

Hess' Law and the First Law of Thermodynamics¹

Chemical thermodynamics deals with the energy changes that accompany chemical reactions. Such energy changes are guiding factors in determining how fast a chemical reaction takes place (chemical kinetics) and how complete the reaction will be (chemical equilibrium). Thermochemistry concerns energy changes manifested as the heat of reaction or change in enthalpy, H . ΔH is the change in enthalpy of a chemical system, $H_2 - H_1$, when it changes from some initial state to a final state. ΔH equals the change in thermal energy only when the process is carried out at constant pressure.

A reaction in which heat is lost by the reactants to the surroundings is said to be exothermic, where ΔH is defined by convention to be a negative value; one in which heat is absorbed is endothermic where ΔH is a positive value. Energy changes also may be manifested as electrical energy measured in terms of voltage required or produced and the amount of chemical change. Mechanical work can also be done by a system, for example when a gas expands against atmospheric pressure.

Enthalpy changes may be classified into more specific categories: (1) the heat of formation is the amount of heat involved in the formation of 1 mole of the substance directly from its constituent elements in their standard states; (2) the heat of combustion is the amount of heat evolved per mole of a combustible substance, such as carbon or methane, undergoing a reaction with excess oxygen; (3) the heats of solution, vaporization, fusion, and sublimation are related to the hydration of molecules or ions or changes in state; (4) the heat of neutralization is the heat evolved when 1 mole of water is produced by the reaction of an acid and a base. In this experiment, we will measure the heats of neutralization of HCl and of CH_3COOH solutions with a NaOH solution. This data should permit you to observe Hess' Law of heat summation.

Enthalpy changes are usually measured in a calorimeter, a simple version of which is shown in Figure 1. The purpose of the calorimeter is to isolate thermally, the system being investigated or in this case, the solution under study. All of the heat liberated or absorbed by the chemical reaction is to be given to the contents of the calorimeter or absorbed from them.

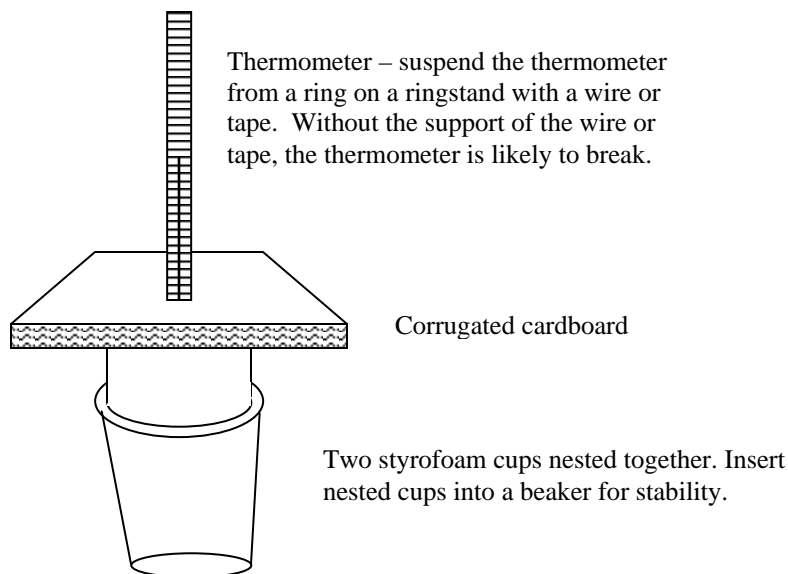


Figure 1

The amount of heat required to raise the temperature of a substance by 1°C is called the heat capacity of that material. The specific heat is the heat capacity per g of the substance. The units of the specific heat are cal/g·°C or J/g·°C. The unit cal is an abbreviation for calorie, the quantity of heat required to heat 1 g of water 1°C. The equivalent heat in joules is 4.184 J to heat 1 g of water 1°C. Use this specific heat to compute the heat released or acquired by water. Use a specific heat that will be given later for several other solutions in the experiment. You will measure the increase (or decrease) in temperature of a given volume of a particular solution. The amount of heat required to produce this change in temperature is calculated by multiplying the volume of the solution by its density, then by its specific heat, and finally by the temperature change. Dimensional analysis shows that this procedure yields the number of joules released or absorbed:

Heat = (Volume of solution)(density of solution)(specific heat)(temperature change)

$$J = (mL) \left(\frac{g}{mL} \right) \left(\frac{J}{g \cdot ^\circ C} \right) (^\circ C)$$

