

# Construction of the JANAF tables and CEA polynomials

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The thermodynamic data contained in the JANAF tables (and calculated from CEA polynomials) can be divided into two categories: *thermal functions*, which describe the intrinsic thermodynamic properties of a chemical species, and *formation functions*, which describe the energy of formation of the chemical species relative to the adopted reference state(s) of the element(s) it contains.

## Thermal Functions

The thermal functions in the NIST-JANAF table include the following values:

$C_p^\circ(T)$	Heat capacity (J K <sup>-1</sup> mol <sup>-1</sup> )
$S^\circ(T) = \int_0^T [C_p^\circ(T)/T]dT$	Molar entropy (J K <sup>-1</sup> mol <sup>-1</sup> )
$H^\circ - H^\circ(T_r) = \int_{T_r}^T C_p^\circ(T)dT$	Enthalpy function (kJ mol <sup>-1</sup> )
$-[G^\circ(T) - H^\circ(T_r)]/T = S^\circ(T) - [H^\circ(T) - H^\circ(T_r)]/T$	Gibbs energy function (J K <sup>-1</sup> mol <sup>-1</sup> )

The basis for the entropy and enthalpy functions is the heat capacity, a key parameter for describing the temperature-dependent thermodynamic properties of each chemical species. The NASA CEA format employs a 7-coefficient power series for calculating the heat capacity  $C_p^\circ(T)/R$  along with integration constants  $b_1$  for  $H^\circ(T)/RT$  and  $b_2$  for  $S^\circ(T)/R$  in the following functions:

$$C_p^\circ(T)/R = a_1T^{-2} + a_2T^{-1} + a_3 + a_4T + a_5T^2 + a_6T^3 + a_7T^4 \quad (1)$$

$$H^\circ(T)/RT = -a_1T^{-2} + a_2(\ln T)/T + a_3 + a_4T/2 + a_5T^2/3 + a_6T^3/4 + a_7T^4/5 + b_1/T \quad (2)$$

$$S^\circ(T)/R = -a_1T^{-2}/2 - a_2T^{-1} + a_3(\ln T) + a_4T + a_5T^2/2 + a_6T^3/3 + a_7T^4/4 + b_2 \quad (3)$$

To reconstruct the JANAF tables from the CEA polynomials, the heat capacity  $C_p^\circ$  and entropy  $S^\circ$  can be calculated directly from their respective functions and the gas constant  $R$ . The enthalpy function  $H^\circ - H^\circ(T_r)$  describes the enthalpy change associated with changes in temperature. Taking  $T_r = 298.15$  it may be calculated by integration of the heat capacity function:

$$H^\circ(T) - H^\circ(298.15) = \int_{298.15}^T C_p^\circ(T)dT \quad (4)$$

or from the enthalpy function itself (which contains the integrated form of the  $C_p$  function):

$$H^\circ - H^\circ(298.15) = \left( \frac{H^\circ(T)}{RT} \right) \frac{RT}{1000} - \left( \frac{H^\circ(298.15)}{R \cdot 298.15} \right) \frac{R \cdot 298.15}{1000} \quad (5)$$

where the factor of 1000 is used to convert the function to kJ mol<sup>-1</sup>. For higher temperature intervals,  $T_r$  can be defined to allow consistent calculation of the enthalpy function from 298.15 K,

$$H^\circ(T) - H^\circ(298.15) = H^\circ(T_r) + \int_{T_r}^T C_p^\circ(T)dT \quad (6)$$

The Gibbs energy function (gef) is effectively an entropy calculation (sometimes called the third-law method) that relates the  $G^\circ(T)$  to  $H^\circ(T_r)$ , where  $T_r$  is typically taken to be 298.15 K. The  $\Delta_{\text{gef}}$  value for a chemical reaction can be used to

- calculate the reaction enthalpy  $\Delta H^\circ(T_r)$  from any measurement at equilibrium, or
- calculate the Gibbs energy of a reaction  $\Delta G^\circ(T)$  at any temperature if  $\Delta H^\circ(298.15)$  is known.

