3.7 EMPIRICAL HEAT-CAPACITY EXPRESSIONS

Although theoretical values of C_V can be determined for ideal gases (see Sec. 3.8), the equations for C_V for the condensed states of matter are much more complex, and empirical relations of the types

$$C_P = a + bT + cT^2 + dT^3 \tag{3.22a}$$

$$C_P = a + bT + c'T^{-2} \tag{3.22b}$$

are often used for these phases and also to represent actual data for gases.

EXAMPLE 3.8. The values of a and b in (3.22a) for aluminum are 20.7 J K^{-1} mol^{-1} and 0.012 4 J K^{-2} mol^{-1}, respectively. Calculate ΔH for heating aluminum from 25 °C to 100. °C.

Using (3.15) gives

$$\begin{aligned}\Delta H &= \int_{T_1}^{T_2} (a + bT)\,dT = a(T_2 - T_1) + \tfrac{1}{2}b(T_2^2 - T_1^2)\\ &= (20.7\ \text{J K}^{-1}\ \text{mol}^{-1})(373\ \text{K} - 298\ \text{K}) + \tfrac{1}{2}(0.012\,4\ \text{J K}^{-2}\ \text{mol}^{-1})[(373\ \text{K})^2 - (298\ \text{K})^2]\\ &= 1\,860\ \text{J mol}^{-1}\end{aligned}$$

3.8 C_V FOR IDEAL GASES

For 1 mol of an ideal gas, $C_V = (\partial E(\text{thermal})/\partial T)_V$. The contributions are

$$C_V(\text{trans}) = \tfrac{3}{2}R \tag{3.23a}$$

$$C_V(\text{rot}) = \begin{cases} R & \text{for a diatomic or linear polyatomic molecule} \\ \tfrac{3}{2}R & \text{for a nonlinear polyatomic molecule}\end{cases} \tag{3.23b}$$

$$C_V(\text{vib}) = \sum_{i=1}^{3A-5\text{ or }3A-6} \frac{Rx_i^2 e^{x_i}}{(e^{x_i}-1)^2} \tag{3.23c}$$

$$C_V(\text{elec}) = R\left[\frac{Q''}{Q} - \left(\frac{Q'}{Q}\right)^2\right] \tag{3.23d}$$

where x_i, Q, and Q' have been previously defined by (3.7) and (3.8) and

$$Q'' = \sum_j g_j \left(\frac{\varepsilon_j}{kT}\right)^2 e^{-\varepsilon_j/kT} \tag{3.8c}$$

If nuclear contributions are included, (3.23d) is used to determine these contributions.

EXAMPLE 3.9. The heat capacity ratio C_P/C_V for a gas was experimentally measured as 1.38. If the empirical formula is ABA, what conclusions can be made concerning the structure?

Assuming the gas to be ideal, (3.18) gives

$$C_P = C_V + R$$

which upon substitution into the desired ratio gives

$$\frac{C_V + R}{C_V} = 1.38 \qquad \text{or} \qquad C_V = 2.63R$$

If vibrational contributions are neglected, $C_V = 2.5R$ for a linear triatomic gas and $C_V = 3.0R$ for a nonlinear triatomic gas. Assuming the difference of $0.13R$ to be from vibrational contributions, the gas is linear.

3.9 C_V FOR CONDENSED STATES

Many metals at room temperature have an average value of $C_P = 25.9$ J K^{-1} mol^{-1}. Using this in combination with (3.13) generates the *law of Dulong and Petit*, which can be used to determine