**Calorimetric Determination of Reaction Enthalpies**

\[ \text{H}^+(\text{aq}) + \text{OH}^- \rightarrow \text{H}_2\text{O} \]

\[ \text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O} \]

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

**Purpose:**
Determine the enthalpy of dissociation of \( \text{CH}_3\text{COOH} \)

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

\( \Delta H_{\text{dis}} \)

**Techniques:**
- Calorimetry
- Temperature Measurement vs Time

**Apparatus:**
- Calorimeter
- Precision Thermometer
- Clock

**Concentration:**
- Strong/Weak Acids and Bases
- Dissociation
- Neutralization
- Heat
- Limiting Reagents
- Heat Capacity
- Enthalpy
- Calorimetric Constant
- Endothermic
- Exothermic
- Hess' Law
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**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.

\[ q = C m \Delta T \]

\( \Delta T = T_{\text{final}} - T_{\text{initial}} \)

* Or other changes, such as melting or boiling

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

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

\[ q = \Delta H_{\text{cal}} \]
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
- 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

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

$$m_c C_c (T_{fin} - T_c) = -m_h C_h (T_{fin} - T_h)$$

$T_{fin} > T_c$ so, $q_{cold} > 0$

$T_{fin} < T_h$ so, $q_{hot} < 0$

**CALIBRATION**

E.g., suppose we add:

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

$$30 \times (T_{fin} - 25) = -60 \times (T_{fin} - 50)$$

$$T_{fin} = (60 \times 50 + 30 \times 25) / (60 + 30) = 42°C$$

**Actual $T_{fin}$ 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 some temperature change as its cold water contents.

Note: We put the cold water initially in the calorimeter!

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

Now, we have

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

Redo the mixing accounting for the calorimeter

$$T_{cal} = 30 \times 25°C = -q_{hot} = q_{cold}$$
Suppose the measured final temperature of the above mixture, $T_{\text{fin}} = 40^\circ C$.

The hot water loses:

$$q_{\text{hot}} = 60 \text{ g} \times 4.18 \text{ J/g} \cdot \text{C} \times (T_{\text{fin}} - 50) = -2510 \text{ J}$$

The cold water gains:

$$q_{\text{cold}} = 30 \text{ g} \times 4.18 \text{ J/g} \cdot \text{C} \times (T_{\text{fin}} - 25) = 1880 \text{ J}$$

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

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

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

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

Instead of 42$^\circ C$ as we calculated earlier in the ideal case.

**TEMPERATURE MEASUREMENT Considerations**

1. Temperatures of objects not at room temperature (RT) will change in time. [Newton's Law: $\Delta T / \Delta t = k (T - T_0)$]

2. When liquids of different temperatures are mixed, the final equilibrium temperature is not achieved instantaneously.

3. Some chemical reactions may occur slowly.

How can we account for these?

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

This procedure (extrapolation to $t = 0$) 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 at the moment of mixing.

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:

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

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

$H_{\text{fin}} > H_{\text{init}}$ - Final state has higher enthalpy (System absorbs heat)

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

$H_{\text{fin}} < H_{\text{init}}$ - Final state has lower enthalpy (System gives up heat)

We wish to Measure $\Delta H$ of dissociation of CH$_3$COOH

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

undissociated  dissociated

$\Delta H$ is for 1 mole of undissociated reactant fully dissociating to 1 mole of each product

Problems:

1. How do you make a solution of the **undissociated starting material** to put in the calorimeter (without having it dissociate immediately through the above reaction to achieve equilibrium)?

2. The ionization equilibrium lies very close to the reactant (i.e., When it does dissociate, the reaction does not produce much product)

$$[ 1.0 \text{ M CH}_3\text{COOH} \text{ ionizes to produces only 0.013 M CH}_3\text{COO}^- ]$$
Reactions of strong or weak acids with strong bases (neutralization) do not suffer from these problems.