In other words, the  $\Delta_{\text{gef}}$  accounts for changes in the Gibbs free energy of a reaction system due to changes in the entropy and enthalpy of reactant(s) and product(s) as a function of temperature.

## Formation Functions

The formation functions in the NIST-JANAF tables include the following values:

$$\Delta H_f^\circ(T) \quad \text{Enthalpy of formation (kJ mol}^{-1}\text{)}$$

$$\Delta G_f^\circ(T) = -RT \ln K_f \quad \text{Gibbs energy of formation (kJ mol}^{-1}\text{)}$$

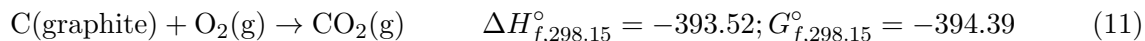
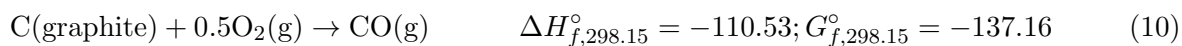
$$\log_{10} K_f = -\Delta G_f^\circ / \ln(10) RT \quad \text{Equilibrium constant for formation reaction}$$

For a given species, the  $\Delta H_f^\circ(T)$  and  $\Delta G_f^\circ(T)$  values correspond to the enthalpy and Gibbs free energy change, respectively, *for the formation reaction of that species*. The *formation reaction* is defined as the reaction that produces 1 mole of the species in question “from the elements” - typically the elements in their most stable state under standard conditions. This adopted *standard reference state* serves as a reference to which the  $\Delta H_f^\circ(T)$  and  $\Delta G_f^\circ(T)$  values for all other forms of an element - or any species involving that element - are considered. For this reason, great care must be taken when adopting  $\Delta H_f^\circ(T)$  and  $\Delta G_f^\circ(T)$  from multiple sources to ensure consistent calculation to common reference states. The selected reference states in the NASA CEA database (Gordon and McBride 1994, McBride and Gordon 1996) are listed in Zehe et al. (2001). The reference states adopted in the NIST-JANAF database are described in Chase (1998).

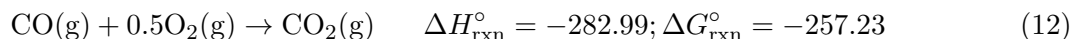
By definition, the  $\Delta H_f^\circ(T) = 0$ ,  $\Delta G_f^\circ(T) = 0$ , and  $\log_{10} K_f = 0$  for the adopted reference states. This is because formation functions must correspond to the *formation reaction* for the chemical species under consideration. The formation reaction of a species that is a reference state (“from the elements”) is thus a formation from itself, e.g.:



For other species, the  $\Delta H_f^\circ$  and  $\Delta G_f^\circ$  values refer to their respective formation reactions from the elements, e.g. at 298.15 K:



By common reference to standard reference states, the  $\Delta H_f^\circ$  and  $\Delta G_f^\circ$  values – and likewise the relative abundances of products and reactants at equilibrium – for *any* reaction can be determined, even if the reaction does not involve the reference state itself, e.g. at 298.15 K:



Usage of the thermal functions described here can be illustrated by considering an example reaction, such as the formation of CO<sub>2</sub> from the reference states C(graphite) and O<sub>2</sub>(g):



The NIST-JANAF tables show the following values:

<b>Oxygen, O<sub>2</sub>(g) Reference State</b>							
J K <sup>-1</sup> mol <sup>-1</sup>				kJ mol <sup>-1</sup>			
<i>T</i> /K	<i>C<sub>p</sub></i> <sup>°</sup> ( <i>T</i> )	<i>S</i> <sup>°</sup>	$-[G^\circ(T) - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	log <i>K<sub>f</sub></i>
298.15	29.376	205.147	205.147	0.	0.000	0.000	0.000
500	31.091	220.693	208.524	6.084	0.000	0.000	0.000
1000	34.870	243.578	220.875	22.703	0.000	0.000	0.000

