1.8: Hess' Law

Sometimes we can use available information about the energetics of reactions to predict the energetics of a new reaction. To see how, we'll look at a relatively simple reaction: the combustion of carbon.

A couple of things could happen when we burn some carbon. Burning typically results in the combination of the elements in a material with oxygen. So we are just talking about combining carbon with oxygen to make a new compound. There are two possibilities. Either the reaction forms carbon monoxide, or it forms carbon dioxide.

The first reaction is:

$$2\,\mathrm{C} + \mathrm{O_2} \rightarrow 2\,\mathrm{CO} \tag{1.8.1}$$

That reaction is exothermic. It releases about 25 kcal per mol of CO produced.

Note that the reaction has been balanced to keep track of the exact numbers of atoms involved in the transaction. Because only one oxygen atom is needed, and the oxygen molecules comes with two oxygen atoms, the oxygen molecule can actually convert two carbon atoms into carbon monoxide.

The second reaction is:

$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2} \tag{1.8.2}$$

That reaction is also exothermic. It releases about 90 kcal per mol of CO_2 produced.

Because energy is released, or produced, by each reaction, we can think about the energy as another product of the reaction. We'll just list it on the product side of the equation with the other products.

$$2\,\mathrm{C} + \mathrm{O_2} \rightarrow 2\,\mathrm{CO} + 50\,\frac{\mathrm{kcal}}{\mathrm{mol}} \tag{1.8.3}$$

and

$$\mathrm{C} + \mathrm{O_2} \rightarrow \mathrm{CO_2} + 90\,\frac{\mathrm{kcal}}{\mathrm{mol}} \tag{1.8.4}$$

There's a third reaction that is related to these two reactions. It's the combustion of carbon monoxide.

$$2CO + O_2 \rightarrow 2CO_2 \tag{1.8.5}$$

Again, the reaction is exothermic, releasing about 65 kcal per mole of CO_2 produced. It would release 130 kcal for the reaction as written, because we are showing the production of two moles of CO_2. Rewriting the equation to include the energy produced:

$$2CO + O_2 \rightarrow 2CO_2 + 130\frac{kcal}{mol} \tag{1.8.6}$$

What if we conducted this reaction in stages? What if we combusted the carbon to carbon monoxide, then took the carbon monoxide and allowed it to react further to get carbon dioxide?

$$2C + O_2 \rightarrow 2CO + 50\frac{kcal}{mol} \tag{1.8.7}$$

$$2CO + O_2 \rightarrow 2CO_2 + 130\frac{kcal}{mol} \tag{1.8.8}$$

Imagine this is a pair of algebraic equations. What would happen if we added them together?

$$2C + O_2 = 2CO + 50\frac{kcal}{mol} \tag{1.8.9}$$

$$2CO + O_2 = 2CO_2 + 130\frac{kcal}{mol} \tag{1.8.10}$$

Sum: $2C + 2CO + 2O_2 = 2CO + 2CO_2 + 180\frac{kcal}{mol}$

Note that the CO appears on both sides and would cancel.

$$2C + 2O_2 = 2CO_2 + 180\frac{kcal}{mol} \tag{1.8.11}$$

We can drop the factor of 2:

$$C + O_2 = CO_2 + 90\frac{kcal}{mol} \tag{1.8.12}$$

So two reactions, one after the other, would add up to a third. In addition, the energies of those two reactions, added together, give the energy of the third.

This result is a pretty important aspect of thermodynamics. Enthalpy is a state function. that means it does not matter how a reaction is performed. Whether we convert carbon directly into carbon dioxide or we convert it to carbon monoxide, then continue, the e nergy involved is the same overall. That's because the energy of the reaction is a property of the products and the reactants only. It is independent of how we get from one to the other.

One more note on the reactions above. The enthalpies for these reactions, if measured in the correct way, are sometimes called the heats of formation of the compounds. The heat of formation refers to the energy change when the compounds are formed from the elements under standard conditions. We're not going too deeply into what those standard conditions are here. However, because C is the elemental form of carbon and O_2 is the elemental form of oxygen, we would loosely consider the energies listed above to be heats of formation.

- When you hear the phrase "heat of formation", we're just talking about the formation of the compound from the elements.

Exercise 1.8.1

a. If the heat of formation of potassium chloride, KCl, is -104 kcal/mol, and the heat of formation or potassium chlorite, $KClO_2$, is -95 kcal/mol, then what is the heat of reaction when potassium chloride reacts with oxygen to produce potassium chlorite?
b. If the heat of formation of tantalum(IV) oxide, TaO_2, is -40 kcal/mol, and the heat of formation of tantalum(V) oxide, Ta_2O_5, is -490 kcal/mol, then what is the heat of reaction for the combustion of TaO_2 to Ta_2O_5?
c. If the heat of formation of carbon monoxide, CO, is -25 kcal/mol and the heat of formation of tetracarbonyl nickel, $Ni(CO)_4$, is -145 kcal/mol, then what is the heat of reaction for the formation of tetracarbonyl nickel from nickel and carbon monoxide?

Answer
Answer a

We could write the equations for the reactions, including the energy change involved:

K + 0.5 Cl_2 → KCl + 104 kcal/mol

There is a 0.5 in front of the Cl_2. Although chlorine is diatomic in its elemental state, we only need half the number of Cl_2 molecules as we need potassium atoms if we are to form potassium chloride.

K + 0.5 Cl_2 + O_2 → $KClO_2$ + 95 kcal/mol

In both cases, the heat of formation is negative, so we are writing that energy as a product of the reaction.

If we write the first reaction in reverse,

104 kcal/mol + KCl → K + 0.5 Cl_2

then we are saying that the reverse reaction would require the input of energy.

We will combine those two equations by adding them together:

K + 0.5 Cl_2 + O_2 → $KClO_2$ + 95 kcal/mol

104 kcal/mol + KCl → K + 0.5 Cl_2

Sum:

104 kcal/mol + KCl + K + 0.5 Cl_2 + O_2 → K + 0.5 Cl_2 + $KClO_2$ + 95 kcal/mol

Simplifying (the 0.5 chlorine molecules and potassium atoms appear on both sides, so they cancel):

$104\ kcal/mol + KCl + O_2 \rightarrow KClO_2 + 95\ kcal/mol$

Now we use more algebra and combine the numerical part together:

$104\ kcal/mol - 95\ kcal/mol + KCl + O_2 \rightarrow KClO_2 + 95\ kcal/mol - 95\ kcal/mol$

Which leaves:

$9\ kcal/mol + KCl + O_2 \rightarrow KClO_2$

The energy is added on the left. It is needed for the reaction. The heat of reaction, $\Delta H_{rxn} = +\ 9\ kcal/mol$. It's an endothermic reaction.