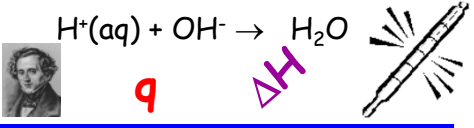



$\Delta T$   $H^+(aq) + OH^- \rightarrow H_2O$   $q$   $\Delta H$



**Calorimetric Determination of Reaction Enthalpies**

$CH_3COOH + OH^- \rightarrow CH_3COO^- + H_2O$

$CH_3COOH$    $HCl$   $NaOH$

**Purpose:**  
Determine the enthalpy of dissociation of  $CH_3COOH$   
 $CH_3COOH(aq) \rightarrow CH_3COO^-(aq) + H^+(aq) \quad \Delta H_{dis}$


**Techniques:**  
Calorimetry      Temperature Measurement vs Time

**Apparatus:**  
Calorimeter      Precision Thermometer      Clock

**Concepts:**  
Strong/Weak Acids and Bases      Dissociation  
Neutralization      Limiting Reagents      Heat  
Heat Capacity      Enthalpy      Calorimeter Constant  
Endothermic      Exothermic      Hess' Law  
0<sup>th</sup> & 1<sup>st</sup> Laws of Thermodynamics

2

**The Measurement of Heat and Temperature**

We cannot measure *heat, q*, directly, but can measure its effect on substances,  - namely *temperature changes,  $\Delta T$* , when *heat* flows *into*, or *from*, a substance.

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

$q = C m \Delta T$        $\Delta T = T_{final} - T_{initial}$

The proportionality constant, *C*, is called the *Specific Heat* of the substance. For water,  $C = 4.18 \text{ J / g K}$

\* Or other changes, such as *melting* or *boiling*


3

$q = C m \Delta T$

*absorbed* heat is *positive*.  
 $\Delta T > 0 ; q > 0$


*liberated* heat is *negative*.  
 $\Delta T < 0 ; q < 0$

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



4

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



**MUST INSULATE !**  
( Use Covered, Nested Styrofoam Cups )


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

**MUST CALIBRATE !**

**How?** Determine heat absorbed by calorimeter when a known amount of *heat* is added to contents with known effects of heat.

**I.e., determine its *Calorimeter Constant***

5



High precision thermometer

**\$60**

**Hg**

6

**CALIBRATION**

How do we calculate  $T_{mix}$  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**
- 90 g of water at  $T_{mix}$

**Ideally** heat **absorbed** by cold water = - heat **lost** by hot water

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

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

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

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

**The Ideal Case**

60 g  $T_{hot}$  50°C

30 g  $T_{cold}$  25°C

90 g  $T_{mix}$  42°C

$$-q_{hot} = q_{cold}$$

Actual  $T_{mix}$  will differ from **ideal** because of heat exchange with container - i.e., calorimeter

Assume **calorimeter**

- is initially at the temperature of the **cold** water &
- it experiences same temperature change as its cold water contents.

Note: The cold water should be in the calorimeter before mixing!

Some heat **lost** by the **hot** water goes to **increasing temperature of calorimeter as well as the cold water**

Now, we have

$$-q_{hot} = q_{cold} + q_{cal} \quad \text{So, } q_{cal} = -q_{hot} - q_{cold}$$

**Accounting for the Calorimeter**

60 g  $T_{hot}$  50°C

30 g  $T_{cold}$  25°C

? °C  $T_{mix}$

$$-q_{hot} = q_{cold} + q_{cal}$$

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

The hot water loses:

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

The cold water gains:

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

The calorimeter gains:

$$q_{cal} = -q_{hot} - q_{cold} = 2510 - 1880 = 630 \text{ J}$$

$\Delta T$  of calorimeter =  $\Delta T$  of cold water = +15 °C

So, it behaves like an object with a specific heat of

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

Instead of 42°C

-2510

+1880

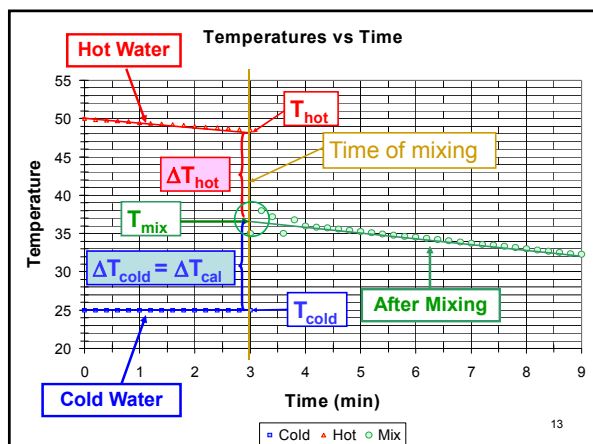
630

**TEMPERATURE MEASUREMENT Considerations**

- Temperatures of objects not at room temperature (RT) will **change in time**.  
[ Newton's Law:  $dT/dt = k(T - T_0)$  ]
- When liquids of different temperatures are mixed, the final equilibrium temperature is **not achieved instantaneously**.
- Some chemical reactions may **occur slowly**

How do we account for the above?

