provided for hot molecules by the ExoMol project, [37] (b) the so-called total internal partition sums (TIPS) provided by the HITRAN atmospheric database [38–40], (c) the diatomic partition functions provided by Barklem and Collet (BC) [41], and (d) by fitting directly to the specific heats given as part of the JANAF database [42]. The polynomials we generate are considered alongside those already available from NASA [13] and the Burcat database [21,33]. We also consider a number of key molecules for which recent studies of the partition functions are available. For the many species where this approach provides more than one set of polynomials, we recommend the NASA polynomial that we consider the most reliable due to the quality of the underlying molecular data. While Marzouk [43] performed an inter-comparison of the shorter five-term NASA polynomials; we are unaware of a similar study for the more accurate seven-term polynomials which we consider here.

2. Methodology

Although older variations of the NASA polynomials used lower-order polynomials, here we concentrate on the so-called seven-term polynomials which are the most recent and most widely available form. In this representation the specific heat is given by seven polynomial coefficients a_i , $i = 1, 7$:

$$\frac{C_p(T)}{R} = \frac{a_1}{T^2} + \frac{a_2}{T} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4, \quad (1)$$

where R is the ideal gas constant. These formula are considered valid in the range $200 \leq T \leq 6000$ K; although in most applications, including ours, this temperature range is split in to two with separate coefficients being provided for $200 \leq T \leq 1000$ K and $1000 \leq T \leq 6000$ K.

The coefficients can also be used to represent the temperature dependence of the enthalpy of formation:

$$\frac{\Delta_f H^0}{RT} = -\frac{a_1}{T^2} + a_2 \frac{\ln T}{T} + a_3 + \frac{a_4}{2}T + \frac{a_5}{3}T^2 + \frac{a_6}{4}T^3 + \frac{a_7}{5}T^4 + \frac{b_1}{T} \quad (2)$$

and entropy

$$\frac{S^0}{RT} = -\frac{a_1}{T^2} - \frac{a_2}{T} + a_3 \ln T + a_4T + \frac{a_5}{2}T^2 + \frac{a_6}{3}T^3 + \frac{a_7}{4}T^4 + b_2 \quad (3)$$

although in each case an extra coefficient, b_1 and b_2 respectively, are required; these terms arise as constants of integration and require further information to characterise them.

2.1. Internal partition and thermodynamic functions

Direct experimental measurement of thermodynamic properties, such as the heat capacity, is difficult. However, they can be expressed in terms of the partition function, $Q(T)$, which in turn can be calculated from spectroscopic data. For an ideal gas, translational and internal energy are independent of each other. Thus, the partition function can be separated into a translational partition function, Q_{trans} , and an internal partition function, Q_{int} . Within the assumption of an ideal gas, the translation part simply leads to a contribution to the specific heat of $\frac{5}{2}R$, so below we simply consider the contribution of Q_{int} .

In general the internal partition function can be written as:

$$Q_{\text{int}} = \sum_i g_i (2J_i + 1) \exp\left(-\frac{E_i}{kT}\right) \quad (4)$$

where k is Boltzmann's constant and J_i is the rotational quantum number of the state; g_i and E_i are the nuclear spin statistical weight and internal energy, respectively, and i runs over bound states of the molecule. In general we take this sum as running over all rotation, vibration and electronic (rovibronic) states of the molecule lying below dissociation. This therefore accounts for effects due to fine structure etc but not the differences in energy between hyperfine components which are allowed for via the nuclear spin statistical weight, g_i . In practice, while electronically excited states are considered for most diatomic molecules we study, for most polyatomics it is assumed that all electronically excited states lie above the dissociation limit or do not contribute significantly to the partition sum so that the summation only runs over the many bound rotation-vibration states in these systems. Unlike atoms, molecules generally only support a finite number of bound states meaning that these partition sums are convergent.

When considering partition functions below we neglect any contribution of quasibound states as the contribution of these states is generally small, although there are exceptions [44]. We note that some compilations, such as the ESA consider the influence of quasibound states for the strongly bound CO and CN

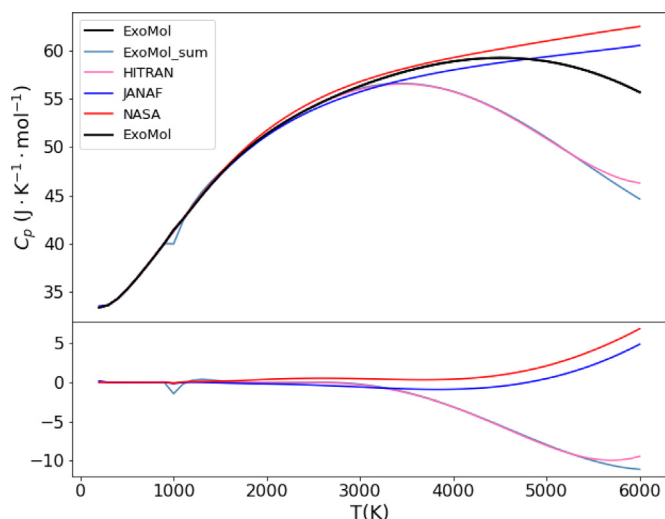


Fig. 1. Comparison of NASA polynomial representations of $C_p(T)$ for H_2^{16}O . The lower panel shows the differences to our recommended polynomials which are based on data from the ExoMol database.

