Hess's Law
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General Chemistry I

Goal:	To determine the standard enthalpy of reaction by two different methods thus demonstrating the concept of path independence.
Previous Skills:	Allowed manipulations of thermochemical equations. Write a thermochemical equation using standard enthalpies of formation.

We will calculate the standard enthalpy of reaction for the following equation-

$$N_2O(g) + NO_2(g) \rightarrow 3NO(g) \qquad \Delta H^0 = ?\ kJ$$

using two related but different methods.

Example #1: Use of Given Thermochemical Equations

The standard enthalpy of reaction can be calculated using the given thermochemical equations-

(1) $N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H^0 = +180.7\ kJ$

(2) $2NO(g) + O_2(g) \rightarrow 2NO_2(g) \qquad \Delta H^0 = -113.1\ kJ$

(3) $2N_2O(g) \rightarrow 2N_2(g) + O_2(g) \qquad \Delta H^0 = -163.2\ kJ$

The idea is to use each of the three given thermochemical equations and manipulate them in some way such that when the chemical equations are added up, it equals the original chemical equation.

Looking at the original equation, we can see that it has $N_2O(g)$ in it as a reactant and so does thermochemical equation #3. However, we need to multiply it by 1/2.

$$N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H^0 = -81.6\ kJ$$

Looking at the original equation, we can see that it has $NO_2(g)$ as a reactant. Thermochemical equation #2 does have $NO_2(g)$ in it but it's as a product so we need to flip it. Additionally, we also need to multiply everything by 1/2.

$$NO_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g) \qquad \Delta H^0 = +56.6\ kJ$$

We need to use all three of the given thermochemical equations and we have yet to use thermochemical equation #1. Trying to figure out how to use it is a little tricky and can be approached a couple of ways. If you look at what we've done to thermochemical equations #2 and #3, you'll see that we have a total of 1 $O_2(g)$ at this point. Since the original chemical equation does not have any $O_2(g)$ in it, we need to use our final thermochemical equation in such a way that all of the $O_2(g)$ is eliminated. Remembering linear equations, we can deduce that thermochemical equation #1 must be used just as it is written-

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H^0 = +180.7 \text{ kJ}$$

Let's summarize our equations and add them up.

$$N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H^0 = -81.6 \text{ kJ}$$

$$NO_2(g) \rightarrow NO(g) + \frac{1}{2}O_2(g) \qquad \Delta H^0 = +56.6 \text{ kJ}$$

$$N_2(g) + O_2(g) \rightarrow 2NO(g) \qquad \Delta H^0 = +180.7 \text{ kJ}$$

$$N_2O(g) + NO_2(g) \rightarrow 3NO(g) \qquad \Delta H^0 = +155.7 \text{ kJ}$$

Since our manipulated chemical equations add up to the original chemical equation, we can add up the manipulated standard enthalpies of reaction to get the standard enthalpy of reaction for the original chemical equation.

Example #2: Use of Standard Enthalpies of Formation.

Let's look at the original chemical equation-

$$N_2O(g) + NO_2(g) \rightarrow 3NO(g)$$

We need to write enthalpies of formation thermochemical equations for each of the chemical species using table values.

(1) $N_2(g) + \frac{1}{2}O_2(g) \rightarrow N_2O(g) \qquad \Delta H_f^0 = +82.0 \text{ kJ/mol}$

(2) $\frac{1}{2}N_2(g) + O_2(g) \rightarrow NO_2(g) \qquad \Delta H_f^0 = +33.1 \text{ kJ/mol}$

(3) $\frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) \rightarrow NO(g) \qquad \Delta H_f^0 = +90.3 \text{ kJ/mol}$

You need to remember how to write these. Look back at your lecture notes. Also, remember that if there were any chemical species in the original thermochemical equation in their natural state, we would not write any enthalpy of formation equations for them. Why?

Enthalpy of formation equations #1 and #2 do need to be flipped and multiplied by 1 mol. While enthalpy of formation equation #3 does not need to be flipped, we do need to multiply it by 3 mol.

$$N_2O(g) \rightarrow N_2(g) + \frac{1}{2}O_2(g) \qquad \Delta H^0 = -82.0 \text{ kJ}$$

$$NO_2(g) \rightarrow \frac{1}{2}N_2(g) + O_2(g) \qquad \Delta H^0 = -33.1 \text{ kJ}$$

$$\frac{3}{2}N_2(g) + \frac{3}{2}O_2(g) \rightarrow 3NO(g) \qquad \Delta H^0 = +270.9 \text{ kJ}$$

$$N_2O(g) + NO_2(g) \rightarrow 3NO(g) \qquad \Delta H^0 = +155.8 \text{ kJ}$$

The standard enthalpy of reaction calculated this way matches very closely to that calculated initially, +155.7 kJ. This is likely due to rounding in the given data.

The standard enthalpy of reaction was calculated using two different, but related, methods and we came up with the same number. This demonstrates that enthalpy is path independent.