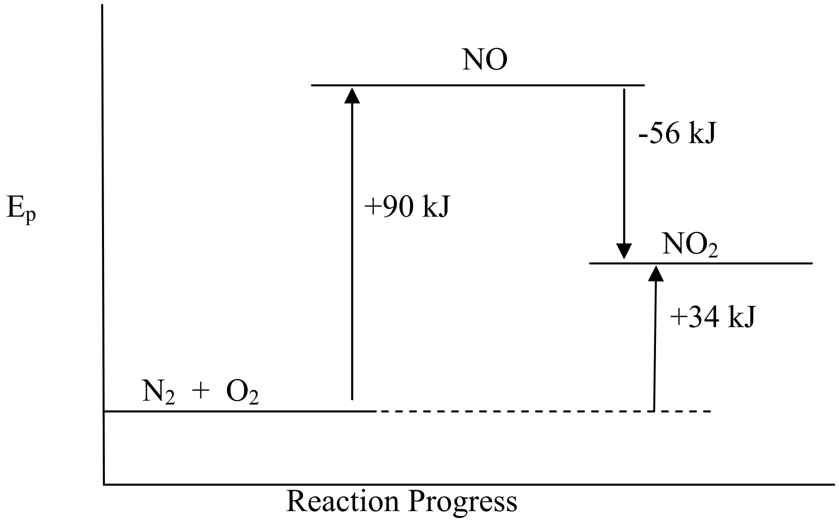
Section 5.4: Hess's Law of Additivity of Reaction Enthalpies

Calorimetry is an accurate technique used to determine changes in enthalpy. How is the enthalpy of chemical systems that can not be determined by this technique calculated?

The calculations are based on the principle that overall changes in some properties of a system are independent of the way the system changes from the initial state to the final state. An analogy for this idea is the construction of a brick wall, the net vertical distance that the bricks rise is the same whether they go up in one stage or in two stages.

The same principle applies to enthalpy changes: if a set of reactions occurs in different steps but the initial reactants and final products are the same, the overall enthalpy change is the same.

Potential Energy Diagram Showing Additive Enthalpy Changes



In this potential energy diagram, $N_{2(g)}$ and $O_{2(g)}$ combine to form NO_2, nitrogen dioxide. There are two different paths to reach the products: (i) N_2 and O_2 gases react to form NO, nitrogen monoxide, a reaction for which ΔH = +90 kJ. Then, NO, nitrogen monoxide combines with more O_2 to form $NO_{2(g)}$, a reaction that releases energy, ΔH = -56 kJ.

(ii) In the second path N_2 and O_2 react directly to form NO_2.

In both paths the overall enthalpy change, ΔH = +34 kJ, is the same.

Predicting ΔH Using Hess's Law

Based on experimental evidence, similar to the experiment you performed in class, a mathematical relationship was developed to help predict the overall ΔH for a series of related chemical reactions.

Hess's Law states: The value of the ΔH for any reaction that can be written in steps equals the sum of the values of ΔH for each of the individual steps.

The law can be restated as: if two or more equations with known enthalpy changes, ΔH, can be added together to form the overall equation for the reaction, then their individual enthalpy changes are also additive.

$$\Delta \mathbf{H}_{\mathbf{overall}} = \Delta \mathbf{H}_1 + \Delta \mathbf{H}_2 + \Delta \mathbf{H}_3 + \ldots$$

or

$$\Delta \mathbf{H}_{\mathbf{overall}} = \sum \Delta \mathbf{H}_{\mathbf{known}}$$

Hess's Law allows for the determination of enthalpy changes without the direct use of calorimetry.

Two rules must be followed:

(i) If a chemical equation is reversed, then the sign of ΔH changes.
(ii) If the coefficients of a chemical equation are altered by multiplying or dividing by a constant factor, then the ΔH is altered in the same way.

Enthalpy is a ***state function***

(i) It depends only upon the ***initial and final state*** of the reactants/products and ***not on the specific pathway*** taken to get from the reactants to the products
(ii) Whether one can arrive at the products via either a single step or multi-step mechanism is unimportant as far as the enthalpy of reaction is concerned - they should be equal

Determining ΔH for the reaction

$$\mathbf{C_{(s)} + \tfrac{1}{2}\, O_{2(g)} \rightarrow CO_{(g)}}$$

is difficult because some CO_2 is also typically produced.
However, complete oxidation of either C or CO to yield CO_2 is experimentally pretty easy to do:

(1) $\mathbf{C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)}}$ $\quad \Delta H = -393.5\ \text{kJ}$

(2) $\mathbf{CO_{(g)} + \tfrac{1}{2}O_{2(g)} \rightarrow CO_{2(g)}}$ $\quad \Delta H = -283.0\ \text{kJ}$

We can invert reaction number 2 (making it ***endothermic***) and have CO(g) as a ***product.*** (This describes the decomposition of CO_2 to produce CO and O_2)

(3) $\mathbf{CO_{2(g)} \rightarrow CO_{(g)} + \tfrac{1}{2}O_{2(g)}}$ $\quad \Delta H = +283.0\ \text{kJ}$

Thus, we now have two equations, (1) and (3) with known enthalpies of reaction:
the first describes the combustion of carbon and oxygen to produce CO_2 and
the second describes how CO_2 can be decomposed to produce carbon monoxide (and oxygen).

We can combine these together to describe the production of carbon monoxide from the combustion of carbon and oxygen. Canceling out identical compounds from the left and right hand sides of this reaction gives

(1) $\mathbf{C_{(s)}} + \overset{\mathbf{\frac{1}{2}O_2}}{\cancel{\mathbf{O_{2(g)}}}} \rightarrow \cancel{\mathbf{CO_{2(g)}}}$ $\Delta H = -393.5\ \text{kJ}$

(3) $\cancel{\mathbf{CO_{2(g)}}} \rightarrow \mathbf{CO_{(g)}} + \cancel{\mathbf{\tfrac{1}{2}O_{2(g)}}}$ $\Delta H = +283.0\ \text{kJ}$

Algebraically adding the two equations to yield the overall equation with the associated overall enthalpy:

$$\mathbf{C_{(s)}} + \tfrac{1}{2}\,\mathbf{O_{2(g)}} \rightarrow \mathbf{CO_{(g)}} \qquad \Delta H = -110.5\ \text{kJ}$$

H.W.
Read section 5.4 in your textbook and study the examples provided.
Pg. 326 do 1 to 3
pg. 239 do 4 and 5