molecules [10]. To remain self-consistent we follow the HITRAN and ExoMol convention of using partition functions which include the full nuclear spin degeneracy; astronomers such as Barklem and Collet [41] generally use a reduced convention. Use of either convention consistently should give the correct specific heat but the astronomers convention will not give the correct entropy.

We test two methods of calculating the temperature-dependent specific heat. Martin et al. [45] provide the theoretical framework for calculating thermodynamic properties based on molecular energy levels. They define the following functions:

$$Q' = T \frac{dQ}{dT} \quad (5)$$

$$Q'' = T^2 \frac{d^2Q}{dT^2} \quad (6)$$

which can be used to compute

$$C_p(T) = R \left[\frac{Q''}{Q} - \left(\frac{Q'}{Q} \right)^2 \right] \quad (7)$$

In practice this can be done in two ways: (1) by numerical differentiation of the partition function as a function of T or (2) by differentiation of Eq. 4 and then summation of the energy levels [45]. We test both methods below for ExoMol data where we have access to both the complete set of energy levels and the partition functions.

Having obtained $C_p(T)$ we then performed least square fits to obtain NASA polynomials. As recommended by the most recent NASA release [13] this was done in two temperature ranges $200 \leq T \leq 1000$ K and $1000 \leq T \leq 6000$ K. In some cases the data generated did not reliably cover the entire range 200 to 6000 K, in which case fits were performed over the reduced range but polynomials are still provided for the two regions. Fitting was actually performed for the functions $T^2 C_p(T)$ as this is a simple polynomial function unlike the actual NASA polynomials. The fitting in two ranges can lead to issues of continuity at 1000 K which for some NASA fits was avoided by "pinning" the fits at this point. We chose not to use this technique and did encounter occasional discontinuities at 1000 K, see for example the ExoMol_sum fit for water shown in Fig. 1 below. However, our recommended fits do not suffer from this problem.

2.2. Data sources

Our work is based on the use of four main data sources.

ExoMol: The ExoMol project [46] provides high-resolution spectroscopic data for molecules found in hot astronomical environments. ExoMol calculates extensive molecular line lists using a mixture of first principles quantum mechanical methods and fine-tuning to empirical data, producing both partition functions and comprehensive lists of energy levels in the so-called States file [47]. At the time of this work the ExoMol database [37] contained extensive line lists for 85 molecules. ExoMol provides line lists for many isotopologues; however in this work we only considered data for the main (parent) isotopologue and used data from the recommended (generally the most recent) line list for each molecule. While the line lists all cover extended temperatures ranges, the actual upper temperature (T_{max}), which is specified for each line list, varies between line lists but only reaches 6000 K for a few diatomic species.

HITRAN is a compilation of spectroscopic parameters that can be used to predict and simulate the transmission and emission of light in the atmosphere of the Earth; data is largely limited to terrestrial temperatures. The latest release, HITRAN2020 [48], provides state resolved data for 57 molecules and 181 isotopologues. Partition functions are provided as separate downloadable files [38,39] with relatively high T_{max} , in part because they are also used by the HITEMP database [49,50]. Again only data from the parent isotopologue was considered here.

BC: Barklem and Collet [41] provide partition functions for 291 diatomic molecules constructed using the relatively old experimental data compiled by Huber and Herzberg [51] with updated zero-point energies from Irikura [52]. BC partition functions are provided on a non-uniform grid of 42 points extending up to 10 000 K for all species. However, only 13 of these grid points lie in the range 200 – 6000 K which is of interest to us, including both 200 K and 6000 K. We followed BC's recommendation and used cubic splines to interpolate between these points.

JANAF: The JANAF Thermochemical Tables were released and updated in a series of publications up to about 20 years ago [42,53,54] with the main source considered here being the 1998 release [42]. JANAF provides tabulated values of $C_p(T)$, $S^0(T)$ and $\Delta_f H^0(T)$ on a uniform grid of temperatures in 100 K steps up to 6000 K. In this work we fitted $C_p(T)$ using NASA polynomials.

The results we obtained using these sources are compared below with those provided by the 2002 release of the NASA Glenn database, [13] and the compilations of Burcat, [21,33] and ESA [10,12].