Correction must be made for the heat absorbed by or evolved from the calorimeter. Also, if the temperature difference between the calorimeter and the surroundings is appreciable, and if the insulation is insufficient, it may be advisable to take a series of temperature-time readings and to extrapolate a graph of these data back to the time of mixing, to obtain a correct temperature change, $\Delta T(^\circ C)$ for the reaction. (See Figure 2)

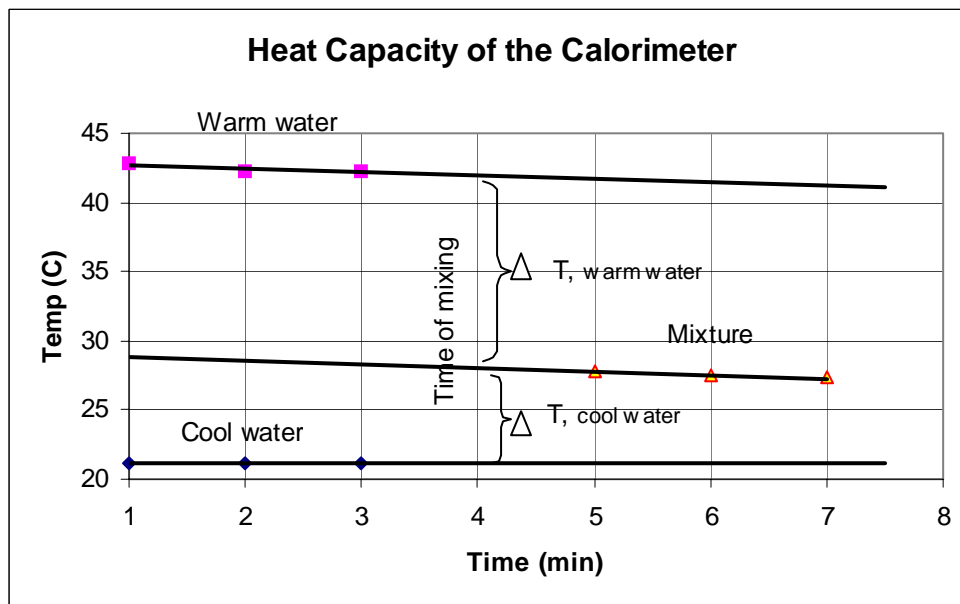


Figure 2

The above graph can be generated using the Excel chart wizard. Extrapolate by adding a trendline for each series (select points for a series, then add trendline), and then use options for the trendline to forecast forward or backward (0.5 unit).

Calculate the heat lost by the warmer water, and the heat gained by the cooler water. (Mass of water x $\Delta T_{\circ C}$ x specific heat. Assume that the density of water = 1.0 g/mL, and

the specific heat = $4.184 \text{ J/g}\cdot\text{°C}$.) The difference, representing the joules gained by the calorimeter, divided by the temperature increase of the cooler water, gives the heat capacity of the calorimeter in $\text{J}/\text{°C}$. It is unnecessary to express this result on a gram basis. It simply measures the amount of heat required to raise the Styrofoam cup (and thermometer) 1°C . Repeat this determination as a check, and average your results.

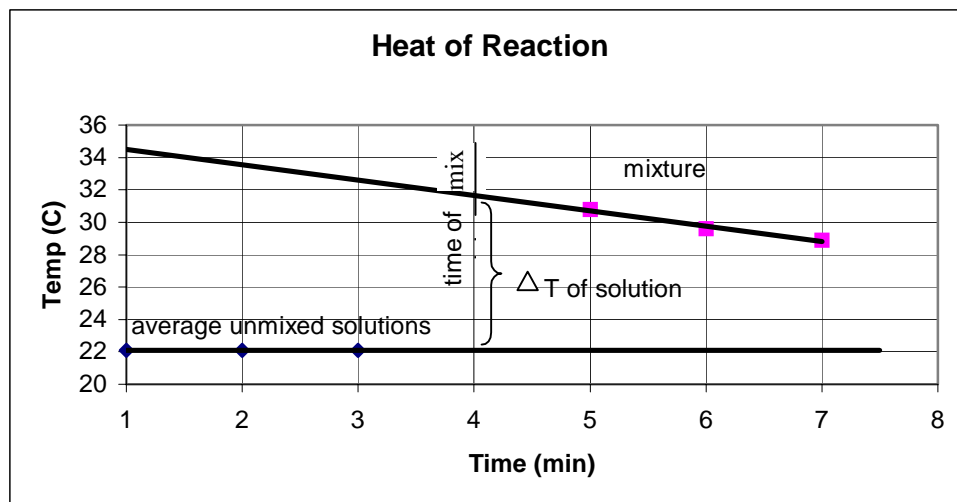


Figure 3

The following examples will illustrate how the heat capacity of the calorimeter may be determined, and later used as a correction factor.

