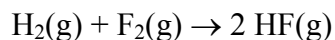


The Additivity of Enthalpy Changes

Background

During chemical changes bonds are broken and/or formed. These changes in bonding always involve energy changes: energy is required to overcome the attractive forces that enable a bond to form, and energy is released when bonding entities achieve a more stable configuration in which attractive forces exceed repulsive forces. These energy changes may be manifested as light, sound, electrical work, pressure/volume work, or heat--to name a few possibilities. It can be demonstrated that heat changes in reactions are directly connected to the energy of bonds by comparing the changes in bond energy to the overall measured energy changes for the same chemical process. For example, for the synthesis of hydrogen fluoride gas from the elements:



the experimentally determined bond energies are given in the table below.

bond	H-H	F-F	H-F
bond energy, kJ/mol	436.4	156.9	568.2

If the simple assumption is made that the bonds in the reactants are broken and the bonds in the products are formed, the energy input for breaking bonds would be 436.4 kJ + 156.9 kJ while the energy output from the formation of the product bonds would be 2(568.2 kJ). The result is a net energy output of 543.1 kJ. The experimentally determined energy output (found by measuring heat) for the reaction as written is 537.2 kJ. This is good agreement. Heat changes are frequent enough in laboratory-scale reactions and they are relatively easy to determine based on temperature changes.

The most common way to determine the amount of heat absorbed or released during a chemical change is to run the reaction in an insulated container and to measure the initial and final temperatures of the *system*. The thermometer itself (or digital temperature probe) is actually part of the surroundings, i.e., not part of the chemical system under observation. In the case of a reaction which gives off heat we might therefore write:

$$\text{heat lost by system} = \text{heat gained by surroundings}$$

The opposite would be true for a reaction which absorbs heat [and both statements assume that no heat is "lost" in the transfer]. The first case describes a reaction which is *exothermic*. The latter case is called *endothermic*.

By convention, changes in heat are relative to the system and therefore signs are used to indicate the direction of heat flow during a chemical change. If we assign the variable q to heat, we might write the statement above as:

$$-q_{\text{sys}} = +q_{\text{surr}}$$

There are two typical ways to measure q . In the most common, the system is "open" to the surroundings so that any gases formed will leave and the pressure will remain constant (although the volume will change if gases are involved since the temperature is changing). This heat term is designated as q_p .

Adapted from A Laboratory Demonstration of the Conservation of Energy, Kalbus, Mantei and Petrucci, *J. of College Science Teaching*, Feb. 1983, p. 277-278

In *bomb calorimetry*, a closed system (with a constant volume) prevents the escape of any gases that might form. Heat measured under those conditions is designated q_v . These two quantities will differ by a quantity known as "pressure-volume work", $P\Delta V$, which has to do with how much work the system can do on the surroundings due to a volume change at constant pressure. The total change in internal energy is equal to the heat measured at constant volume since:

$$\Delta E = q + w \quad (\text{where } w = \text{"work"})$$

$$\text{so } \Delta E = q + P\Delta V$$

and if V is fixed, then $\Delta V = 0$, so $P\Delta V = 0$ and

$$\Delta E = q_v.$$

In reactions which either consume or produce gases such work may be done in an open system, however, but for reactions occurring only in condensed phases this work is negligible or non-existent. Because chemists are not generally concerned as much with work as with energy in the form of heat, measurements are generally made under constant pressure (which is much easier to do), i.e., in a vessel open to the atmosphere. Under those conditions:

$$q_p = \Delta E + P\Delta V$$

[the sign conventions are incredibly bewildering in thermochemistry]

Heat is routinely determined as q_p in the laboratory using a device known as a *calorimeter*. At its simplest, this is an insulated container which is designed to minimize heat losses, hopefully restricting the heat exchange to the system and the thermometer. In reality, each calorimeter has associated with it a *heat capacity*. This is the amount of energy needed to raise the temperature of the calorimeter by one degree. That means some heat will end up exchanging with the container itself. In very accurate work this must be taken into account. To relate the temperature change in a calorimeter system to the heat change, the following expression is used:

$$q_p = \text{mass}_{\text{system}} \times (t_{\text{initial}} - t_{\text{final}}) \times s_{\text{system}} + (t_{\text{initial}} - t_{\text{final}}) \times C_{\text{calorimeter}}$$

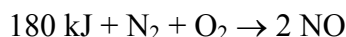
Where t is the temperature [units of $^{\circ}\text{C}$ or K may be used], s is the *specific heat* of the system [the amount of heat needed to raise the temperature of one gram by one degree], and C is the heat capacity of the calorimeter, also known as the *calorimeter constant*.

[The expression above has been written with particular care so that the sign of q_p (which is for the system) will be correct. In practice the change in temperature is sometimes treated as an absolute value to simplify number crunching and then the appropriate sign is added to the answer.]

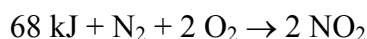
The heat term q_p is equivalent to an important thermodynamic quantity, the *enthalpy change* or ΔH [generally speaking, ΔH is given as a molar quantity while q_p is an arbitrary value for the given experimental amounts]. Enthalpy (H) is a property of substances which is not directly measurable. It is possible to measure changes in enthalpy, however, and these are largely associated with the bond rearrangement mentioned at the beginning of this discussion or with alterations in intermolecular attractions.

Enthalpy is an example of a *state property*. Its magnitude depends on the original state or final state of the substance and not the method of transformation. **Therefore ΔH must be independent of pathway since the reactants and products could be the same for different processes which start and end with the same materials.** That sentence states, in so many words, the underlying principle behind Hess's Law of the additivity of reaction enthalpies. It also addresses more indirectly the First Law of Thermodynamics (*energy is conserved*) since the heats that pass between steps in an overall process must tally up so that the overall heat change is the same regardless of how many steps there are between the same points A and B.

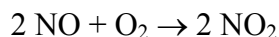
Using a simple set of related reactions the logic behind this relationship can be demonstrated. Consider the reaction to form nitrogen monoxide (NO) from the elements:



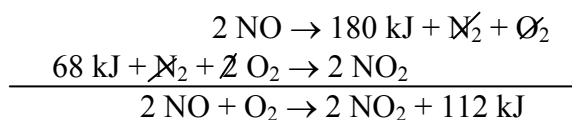
This reaction is endothermic. The same elements can also react to form nitrogen dioxide under different conditions:



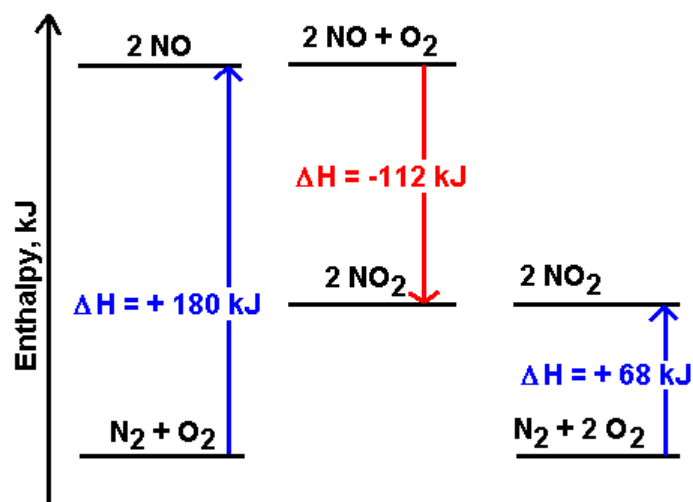
Nitrogen dioxide can also be produced from the reaction of NO and O₂:



The enthalpy change of this process can be determined by comparing the enthalpy changes for the related reactions since this process is an algebraic combination of the others:



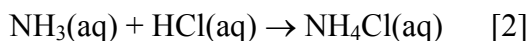
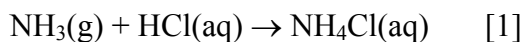
The diagram below shows the same information in another way.



These principles can be applied to a number of simple reaction systems. In this experiment our attention is focused on the reaction between ammonia and hydrogen chloride:



At room temperature both ammonia and hydrogen chloride are gases and generally aqueous solutions of the compounds are used in the lab. Each concentrated solution exerts a fairly high partial pressure of the dissolved gas and the gas can be displaced from the solution by forcing in another gas. This technique can be used to help compare the reaction by two pathways:

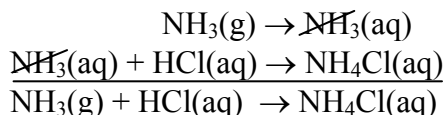


For reaction [1] air is bubbled through a solution of concentrated ammonia and displaces some ammonia gas which is directed into a solution of hydrochloric acid until a suitable indicator signals that the HCl has completely reacted. The temperature change of the HCl is monitored. During this process the temperature change of the ammonia solution also gives information about the heat flow for this process:



For reaction [2], a slight excess of aqueous concentrated ammonia is added directly to a solution of hydrochloric acid. The temperature change of this system yields heat information about the reaction of the aqueous species.