3. Results

In total, the sources specified above enabled the determination of NASA polynomials for 464 molecules of which 44 are cations and 9 are anions; for 197 of these species there are no seven-term NASA polynomials currently available. Table 1 lists the molecules we consider and specifies the data source that was used to determine the NASA polynomials, or for the NASA Glenn and Burcat compilations, where the compilations were obtained. In the supporting material we provide a spreadsheet giving the new NASA polynomials for the molecules in the table and plots of $C_p(T)$ versus T , which compares NASA polynomials for each source. A separate spreadsheet containing only the recommended NASA polynomials, as indicated for each molecule in Table 1, is also provided.

Considering now each data source:

ExoMol: the underlying energy levels as well as temperature-dependent partition functions are available in the ExoMol database [37,55]. This allowed us to compute $C_p(T)$ by direct summation of the energy levels using Eq. (7), which we call ExoMol_sum be-

Table 1

Summary of NASA polynomials generated in this work (columns BC, ExoMol and JANAF) and previously available (columns NASA, Burcat and other). Recommended polynomials are denoted by ✓ and other available polynomials by x; (✓) is used to signify cases for which our recommendation is only tentative. See text for details of the data sources.

species	BC	ExoMol	HITRAN	JANAF	NASA	Burcat	Other
AgCl	✓						
AgF	✓						
AgH	✓						
Al ₂	✓						
AlC				✓			
AlCl	✓						
AlF	✓						
AlH	x	✓					
AlH ⁺	✓						
AlN	✓						
AlO	x	✓					
AlS	✓						
AlSe	✓						
As ₂	✓						
AsCl	✓						
AsF	✓						
AsH	✓						
AsH ₃		✓					
AsN	✓						
AsO	✓						
AsO ⁺	✓						
AsP	✓						
AsS	✓						
AuCl	✓						
AuH	✓						
B ₂	x				(✓)		
BC				x	(✓)		
BCl	x				(✓)		
BF	x				(✓)		
BH	x				(✓)		
BN	x				(✓)		
BO	x				(✓)		
BO ⁺	✓						
BS	x				(✓)		
BaCl	x				(✓)		
BaF	x				(✓)		
BaH	x				(✓)		
BaO	x				(✓)		
BaS	x				(✓)		
BeC ₂				✓			
BeCl	x				(✓)		
BeF	x				(✓)		
BeH	x	✓			x		
BeH ⁺	✓						
BeO	x				(✓)		
BeS	x				(✓)		
BiH	✓						
BiO	(✓)					x	
BiS	✓						
BrCN				(✓)		x	
BrCl	x				(✓)		
BrF	x				(✓)		
BrO	x				✓	x	
C ₂	x	✓		x	x	x	x[26]
C ₂ ⁺	✓						
C ₂ ⁻	x			x	(✓)	x	ESA
C ₂ Cl ₂				x	✓		
C ₂ Cl ₄				x	✓		
C ₂ Cl ₆				x	✓		
C ₂ F ₂				x	✓	x	
C ₂ F ₄				x	✓	x	
C ₂ F ₆				x	✓	x	
C ₂ H				x	✓	x	
C ₂ H ₂		x	x	✓		x	
C ₂ H ₄		x	✓	x			
				x		✓	
C ₂ H ₄ O							
C ₂ H ₆			✓	x			
C ₂ HCl				x	✓	x	
C ₂ HF				x	✓	x	

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Table 1 (continued)

species	BC	ExoMol	HITRAN	JANAF	NASA	Burcat	Other
C ₂ N				(✓)		x	
C ₂ N ₂			✓		x	x	
C ₂ O				x	✓	x	
C ₃				x	✓	x	ESA
C ₃ H ₄			✓			x	
C ₃ O ₂				x	✓	x	
C ₄				x	(✓)	x	
C ₄ H ₂			x		✓	x	
C ₄ N ₂				x	✓		
C ₅				x	(✓)	x	
CBr	x			x	✓	x	
CBr ₄				x	✓	x	
CBrF ₃				✓		x	
CCl	✓		x	x			
CCl ₂				x	(✓)		
				✓			
CCl ₂ F ₂							
CCl ₃				x	(✓)		
CCl ₃ F				✓		x	
CCl ₄				x	✓		
CClF ₃				✓			
CF	x			✓	x		
CF ₂				x	✓	x	
CF ₃				x	✓		
				✓			
CF ₃ CN				✓			
CF ₃ OF				✓			
				✓			
CF ₃ SF ₅							
CF ₄			x	x	✓		
CH	✓			x	x	x	
CH ⁺	✓						
CH ⁻	✓						
CH ₂				x	✓	x	
					✓		
CH ₂ Cl ₂				✓			
CH ₂ ClF				✓	x		
CH ₂ F ₂							
CH ₃		x	x	x	✓	x	
			x		✓	x	
CH ₃ Br			x		✓	x	
CH ₃ CN							
CH ₃ Cl		x	x	x	✓		
CH ₃ F		x	✓	x	x	x	
CH ₃ I			✓			x	
			✓		x	x	
CH ₃ OH							
CH ₄		x	x	x	✓		
				✓			
CHCl ₂ F							
CHCl ₃				x	✓	x	
				✓			
CHClF ₂							
CHF				x	(✓)	x	
CHF ₃				✓	x	x	
CHP				✓		x	
ClF ₃				✓			
CN	x		x	x	✓	x	ESA
CN ⁺	✓						
CN ⁻	✓						
(CN) ₂				✓			
CNI				✓			
CNN				✓	x	x	
CO	x		x	x	✓		ESA
CO ⁺	✓						
CO ₂		x	x	✓	x	x	ESA
CO ₂ ⁻				✓		x	
COCl				✓	x		
COCl ₂			x	x	✓		
COCIF				✓			

