$$\bar{u}^*_{el}\big|_{T<<\theta_d} = -\bar{R}\,\theta_d \qquad \text{(IIIC-B2)}$$

With this result we are able to determine the net energy change when a molecule is formed from its constituent atoms. For reference purposes these *formation reactions* are normally considered to occur at fixed temperature and pressure. Under these conditions the heat of the reaction is called the *enthalpy of formation*, $\Delta\bar{h}_f$.

Example B1. Determine the change in enthalpy when oxygen is formed from its constituent atoms at 298 K and atmospheric pressure.

The defining reaction is $2O \Rightarrow O_2$. Under these conditions both atomic and molecular oxygen are perfect gases. Thus the enthalpy change is

$$\Delta\bar{h}_f(T_o) = \bar{h}^*_{O_2}(T_o) - 2\bar{h}^*_O(T_o)$$

To determine the value we must use an absolute or a common reference base. We have chosen the atom in its lowest electronic level as a basis for our calculations.[23] Thus using the formulae of Table IIIC-1 and the data of Tables IIIC-2 and B1, we find

$$\bar{h}^*_{O_2}(298\text{ K}) = \bar{R}\left\{\frac{7}{2}T + \theta_v\left[\frac{1}{2} + \frac{1}{\left(e^{\theta_v/T} - 1\right)}\right] - \theta_d\right\} = 8.314\text{ J/(g mol K)}\left\{\left(\frac{7}{2}\right)\cdot 298\text{ K}\right.$$

$$\left. + 3392\text{ K}\left[\frac{1}{2} + \frac{1}{e^{(3392\text{ K}/298\text{ K})} - 1}\right] - 5.90\cdot 10^4\text{K}\right\} = -4.737\cdot 10^5\text{ J/(g mol)}$$

$$\bar{h}^*_O(298\text{ K}) = \frac{5}{2}\bar{R}T = \left(\frac{5}{2}\right)\cdot 8.314\text{ J/(g mol K)}\cdot 298\text{ K} = 6196\text{ J/(g mol)}$$

Thus

$$\Delta\bar{h}_f(298\text{ K}) = -4.588\cdot 10^5 - 2\cdot 6196 = -4.861\cdot 10^5\text{ J/(g mol)}$$

Exmp. B1 affirms our expectation that the major portion of chemical energy results from the formation and or destruction of molecular bonds. Though we have only considered the formation reaction of a homonuclear diatomic molecule, the formation of compound molecules from unlike elements or new compounds from molecular reactants are simply extensions of the same techniques. Combustion processes are considered in Units VIB and C. The calculations for combustion analysis depend upon absolute property data developed by the methods of this unit.

---

[23]The JANAF Tables use the elements in their natural state as the reference basis. Thus the enthalpy of formation of O_2 is defined as zero; but atomic oxygen has an enthalpy of reaction of opposite sign and half the value of the result obtained here.

Ans. B1.

$$\bar{u}_{el} = \bar{R}T^2\left(\frac{\partial \ln Z_{el}}{\partial T}\right)_{\bar{v}} = \bar{R}T^2\left[\frac{\partial}{\partial T}\left(g_{el,}\ e^{\theta_d/T}\right)\right]_{\bar{v}} = -\bar{R}\theta_d$$

$$\bar{c}_{v,el} = \left(\frac{\partial \bar{u}_{el}}{\partial T}\right)_{\bar{v}} = 0 \qquad \bar{s}_{el} = \frac{\bar{u}_{el}}{T} + \bar{R}\ln Z_{el} = \bar{R}\left[-\frac{\theta_d}{T} + \ln(g_{el,1}) + \frac{\theta_d}{T}\right] = \bar{R}\ln g_{el,1}$$