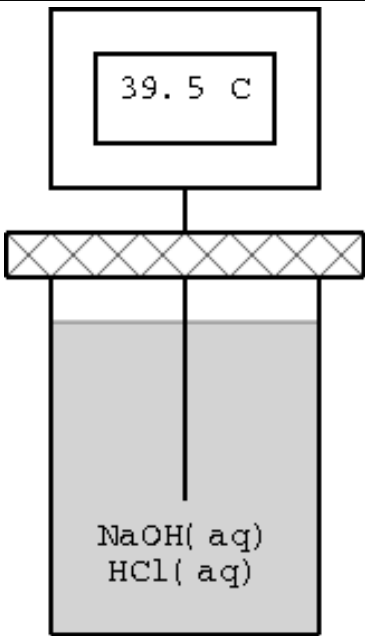


Introduction

We've discussed thermochemical equations previously, and that they could be used for calculating the heat transfer (enthalpy change) in chemical reactions. So far, these heats have been just given to you in a thermochemical equation. This note pack will tell you how you can find out the heat (enthalpy change) of reaction of a reaction if the information is **not** simply provided in advance.

Calorimetry

One of our labs is a **calorimetry** experiment. It involves taking a known quantity of reactants and **measuring** their enthalpy change experimentally. To do this, we use an instrument called a calorimeter. In our lab, this is a rather simple device made from Styrofoam cups and a thermometer.

	<ul style="list-style-type: none"> <li>• The system: The chemical reaction - the reactants and products.</li> <li>• The surroundings: The water the reactants are dissolved in and the cup.</li> <li>• The heat produced (or required) is measured by monitoring the temperature change of the contents of the calorimeter, and using the <b>specific heat</b> of water to calculate the amount of heat involved.</li> </ul>
Illustration 1 - Coffee cup calorimeter	

The calorimeter pictured contains hydrochloric acid solution combined with sodium hydroxide solution - an acid-base reaction. How do we get the heat the reaction produces from the temperature change we measure?

To figure this out, we observe that a certain amount of heat is produced by the reaction. This heat flows from the reagents to the surroundings. The surroundings then increase in temperature. How much heat, though, does it take to increase the temperature of a calorimeter and a bunch of water?

If we know the volume of water in the calorimeter, we can figure this out from the

**specific heat.** The **specific heat** is the **heat required to raise the temperature of 1 gram of a substance by 1 degree Celsius**. This property is tabulated for many substances, and can be used almost like a conversion factor.

$$Q_{\text{substance}} = s \times m \times \Delta T$$

where

- $Q_{\text{substance}}$  = the heat
- $s$  = the specific heat
- $m$  = the mass of the substance
- $\Delta T$  = the **final temperature** of the substance **minus the initial temperature** of the substance.

The specific heat of **water** is  $4.184 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}$

For example, you can find the heat change if 50.0 g water is cooled from 100.0 °C to 25.0 °C:

$$Q_{\text{water}} = \left(4.184 \frac{\text{J}}{\text{g} \cdot ^\circ\text{C}}\right) \times (50.0 \text{ g}) \times (25.0 ^\circ\text{C} - 100.0 ^\circ\text{C}) = -15700 \text{ J}$$

$$Q_{\text{water}} = -15700 \text{ J (or -15.7 kJ)}$$

The sign of  $Q$  is negative. This water has **lost heat**, and the process of cooling is **exothermic**.

What about the calorimeter (the cup)? If we know the **heat capacity** of the calorimeter, we can find the amount of heat required to change the temperature of the calorimeter. The **heat capacity** is the **amount of heat required to raise the temperature of an object by 1 degree Celsius**. This property can be used as a conversion factor.

$$Q_{\text{object}} = C \times \Delta T$$

where

- $Q_{\text{object}}$  = the heat
- $C$  = the heat capacity
- $\Delta T$  = the **final temperature** of the substance **minus the initial temperature** of the substance.

You can then calculate the heat transfer in the calorimeter as:

$$Q_{\text{system}} + Q_{\text{water}} + Q_{\text{cup}} = 0, \text{ or}$$

$$Q_{\text{system}} = -(Q_{\text{water}} + Q_{\text{cup}})$$

The sign on the heat change of the system is **opposite** the sign of the heat change on the surroundings (the cup and water). This is because heat flows from one to the other. A loss from the system is a gain to the surroundings!