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Table 1 (continued)

species	BC	ExoMol	HITRAN	JANAF	NASA	Burcat	Other
COF				✓	x		
COF ₂			✓	x	x	x	
COS				✓	x		
CP	✓			x	x		
CS	x	x	✓	x	x		
CS ⁻	✓						
CS ₂			x	✓	x		
CSe	✓						
				x	✓		
Ca(OH) ₂							
CaCl	x			x	✓		
CaCl ₂				x	✓		
CaF	x			x	✓		
CaF ₂				x	✓		
CaH	x	✓			x		
CaI				x	(✓)		
CaI ₂				x	✓		
CaO	x	✓			x		
CaOH	x			x	✓		
				✓			
CaOH ⁺							
CaS					(✓)		
CdCl	✓						
CdF	✓						
CdH	✓						
CdH ⁺	✓						
Cl ₂	x				(✓)		
ClCN				x	(✓)		
ClO	✓		x	x	x		
			✓			x	
ClONO ₂							
CoH	✓						
CrH	✓						
CrO	✓				x	x	
CrS	✓						
Cs ₂	(✓)				x		
CsCl	(✓)				x		
CsF	(✓)				x		
CsH	✓						
Cu ₂	x				✓	x	
CuCl	x				✓	x	
CuF	x				x	✓	
CuH	✓						
CuO	x				x	✓	
CuS	✓						
F ₂	x				✓		
FCN				x	✓	x	
FO	✓				x		
				✓			
Fe(CO) ₅							
FeCl	✓				x		
FeH	✓						
FeO	✓				x		
FeO ⁻	✓						
GaCl	✓				x		
GaF	x				✓		
GaH	x				✓		
GaO	✓				x		
GeCl	✓				x		
GeF	✓				x		
GeH	✓						
GeH ₄		x				✓	
GeO	✓				x		
GeS	✓				x		
GeSe	✓						
GeTe	✓						
H ₂	x	x	x	x	✓		ESA
H ₂ ⁺	x	✓		x	x		
H ₂ ⁻	x			x	✓	x	
H ₂ CO		x	x	✓			
H ₂ O		✓	x	x	x		x[23,25]
H ₂ O ₂		✓	x	x	x	x	
H ₂ S		✓	x	x	x		
H ₃ ⁺		✓				x	

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Table 1 (continued)

species	BC	ExoMol	HITRAN	JANAF	NASA	Burcat	Other
H ₃ O ⁺		✓		x	x		
HBr	x		✓		x	x	
HBr ⁺	✓						
HC ₃ N			✓				
HCN		✓	x	x	x		x[27]
HCO				x	✓		
HCOF				✓			
			✓	x			
HCOOH							
HCl	x		✓		x		
HCl ⁺	✓						
HF	x	x	x		✓		
HF ⁺	✓						
HI	x		x	x	✓		
				x	✓		
HNCO				✓			
HNNH							
HNO				x	(✓)		
HNO ₃		x	✓		x	x	
HO ₂			x		✓	x	
HOBr			✓			x	
HOCl			✓		x	x	
				✓		x	
HONO				✓			
HONO ₂				✓			
HOO				✓			
HS	x	x		x	(✓)	x	
HS ⁻	✓						
He ₂ ⁺	✓						
HeH ⁺	x	✓				x	
HfO	✓						
HgCl	✓						
HgF	✓						
HgH	✓			x			
HgH ⁺	✓						
HoF	✓						
I ₂	x				✓		
ICl	✓						
IF	x						✓
IO	✓						
InCl	x				✓		
InF	x				✓		
InH	x				✓		
InO	x				(✓)		
IrC	✓						
K ₂	x				(✓)		
KBr	✓						
KCN				x	✓		
				✓			
(KCN) ₂							
KCl	x	✓			x		
KF	x				(✓)		
KH	x			(✓)	x		
KI	✓						
KO	x				(✓)		
KOH		x		x	✓		
KOH ⁺				✓			
				✓			
(KOH) ₂							
LaF	✓						
LaO	✓						
LaS	✓						
Li ₂	x				(✓)		
LiCl	x				✓		
LiF	x				✓		
LiH	x	✓		x	x		
LiNa	✓						
LiO	x				(✓)		
LiOH				(✓)	x		
				✓			
LiOH ⁺							

