

## Calorimetric Determination of Reaction Enthalpies

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### Purpose:

Determine  $\Delta H_{\text{dis}}$ , the enthalpy of dissociation of  $\text{CH}_3\text{COOH}$

### Techniques:

Calorimetry      Temperature Measurement vs Time

### Apparatus:

Calorimeter      Precision Thermometer

### Concepts:

Strong/Weak Acids and Bases      Dissociation  
Neutralization      Limiting Reagent      Heat  
Heat Capacity      Enthalpy      Calorimetric Constant  
Endothermic      Exothermic      Hess' Law  
1st & 2nd Laws of Thermodynamics

### The Measurement of Heat and Temperature

Cannot measure *heat*,  $q$ , directly, but

can measure its effect on a substance - namely *temperature change*,  $\Delta T$ ; when *heat* flows *into*, or *from*, the substance.

For reasonable changes in *temperature*, for a given *mass* of a substance,  $m$ ,  $q$  is proportional to the mass,  $m$  and the temperature change,  $\Delta T$ .

$$q = C m \Delta T$$

Proportionality constant,  $C$ , is called the *Heat Capacity* per gram of the substance (specific heat).

$$q = C m \Delta T$$

By convention, absorbed heat is positive.

( liberated heat is negative )

For water,  
 $C = 4.18 \text{ J / g K}$

*Calorimeter* - a device that measures *temperature changes* accompanying *heat changes* in its contents

*Calorimeters* - constructed to minimize *heat exchange* with *environment* so effects of heat are entirely on the *calorimeter and its contents*.

Must be able to separate effects of *heat* on *calorimeter* from effects on *its contents*.

Determine heat absorbed by calorimeter when known amount of *heat* is added to its contents.

I.e., determine the Calorimetric Constant for the calorimeter,  $C_{\text{cal}}$

### CALIBRATION

How do we calculate  $T_{\text{mix}}$  when two samples of water of known mass and *temperature* are mixed?

E.g., suppose we add:

60 g of *hot* water at 50°C to  
30 g of *cold* water at 25°C

Ideally 90 g of water at  $T_{\text{mix}}$   
heat absorbed by cold water = heat lost by hot water

$$q_{\text{cold}} = m_c C_c \Delta T_c = - q_{\text{hot}} = - m_h C_h \Delta T_h$$

$$30 \text{ g} * 4.18 \text{ J/g} * (T_{\text{mix}} - 25) = - 60 \text{ g} * 4.18 \text{ J/g} * (T_{\text{mix}} - 50)$$

$$30 * (T_{\text{mix}} - 25) = - 60 * (T_{\text{mix}} - 50)$$

$$T_{\text{mix}} = (60 * 50 + 30 * 25) / (60 + 30) = 42^\circ\text{C}$$

Suppose the measured final temperature  $T_{\text{mix}}$  of the above mixture is  $40^{\circ}\text{C}$

The hot water loses:

$$q_{\text{hot}} = 60 \text{ g} * 4.18 \text{ J/gC}^{\circ} * (T_{\text{mix}} - 50) \\ = -2510 \text{ J}$$

The cold water gains:

$$q_{\text{cold}} = 30 \text{ g} * 4.18 \text{ J/gC}^{\circ} * (T_{\text{mix}} - 25) \\ = 1880 \text{ J}$$

$$q_{\text{cal}} = -q_{\text{hot}} - q_{\text{cold}}$$

$\Delta T$  of calorimeter =  $\Delta T$  of cold water =  $15^{\circ}\text{C}$   
So, it behaves like an object with a heat capacity

$$C_{\text{cal}} = q_{\text{cal}} / \Delta T_{\text{cal}} = 630 / 15 = 42 \text{ J} / \text{C}^{\circ}$$

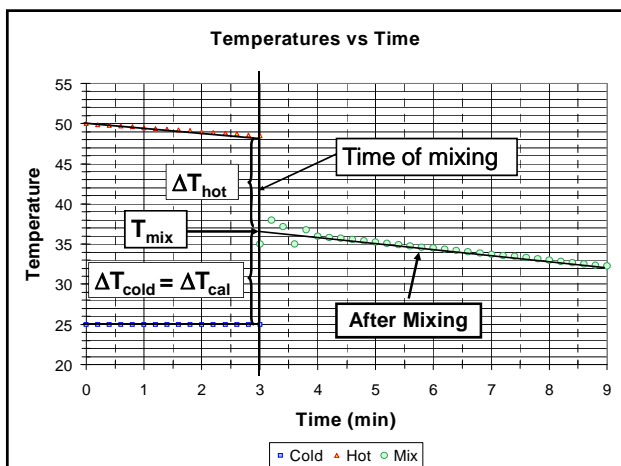
## TEMPERATURE MEASUREMENT

### Considerations

1. Temperatures of objects not at room temperature (RT) will *change in time*.
2. When liquids of different temperatures are mixed, the final equilibrium temperature is *not achieved instantaneously*.
3. Chemical reactions may *not occur instantaneously*.