Example 1 Heat Capacity of the Calorimeter Data

Temperatures at Time of Mixing

Warm Water 37.9°C

Cool Water 20.9°C

Mixture 29.1°C

Heat lost by warm water: $(50. \text{ g})(8.8\text{°C})(4.18 \text{ J/g}\cdot\text{°C}) = 1,800 \text{ J}$

Heat gained by cool water: $(50. \text{ g})(8.2\text{°C})(4.18 \text{ J/g}\cdot\text{°C}) = 1,700 \text{ J}$

Heat gained by calorimeter: $1,800 - 1,700 \text{ J} = 100 \text{ J}$

Heat capacity of the calorimeter: $100\text{J}/8.2\text{°C} = 12 \text{ J}/\text{°C}$ (but 1 sig fig)

Example 2 Use the heat capacity of the calorimeter in the calculation of the heat of a reaction: During a reaction in this calorimeter 100 mL of a solution increases in temperature by 6.5°C .

Heat gained by the water: $(100\text{g})(6.5\text{°C})(4.18 \text{ J/g}\cdot\text{°C}) = 2700 \text{ J}$

Heat gained by the calorimeter: $(12 \text{ J}/\text{°C})(6.5\text{°C}) = 80 \text{ J}$

Heat of reaction: $2700 \text{ J} + 80 \text{ J} = 2,780 \text{ J}$ or 2800 J

EXPERIMENTAL PROCEDURE

Special Supplies: 2 thermometers, foam plastic hot-cold cups (Styrofoam) for use as calorimeters, 250 mL beakers, corrugated cardboard for calorimeter covers.

A. Heat Capacity of the Calorimeter

Compare your two thermometers by immersing them together in water at room temperature for 1 minute in a small beaker, and reading the temperature of each as nearly as possible to the nearest 0.1°C . Always take readings with the thermometer bulb suspended 1 to 2 cm from the bottom of the calorimeter. Be careful to avoid parallax in your readings. Record the temperatures. Prepare two calorimeters, each similar to the form illustrated in Figure 1 but secure the calorimeters by placing each of them in a 250-mL beaker. Always use the same thermometer (thermometer 1) in the calorimeter in which the temperature change occurs, and in all subsequent readings apply any necessary correction to the other, so that the readings of both thermometers will always correspond.

Heat 50.0 mL of tap water $15\text{-}20^{\circ}\text{C}$ above room temperature in a small beaker. Place 50.0 mL of tap water at room temperature in one calorimeter (thermometer 1), and 50.0 mL of the heated tap water in the other. With the lids and the thermometers in place, make careful temperature readings ($\pm 0.1^{\circ}\text{C}$ of each at 1-minute intervals for 3 minutes). At the next minute interval (at 4 minutes), pour the warmer water quickly as completely as possible into the other calorimeter, and continue the readings for the next 3 minutes (minute 5 to 7). Use the thermometer in the cooler water to record subsequent temperatures. Repeat the procedure for a second trial. You can extrapolate the temperatures of the separate samples and of the mixture back to the time of mixing by making a graph on which you plot the temperature of each along the ordinate (vertical axis) and the mixing time for each along the abscissa (horizontal axis). A sample graph is illustrated in Figure 2.

B. The Heat of Neutralization of $\text{HCl}(\text{aq})$ and $\text{NaOH}(\text{aq})$

Place 50.0 mL of 1.0 M HCl in one calorimeter (thermometer 1), and 50.0 mL of 1.0 M NaOH in the other calorimeter. With the lids and thermometers in place, read the temperature ($\pm 0.1^{\circ}\text{C}$) for 3 minutes at 1-minute intervals, quickly mix the NaOH thoroughly into the HCl solution, and continue the readings for 3 minutes at 1-minute intervals. Repeat the procedure for a second trial but **rinse the calorimeter with water between each part of the experiment**. Extrapolate the temperatures back to the time of mixing for each solution as in part A, and calculate the heat of neutralization per mole of water produced. Refer to Figure 3. **The density of the 0.5 M NaCl mixture solution produced is 1.02 g/mL and its heat capacity is 4.02 J/g $\cdot^{\circ}\text{C}$.**