(continued on next page)

Table 1 (continued)

species	BC	ExoMol	HITRAN	JANAF	NASA	Burcat	Other
(LiOH) ₂				✓			
LuF	✓						
LuO	✓						
Mg(OH) ₂				x	(✓)		
Mg ₂	✓						
MgCl	x				✓		
MgF	x				✓		
MgH	x	✓		x	x		
MgH ⁺	✓						
MgO	x	✓		x			
MgOH				x	✓		
MgOH ⁺				✓			
MgS	✓				x		
MnCl	✓						
MnF	✓						
MnH	✓						
MnO	✓						
N ₂			x	✓	x		ESA
N ₂ ⁺	✓						
N ₂ H ₄				x	(✓)		
N ₂ O			x		✓	x	ESA
NCN				x	✓	x	
NCO				x	✓		ESA
NCI	✓						
NF	✓				x		
NF ₃			x		✓		
NH	✓			x	x	x	
NH ⁺	✓						
NH ₂				x	✓	x	
NH ₃		x	x		x	✓	x[28]
NO	x	✓	x	x			ESA
NO ⁺	x		✓				ESA
NO ₂			x	✓	x	x	ESA
NS	x	✓					
NS ⁺	✓						
Na ₂	✓				x		
NaCN				✓	x		
(NaCN) ₂				✓			
NaCl	✓	x			x		
NaF	x				(✓)		
NaH	x	✓		x	x		
NaO	x	✓		x	x		
NaOH		x		x	✓	x	
NaOH ⁺				✓			
(NaOH) ₂				✓			
NbO	✓			x			
Ne ₂ ⁺	✓						
NeH ⁺	✓						
Ni(CO) ₄				✓			
NiF	✓						
NiH	✓						
NiO	+				(✓)		
O ₂	x		x	x	✓	x	ESA
O ₂ ⁺	x			✓			
O ₂ ⁻				x	✓		ESA
O ₂ Mo(OH) ₂				✓			
O ₂ S(OH) ₂				✓			
O ₂ W(OH) ₂				✓			
O ₃			x	✓	x	x	ESA
OCS		✓					
OH	x		x	x	(✓)	x	
OH ⁺	(✓)			x			

(continued on next page)

Table 1 (continued)

species	BC	ExoMol	HITRAN	JANAF	NASA	Burcat	Other
OH ⁻	(✓)			x	x		
P ₂	x			x	✓		
P ₂ ⁺	✓						
cis-P ₂ H ₂		✓					
trans-P ₂ H ₂		✓					
(P ₂ O ₃) ₂				✓			
(P ₂ O ₅) ₂				✓			
P ₄				x	✓	x	
PCl	x				✓		
PF	x				✓		
PF ₃		x			✓	x	
PH	x	✓		x	x		
PH ⁺	✓						
PH ₂				x	✓	x	
PH ₃		✓	x	x	x	x	
PN	x	✓			x		
PO	x	✓		x	x		
PO ⁺	✓						
PO ₂				x	✓	x	
PS	x	✓		x	x	x	
Pb ₂				x	(✓)		
PbCl	x				(✓)		
PbF	x				✓		
PbH	x			✓			
PbO	✓			x	x		
PbS	✓			x	x		
PtC	✓						
PtH	✓					x	
PtO	✓						
RbCl	✓						
RbF	✓						
RbH	✓						
RbO	✓						
RhC	✓						
S ₂	✓				x		
S ₂ ⁺	✓						
SF	x				(✓)		
SF ₆			✓		x		
SH ⁺	✓						
SO	x		x	✓	x		
SO ⁺	✓						
SO ₂		x	✓	x	x		
SO ₃		x	x	x	✓		
SSO				✓			
Sb ₂	(✓)					x	
SbCl	✓						
SbF	✓					x	
SbH	✓						
SbO	✓						
SbP	✓						
ScCl	✓						
ScF	✓						
ScH		✓					
ScO	✓						
ScS	✓						
Se ₂	✓						
SeCl	✓						
SeF	✓						
SeH	✓						
SeN	✓						
SeO	✓						
SeS	✓						
Si ₂	x				(✓)		
Si ₂ C				x	(✓)		
SiC	✓						
SiC ₂				x	(✓)		
SiCl	x			x	✓		
SiF	✓				x		
SiH	x	(✓)		x	x		

(continued on next page)