How do we account for these?

Make periodic temperature measurements and extrapolate back and forth to the time of interest.



This procedure enables us to tell what the temperature changes would have been if:

- the mixing had been *instantaneous*, and
- the temperature of the calorimeter and its contents equilibrated *instantaneously*

We use this technique in each of the three calorimetric measurements we make in this exercise.

## RELATIONSHIP BETWEEN $q$ AND $H$

Under the conditions of this exercise - constant pressure, and assuming only PV work, -

heat *absorbed* or liberated by a process is equal to the enthalpy change in the process:

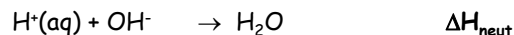
$$q = H_{\text{fin}} - H_{\text{init}} = \Delta H$$

A process for which  $\Delta H > 0$  is called Endothermic

A process for which  $\Delta H < 0$  is called Exothermic

## What will we measure?

1. Determine *calorimetric constant*,  $C_{\text{cal}}$
2. Determine *heat of neutralization of  $\text{CH}_3\text{COOH}$* , i.e.,  $q = \Delta H_{\text{CH}_3\text{COOH}}$  for the reaction:  
$$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$$
3. Determine *heat of neutralization of HCl*,

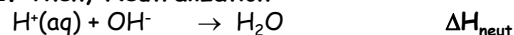


But, reaction of NaOH with  $\text{CH}_3\text{COOH}$  can be represented as occurring in two steps:

1. **First, Dissociation:**



2. **Then, Neutralization:**



**Hess' Law** tells us that  $\Delta H$  for any reaction is the sum of the  $\Delta H$ 's for any reactions the **net result** of which is the same.

(i.e.,  $\Delta H$  is independent of the path of a process)

Rearranging,

$$\Delta H_{\text{dis}} = \Delta H_{\text{CH}_3\text{COOH}} - \Delta H_{\text{neut}}$$

### Procedure - Calculations

#### 1. Calibration - Determination of $C_{\text{cal}}$

**Mix** two samples of **measured volumes** and **temperatures** of water.

**Measure** temperature changes at mixing, *graphically*

$$[\Delta T_{\text{hot}}, \Delta T_{\text{cold}} = \Delta T_{\text{cal}}]$$

Using **given** heat capacity of water ( $4.18 \text{ J / g}^\circ\text{C}$ ), and **measured** temperature changes, **calculate** measured heat exchange

$$[q_{\text{hot}}, q_{\text{cold}}, q_{\text{cal}}]$$

From these, **calculate** the effective heat capacity of the calorimeter,  $C_{\text{cal}}$ , **as described earlier**

**In the example that follows, we assume that our calculated value of  $C_{\text{cal}} = 42 \text{ J / }^\circ\text{C}$**

#### 2. Determine $\Delta H_{\text{HCl}}$ for HCl + NaOH

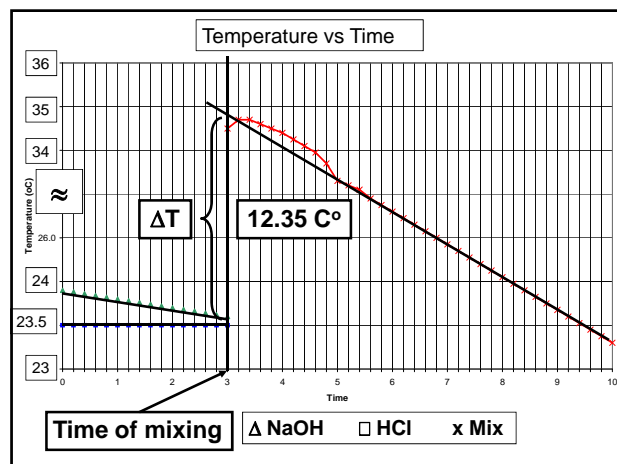
**Mix** samples of **measured volumes** and **temperatures** and **given concentrations** of HCl and NaOH \*

$$\begin{array}{ll} V_{\text{HCl}} = 50.0 \text{ mL} & V_{\text{NaOH}} = 55.0 \text{ mL} \\ T_{\text{HCl}} = 24.0^\circ\text{C} & T_{\text{NaOH}} = 24.2^\circ\text{C} \\ M_{\text{HCl}} = 2.20 \text{ M} & M_{\text{NaOH}} = 2.30 \text{ M} \end{array}$$