C. The Heat of Neutralization of $\text{CH}_3\text{COOH}(\text{aq})$ and $\text{NaOH}(\text{aq})$.

Repeat the procedure of part B, this time using 50.0 mL of 1.0 M CH_3COOH (thermometer 1) and 50.0 mL of 1.0 M NaOH . Rinse out the calorimeters before the first trial, before the second trial and when you have completed the experiment. Calculate the heat of neutralization as before. **Assume the density of the 0.5 M NaCH_3COO mixture solution is 1.02 g/mL and its heat capacity is 4.02 J/g $\cdot^{\circ}\text{C}$.**

¹Roberts, et al.; Frantz/Malm's Chemical Principles in the Laboratory, 2nd edition, Freeman, 1977

HESS' LAW

Name _____

DATA**Comparison of Thermometer Readings**

	Thermometer 1 Reading	Thermometer 2 Reading
Temperature of Water		

 Thermometer 2 Reading – Thermometer 1 Reading = (include sign)

Add/subtract the above difference to all Thermometer 2 Readings below.
A. The Heat Capacity of the Calorimeter (Calorimeter for Thermometer 1)**Trial 1 Temperatures**

Time	@ 1 min	@ 2 min	@ 3 min	@ 5 min	@ 6 min	@ 7 min
Warm water				Mixture temperatures		
Corrected warm temp						
Cool water						

↓ time of mixing →

Trial 2 Temperatures

Time	@ 1 min	@ 2 min	@ 3 min	@ 5 min	@ 6 min	@ 7 min
Warm water				Mixture temperatures		
Corrected warm temp						
Cool water						

Graph the data using the temperatures indicated on thermometer 1 and the corrected temperatures for thermometer 2 versus time. Extrapolate the temperatures to the time of mixing (minute 4) and list those temperatures here.

Trial 1

Warm water temperature	Cool water temperature	Mixture temperature

Trial 2

Warm water temperature	Cool water temperature	Mixture temperature

HESS' LAW

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B. The Heat of Neutralization of HCl(aq) and NaOH(aq)

Trial 1 Temperatures

Time	@ 1 min	@ 2 min	@ 3 min	@ 5 min	@ 6 min	@ 7 min
NaOH(aq)				Combination temperatures		
Corrected NaOH temp						
HCl(aq)						

average premix
temperature _____

← time of mixing →

Trial 2 Temperatures

Time	@ 1 min	@ 2 min	@ 3 min	@ 5 min	@ 6 min	@ 7 min
NaOH(aq)				Combination temperatures		
Corrected NaOH temp						
HCl						

average premix
temperature _____

Graph the data using the average premix temperatures and the mixture temperatures versus time (only two lines). Extrapolate the temperatures to the time of mixing (minute 4) and list those temperatures here.

	Trial 1	Trial 2
Average temperature of separate solutions		
Mixture temperature at time of mixing		

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C. The Heat of Neutralization of $\text{CH}_3\text{COOH}(\text{aq})$ and $\text{NaOH}(\text{aq})$

Trial 1 Temperatures

Time	@ 1 min	@ 2 min	@ 3 min	@ 5 min	@ 6 min	@ 7 min
NaOH(aq)				Combination temperatures		
Corrected NaOH temp						
$\text{CH}_3\text{COOH}(\text{aq})$						

average premix temperature _____ _____ _____

← time of mixing →
 ↓
 ↓

Trial 2 Temperatures

Time	@ 1 min	@ 2 min	@ 3 min	@ 5 min	@ 6 min	@ 7 min
NaOH(aq)				Combination temperatures		
Corrected NaOH temp						
$\text{CH}_3\text{COOH}(\text{aq})$						

average premix temperature _____ _____ _____

Graph the data using the average premix temperatures and the mixture temperatures versus time (only two lines). Extrapolate the temperatures to the time of mixing (minute 4) and list those temperatures here.

	Trial 1	Trial 2
Average temperature of separate solutions		
Mixture temperature at time of mixing		

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CALCULATIONSUse extrapolated temperatures to determine ΔT in each instance.**A. The Heat Capacity of the Calorimeter**

	Example Calculation	Trial 1 value	Trial 2 value
Heat lost by warm water			
Heat gained by cool water			
Heat gained by calorimeter			
Heat capacity of calorimeter			

Average Heat Capacity of Calorimeter:

B. The Heat of Neutralization of HCl(aq) and NaOH(aq)

	Example Calculation	Trial 1 value	Trial 2 value
Heat gained by mixing solns.			
Heat gained by calorimeter (use ave. ht. capacity)			
Total heat of reaction			
Number of moles of water formed			
Heat of neutral per mole of water formed			

Average Heat of Neutralization per mole of water formed:

