SECTION 14: THE FORMAL DEFINITION OF ENTHALPY

If we wanted to look at more general cases, such as situations where the pressure changes during the reaction, or the initial and final temperatures are not equal, we will need a better definition of enthalpy. The formal definition of enthalpy is:

\[ H = E + PV \]

Note that this is a definition of \( H \), not \( \Delta H \). As such, it has no real practical use, because we cannot measure the total energy of a chemical system. To relate \( \Delta H \) to \( \Delta E \), we will need to do the following manipulations:

\[
\Delta H = H_{\text{final}} - H_{\text{initial}} \\
= (E_{\text{final}} + P_{\text{final}}V_{\text{final}}) - (E_{\text{initial}} + P_{\text{initial}}V_{\text{initial}}) \\
= (E_{\text{final}} - E_{\text{initial}}) + (P_{\text{final}}V_{\text{final}} - P_{\text{initial}}V_{\text{initial}}) \\
= \Delta E + (P_{\text{final}}V_{\text{final}} - P_{\text{initial}}V_{\text{initial}})
\]

For solids and liquids, the PV term is essentially zero and can be ignored. For gases, we can use the ideal gas law:

\[
\Delta H = \Delta E + n_{\text{final}}RT_{\text{final}} - n_{\text{initial}}RT_{\text{initial}} \\
= \Delta E + R(n_{\text{final}}T_{\text{final}} - n_{\text{initial}}T_{\text{initial}})
\]

This is a general expression and can be used under any circumstances. For cases when the initial and final temperatures are equal, we can factor out T, and the expression reduces to:

\[
\Delta H = \Delta E + RT(n_{\text{final}} - n_{\text{initial}}) \\
= \Delta E + RT\Delta n_{\text{gases}}
\]

…which is the equation from the previous section.