**Measure** temperature change at mixing time graphically, E.g., suppose the result is:

$$\Delta T = 12.35^\circ\text{C}$$

\* From here on, **Measured** Quantities are in Red and **Given** Quantities are in Green



Using **volumes** and **given concentrations** of HCl and NaOH, **Calculate** moles of reactants and the limiting stoichiometry

$$\begin{aligned} n_{\text{HCl}} &= V_{\text{HCl}} * M_{\text{HCl}} \\ &= 50.0 * 2.20 \\ &= 0.110 \text{ mol} \end{aligned}$$

$$\begin{aligned} n_{\text{NaOH}} &= V_{\text{NaOH}} * M_{\text{NaOH}} \\ &= 55.0 * 2.30 \\ &= 0.127 \text{ mol} \end{aligned}$$

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**We can neutralize only 0.110 mol HCl**

Using the given *heat capacity, densities and measured volumes* of the solutions and the *measured temperature change*, analyze the heat exchange,  $q$ , - correcting for the calorimeter

$$\begin{aligned} \text{Heat Capacity} &= 3.97 \text{ J/g } ^\circ\text{C} \\ \text{Density} &= 1.02 \text{ g/mL} \\ C_{\text{cal}} \text{ (from part 1)} &= 42.0 \text{ J/}^\circ\text{C} \end{aligned}$$

$$\text{Tot Vol of Sol} = 50.0 + 55.0 = 105.0 \text{ mL}$$

$$\text{Tot Wt Sol} = 1.02 * 105.0 = 107 \text{ g}$$

$$q_{\text{SOL}} = 3.97 \text{ J/g}^\circ\text{C} * 107 \text{ g} * 12.35 \text{ }^\circ\text{C} = 5250 \text{ J}$$

$$q_{\text{cal}} = 42.0 \text{ J/}^\circ\text{C} * 12.35 \text{ }^\circ\text{C} = 519 \text{ J}$$

$$q_{\text{RXN}} = q_{\text{SOL}} + q_{\text{cal}} = 5250 \text{ J} + 519 \text{ J} = 5770 \text{ J}$$

I.e., The neutralization of 0.110 mol of HCl liberated 5770 J

$$\Delta H_{\text{HCl}} = - 5770 \text{ J} / 0.110 \text{ mol} = - 5.24 \times 10^4 \text{ J/mol}$$

### 3. Determine $\Delta H_{\text{CH}_3\text{COOH}}$ for $\text{CH}_3\text{COOH} + \text{NaOH}$

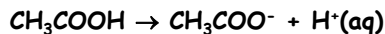
Suppose the result for this part of the exercise was:

$$\Delta H_{\text{CH}_3\text{COOH}} = - 4.37 \times 10^4 \text{ J/mol}$$

#### 4. Now we can invoke Hess' Law, namely

$$\begin{aligned} \Delta H_{\text{dis}} &= \Delta H_{\text{CH}_3\text{COOH}} - \Delta H_{\text{HCl}} \\ &= - 4.37 \times 10^4 - (- 5.24 \times 10^4) \\ &= + 8.7 \times 10^3 \text{ J / mol} \end{aligned}$$

I.e., we have determined the enthalpy of the reaction:



$$\Delta H_{\text{dis}} = + 8.7 \text{ kJ / mol}$$

#### Procedure

1. Work in *assigned Pairs*
2. **Do not remove** Precision Thermometers from their special clamps!
3. In Part 1, if the temperature of *hot tap water* is **40°C or above**, you may use hot tap water instead of heating water.
4. Each pair will submit **3 plots**. Put both names on all plots and attach all 3 plots to **ONE** of the two lab reports. No need to make copies for each report.

Make sure you read thermometers to their *full precision*:

Desk thermometers to nearest  $\pm 0.2 \text{ }^\circ\text{C}$

Precision thermometers to nearest  $\pm 0.02 \text{ }^\circ\text{C}$

Maximum Temperature - 50°C

In plotting, use temperature scales that will provide *appropriate precision*.

You may "*break*" the temperature scale if that is helpful.

Read the temperatures from the graphs with appropriate precision

#### Next Lecture / Exercise

#### Complexometric Determination of Calcium SUSB-017

Read SUSB-017 and do pre-lab

Test Exercise – 100 points

You are welcome to bring your own Calcium-containing tablet