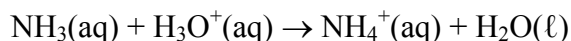
The heat change for reaction [1] can be determined using these two heat changes appropriately, noting that only the beginning and final states are important, not the pathway. Thus the reactions can be combined as follows:



and a similar manipulation of the calculated heat changes should give q_p for reaction [1].

It should be recognized that these reactions as written are themselves only representative of other changes which result in the overall transformation, and they are not very realistic. For example, the interactions between gaseous ammonia and water are mainly hydrogen bonding but because the ammonia is also protonated to a small extent by water (forming NH_4^+ and OH^-) there is a hidden energy term there.

Additionally, while the primary non-water species in aqueous ammonia is certainly $\text{NH}_3(\text{aq})$, in HCl the primary reacting species is probably H_3O^+ or its equivalent. Also, no appreciable amount of $\text{NH}_4\text{Cl}(\text{aq})$ exists in the final mixture, i.e., there is no ion-ion attraction to consider. A more accurate representation of the aqueous reaction might be:



Each of the processes discussed might be represented in alternative ways but even they would ultimately be related by the energy changes in each.

The Experiment

There are three parts to this experiment:

- determine q_p for reaction [1]
- determine q_p for reaction [2]
- determine q_p for reaction [3]

The following non-locker materials will be provided:

- concentrated $\text{NH}_3(\text{aq})$ [fume hood]
- 1.0 M HCl
- methyl red indicator
- gas generator for displacing ammonia
- 600 mL beaker w/insulation
- piston pumps
- expanded polystyrene calorimeter
- CBL w/thermometer probe

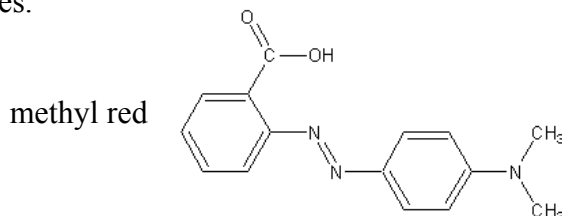
The Chemicals

Ammonia is a gas at room temperature. Laboratory solutions of aqueous ammonia have sometimes been erroneously called "ammonium hydroxide" although there is little evidence for the existence of that compound. Aqueous solutions of ammonia are basic.

Ammonia gas can be manufactured from industrial gases associated with the processing of "coke", a spongy form of carbon obtained from processing coal and essential in steel-making. In the Haber-Bosch process nitrogen and hydrogen from these industrial gas mixtures are combined at high temperature and pressure in the presence of a catalyst to form ammonia. The gas and its aqueous solutions are colorless with a very pungent odor (lower limit of human perception: 0.04 g/m^3). Mixtures of ammonia gas and air can explode when ignited under favorable conditions. At room temperature ammonia is soluble to the extent of 31% in water, only 16% in methanol. It is used in the manufacture of nitric acid, explosives, fertilizers and in refrigeration. In anhydrous liquid form it is a good solvent for many elements and compounds, notably the alkali metals which yield blue solutions when dissolved in liquid ammonia.

Inhalation of the concentrated vapor causes swelling in the respiratory tract, spasms and asphyxia.

Methyl red (or *o*-[[*p*-dimethylamino)phenyl]azo]benzoic acid) is an azo dye used as an indicator in a 0.1% alcohol solution. At pH 4.4 it is red and turns yellow at pH 6.2. It is used for titrating ammonia and weak organic bases.



Hydrochloric acid is also known as muriatic acid. It is the same liquid acid that is often used in controlling the pH of swimming pool water. It is sometimes colored yellow by iron impurities, traces of chlorine and organic matter. Reagent grade HCl contains about 38% hydrogen chloride gas, close to the limit of its solubility at room temperature.

Hydrochloric acid in concentrated form (12 M) has the sharp, choking odor of hydrogen chloride. It is used in the production of other chlorides and in refining some ores (tin and tantalum), cleaning metal products, removing scale from boilers and heat-exchange equipment, and as an important laboratory reagent (often in diluted form).

Concentrated solutions cause severe burns; permanent visual damage may occur. Inhalation causes coughing, choking; inflammation and ulceration of the respiratory tract may occur. Ingestion can be fatal.