Make **periodic** temperature measurements and **extrapolate** 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 had *equilibrated instantaneously*

We use time extrapolation in each of the calorimetric measurements 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:

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

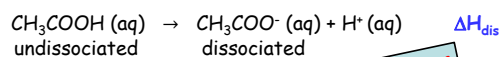
A process for which  $\Delta H > 0$  is called **Endothermic**

$$H_{fin} > H_{init} - \text{Final state has higher enthalpy}$$

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

$$H_{fin} < H_{init} - \text{Final state has lower enthalpy}$$

### We wish to Measure $\Delta H$ of Dissociation of $CH_3COOH$



$\Delta H$  is per mole

Problems:

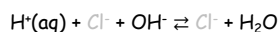
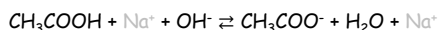
1. How do you make a solution of the pure **undissociated starting material** to put in the calorimeter? (It dissociates immediately to its equilibrium extent)
2. The ionization reaction stops when it reaches equilibrium which lies very close to the reactant side. (i.e., When it does dissociate, the reaction does not produce much product)

Weak Acid

[ 1.0 M  $CH_3COOH$  ionizes to produce only 0.013 M  $CH_3COO^-$  ]

### What About Neutralization Reactions?

The reaction of acetic acid with a strong base does not suffer from these problems.



But, the reaction of NaOH with  $CH_3COOH$  can be represented as occurring in two steps:

1. **First, Dissociation:**



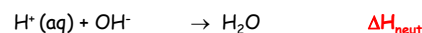
2. **Then, Neutralization:**



Reaction 1 is the one in which we are interested!

What about Reaction 2?

The neutralization reaction:



does not involve the original acetic acid or any other specific acid in any way.

Indeed, it is the net ionic equation one would write for the reaction of hydrochloric acid, or any strong, monoprotic acid, with sodium hydroxide, e.g., HBr, HNO<sub>3</sub>, HI, HClO<sub>3</sub>, HClO<sub>4</sub>

So,  $\Delta H_{neut}$  could be the  $\Delta H$  for the neutralization of hydrochloric acid with sodium hydroxide - which should be easily measurable.

**HESS**

**Hess' Law**:  $\Delta H$  for a reaction that can be written as a series of steps is equal to the sum of  $\Delta H$ 's for the individual steps.

$$\begin{array}{l} \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+ \quad \Delta H_{\text{dis}} \\ \text{H}^+ + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad \Delta H_{\text{neut}} \\ \hline \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \quad \Delta H_{\text{CH}_3\text{COOH}} \end{array}$$

From Hess' Law  
 $\Delta H_{\text{CH}_3\text{COOH}} = \Delta H_{\text{dis}} + \Delta H_{\text{neut}}$

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

From  $\text{CH}_3\text{COOH}$  neutralization

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What will we Measure & Compute?

- Determine *calorimeter constant*,  $C_{\text{cal}}$
- Determine "heat of" neutralization of **Weak acid**  
 $\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \quad \Delta H_{\text{CH}_3\text{COOH}}$
- Determine "heat of" neutralization of **Strong acid**,  $\text{HCl}$   
 $\text{H}^+(\text{aq}) + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad (\Delta H_{\text{HCl}} =) \Delta H_{\text{neut}}$
- Compute "heat of" dissociation of  $\text{CH}_3\text{COOH}$   
 $\Delta H_{\text{dis}} = \Delta H_{\text{CH}_3\text{COOH}} - \Delta H_{\text{neut}}$

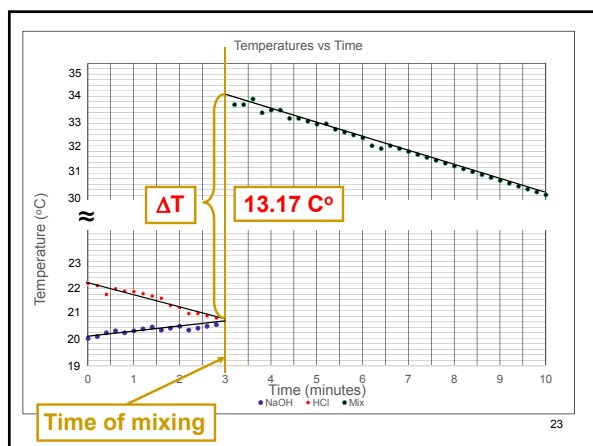
20

**Procedure**

- Calibration - Determination of  $C_{\text{cal}}$**   
Mix two samples of water with measured volumes (to get weights) and temperatures.  
Determine temperature changes at mixing, graphically  
 $[\Delta T_{\text{hot}}, \Delta T_{\text{cold}} = \Delta T_{\text{cal}}]$   
 Using given heat capacity of water ( $4.18 \text{ J/g} \cdot \text{C}^\circ$ ), density, and temperature changes, calculate heat exchange  
 $[q_{\text{hot}}, q_{\text{cold}}, q_{\text{cal}}]$   
 From these, calculate the calorimeter constant,  $C_{\text{cal}}$ .  
 In the example that follows, let us assume that our calculated value of  $C_{\text{cal}}$  is  $42 \text{ J/C}^\circ$

