Construction of the JANAF tables and CEA polynomials

Channon Visscher, Dordt University; Space Science Institute

The thermodynamic data contained in the JANAF tables (and calculated from CEA polynomials) can be divded 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^{-1} mol^{-1})

$S^\circ(T) = \int_0^T [C_p^\circ(T)/T]dT$ Molar entropy (J K^{-1} mol^{-1})

$H^\circ - H^\circ(T_r) = \int_{T_r}^T C_p^\circ(T)dT$ Enthalpy function (kJ mol^{-1})

$-[G^\circ(T) - H^\circ(T_r)]/T = S^\circ(T) - [H^\circ(T) - H^\circ(T_r)]/T$ Gibbs energy function (J K^{-1} mol^{-1})

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:

$$C_p^\circ(T)/R = a_1 T^{-2} + a_2 T^{-1} + a_3 + a_4 T + a_5 T^2 + a_6 T^3 + a_7 T^4 \tag{1}$$

$$H^\circ(T)/RT = -a_1 T^{-2} + a_2 (\ln T)/T + a_3 + a_4 T/2 + a_5 T^2/3 + a_6 T^3/4 + a_7 T^4/5 + b_1/T \tag{2}$$

$$S^\circ(T)/R = -a_1 T^{-2}/2 - a_2 T^{-1} + a_3 (\ln T) + a_4 T + a_5 T^2/2 + a_6 T^3/3 + a_7 T^4/4 + b_2 \tag{3}$$

To reconstruct the JANAF tables from the CEA polynomials, the heat capacity C_p° and entropy S° 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:

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

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

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

where the factor of 1000 is used to convert the function to kJ mol^{-1}. For higher temperature intervals, T_r can be defined to allow consistent calculation of the enthalpy function from 298.15 K,

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

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 Δgef 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 Δgef 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:

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

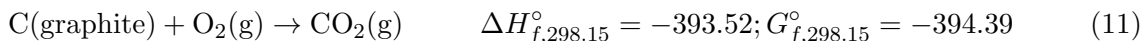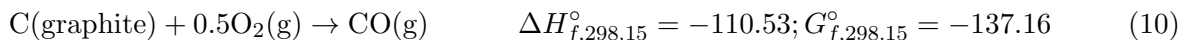$$\Delta G_f^\circ(T) = -RT \ln K_f \qquad \text{Gibbs energy of formation (kJ mol}^{-1})$$

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

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.:

$$\text{C(graphite)} \rightarrow \text{C(graphite)} \qquad \Delta H_f^\circ = 0; G_f^\circ = 0 \qquad (7)$$
$$\text{O}_2(\text{g}) \rightarrow \text{O}_2(\text{g}) \qquad \Delta H_f^\circ = 0; G_f^\circ = 0 \qquad (8)$$
$$\text{P(cr; white)} \rightarrow \text{P(cr; white)} \qquad \Delta H_f^\circ = 0; G_f^\circ = 0 \qquad (9)$$

For other species, the ΔH_f° and ΔG_f° values refer to their respective formation reactions from the elements, e.g. at 298.15 K:

$$\text{C(graphite)} + 0.5\text{O}_2(\text{g}) \rightarrow \text{CO(g)} \qquad \Delta H_{f,298.15}^\circ = -110.53; G_{f,298.15}^\circ = -137.16 \qquad (10)$$
$$\text{C(graphite)} + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \qquad \Delta H_{f,298.15}^\circ = -393.52; G_{f,298.15}^\circ = -394.39 \qquad (11)$$

By common reference to standard reference states, the ΔH_f° and ΔG_f° 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:

$$\text{CO(g)} + 0.5\text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g}) \qquad \Delta H_{\text{rxn}}^\circ = -282.99; \Delta G_{\text{rxn}}^\circ = -257.23 \qquad (12)$$