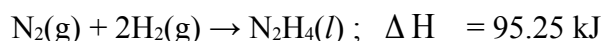
### Hess's Law

What if you're interested in a heat of reaction and you either don't have a calorimeter handy or you just don't have time to get a heat of reaction experimentally? We can use a certain property of the enthalpy to actually calculate heats of reaction from tabulated heats. [*Enthalpy change is the same thing as the heat of reaction at constant pressure!*]

Hess's Law states that **the sum of the enthalpy changes in individual steps in a chemical reaction is equal to the enthalpy change of the overall reaction**. In short, if  $A \rightarrow B$  and  $B \rightarrow C$ , the enthalpy change of  $A \rightarrow C$  is the same as the sum of the enthalpy changes of  $A \rightarrow B$  and  $B \rightarrow C$ . This is easier to grasp if you think of the enthalpy as if it's a location. No matter how you **get** to Columbia from Florence, you're still the same distance from Florence when you arrive there.

You can add up these enthalpies for any reaction you choose. However, the reactions that you will find tabulated in books are so-called **formation reactions**. **Formation reactions** are reactions that form **one mole** of a substance **from its elements at their standard states**. For thermodynamics, standard state is defined as 25 °C and 1 atm pressure. [*This is different from STP for gases!*] Elements at their standard states are defined as having an enthalpy of formation of **zero**.

For example, let's take the compound hydrazine ( $N_2H_4$ ). If you look in a set of tables of thermodynamic data, you would find this reaction.



This is the formation reaction of hydrazine. Nitrogen and hydrogen are in the form of diatomic molecules, since this is how they exist at 25 °C and 1 atm pressure. Hydrazine is a liquid at 25 °C and 1 atm pressure, so it appears that way in the formation reaction.

You can add and subtract formation reactions to make nearly any chemical reaction you choose - and that's the reason the enthalpies of formation reactions are tabulated. It's not necessary, though, to even write down the formation reactions themselves. You can find the enthalpy of reaction of an arbitrary reaction by summing the heats of formation of the products and subtracting the sum of the heat of formation of the reactants. **Each heat of formation should be multiplied by its stoichiometric coefficient in the reaction.**

Let's do an example. Acetone ( $CH_3COCH_3$ ) is a solvent you may be familiar with - it used to be a common fingernail polish remover. It's currently an ingredient in many solvents you'd buy at a home store for removing paint. Acetone is also extremely flammable. *What is the enthalpy of reaction for the combustion of acetone?*



We'll use Hess's Law to answer this question. First, we'll look up all the **enthalpies of formation** of the products and reactants. I used the CRC Handbook of Chemistry and Physics (available in most libraries and in the lab) to get the numbers in this note pack. Your textbook has some of these heats of formation tabulated.

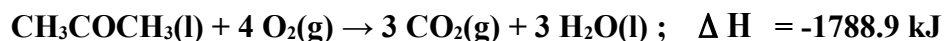
<i>Reactants</i>	<i>Products</i>
$\text{CH}_3\text{COCH}_3(l); \Delta H_f = -248.1 \text{ kJ/mol}$	$\text{CO}_2(g); \Delta H_f = -393.5 \text{ kJ/mol}$
$\text{O}_2(g); \Delta H_f = 0.0 \text{ kJ/mol}$ (a pure element at standard state!)	$\text{H}_2\text{O}(l); \Delta H_f = -285.8 \text{ kJ/mol}$

Now that we have our data, we can find the enthalpy change. The enthalpy change of the reaction is:

- Reactants:  $1 \times (-248.1 \text{ kJ}) + 4 \times (0 \text{ kJ}) = -248.1 \text{ kJ}$
- Products:  $3 \times (-393.5 \text{ kJ}) + 3 \times (-285.8 \text{ kJ}) = -2037.0 \text{ kJ}$

$$\text{Reaction} = \text{Products} - \text{Reactants} = -2037.0 \text{ kJ} - (-248.1 \text{ kJ}) = \mathbf{-1788.9 \text{ kJ}}$$

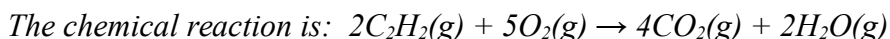
So, the enthalpy change for the combustion of one mole of acetone (see the equation) is -1788.9 kJ. As you would expect, the combustion of acetone is exothermic. You could write the thermochemical equation for the combustion of acetone this way:



### Putting it all together

We've discussed enthalpies of reaction and how to get them from both experimental data and from looking up enthalpies of formation in the literature. We know how to calculate the heat of reaction. Let's do an example that fits most of the pieces together.

*Acetylene ( $\text{C}_2\text{H}_2$ ,  $FW = 26.04$ ), a common fuel for welding torches, burns in oxygen to form carbon dioxide gas and gaseous water. How much heat is produced if 424.2 g of acetylene is burned? What volume of  $\text{CO}_2$  gas would be produced at 25 °C and 1.00 atm pressure by the combustion?*



This problem involves use of the gas laws and the heat of reaction. How do we start this problem? The first thing you should realize is that this problem is at its heart a simple stoichiometry problem. Tacked onto it are the application of Hess's Law (to find the enthalpy of reaction) and the ideal gas equation (to find the volume of  $\text{CO}_2$  gas).

Let's do the heat problem first. To solve this, we first need the enthalpy of reaction. We have to look up the required heats of formation.

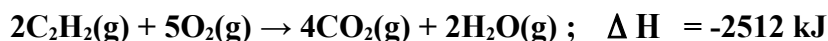
<i>Reactants</i>	<i>Products</i>
$\text{C}_2\text{H}_2(\text{g}); \Delta H_f = 227 \text{ kJ/mol}$	$\text{CO}_2(\text{g}); \Delta H_f = -393.5 \text{ kJ/mol}$
$\text{O}_2(\text{g}); \Delta H_f = 0.0 \text{ kJ/mol}$ (element at standard state)	$\text{H}_2\text{O}(\text{g}); \Delta H_f = -241.8 \text{ kJ/mol}$

Let's sum up the products and reactants:

- Reactants:  $2 \times (227 \text{ kJ}) + 5 \times (0 \text{ kJ}) = 454 \text{ kJ}$
- Products:  $4 \times (-393.5 \text{ kJ}) + 2 \times (-241.8 \text{ kJ}) = -2057.6 \text{ kJ}$

$$\text{Reaction} = \text{Products} - \text{Reactants} = -2057.6 \text{ kJ} - (454 \text{ kJ}) = \mathbf{-2512 \text{ kJ}}$$

So, we can write the equation as:



Now, we can solve this just like we solved the problem in the previous note pack. First, find the number of moles acetylene, then find the heat change.

$$424.2 \text{ g C}_2\text{H}_2 \times \frac{1 \text{ mol C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2} \times \frac{-2512 \text{ kJ}}{2 \text{ mol C}_2\text{H}_2} = \mathbf{-20461 \text{ kJ}}$$

So,  $\mathbf{Q = -20460 \text{ kJ (rounded)}}$ . The reaction is exothermic, and you could also say that  $\mathbf{20460 \text{ kJ of heat were released}}$ .

Now on to the ideal gas law part of the problem. First, find the moles of acetylene that reacted, then relate to moles of  $\text{CO}_2$  formed, and then use the ideal gas equation to find the volume at the given conditions.

Find moles ...

$$424.2 \text{ g C}_2\text{H}_2 \times \frac{1 \text{ mol C}_2\text{H}_2}{26.04 \text{ g C}_2\text{H}_2} \times \frac{4 \text{ mol CO}_2}{2 \text{ mol C}_2\text{H}_2} = \mathbf{32.58 \text{ mol CO}_2}$$

Now, we set up the ideal gas equation,  $PV = nRT$

The variables:

$P = 1.00 \text{ atm}$  (given)

$R = 0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}$  (gas constant)

$V = ???$  (trying to find this)

$T = 298 \text{ K}$  (converted from Celsius)

$n = 32.58 \text{ mol CO}_2$  (calculated)

$$V = \frac{n \times R \times T}{P} = \frac{(32.58 \text{ mol}) \times (0.08206 \frac{\text{L}\cdot\text{atm}}{\text{mol}\cdot\text{K}}) \times (298 \text{ K})}{(1.00 \text{ atm})} = \mathbf{797 \text{ L}}$$

**$V = 797 \text{ L CO}_2$  gas produced.**

### Summary

In this pack, we've learned how enthalpies of reaction were found (both experimentally and from the literature). We've also worked through an exercise where we had to pull together concepts we learned previously to solve a problem involving both the heat of reaction and gas formation. If you understand the examples here, you should be well-prepared for any problems you see later in the course.