Acetic Acid

\[
\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}
\]

Hydrochloric Acid

\[
\text{H}^+(aq) + \text{OH}^- \rightarrow \text{H}_2\text{O}
\]

But, reaction of OH\(^-\) with CH\(_3\)COOH can be represented as occurring in two steps:

1. First, Dissociation:
   \[
   \text{CH}_3\text{COOH} \rightarrow \text{CH}_3\text{COO}^- + \text{H}^+(aq)
   \]
   \[\Delta H_{\text{dis}}\]

2. Then, Neutralization:
   \[
   \text{H}^+(aq) + \text{OH}^- \rightarrow \text{H}_2\text{O}
   \]
   \[\Delta H_{\text{neut}}\]

Reaction 1 is the one in which we are interested! What about Reaction 2?

The neutralization step:

\[
\text{H}^+(aq) + \text{OH}^- \rightarrow \text{H}_2\text{O} \quad \Delta H_{\text{neut}}
\]

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 with sodium hydroxide\(^1\).

So, \(\Delta H_{\text{neut}}\) must be the \(\Delta H\) for the neutralization of e.g., hydrochloric acid with sodium hydroxide - which should be easily measurable.

\(^1\) or any other strong acid or strong base.

**Hess' Law:** \(\Delta H\) for a reaction carried out in a series of steps is equal to the sum of \(\Delta H\)'s for the individual steps.

\[
\Delta H_{\text{CH}_3\text{COOH}} = \Delta H_{\text{dis}} + \Delta H_{\text{neut}}
\]

\[\text{From CH}_3\text{COOH neutralization}\]

Using Hess' Law

\[
\Delta H_{\text{CH}_3\text{COOH}} = \Delta H_{\text{dis}} + \Delta H_{\text{neut}}
\]

What we seek

From HCl neutralization

\[
\Delta H_{\text{HCl}} = \Delta H_{\text{dis}} - \Delta H_{\text{neut}}
\]

2. Determine \(\Delta H_{\text{HCl}}\) for HCl + NaOH

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

\[
\begin{align*}
V_{\text{HCl}} &= 50.0 \text{ mL} \\
M_{\text{HCl}} &= 2.20 \text{ M} \\
V_{\text{NaOH}} &= 55.0 \text{ mL} \\
M_{\text{NaOH}} &= 2.30 \text{ M}
\end{align*}
\]

Confirm limiting reagent

\[
\begin{align*}
\text{mmol HCl} &= 50.0 \times 2.20 = 110 \\
\text{mmol NaOH} &= 55.0 \times 2.30 = 127
\end{align*}
\]

Measure initial temperatures and temperature change at mixing time graphically.

Note: We measure solution volumes instead of weights so we need densities.

**Procedure - Calculations**

1. 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 J/g°C), density (1.00 g/mL) and measured temperature changes, calculate heat exchanged

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

   From these, calculate the effective heat capacity of the calorimeter, \(C_{\text{cal}}\), as described earlier.

   In the example that follows, we assume that the value of \(C_{\text{cal}} = 42 \text{ J/}^\circ\text{C}\).
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:

$$\Delta H_{\text{CH}_3\text{COOH}} = -5.61 \times 10^4 \text{ J/mol}$$

4. Now we invoke Hess’ Law, namely

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

$$= -5.61 \times 10^4 - (-5.24 \times 10^4)$$

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

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

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

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

* The difference between two comparable negative numbers.

Precision is critical in this exercise!
Make sure you read thermometers to their full precision:
Desk thermometers to nearest ±0.2 °C
Precision thermometers to nearest ±0.02 °C
(Maximum Temperature 50°C)

In plotting, use temperature scales that provide appropriate precision. Try to read to ±0.02 °C
You should “break” the temperature axis to expand scale if that is helpful.
Read the temperatures from graphs with appropriate precision

The Last Word

“In this house, we obey the laws of thermodynamics.”

Homer Simpson

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