

Estimating ΔG° (Exercise 13.7)

Problems P13.29, P13.30, P13.31, and P13.32 require the following:

P13.29. The volume of a spherical molecule can be estimated as if it were a sphere. The van der Waals parameter b for the molecule under concern can be found in Appendix 1, which relates this relationship by considering a sphere of diameter of radius r , with volume $V = \frac{4}{3}\pi r^3$. When water volume contained in the molecule that is perturbed by the action of electrostatic forces is assumed to be negligible, the volume for b can be approximated by Equation 13-10, which relates b to the radius of sphere of $r = \frac{1}{2}d$, where d is the value of a **van der Waals** molecular diameter from the value of its van der Waals parameter.

The van der Waals a is $\left(\frac{4}{3}\pi r^3\right) \times \left(\frac{4}{3}\pi r^3\right) \times \left(\frac{1}{V_m}\right) \times \left(\frac{1}{V_m}\right)$ per molecule. Therefore,

for $a(\text{J} \cdot \text{m}^3 \cdot \text{mol}^{-2})$ and $V_m(\text{m}^3 \cdot \text{mol}^{-1})$ units, the value for b is as follows (Table 1.1):

$$b = \frac{\frac{3a}{4\pi}}{\left(\frac{4}{3}\pi r^3\right)} = \left(\frac{3a(\text{J} \cdot \text{m}^3 \cdot \text{mol}^{-2})}{4\pi \times 4.189 \times 10^{-31} \text{ m}^3}\right) = \frac{1.43 \times 10^{-28} \text{ m}^3}{\text{mol}}$$

P13.29. Estimate the specific enthalpy of vaporization of **carbon** from the values of the van der Waals constants. Use the b value for the carbon parameter in Table 1.1.

$$\begin{aligned} \Delta H^\circ &= \frac{RT_c}{1.7} = \frac{(8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \times (3642 \text{ K})}{1.7} = \frac{2790 \text{ J}}{\text{mol}} = \frac{0.00279 \text{ kJ}}{\text{mol}} \\ &= \frac{1.1 \times 10^4 \text{ J} - [1.1 \times (0.114 \times 10^4 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}) \times (3642 \text{ K})]}{1.7} = \frac{1.06 \times 10^4 \text{ J}}{\text{mol}} \\ &= \frac{1.06 \text{ kJ} \cdot \text{mol}^{-1} \times 10^3 \text{ mol}^{-1}}{1.1 \times 10^4} \end{aligned}$$

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