

# Combustion Chemistry

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Chapter 8

## Thermochemical Data for Combustion Calculations

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### 1. Introduction

The thermodynamic and thermochemical properties of molecules, radicals, and atoms are involved one way or another in almost every computational aspect of combustion science. In most chemical kinetics and equilibrium calculations, such as kinetics of reactions behind shock waves or in nozzle flow, adiabatic flame calculations, and detonation processes, to mention a few, these thermodynamic and thermochemical properties must be found at a number of temperatures, usually determined by an automatic iteration process.

There are two ways to handle the task of representing properties of individual species. In the first one the properties of the substances are provided in a tabular form at predetermined temperature intervals and the values needed are calculated by interpolation. This method requires large memory storage, handling thousands of thermodynamic values, and does not permit use beyond the temperature limits of the table. A second and more commonly used technique is representation of the properties of each species by polynomials that allow direct calculation of the thermodynamic properties at any temperature, including limited extrapolation beyond the fitted range of the polynomial.

Polynomials as discussed in this chapter may also include exponential and logarithmic forms.

### 2. The polynomial representation

We differentiate between two kinds of properties, thermodynamic and thermochemical.



The three thermodynamic properties,  $C_p^\circ$ —the heat capacity at constant pressure,  $H^\circ$ —the enthalpy, and  $S^\circ$ —the entropy, can be calculated directly from molecular spectroscopic data using statistical mechanics equations. (The superscript  $^\circ$  denotes the ideal gas standard state of 1 atm pressure; the amount of matter is taken as one mole. To conform to the usage in common tables of properties, we use subscript  $T$  to denote the value of a property at temperature  $T$ .) The three properties are interrelated by

$$H_T^\circ = H_{T_{\text{ref}}}^\circ + \int_{T_{\text{ref}}}^T C_p^\circ dT \quad (1)$$

$$S_T^\circ = S_{T_{\text{ref}}}^\circ + \int_{T_{\text{ref}}}^T C_p^\circ d \ln T \quad (2)$$

and by definition the Gibbs free energy is derived from them by

$$G_T^\circ = H_T^\circ - TS_T^\circ \quad (3)$$

The other properties are thermochemical ones, those which take cognizance of the chemical reactions undergone by the substance. The basic thermochemical property is the standard heat of formation  $\Delta H_f^\circ$ , which determines the heat balance when one mole of the substance is formed in its standard state from its constituent elements in their standard states. The heat of formation is used to calculate the standard Gibbs free energy of formation, another thermochemical property

$$\Delta G_{fT}^\circ = \Delta H_{fT}^\circ - T\Delta S_{fT}^\circ \quad (4)$$

The thermochemical standard free energy of formation is calculated practically as a difference of the standard free energy of the compound minus the standard free energy of the constituent elements (McBride and Gordon, 1967)

$$\Delta G_{fT}^\circ = G_T^\circ(\text{compound}) - G_T^\circ(\text{elements}) \quad (5)$$

From Eq. (3)  $\Delta G_{f0}^\circ = \Delta H_{f0}^\circ$ . The free energy of formation is also related to the equilibrium constant of formation  $K_p$

$$\Delta G_{fT}^\circ = -RT \ln K_p \quad (6)$$

(But note that

$$G_T^\circ \neq -RT \ln K_p \quad (7)$$

as there is no meaning to  $K_p$  except for a chemical reaction.)

Since the value of  $H_{T_{\text{ref}}}^\circ$  in Eq. (1) is arbitrary, a convention is adopted by which

$$H_{T_{\text{ref}}}^\circ = \Delta H_{fT_{\text{ref}}}^\circ \quad (8)$$

Thus, engineers refer to a thermochemical rather than a thermodynamic property

$$H_T^\circ = \Delta H_{fT_{\text{ref}}}^\circ + \int_{T_{\text{ref}}}^T C_P^\circ dT \quad (9)$$

usually called the "absolute enthalpy" and sometimes called "sensible enthalpy." (Its notation in the Russian literature on thermochemical properties has different symbols. Thus, the thermochemical enthalpy is designated as  $I_T$ . But in Eq. (3), the enthalpy that defines  $G_T^\circ$  is known only if it is defined through Eq. (9). Therefore,  $G_T^\circ$  becomes a thermochemical property also, but still not the  $\Delta G_{fT}^\circ$  defined by Eq. (4). In the Russian literature it is designated  $Z_T^\circ$  to differentiate it from the thermodynamic property.)

Thermodynamic polynomials found their use in engineering practice long ago. Engineers prefer to start with polynomial representations of  $C_P$ , essentially because this enables calculation of other properties through simple integration. The use of  $C_P$  polynomials is thus found quite commonly in engineering thermodynamics textbooks (e.g., Holman, 1974; Wark, 1977). A number of papers are devoted to different techniques of determining and using  $C_P$  polynomials (Huang and Daubert, 1974; Parsut and Danner, 1972; Prothero, 1969; Reid, Prausnitz, and Sherwood, 1977; Tinh *et al.*, 1971; Thompson, 1977; Wilhoit, 1975; Yuan and Mok, 1968; Zeleznik and Gordon, 1960). The main problem with these polynomials is the accuracy with which they reproduce the original values of  $C_P$  and other values, particularly of enthalpy and entropy, obtained by integration. While other kinds of polynomials have been suggested and used (Thompson, 1977; Wilhoit, 1975), the most widely used one is the power series  $a + bT + cT^2 + dT^3 + \dots$ . It was found long ago that if a large temperature range is covered by a single such polynomial, then even the original data is poorly reproduced. The fundamental reason for this is that the  $C_P$  function, and to a lesser extent the other thermodynamic properties, have a characteristic "knee" between 900 and 2000 K. Thus, a single polynomial may fit poorly to the changing slopes.

To overcome this difficulty Duff and Bauer (1962) proposed two different polynomials with overlapping ranges. Later, "pinned polynomials" were suggested by McBride and Gordon (1967) and Zeleznik and Gordon (1960). These polynomials are constrained to fit exactly the  $C_P$  value at a temperature that is an endpoint of one polynomial and a starting point to the second, and to give equal values of the other thermodynamic functions at that temperature. McBride and Gordon preferred 1000 K as the common temperature, while Prothero (1969) argues that 2000 K is a better choice.

While most authors (Parsut *et al.*, 1972; Reid *et al.*, 1977; Tinh *et al.*, 1971; Yuan *et al.*, 1968) fit  $C_P$  values only and use the  $C_P$  polynomial to calculate the rest of the thermodynamic properties, McBride *et al.* (1967) and Zeleznik and Gordon (1960), suggested the simultaneous least squaring of three properties,  $C_P^\circ$ ,  $S_T^\circ$ , and  $H_T^\circ - H_{\text{ref}}^\circ$ . This procedure generally gives better reproducibility of all the properties and low deviation. For example, the typical fourth-degree least-squares fit to  $C_P$  values gives a fit with a maximal error of around 4% in the 1000–5000 K range. In the 300–1000 K range the fitting is easier,

normally with lower error percentages; the rest of the thermodynamic properties calculated by integration of the  $C_p$  values will have a still lower percent error. Simultaneous least squaring of three properties, however, causes the maximal error of  $C_p$  to be the same as before but the other thermodynamic properties to be fit with usually half the error of the  $C_p$ -alone method.

The polynomials from simultaneous fitting are known as the NASA thermodynamic polynomials because of their use in a variety of NASA computer programs (Bittker and Scullin, 1972; 1984; Gordon and McBride, 1971; McLain and Rao, 1976; Svehla and McBride, 1973). In Appendix A a program written according to Zeleznik and Gordon (1961) to calculate NASA polynomials by simultaneous least squaring is presented.

The NASA polynomials are usually fitted in the temperature range 300 to 5000 K. The reason for choosing this range is practical. Combustion calculations require thermodynamic and thermochemical properties between room temperature and 3000 or (for special fuels or detonations) 4000 K. In the course of automatic calculations, as well as in some exotic conditions such as spaceship reentry, knowledge of properties to 6000 K is required. Thus, the polynomials discussed here follow the bulk of existing tables (such as JANAF and TSIV as discussed later) by being fit in the range 300–5000 K. Extrapolation to 6000 K is easily done with little error. Extrapolation below 300 K, seldom needed in combustion research, is less accurate. In some cases the polynomials were fit up to 3000 K only.

### 3. Extrapolation

Extrapolating a polynomial outside the temperature range where it was fitted calls for caution. Not only does the uncertainty increase, but the curve often deviates in a direction opposite to the normal trend. This may be a serious drawback, since most thermodynamic data tabulations, as discussed in the next section, cover temperature ranges too low for combustion calculations. Thus, when these data have to be extrapolated to higher temperatures, the polynomials usually used for this purpose may give improper results (see Fig. 1).

To overcome this inconvenience, different types of polynomials have been developed. The basic concept is to force the  $C_p^{\circ}$  curve to approach asymptotically the correct classical upper value  $C_p^{\circ}(\infty)$ . Although this offers problems for molecules with hindered internal rotations and electronically excited species (radicals and ions), it is satisfactory for most molecules, and even for the exceptional species it provides an adequate approximation.

One method, proposed by Wilhoit (1975), uses the following fitting function for the heat capacity

$$C_p^{\circ} = C_p^{\circ}(0) + [C_p^{\circ}(\infty) - C_p^{\circ}(0)]y^2 \left[ 1 + (y - 1) \sum_{i=0}^n a_i y^i \right] \quad (10)$$

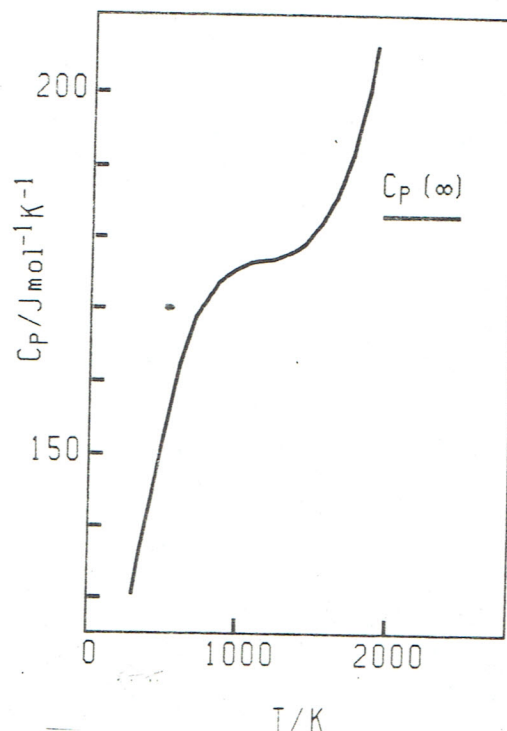


Figure 1. Heat capacity polynomial fit for  $\text{CCl}_2\text{F-CF}_2\text{Cl}$  (Freon 113) from the data compilation of Reid, Prausnitz, and Sherwood (1977) showing the unrealistic upwards curvature above 1300 K. Data points were fitted up to 1500 K.

where  $y = T/(T + B)$  varies from 0 to 1. The symbol  $B$  represents a scaling factor that determines how rapidly  $C_p^{\circ}$  approaches  $C_p^{\circ}(\infty)$ . For most polyatomic molecules it is in the range 300–1000 K, with small molecules near the high end and larger ones in the 300–500 K range.  $C_p^{\circ}(0)$  is the low-temperature limit heat capacity,  $(7/2)R$  for linear molecules (except hydrogen) and  $4R$  for nonlinear molecules;  $C_p^{\circ}(\infty)$  is the classical high-temperature value,  $(3N-3/2)R$  for linear molecules and  $(3N-2)R$  for nonlinear ones; and  $N$  is the number of atoms in the molecule.

The coefficients  $a_i$  can be calculated by a least-squares fit of the function

$$\frac{C_p^{\circ} - C_p^{\circ}(0) - y^2[C_p^{\circ}(\infty) - C_p^{\circ}(0)]}{[C_p^{\circ}(\infty) - C_p^{\circ}(0)]y^2(y-1)} = \sum_{i=0}^n a_i y^i \quad (11)$$

Heat capacity values and an assumed  $B$  are used to compute the left-hand side of Eq. (11) for a range of  $y$  values. The results for different values of  $B$  are computed and  $B$  modified until the best agreement is obtained. The enthalpy

Table 1. Parameters for Wilhoit Polynomials.

Compound	Range (K)	$C_p(\infty)/R$	$10^3 \text{ RMSD}$	B(K)	I/R(kK)	J/R	$a_0$	$a_1$	$a_2$	$a_3$	Notes
O <sub>2</sub>	50-3000	4.5	22	1500	167.575	-2.59	8.594	-84.33	166.26	-107.80	a
H <sub>2</sub>	50-3000	4.5	38	500	-86.682	-5.50	4.280	-126.19	326.53	-234.56	a
H <sub>2</sub> O	50-3000	7	7	1000	-25.868	-20.84	0.502	6.59	-24.64	14.30	a
F <sub>2</sub>	50-3000	4.5	35	700	-16.719	-2.20	6.755	-52.84	79.98	-39.54	a
HF	50-3000	4.5	15	1000	-47.191	-5.98	-1.090	14.57	-19.71	2.60	a
Cl <sub>2</sub>	50-3000	4.5	25	700	77.789	0.06	7.966	-111.71	252.84	-168.06	a
HCl	50-3000	4.5	13	1000	-14.11	-4.39	-1.292	23.63	-60.54	34.16	a
N <sub>2</sub>	50-3000	4.5	14	1000	37.957	-3.80	-0.745	24.94	-84.07	63.37	a
NO	50-3000	4.5	94	500	25.041	-1.57	-52.396	292.64	-507.88	275.32	a, b
NO <sub>2</sub>	50-3000	7	27	1000	-143.24	-14.79	5.708	-61.55	116.27	-69.34	a, b
N <sub>2</sub> O	50-3000	7	45	700	-26.207	-42.76	3.684	-39.48	70.03	-38.03	a
N <sub>2</sub> O <sub>4</sub>	50-3000	16	88	500	58.984	-65.66	-8.828	27.33	-43.36	24.44	a, b
NH <sub>3</sub>	50-3000	10	19	1000	-24.11	-41.14	2.447	-12.95	10.35	-2.55	a
CO	50-3000	4.5	20	1500	135.959	-3.48	3.694	-15.32	-22.26	44.28	a
CO <sub>2</sub>	50-3000	7.5	28	700	-40.905	20.80	4.520	39.40	66.77	36.12	a
CH <sub>4</sub>	60-3000	13	53	1500	291.547	-66.23	5.017	-46.20	76.38	-40.15	c
CH <sub>3</sub> F	100-1500	13	31	500	36.772	-52.06	-0.195	14.72	-41.24	26.03	d
CH <sub>3</sub> Cl	100-1500	13	37	500	22.202	-50.79	1.444	-1.84	-16.82	12.33	e
CH <sub>3</sub> NO <sub>2</sub>	298-1000	19	3	335	1.23390	-78.377	0.8484	1.291	-6.719	2.673	f
CH <sub>3</sub> OH	100-1500	16	45	500	67.414	-69.72	-3.042	23.35	-49.21	28.71	g
C <sub>2</sub> H <sub>2</sub>	50-2500	9.5	84	700	-149.907	-42.36	4.480	-44.45	88.47	-55.17	h
C <sub>2</sub> H <sub>4</sub>	50-1500	16	62	500	34.557	-71.31	1.23	3.46	-20.04	14.28	i
C <sub>2</sub> H <sub>5</sub> F	100-1500	22	43	500	39.983	-104.68	-0.125	2.71	-12.87	9.00	j
C <sub>2</sub> H <sub>5</sub> Cl	100-1500	22	42	500	27.789	-103.65	-0.023	0.04	-6.79	5.27	j
C <sub>2</sub> H <sub>5</sub> OH	273-1000	25	15	500	54.945	-121.66	0.021	0.23	-6.34	4.93	a, c
C <sub>2</sub> H <sub>5</sub> NO <sub>3</sub>	298-1000	31	5	300	-0.709	-139.90	1.0257	-4.4261	5.702	-4.287	f
CCl <sub>2</sub> FCF <sub>2</sub> Cl	298-1000	22	25	500	197.499		-16.91	54.94	-83.20	46.70	k
C <sub>2</sub> H <sub>6</sub>	50-1500	22	35	500	0.111	108.26	0.682	0.94	-8.60	4.98	l
C <sub>3</sub> H <sub>6</sub>	50-1500	25	42	500	4.959	-123.55	-0.094	1.09	-7.24	4.32	i
C <sub>3</sub> H <sub>8</sub>	50-1500	31	94	500	-12.832	-161.14	0.077	-0.76	-2.59	1.12	i
C <sub>3</sub> H <sub>6</sub> O(m)	273-1000	28	15	500	63.804	-140.04	-1.866	8.70	-19.72	11.74	a
C <sub>3</sub> H <sub>8</sub> O(m)	273-1000	34	23	500	106.470	-175.26	-2.419	10.35	-21.42	12.63	a, e

C <sub>3</sub> H <sub>8</sub> O(g)	273 1000	34	47	500	50,803	-176.12	0.014	-3.11	1.16	0.48	a, c
1-n-C <sub>4</sub> H <sub>8</sub>	298 1500	34	15	500	-11,629	-176.31	0.3198	-3.942	3.079	-1.583	a
n-C <sub>4</sub> H <sub>10</sub>	50 1500	40	195	500	52,689	-215.88	-3.029	12.30	-22.62	11.82	c
i-C <sub>4</sub> H <sub>10</sub>	50 1500	40	143	500	1,783	-216.21	-0.556	-0.10	-2.51	1.15	c
1-n-C <sub>5</sub> H <sub>10</sub>	298 1500	43	10	350	1,374	-216.22	0.7411	-3.058	6.754	-6.368	a
1-n-C <sub>5</sub> H <sub>12</sub>	200 1500	49	100	350	42,984	-255.18	-4.2985	20.66	-32.005	14.108	a
1-n-C <sub>6</sub> H <sub>12</sub>	298 1500	52	15	300	13,846	-259.39	-0.03395	-0.1838	2.63	-4.248	a
n-C <sub>6</sub> H <sub>14</sub>	200-1000	58	60	350	170,074	-306.40	-5.785	28.76	-47.74	24.30	a
1-n-C <sub>7</sub> H <sub>14</sub>	298 1500	61	25	300	21,795	-308.81	-0.5105	1.49876	0.283	-3.053	a
n-C <sub>7</sub> H <sub>16</sub>	200-1000	67	200	350	227,261	-358.23	-6.212	30.58	-50.97	26.36	a
1-n-C <sub>8</sub> H <sub>16</sub>	298 1500	70	25	300	28,141	-358.06	-0.7283	2.114	-0.481	-2.66	a
n-C <sub>8</sub> H <sub>18</sub>	298 1000	76	25	335	15,981	-400.25	-0.7887	1.95133	-1.1749	-1.8469	f
i-C <sub>8</sub> H <sub>18</sub>	200 1000	76	35	350	108,576	-407.60	-0.347	-0.29	2.33	-4.43	a
cis-C <sub>10</sub> H <sub>18</sub>	298 1000	82	25	500	183,861	-470.17	1.193	-5.322	-1.15	3.80	p
trans-C <sub>10</sub> H <sub>18</sub>	298-1000	82	45	500	127,054	-471.33	0.4636	-1.39	-8.01	7.702	p
c-C <sub>5</sub> H <sub>10</sub>	300 1500	43	20	500	-87,506	-230.86	4.426	-18.96	21.59	-9.78	a
c-C <sub>6</sub> H <sub>12</sub>	298 1500	52	15	400	-14,663	-278.86	0.442	3.96	-15.58	9.05	a
c-C <sub>5</sub> H <sub>8</sub> (w)	298-1500	37	20	500	-39,257	-193.87	4.155	-16.95	17.07	-6.66	a
c-C <sub>6</sub> H <sub>10</sub> (x)	298 1500	46	15	500	-105,678	-249.28	4.059	-21.67	28.71	-13.91	a
C <sub>7</sub> H <sub>6</sub> (q)	273 1500	34	15	500	-113,424	-177.84	5.932	-30.19	41.04	-20.00	a
C <sub>10</sub> H <sub>8</sub>	50 1500	52	20	1000	-2658.86	-320.92	-0.959	-32.67	83.39	-59.78	r
C <sub>7</sub> H <sub>8</sub> (s)	273 1500	43	20	500	-103,336	-230.22	2.846	-16.34	20.72	-10.08	a
C <sub>6</sub> H <sub>5</sub> OH(l)	50 1500	37	35	700	367,423	-205.54	1.792	-28.06	53.40	-31.56	p
(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> (u) ·	298 1000	64		500	-47,371	-356.03	2.491	-17.42	22.81	-10.12	f

<sup>a</sup> API tables.

<sup>b</sup> Chao *et al.* (1974).

<sup>c</sup> McDowell and Kruse (1963).

<sup>d</sup> Rogers *et al.* (1977).

<sup>e</sup> Chen *et al.* (1975).

<sup>f</sup> Stull *et al.* (1969); reconstructed enthalpy is H<sub>1</sub>-H<sub>298</sub>.

<sup>g</sup> Chen *et al.* (1977).

<sup>h</sup> Chao (unpublished).

<sup>i</sup> Chao and Zwolinsky (1975).

<sup>j</sup> Chao *et al.* (1974).

<sup>k</sup> Freon 113; Reid *et al.* (1977); entropy not available.

<sup>l</sup> Chao *et al.* (1973).

<sup>m</sup> Acetone.

<sup>n</sup> 1-Propanol; Wilhoit and Zwolinsky (1973).

<sup>o</sup> 2-Propanol; Wilhoit and Zwolinsky (1973).

<sup>p</sup> Decalin; Miyazawa and Pitzer (1958).

<sup>q</sup> Benzene; API tables.

<sup>r</sup> Naphthalene; Chen *et al.* (1979).

<sup>s</sup> Toluene; API tables.

<sup>t</sup> Phenol; Kudchadker *et al.* (1978).

<sup>u</sup> Biphenyl; Stull *et al.* (1969).

<sup>w</sup> Cyclopentene.

<sup>x</sup> Cyclohexene.

and entropy are obtained by integration of the  $C_p$  equation

$$\frac{H_T^\circ - H_0^\circ}{T} = \frac{I}{T} + C_p^\circ(0) - [C_p^\circ(\infty) - C_p^\circ(0)] \left( 2 + \sum_{i=0}^n a_i \right) \\ \times \left[ y/2 - 1 + \left( \frac{1}{y} - 1 \right) \ln \frac{T}{y} \right] + y^2 \sum_{i=0}^n \frac{y^i}{(i+2)(i+3)} \left( \sum_{j=1}^n f_{ij} a_j \right) \quad (12)$$

in which  $f_{ij} = 3 + j$  for  $i = j$  and  $f_{ij} = 1$  for  $j > i$ .  $I$  is an integration constant set by comparing an enthalpy value given in the literature at some selected temperature with that obtained by integration of  $C_p^\circ$ . The entropy is calculated from

$$S_T^\circ = J + C_p^\circ(\infty) \ln T - [C_p^\circ(\infty) - C_p^\circ(0)] \\ \left[ \ln y + \left( 1 + y \sum_{i=0}^n \frac{a_i y^i}{2+i} \right) y \right] \quad (13)$$

$J$  is an integration constant set by comparing an entropy value given in the literature at some selected temperature to that obtained by integration of  $C_p^\circ$ .

Table 1 shows some polynomial coefficients obtained by Wilhoit (1975) and the present author. (Additional ones can be obtained from a data bank at the Thermodynamic Research Center (TRC), Texas A & M University, College Station, Texas.) In Appendix B a program is given for evaluating the  $a_i$ ,  $B$ ,  $I$ , and  $J$ .

Thompson's method (1977) provides a different polynomial based on similar principles. It also approaches  $C_p(\infty)$  asymptotically. It has fewer parameters and is therefore less accurate, as noted by Thompson himself. Yuan and Mok (1968) propose extrapolation of data using the formula  $C_p^\circ = A + B \exp(-C/T^n)$ . The four parameters to be fit are  $A$ ,  $B$ ,  $C$ , and  $n$ , where  $n$  differs from unity only when data to 6000 K are available.

#### 4. Thermochemical data sources

In order to calculate polynomial coefficients, the thermodynamic and thermochemical property values must be found in tables or calculated from molecular properties by the methods of statistical thermodynamics. The available tables will be described in the following section.

A popular and often quoted source is the "JANAF Thermochemical Tables" (1971), prepared by a team of thermodynamicists at the Dow Chemical Company headed by D. R. Stull and M. W. Chase. This source has thermochemical values for small, mostly inorganic molecules, radicals, and ions up to 6000 K. The calculations are mainly done using the rigid rotator



harmonic oscillator (RRHO) approximation. Values for some species are calculated using anharmonic corrections. Four additional groups of tables were issued since the main volume was published in 1971, with both additions and revisions (JANAF, 1974; 1975; 1978; 1982).

Most of the JANAF tables have been fitted to polynomials by the NASA thermodynamics group. Polynomial coefficients for the species included in the main JANAF volume (1971) have been published (Gordon and McBride, 1971) and are supplied with the NASA SP-273 computer program.

A second source comparable to the JANAF tables published in the Soviet Union by Gurvitch *et al.* (1967) is not well known in the Western hemisphere. Gurvitch *et al.* published with their tables a set of nine-term polynomials that cover the temperature range 0–5000 K. This set of polynomials was reprinted in a later publication of Alemasov *et al.* (1974). Unfortunately, the explanation of how to use these polynomials is not clear, making their use guesswork.

The latest edition of the publication of Gurvitch *et al.* (1978) has gained much prestige although only the Russian version is as yet available. The spectroscopic data are well documented and a good discussion of the thermochemical data is provided. The tables list  $C_p^\circ$ ,  $H_T^\circ - H_0^\circ$ ,  $\phi = (G_T^\circ - H_0^\circ)/T$ ,  $S_T^\circ$ , and  $\log K_p$ . However,  $K_p$  is calculated for equilibrium with gaseous atoms rather than reference elements as in most sources (JANAF, 1971; 1974; 1975; 1978; Amer. Petrol Inst.: Stull, Westrum, and Sinke, 1969).  $\Delta H_f^\circ$  is given only at 0 and 298.15 K. A seven-coefficient polynomial is fitted for  $\phi$  only in the temperature range 500–6000 K. This polynomial is unsuitable for most combustion research since the room-temperature end is missing and extrapolation into this range introduces a large error.

A publication devoted to stable organic molecules is the API-TRC Project 44. This is a reliable thermodynamic data source calculated either by statistical mechanics formulas or by approximation methods developed by Pitzer, Rossini, and their co-workers over the years. The main problems of this source are the following: First, it covers temperatures up to 1000 K only (for some older calculations up to 1500 K). In most cases this range is too low for combustion calculations; Wilhoit's extrapolation method is recommended if these tables are to be used at higher temperatures. Also, this source, owing to its high cost, is not available in many libraries. Where it is available it is usually not complete, and because of its complex indexing system, updating the looseleaf supplements and finding the desired table are difficult. In addition, it is almost impossible to determine which data sources were used for the calculation of thermochemical values, and the spectroscopic values used are not quoted as they are in the JANAF tables. (In 1984 the first n-alkyl radical, tables of thermodynamic properties, were published by the API-TRC Project).

Most of these drawbacks were corrected by Stull, Westrum, and Sinke (1969). In a regular-size volume the authors have included the ideal gas thermodynamic functions of the API Project 44 as well as others that were not

included in this publication. It contains data for 918 compounds. All values are given, in the JANAF format, for the temperature range 298–1000 K. A complete list of references and comments regarding the calculations and the validity of the spectroscopic and thermal data are appended to each table. It contains an additional data table for organic molecules on which limited thermodynamic data is available.

Reid, Prausnitz, and Sherwood (1977) provide ideal gas  $C_p$  data for 468 organic molecules as four-term polynomials. The valid temperature range of these polynomials is not mentioned, nor is the data source, presumably mostly Thinh *et al.* (1971). The absolute enthalpy polynomial (probably in the range 273–1000 or 298–1500 K) can also be found since the value of  $\Delta H_{f,298}^\circ$  is mentioned. The entropy cannot be calculated since the integration constant is not given. However, as mentioned earlier, these polynomials are useless anyway for high-temperature combustion calculation since they cannot be extrapolated far outside the range where they were fitted.

When making combustion calculations one usually needs in addition to the thermochemical properties of the stable organic molecules those of organic radicals or even ions. Unfortunately, in this domain there are very few sources of data.

Duff and Bauer (1961) calculated some thermodynamic properties of complex organic radicals. The values were given only in polynomial form because of the uncertainties in the data obtained. As mentioned earlier, the values were fitted to two polynomials with overlapping temperature ranges: 300–2000 K and 1500–6000 K. (Note: in the *J. Chem. Phys.* publication, Parts I and II of Table I were interchanged. The original report gives more details and is therefore recommended.) This publication should be considered as a pioneer work, and many of the spectroscopic values recommended in it are still valid today.

The only other publication in which calculations of the thermodynamic properties of a large number of organic radical species are reported is the NASA report of G. S. Bahn (1973), which includes many serious mistakes. These tables were later published as coefficients for NASA-type polynomials by Wakelyn *et al.* (1975). Although the approximation idea used by Bahn is interesting,  $\Delta H_{f,0}^\circ$  values are sometimes used in place of  $\Delta H_{f,298}^\circ$  values as if they were the same, which usually causes the "absolute enthalpy" values to be inconsistent; in most cases it is unclear to which of the possible isomers the calculated species belong or even whether the species mentioned is a chain or a ring compound; some values are simply wrong. It can be shown that these tables or polynomials may lead to serious mistakes if used in chemical kinetics or equilibrium calculations (Van Zeggeren and Storey, 1970).

In Appendix C a table of polynomial coefficients and ancillary information is given. Most of the entries are based on the most accurate data currently available. Some of them, although approximate, were included to provide better representation than the values given by Bahn (1973) or Wakelyn and McLain (1975).

When properties of deuterated species are needed, the monograph of Haar, Friedman, and Beckett (1961) is almost the only existing compilation. The Russian monographs (Gurvitch, 1967; 1978) present data for some deuterated and tritiated species, as do the recent JANAF supplement (1982) and a report of the author (Burcat, 1980). Thermodynamic properties for other isotopic species have to be searched for in the primary literature (Chen, Wilhoit, and Zwolinski, 1977; Chen, Kudchadker, and Wilhoit, 1979).

Finally, a word about statistical thermodynamic calculation methods. Most of the published tables used the rigid rotor harmonic oscillator (RRHO) approximation method. These calculations are accurate for most molecules up to 1500 K. The JANAF (1971) calculations were based mainly on the RRHO approximation. When values at temperatures above 3000 K are desired, however, the RRHO values are too low. Unfortunately, anharmonicity constants are still known only for very few molecules. Some publications do include values obtained using anharmonicity corrections (Burcat, 1980; McBride *et al.*, 1963; McDowell and Kruse, 1963). There are still uncertainties regarding the best way to calculate anharmonic corrections. McBride and Gordon (1967) discuss the alternatives, of which NRRAO2 appears to be the best.

## 5. Approximation methods

In many cases it may be found that the molecule of interest has not been spectroscopically investigated or that the spectroscopic knowledge is too limited to calculate the thermodynamic properties by ordinary statistical mechanics methods. Approximation methods have to be used.

Benson and Buss (1958) have classified the different approximations possible through additivity of properties. They called the roughest approximation possible, approximation of molecular thermodynamic property through summation of the thermodynamic properties of the individual atoms in the molecule, a "zero additivity rule." The first additivity rule is then summation of the properties of the bonds in the molecule. Graphical extrapolations and interpolations of thermodynamic properties based on the chemical formula, as done by Bahn (1973), fit in between the zero and first additivity rules.

The second additivity rule (also used in Benson, 1976; Benson and O'Neal, 1970; O'Neal and Benson, 1973) utilizes the contribution of groups of atoms. A second-order group is a central atom and its attached ligands, at least one of which must be polyvalent. Benson and co-workers evaluated a large number of group properties, mainly by averaging properties of many molecules or by using kinetic information and least-squares-fitting the values rather than relying on any single input. The properties of the entire molecule or radical are evaluated by summing up all the group contributions. In addition, some third-order corrections have to be added for specific molecules such as ring

compounds or those having gauche or cis interactions or other steric factors. The cited publications include tables of thermodynamic and thermochemical properties. Most values are compiled or calculated for  $\Delta H_f^\circ$ ,  $S^\circ$ , and  $C_p^\circ$  at 298 K. For some species the calculation of  $C_p$  was continued for temperatures up to 1500 K.

Benson's method, although supposedly simple and easy to use, turns out in practice to be so complex that few have discovered how to use it. It has been programmed so that properties of unknown molecules can be evaluated automatically for any temperature between 300 and 1500 K in a code named CHETAH, the ASTM Chemical Thermodynamic and Energy Release Evaluation Program (Seaton, Freedman, and Treveek, 1974). This program calculates the thermodynamic properties  $\Delta H_f^\circ$ ,  $S^\circ$ ,  $C_p^\circ$ , and the heat of combustion  $\Delta H_c$  of the requested molecule as a side procedure. (Its main objective is evaluation of possible energy release of a given compound in order to characterize the relative hazard of the substance in industrial use.) Properties of radicals cannot be evaluated with this program; they have to be done separately (Benson, 1976, and the cited references above).

A higher quality approximation method for radicals was proposed by Forgeteg and Berces (1967). This method uses the spectroscopic assignment of the parent molecule, from which the vibrations relevant to the atom missing in the radical are deleted. Other vibrations may then be adjusted according to known ratios between bond lengths or force constants in the molecule and the radical. Thereafter the ordinary statistical mechanics formulas can be used to calculate the thermodynamic properties. Benson's additivity method or other estimates can be used to obtain the enthalpy of formation.

Reid *et al.* (1977) present an evaluation of most of the approximation methods available. These methods should only be used, however, as a last resort, after conventional methods have failed.

What should be done when needed thermodynamic properties cannot be found in one of the standard thermodynamic compilations?

First, the literature should be searched for spectroscopic data, and if these are sufficient, the thermodynamic properties can be calculated by statistical mechanics formulas. McBride and Gordon's program (1967) is recommended for this purpose. The latest version, PAC3, includes, among many possible calculation methods, an accurate calculation method for internal rotation contributions, which are important when organic species are involved, and a subroutine which automatically calculates the coefficients of the NASA polynomials. Wilhoit's extrapolation method was recently included to the code.

Among the parameters that have to be known for the calculation of thermodynamic properties are the rotational constants. If these are unknown then the three principal moments of inertia of the molecule have to be calculated from assumed molecular bond lengths and angles. For this purpose there are two documented computer programs (Brinkmann and Burcat, 1979; Ehlers and Cowgill, 1964).

For radicals, chances are that no spectroscopic data can be found for the radical itself, and therefore the parent molecule has to be investigated. Afterwards, the procedure of Forgeteg and Berces (1967) can be applied as described above.

In case no spectroscopic information at all is available about a molecule, then the properties must be estimated by analogies or through Benson's method.

## 6. Thermochemical polynomials in combustion chemistry

Before dealing with the different uses of thermochemical polynomials in combustion, the relevance of using thermochemical properties for elevated temperatures must be discussed. The relevance of the enthalpy or entropy of an organic molecule at 4000 K may be questioned (Chase, Downey, and Syvernd, 1979) since these molecules can hardly exist even at 1000 K for more than a few milliseconds. Modern technical and experimental devices, however, require engineers and scientists to consider the behavior of fuel molecules that have been brought in microseconds or less from ambient temperature to 2000–3000 K or more. It is clear that at such elevated temperatures large molecules dissociate quickly. Some combustion processes, however, proceed on a microsecond time scale. Thus, although large molecules cannot survive a few seconds at combustion temperatures, they can survive a few microseconds, and for studying their behavior over these limited time scales their thermodynamic properties are important.

One of the simplest uses of thermodynamic polynomials is in the calculation of steady-flow gas properties, such as behind a shock wave, assuming "frozen chemistry." In this case the specific enthalpy of the gaseous mixture must be found for the calculation of the flow properties (pressure, temperature, Mach Number, density, etc.). To find the molar enthalpy of the mixture, the polynomial expressions for  $H_T^\circ$  are multiplied by the mole fractions of each component and added. More sophisticated calculations are involved in studying the equilibrium chemistry of a flame or behind a shock wave. In this case the calculation of equilibrium composition is required, using one of the methods that will be discussed in the next section. To find the Chapman-Jouguet detonation velocity, the equilibrium chemistry of the mixture has to be evaluated as well as the specific enthalpy. The equilibrium composition is also needed for calculating adiabatic flame temperatures, exhaust properties of rocket engine nozzles, and stagnation processes in gasdynamic combustion lasers.