Table 1 (continued)

species	BC	ExoMol	HITRAN	JANAF	NASA	Burcat	Other
SiH ⁺	✓						
SiH ⁻	✓						
SiH ₂		✓			x		
SiH ₂ I ₂				x	✓		
SiH ₃ I				x	✓		
SiH ₄		x		x	✓		
SiHI ₃				x	✓		
SiN	x	✓			x		
SiO	x	✓		x	x		
SiO ⁺	✓						
SiO ₂		x		x	✓		
SiS	✓	x			x		
SiSe	✓						
SiTe	✓						
SnCl	✓				x		
SnF	✓				x		
SnH	✓						
SnO	✓				x		
SnS	✓				x		
				x	✓		
Sr(OH) ₂							
SrCl	x				(✓)		
SrF	x				(✓)		
SrH	x				(✓)		
SrO	x			x	(✓)		
SrOH				x	(✓)		
SrS	x				(✓)		
TaO	x				(✓)		
TaO ⁺	✓						
TaO ₂				x	(✓)		
TbO	✓						
Te ₂	✓						
TeH	✓						
TeO	✓						
TeS	✓						
ThO	✓						
TiH	✓						
TiN	✓						
TiO	x	✓		x	x		
TiO ₂				x	✓		
TiS	✓						
TiCl	✓						
TiF	✓						
TiH	✓						
VO	x	✓		x	x		
VO ₂				x	✓		
				✓			
W ₃ O ₈							
WO	✓			x			
WO ₂				x	(✓)		
WO ₃				x	✓		
					(✓)		
(WO ₃) ₂					(✓)		
(WO ₃) ₃					(✓)		
(WO ₃) ₄					(✓)		
YCl	✓						
YF	✓						
YO	✓	x					
YS	✓						
YbCl	✓						
YbF	✓						
YbH	✓						
ZnCl	✓						
ZnF	✓						
ZnH	✓						
ZnH ⁺	✓						
ZrH				✓			
ZrN	x				(✓)		
ZrO	✓			x	x		
ZrO ₂				✓	x		

low, and by numerical differentiation the partition function, which we simply call ExoMol. ExoMol partition functions are tabulated in 1 K steps so this spacing was used for the numerical differentiation. Comparisons showed that the two methods give very similar results; the main exception being the case where the partition function adopted by ExoMol is more complete than the one given by the simple sum over energy levels, see Refs [23,56,57], for discussions of this issue. Our analysis suggests that the maximum temperatures proposed by ExoMol are realistic, but as most of these are lower than 6000 K, the NASA polynomials fitted to ExoMol data therefore cover a reduced temperature range. This final upper temperature is given alongside the recommended NASA polynomials in the supporting information.

HITRAN: no underlying energy levels are provided alongside the HITRAN partition functions [38,39] so $C_p(T)$ was computed by numerically differentiating the partition function. These compilations all give a maximum temperature of at least 3500 K. However, our analysis suggests that this temperature is often rather optimistic and we have found it necessary to specify a lower maximum temperature in many cases. Again the maximum temperature we adopt is given alongside the recommended NASA polynomials in the supporting information.

BC: Barklem and Collet [41] represent their partition functions with relatively few points, only 16 in the range of interest 200 – 6000 K. As recommended we used three point spline interpolation to differentiate these partition functions. While this worked satisfactorily in most cases, there were a few instances where this procedure produced numerically unstable values for $C_p(T)$ from the BC partition functions and these results were not adopted.

JANAF: as JANAF tabulated $C_p(T)$ directly it was only necessary to obtain polynomial fits to these values. In many cases the underlying spectroscopic data used to construct JANAF and the NASA Glenn compilation are essentially the same. In those cases we have favored the NASA compilation in part because JANAF only provides their data on a relatively coarse 100 K grid.

Overall comparing results, with a few exceptions, there is good agreement between all determinations of $C_p(T)$ in the lower (200 – 1000 K) temperature range. However, there are many significant differences at temperatures above 1000 K. Broadly this arises from the way higher lying states are treated. Essentially there are two different approaches: ExoMol, HITRAN and BC compute partition functions using an explicit sum over states. As these compilations of states are rarely complete, these sums can become incomplete at high T . Although in some cases procedures have been adopted to allow approximately for higher states in the system [23,58], in general this approach leads to $C_p(T)$ being underestimated at higher temperatures.

Conversely JANAF and NASA Glenn, and by association, Burcat use approximate models to represent rotational and vibrational energy which are then summed to infinity (such sums can often be calculated using analytic summation formulae). As the number of both vibrational and rotational states in all the systems considered is actually finite, this approach leads to partition functions and $C_p(T)$ values which are overestimated at high T . As can be seen in many cases the behavior of the two approaches often give very different results above 2000 K.