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- Determine  $\Delta H_{\text{HCl}}$  for  $\text{HCl} + \text{NaOH}$   
Mix samples of measured volumes and temperatures and given concentrations of  $\text{HCl}$  and  $\text{NaOH}$  \*  
 $V_{\text{HCl}} = 50.0 \text{ mL} \quad V_{\text{NaOH}} = 55.0 \text{ mL}$   
 $M_{\text{HCl}} = 2.20 \text{ M} \quad M_{\text{NaOH}} = 2.30 \text{ M}$   
Confirm limiting reagent  
 $\text{mmol HCl} = 50.0 * 2.20 = 110$  ← **Limiting Reagent**  
 $\text{mmol NaOH} = 55.0 * 2.30 = 127$   
Measure initial temperatures of  $\text{HCl}$  and  $\text{NaOH}$  and temperature change at mixing time, graphically.  
**Note: We measure solution volumes instead of weights so we need densities ( $1.02 \text{ g/mL}$ ).**



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

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

Tot Volume of Solution =  $50.0 + 55.0 = 105.0 \text{ mL}$   
 Tot Weight of Solution =  $1.02 * 105.0 = 107 \text{ g}$   
 Our measured temperature change at mixing time (from the graph) is:  
 $\Delta T = 13.17 \text{ C}^\circ$  **2 decimals**

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So,  
 $q_{\text{SOL}} = 3.97 \text{ J/g}^\circ\text{C} \times 107 \text{ g} \times 13.17 \text{ }^\circ\text{C} = 5594 \text{ J}$   
 $q_{\text{cal}} = 42.0 \text{ J/}^\circ\text{C} \times 13.17 \text{ }^\circ\text{C} = 553 \text{ J}$

**SIG  
FIGS**

The heat *absorbed* by the solution and the calorimeter was *liberated* by the reaction

$q_{\text{RXN}} = -(q_{\text{SOL}} + q_{\text{cal}}) = -(5594 + 553) \text{ J} = -6147 \text{ J}$

(The sign of the heat of reaction is negative!)

But, how many moles of HCl were neutralized?  
 I.e., The neutralization of **0.110 mol** of HCl *liberated* 6147 J

$\Delta H_{\text{HCl}} = -6147 \text{ J} / 0.110 \text{ mol} = -55.9 \text{ kJ/mol}$

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

**The analysis for this part is identical with the strong acid case.**

The result is again a relatively large negative number.  
 Suppose the result for this part of the exercise is:

$\Delta H_{\text{CH}_3\text{COOH}} = -56.1 \text{ kJ/mol}$

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

$\Delta H_{\text{dis}} = \Delta H_{\text{CH}_3\text{COOH}} - \Delta H_{\text{HCl}}$   
 $= -5.61 \times 10^4 - (-5.24 \times 10^4)$   
 $= -3.7 \times 10^2 \text{ J/mol}^*$

**Sig  
Figs**

We have determined the enthalpy of the reaction:

$\text{CH}_3\text{COOH}(\text{aq}) \rightarrow \text{CH}_3\text{COO}^-(\text{aq}) + \text{H}^+(\text{aq})$

$\Delta H_{\text{dis}} = -3.7 \times 10^2 \text{ J/mol}$


\* The difference between two comparable negative numbers.

**Precision is critical in this exercise!**

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### Notes on the Procedure

1. Work in *assigned Pairs*
2. **Do not remove** Precision Thermometers from their special clamps!
3. 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.



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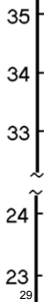
Make sure you read thermometers to their *full precision*:

Desk thermometers to nearest  $\pm 0.2 \text{ }^\circ\text{C}$   
 Precision thermometers to nearest  $\pm 0.02 \text{ }^\circ\text{C}$   
 (Maximum Temperature  $50 \text{ }^\circ\text{C}$ )

In plotting, use temperature scales that provide *appropriate precision*. Try to read to  $\pm 0.02 \text{ }^\circ\text{C}$

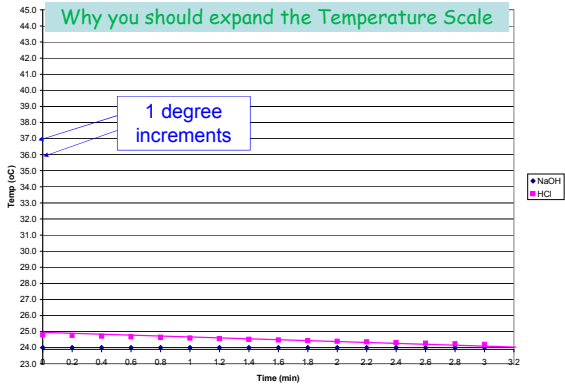
For neutralization reactions, you should *"break" the temperature axis* to expand scale in two regions if that is helpful.

Read the temperatures from graphs with appropriate precision



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### Why you should expand the Temperature Scale



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