In kinetic modeling, one must calculate reverse rate constants of elementary reactions from forward rate constants. This is easily achieved from

$$k_f/k_r = K_c \quad (14)$$

The equilibrium constant calculated from thermochemical polynomials [Eq. (6)] is  $K_p$ . Misidentifying  $K_c$  with  $K_p$  can cause confusion (Golden, 1971) since  $K_c = K_p$  only when the number of moles of products is equal to the number of moles of reactants i.e., when  $\Delta n = 0$ . When this is not the case

$$K_c = K_p(R'T)^{-\Delta n} \quad (15)$$

where  $R' = 82.06 \text{ cm}^3 \text{ atm/mol K}$  or  $0.08206 \text{ l atm/mol K}$ .  $K_p$  is calculated from the free energy of reaction  $\Delta G_r^\circ$

$$\Delta G_r^\circ = \sum G_T^\circ(\text{products}) - \sum G_T^\circ(\text{reactants}) \quad (16)$$

and

$$K_p = \exp(-\Delta G_r^\circ/RT) \quad (17)$$

or from the equilibrium constants for the formation of each substance participating in the reaction, as defined in Eq. (6), through

$$\ln K_p = \sum \ln K_p(\text{products}) - \sum \ln K_p(\text{reactants}) \quad (18)$$

Reviews of the different methods for calculation of equilibrium composition are given by Zeleznik and Gordon (1968), Van Zeggeren and Storey (1970), and by Alemasov (1974). Basically, there are two methods: those based on the calculation of the equilibrium constant  $K$ , and those based on the free energy minimization. Superficially, both would appear to be the same since the two properties are interconnected by Eq. (17). They differ in the method used to solve the system of nonlinear equations: Minimization of free energy is usually preferred for complex systems. The NASA program NASA SP-273 (Gordon *et al.*, 1971) was noted by the reviewers (Alemasov, 1974; Van Zeggeren and Storey, 1970) to be one of the best codes available for calculating equilibrium conditions in a variety of practical situations arising in combustion science. There are others.

## 7. Required accuracy of thermochemical information

Opinions about the accuracy of thermochemical data needed for combustion research are educated guesses rather than facts. Unfortunately, no systematic investigation has been carried out yet on this question.

The "well-determined species," such as those appearing in JANAF tables or API Project 44 tables or those published in the Journal of Physical and Chemical Reference Data, are calculated to the third or fourth digit after the decimal point. In the majority of cases the third digit after the decimal point can be well reproduced but the fourth is sometimes doubtful. However, for most calculations even the second digit after the decimal point is more than is ever necessary. Thus,  $C_p$  and  $S$  may be known to two digits after the decimal

point while there is seldom any need for this degree of accuracy. The value of  $H_T^\circ$ , however, is seldom known to better than 0.01 kJ while it would be preferable to know it to 0.001 kJ. Whether this type of accuracy is really needed in calculations is not clear, although general opinion holds that it is usually not necessary.

One property we would want to know to at least two digits after the decimal point is  $\log K_p$ . The reason for this is that  $K_p$  is the property used to calculate back reaction rate constants when forward reaction rate constants are known or assumed. In chemical kinetics calculations this is of primary importance and a difference of one unit in the second digit of  $\log K_p$  causes a 2% difference in the value of the calculated reverse reaction rate constant. On the other hand, in the calculation of shock tube experimental properties where reactive species are highly diluted in a noble gas or nitrogen, there is hardly any importance to knowledge of the exact properties of any species other than the diluent itself.

Even the thermochemical values for "well-determined species," such as those appearing in JANAF tables, are changed from time to time as physical constants or atomic weights change or mistakes are found. This should concern combustion science only if the changes affect the second digit after the decimal point. On the other hand, it is important to use reliable sources as much as possible, and if there is a choice not to mix different thermodynamic sources since they tend to differ at temperatures higher than 3000 K, where anharmonicity effects may be important.

One must also realize that except for elements, stable compounds which burn cleanly in oxygen, and small molecules or radicals whose electronic spectra in dissociative regions have been thoroughly analyzed, standard enthalpies of formation must be evaluated through difficult experiments subject to interpretive difficulties. This means that the largest errors—by far—in thermochemical calculations arise from uncertain enthalpies of formation. Fortunately, it is a fairly straightforward matter to modify the polynomial representations to change enthalpies of formation when new experimental results become available or sensitivity checks on  $\Delta H_{f,298}^\circ$  are to be made (cf. comments in Appendix C).

There are also some technical uncertainties about whether values calculated by the RRHO method and values calculated including anharmonicity corrections should be used in the same calculations. These uncertainties are under consideration by the JANAF, NBS, and NASA thermodynamics teams. Special care should also be taken when dealing with species such as  $\text{CH}_3$ ,  $\text{CH}_4$ ,  $\text{CD}_4$ ,  $\text{CD}_3\text{H}$ ,  $\text{CD}_2\text{H}_2$ , and  $\text{CDH}_3$  at temperatures beyond 3000 K. The mixed isotopic species have been calculated in this compilation using only the RRHO method, while  $\text{CH}_3$ ,  $\text{CH}_2$ , etc., were calculated using RRHO plus electronic excitation (Appendix C). On the other hand,  $\text{CH}_4$  and  $\text{CD}_4$  were calculated using both anharmonic and simple RRHO methods. It is the author's recommendation to use together species that were calculated by the same method.  $\text{CD}_3$ , etc., should be used together with  $\text{CH}_4$  and  $\text{CD}_4$  of the

anharmonic method, while  $CD_3H$ ,  $CD_2H_2$  and  $CDH_3$  should be used with  $CH_4$  and  $CD_4$  calculated by the simple RRHO method.

For the nonspecialist user of Appendix C who wants to know by which method a species was calculated, the following should be noted:

- (1) Anharmonic corrections were used if anharmonicity constants are given together with the other molecular constants;
- (2) RRHO formulas plus electronic excitation contributions were used if electronic levels are given;
- (3) In all other cases the calculations were done using the RRHO formulas.

As a closing word of caution it should be noted that the values of the polynomial coefficients generally have no meaning by themselves and that virtually the same property values can be generated by different sets of coefficients. Hence, judgment about the actual values of the coefficients is usually not possible, but it is possible to judge how well they collectively represent the thermodynamic functions themselves.

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