The recommendations given below are generally based on assessment of the reliability of the partition function used to compute the specific heat; usually this assessment is largely concerned with the high temperature representation of the partition function. In some cases it is clear which of these results are likely to be more reliable: either when the partition sums have converged or when the extrapolation techniques lead to unrealistically large values for $C_p(T)$ at high temperature. However, in some cases further work is required to determine which of the two or more predicted $C_p(T)$ values is the best approximation; in these cases our recom-

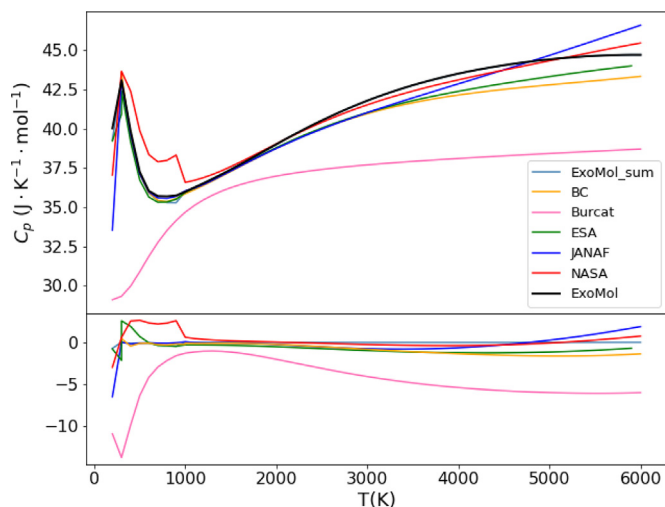


Fig. 2. Comparison of NASA polynomial representations of $C_p(T)$ for $^{12}\text{C}_2$. The lower panel shows the differences to our recommended polynomials which are based on data from the ExoMol database.

mentation is given in brackets and must be regarded as tentative. For most of these tentative cases we have stuck with the NASA Glenn values when available because without further evidence it would seem unwise to recommend alternatives.

Below we explicitly consider four cases where the independent determinations of $C_p(T)$ give conflicting results, as these illustrate some of the general points made above.

The water molecule has the largest number of independent determinations; these are compared in Fig. 1. Generally there is good agreement between these determinations below about 3000 K. Above 3000 K both the ExoMol_sum and HITRAN determinations lie lower than the others; this is due to a lack of completeness of the energy levels in both cases which leads to an underestimation of the partition function at higher temperatures. The ExoMol_sum results used 221 097 energy levels computed as part of the BT2 line list [59], which only considers rovibrational states with total angular momentum $J \leq 50$ and energy up to $30\,000\text{ cm}^{-1}$ above the ground state. The recommended ExoMol result was obtained by differentiating a partition function based on 810 269 energy levels calculated as part of the POKAZATEL line list [60]. The POKAZATEL calculations, for the first time, explicitly obtained estimated energies for every rovibrational bound state supported by the ground state potential energy surface which means $J \leq 72$ and all energies up to $41\,000\text{ cm}^{-1}$. It can be seen in Fig. 1 that using a complete set of bound states leads to a significantly higher $C_p(T)$ above 3000 K. We note that this approach neglects the possible contribution due to quasibound rovibrational levels [61–63], however, there are relatively few of these levels so this contribution is assumed to be small. At high temperatures the NASA and JANAF results for water suggest that $C_p(T)$ is still increasing. As discussed by Vidler and Tennyson [23], this behavior is caused by the use of spectroscopic data that incorrectly allows for an infinite number of vibrational states.

Fig. 2 compares results for the C_2 molecule, an important species in combustion. The specific heat of C_2 is unusual as it shows a local maximum as a function of temperature at about 400 K; this appears to be associated with the somewhat unusual electronic structure of the radical which has another electronically excited state lying just above the ground electronic state. Generally there is good agreement between the various determinations below about 2000 K. The exceptions are (i) the polynomi-

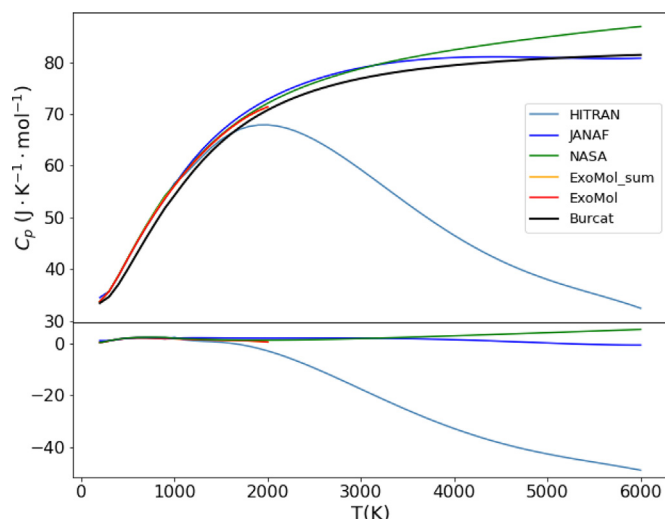


Fig. 3. Comparison of NASA polynomial representations of $C_p(T)$ for ammonia (NH_3). The lower panel shows the differences to our recommended polynomials which are based on data from the compilation due to Burcat.

als found in the Burcat compilation which give results significantly lower than all the other determinations at all temperatures and must be considered inaccurate, and (ii) the NASA Glenn polynomials which behave strangely in the important 500 – 1000 K region; given that the polynomials above 1000 K look reasonable and usually some care was taken in this compilation to ensure that polynomials join smoothly at the break point of 1000 K, it is unclear what is wrong with the region below 1000 K. At high temperature the NASA and JANAF results suggest that $C_p(T)$ is still increasing which is again likely to be due to implicit assumptions about infinite numbers of bound states. Conversely those methods based on finite sums of energy levels, namely BC, ESA and ExoMol, all level off at high temperature. For C_2 we recommend the ExoMol results which are based on empirically determined rovibronic energy levels [26] augmented by an extensive list of computed rovibronic energy levels [64]. The two methods of determining NASA polynomials using ExoMol data give results which are indistinguishable on the scale of the figure.