<b>Carbon, C(graphite) Reference State</b>							
J K <sup>-1</sup> mol <sup>-1</sup>				kJ mol <sup>-1</sup>			
<i>T</i> /K	<i>C<sub>p</sub></i> <sup>°</sup> ( <i>T</i> )	<i>S</i> <sup>°</sup>	$-[G^\circ(T) - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	log <i>K<sub>f</sub></i>
298.15	8.517	5.740	5.740	0.	0.000	0.000	0.000
500	14.623	11.662	6.932	2.365	0.000	0.000	0.000
1000	21.610	24.457	12.662	11.795	0.000	0.000	0.000

<b>Carbon Monoxide, CO</b>							
J K <sup>-1</sup> mol <sup>-1</sup>				kJ mol <sup>-1</sup>			
<i>T</i> /K	<i>C<sub>p</sub></i> <sup>°</sup> ( <i>T</i> )	<i>S</i> <sup>°</sup>	$-[G^\circ(T) - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	log <i>K<sub>f</sub></i>
298.15	29.142	197.653	197.653	0.	-110.527	-137.163	24.030
500	29.794	212.831	200.968	5.931	-110.003	-155.414	16.236
1000	33.183	234.538	212.848	21.690	-111.983	-200.275	10.461

<b>Carbon Dioxide, CO<sub>2</sub></b>							
J K <sup>-1</sup> mol <sup>-1</sup>				kJ mol <sup>-1</sup>			
<i>T</i> /K	<i>C<sub>p</sub></i> <sup>°</sup> ( <i>T</i> )	<i>S</i> <sup>°</sup>	$-[G^\circ(T) - H^\circ(T_r)]/T$	$H^\circ - H^\circ(T_r)$	$\Delta H_f^\circ$	$\Delta G_f^\circ$	log <i>K<sub>f</sub></i>
298.15	37.129	213.795	213.795	0.	-393.522	-394.389	69.095
500	44.627	234.901	218.290	8.305	-393.666	-394.939	41.259
1000	54.308	269.299	235.901	33.397	-394.623	-395.886	20.679