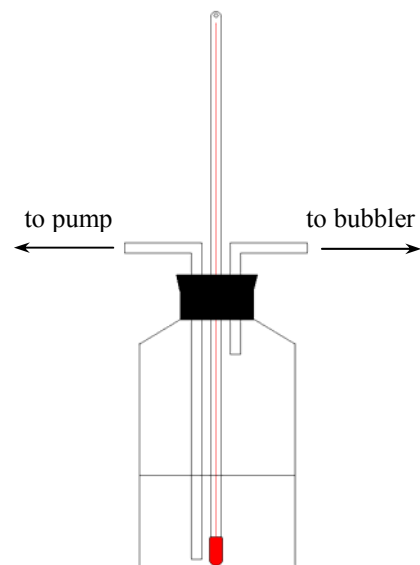
Technique Discussion

Because of the strong, irritating odor of ammonia much of the preparative work of this experiment must be done in the fume hood. To ensure adequate space in the fume hoods, the class will be divided in half [although three determinations are required, two are done simultaneously]. Some students will conduct the reaction of aqueous ammonia with hydrochloric acid--a relatively quick procedure--while others are running the displacement of gaseous ammonia into hydrochloric acid. When equipment becomes available, the remaining determination should be done by each student.

Reaction [2] is the most straightforward to perform. 100.0 mL of 1.0 M HCl is placed in a dry expanded polystyrene calorimeter. These calorimeters should have two cups and should *always* be used in their supporting beakers and with their lids. This not only helps to stabilize them but also adds an additional insulating blanket of air. 8 mL of concentrated ammonia is added in the fume hood. The initial and final temperatures can be measured with a CBL probe. **Be sure to bring your TI-83/84 calculator to lab and have the HCHEM.8XG programs in memory.** To help minimize heat exchange with the air above the acid as the ammonia is poured in, a funnel can be placed in the calorimeter, with its stem resting on the bottom. Added ammonia then goes directly down into the solution rather than reacting at the surface as soon as it makes contact.

8 mL is a slight stoichiometric excess to establish HCl as the definite limiting reagent in all parts of the experiment. This allows all q_p values to be compared without conversion to molar enthalpy values. Because the mixture will have a slight excess of ammonia at the end of the reaction it should be discarded in the fume hood sink.

The gas generator for displacing ammonia is supplied with a standard thermometer. A tube which connects to the air pump leads down into the aqueous ammonia. As air is forced into the solution (which is saturated), ammonia gas is liberated and exhausted through a second tube which terminates in a bubbler. The bubbler is **completely** immersed in HCl which has methyl red added to it. Once the indicator changes, the pump is stopped or disconnected. Initial and final temperatures for both systems should be recorded.



To minimize the release of ammonia into the lab the entire apparatus should be ready to use before the gas generator is filled [in the fume hood]. 100.0 mL of 1.0 M HCl is placed in an expanded polystyrene calorimeter. The cover has two holes, one for a CBL thermometer probe and the other for the bubbler. There should be enough space around one or the other to see the color of the solution. The initial temperature should be recorded.

To minimize heat loss the ammonia gas must be transferred fairly quickly. 50 mL of concentrated ammonia is placed in the generator bottle. The bottle should then be stoppered [twist the stopper slightly to be sure it is firmly seated] and a pinch clamp placed on the hose which will be connected to the pump. To help keep the stopper in place, a strong rubber band may be used across the stopper and under the bottom of the bottle. The bottle should be wrapped in insulating foam and placed in a 600 mL beaker with an insulating pad in the bottom. The initial temperature of the ammonia should be recorded before air is bubbled through the system.

With the bubbler completely immersed in the HCl, the pinch clamp is loosened and the air pump connected. Vigorous bubbling should ensue in both containers. When the indicator signals the reaction is complete the pump should be disconnected and the pinch clamp replaced [the clamp acts as an anti-siphon device]. The final temperatures of both solutions should be recorded after swirling.

The generator should be disassembled in the fume hood. The depleted aqueous ammonia should be poured into the bottle labeled for that purpose [its concentration generally drops from 14.8 to about 10 M]. The generator should be rinsed in the fume hood.

The Report

Your initial calculations should include:

[you may assume the various calorimeter constants all = 0]

1. The temperature changes in each reaction
2. The heat gained or lost by the ammonia solution during dissolution
(the density of concentrated ammonia is 0.90 g/mL, the specific heat is 5.2 J/g°C)
3. The heat gained or lost by the HCl solution during the reaction with gaseous ammonia
(the density of 1 M NH₄Cl is 1.075 g/mL, the specific heat is 3.8 J/g°C)
4. The heat gained or lost by the HCl solution during the reaction with aqueous concentrated ammonia
(same assumptions as in #3)
5. A comparison of the heat changes illustrating the additivity of enthalpies in this cycle

Your conclusion to this experiment should include a brief discussion of the inherent errors in the design and specifically how they relate to your results [as usual....]. Show by diagram (similar to the NO/NO₂ example in the Background section) how the q_p values are related in this system.