Fig. 3 compares results for the ammonia molecule. Again up to about 2000 K there is good agreement between the various methods of determining $C_p(T)$, the exception being HITRAN for which the partition function appears only to be complete up to about 1500 K. Similarly the ExoMol results have a stated upper limit of 2000 K. For this reason we recommend Burcat's results which give good agreement with the ExoMol determination up to 2000 K and behave in the physically expected manner at higher temperatures.

Finally, in Fig. 4 we compare results for the hydrogen peroxide molecule. H_2O_2 has a much lower dissociation limit than the three species considered above. Partly as a result of this the disagreement between the different determinations of $C_p(T)$ is larger for this system. For example the overestimate caused by summing over infinite numbers of bound states leads to the NASA Glenn values being too high above about 800 K; conversely the HITRAN partition function appears to be significantly underestimated at all temperatures above about 300 K despite the claim that the values are converged for T up to 3500 K [38]! Again for H_2O_2 we recommend the ExoMol data which come from the APTY line list calculations [65]. However, these results are only valid below 2000 K but given the low dissociation energy of H_2O_2 this is unlikely to be a problem for most practical applications.

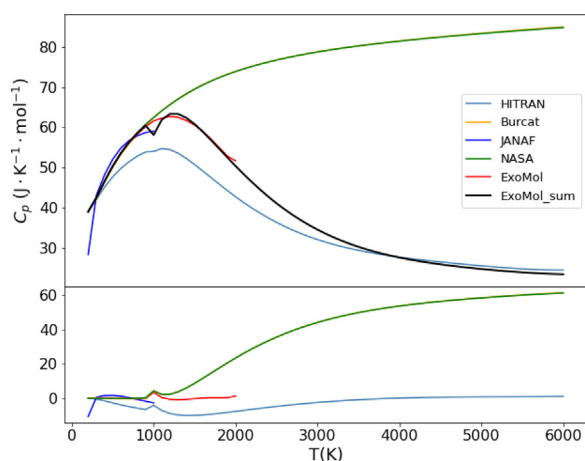


Fig. 4. Comparison of NASA polynomial representations of $C_p(T)$ for hydrogen peroxide (H_2O_2). The lower panel shows the differences to our recommended polynomials which are based on data from the ExoMol database.

4. Conclusions and outlook

The development of thermodynamic and thermochemistry databases has been driven by advances in technology, which require more accurate and complex data. The NASA polynomial format, i.e., a set of coefficients for a standard (polynomial) expansion in temperature to represent thermodynamic quantities such as the specific heat capacity, has proved to be convenient and effective for research, technology development and engineering, including plasma modelling. In this study we reviewed and extended the available seven-term NASA polynomials and considered a total of 464 molecules. While our recommended polynomials generally represented an improvement on what was previously available, there were a significant number of cases where we were unable to arbitrate between the different polynomial representations of the specific heat that produced significantly different answers. There is clearly more work to be done on these species. Furthermore, while we have provided NASA polynomials for 197 molecules for which there was no such representation available, these molecules were selected on the basis that the underlying data was available for us to process, not because these species were necessarily required. For example, the recent release of the Quantemol Database (QDB) [9] which is designed for plasma modelling contains 1818 species which are nearly all molecular. Even with our new results, only about half of these species have specific heats represented in either the five-term or seven-term NASA polynomial representation.

Declaration of Competing Interest

The authors have no conflicts to disclose.

CRediT authorship contribution statement

Rong Wang: Formal analysis, Visualization, Writing – review & editing. **Ugne Balciunaite:** Formal analysis, Writing – original draft. **Juncai Chen:** Formal analysis. **Cheng Yuan:** Formal analysis. **Alec Owens:** Supervision, Writing – review & editing. **Jonathan Tennyson:** Conceptualization, Formal analysis, Methodology, Supervision, Writing – original draft.

Data availability

All data produced in the work are made available as Supplementary materials.

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Supplementary material

See supplementary material for a spreadsheet containing all the NASA polynomials constructed in this work, a graphical representation of the specific heat as a function of temperature for each molecule considered, and a spreadsheet containing our recommended NASA polynomials.

Supplementary material associated with this article can be found, in the online version, at doi:[10.1016/j.jqsrt.2023.108617](#).

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