element	phase	description	T interval
Ag	Ag(cr)	cubic	200-1235.08
	Ag(L)	liquid	1235.08-6000
Al	Al(cr)	cubic	200-933.61
	Al(L)	liquid	933.61-6000
Ar	Ar(g)	ideal gas	200-20000
B	B(b)	beta	200-2350
	B(L)	liquid	2350-6000
Ba	Ba(cr)	crystal	80-1000
	Ba(L)	liquid	1000-6000
Be	Be(a)	alpha	100-1543
	Be(b)	beta	1543-1563
	Be(L)	liquid	1563-6000
Br	Br2(cr)	rhombic	200-265.9
	Br2(L)	liquid	265.9-6000
C	C(gr)	Graphite	200-6000
Ca	Ca(a)	alpha	200-716
	Ca(b)	beta	716-1115
	Ca(L)	liquid	1115-6000
Cd	Cd(cr)	crystal	100-594.258
	Cd(L)	liquid	594.258-6000
Cl	CL2(g)	ideal gas	200-6000
Co	Co(a)	alpha	200-700.1
	Co(b)	beta; below lambda trans	700.1-1394
	Co(b)	beta; above lambda trans	1394-1768
	Co(L)	liquid	1768-6000
Cr	Cr(cr)	below lambda trans	200-311.5
	Cr(cr)	above lambda trans	311.5-2130
	Cr(L)	liquid	2130-6000
Cs	Cs(cr)	crystal	100-301.59
	Cs(L)	liquid	301.59-2000
Cu	Cu(cr)	cubic	200-1358
	Cu(L)	liquid	1358-6000
D	D2(g)	ideal gas	200-20000
e-	e-(g)	ideal gas	298.15-20000
F	F2(g)	ideal gas	200-6000
Fe	Fe(a)	alpha; below lambda trans	200-1042
	Fe(a)	alpha; above lambda trans	1042-1184
	Fe(c)	gamma	1184-1665
	Fe(d)	delta	1665-1809
	Fe(L)	liquid	1809-6000
Ga	Ga(cr)	rhombic	100-302.92
	Ga(L)	liquid	302.92-6000
Ge	Ge(cr)	cubic	200-1211.4
	Ge(L)	liquid	1211.4-6000
H	H2(g)	ideal gas	200-20000
He	He(g)	ideal gas	200-20000
Hg	Hg(cr)	tetragonal	100-234.29
	Hg(L)	liquid	234.29-2000
I	I2(cr)	rhombic	200-386.75
	I2(L)	liquid	386.75-6000
In	In(cr)	tetragonal	100-429.784
	In(L)	liquid	429.784-6000
K	K(cr)	cubic	200-336.86
	K(L)	liquid	336.86-2200
Kr	Kr(g)	ideal gas	200-20000
Li	Li(cr)	crystal	200-453.69
	Li(L)	liquid	453.69-6000
Mg	Mg(cr)	hexagonal	100-923
	Mg(L)	liquid	923-6000
Mn	Mn(a)	alpha	200-980
	Mn(b)	beta	980-1361
	Mn(c)	gamma	1361-1412
	Mn(d)	delta	1412-1519
	Mn(L)	liquid	1519-6000
Mo	Mo(cr)	crystal	200-2896
	Mo(L)	liquid	2896-6000
N	N2(g)	ideal gas	200-20000
Na	Na(cr)	cubic	200-371.01
	Na(L)	liquid	371.01-2300
	Nb(cr)	crystal	200-2750
Ne	Nb(L)	liquid	2750-6000
	Ne(g)	ideal gas	200-20000
Ni	Ni(cr)	below lambda trans	200-631
	Ni(cr)	above lambda trans	631-1728
	Ni(L)	liquid	1728-6000
O	O2(g)	ideal gas	200-20000
P	P(cr)	White	195.4-317.3
	P(L)	liquid	317.3-6000
Pb	Pb(cr)	cubic	200-600.65
	Pb(L)	liquid	600.65-3600
Rb	Rb(cr)	cubic	100-312.47
	Rb(L)	liquid	312.47-2100
Rn	Rn(g)	ideal gas	200-20000
S	S(a)	alpha	200-368.3
	S(b)	beta	368.3-388.36
	S(L)	liquid	388.36-6000
Sc	Sc(a)	alpha	100-1609
	Sc(b)	beta	1609-1814
	Sc(L)	Liquid	1814-6000
Si	Si(cr)	cubic	200-1690

	Si(L)	liquid	1690-6000
Sn	Sn(cr)	tetragonal	200-505.118
	Sn(L)	liquid	505.118-4700
Sr	Sr(a)	alpha	100-820
	Sr(b)	beta	820-1041
	Sr(L)	liquid	1041-6000
Ta	Ta(cr)	crystal	200-3258
	Ta(L)	liquid	3258-6000
Th	Th(a)	alpha	200-1650
	Th(b)	beta	1650-2023
	Th(L)	liquid	2023-6000
Ti	Ti(a)	alpha	200-1156
	Ti(b)	beta	1156-1944
	Ti(L)	liquid	1944-6000
U	U(a)	alpha	200-942
	U(b)	beta	942-1049
	U(c)	gamma	1049-1408
	U(L)	liquid	1408-4000
V	V(cr)	crystal	200-2190
	V(L)	liquid	2190-6000
W	W(cr)	crystal	200-3680
	W(L)	liquid	3680-6000
Xe	Xe(g)	ideal gas	200-20000
Zn	Zn(cr)	crystal	200-692.73
	Zn(L)	liquid	692.73-6000
Zr	Zr(a)	alpha	200-1135
	Zr(b)	beta	1135-2125
	Zr(L)	liquid	2125-6000