THERMOCHEMISTRY
2: CALORIMETRY

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CALCULATING HEAT AND ENTHALPY

We will now learn how to calculate heat (q) and enthalpy (H).

This is done by means of a calorimeter, which can be a closed or isolated system depending on how accurate the data needs to be. Isolated systems are more accurate as there is no loss of energy to the surroundings.

When determining enthalpy, heat capacity (of the system), and specific heat (of an object) should be known. These two data can also be measure by calorimetry.

A reaction is carried out in a closed or isolated environment and the change in heat is measured by thermometer.

HEAT CAPACITY

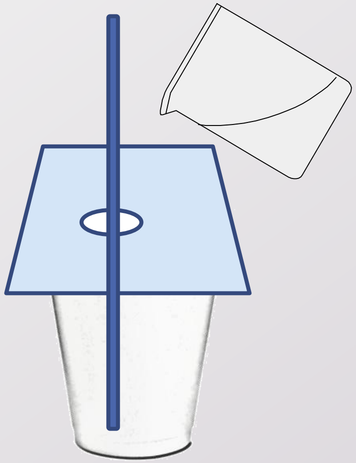
- **Heat capacity (C)** is the amount of heat needed to raise the temperature of the sample of substance by one degree Celsius or Kelvin.

$$\boxed{q = C\Delta t}$$

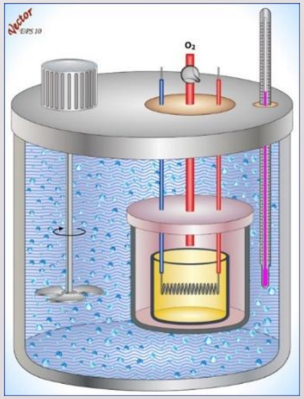
- **Molar heat capacity**: heat capacity of one mole of substance.
- **Specific Heat (s)**: Quantity of heat needed to raise the temperature of **one gram** of substance by **one degree Celsius** (or one Kelvin) at constant pressure.

$$\boxed{q = m \cdot s \cdot \Delta t \textit{ (final-initial)}}$$

- Heat capacity and specific heat are measured using a calorimeter. Any change in temperature can be measured using a thermometer.
- Left figure is for coffee cup calorimeter, used commonly in undergraduate labs.
- Right figure is bomb calorimeter, used mostly in research labs and industry.



Coffee cup calorimeter



Shutterstock Image

Bomb calorimeter

SPECIFIC HEAT OF SOME CHEMICALS

The higher the specific heat the higher the energy required to raise the temperature by 1°. From the data given below it is easy to see why metals are good conductors of heat while water is a good coolant.

Substance	Specific Heat Values in J/g °C
Al (s)	0.900
Au (s)	0.129
C (graphite)	0.720
C (diamond)	0.502
Cu (s)	0.385
Fe (s)	0.444
H_2O	4.184
C_2H_5OH (l) Ethanol	2.46

EXAMPLE 1: SPECIFIC HEAT

A piece of zinc weighing 35.8 g was heated from 20.00 °C to 28.00 °C. How much heat was required? The specific heat of zinc is 0.388 J/(g °C).

Answer: Use specific heat equation.

$$\boxed{\mathbf{q = m \cdot s \cdot \Delta t} \ \textit{(final-initial)}}$$

m = 35.8 g

s = 0.388 J/(g °C)

Δt = 28.00 °C – 20.00 °C = 8.00 °C

$$q = 35.8 \text{ g} \times \left(\frac{0.388 \text{ J}}{\text{g°C}}\right) \times (8.00\text{°C}) = \boxed{111 \text{ J}}$$

EXAMPLE 2: CALORIMETRY

A snack chip with a mass of 2.36 g was burned in a bomb calorimeter. The heat capacity of the calorimeter 38.57 kJ/°C. During the combustion, the water temp rose by 2.70 °C. Calculate the energy in kJ/g for the chip. How much is this in food calories (Cal/g)?

Answer:

$$\boxed{q = -C_{cal}\Delta t} = -(38.57\ \text{kJ/°C})\ (2.70\ \text{°C})$$

$$= -\ 104\ \text{kJ}$$

Energy content is a positive quantity.

$$= 104\ \text{kJ}/2.36\ \text{g} = \boxed{44.1\ \text{kJ/g}}$$

Convert J to Cal. (1 cal = 4.184 J)

$$\frac{44.1\ \text{kJ}}{\text{g}} \times \frac{1\ \text{Cal}}{4.184\ \text{kJ}} = \boxed{10.5\ \text{Cal/g}}$$

EXAMPLE 3: SPECIFIC HEAT

A metal pellet, 85.0 g at an original temperature of 92.5 °C is dropped into a calorimeter with 150.0 g of water at an original temperature of 23.1 °C. The final temperature of the water and the pellet is 26.8 °C. Calculate the specific heat for the metal.

Answer: First find the energy given off to water. $\boxed{\mathbf{q = ms\Delta t}}$

Step 1 $\quad$ *Energy* = q_{water} = $ms\Delta T$ = (150.00 g) (4.184 J/g°C) (3.7 °C)

= 2300 J (water gained energy) = -2300 J (pellet released energy)

Step 2 $\quad$ Find specific heat of pellet using the data for the pellet and energy released from step 1.

$\boxed{\mathbf{q = ms\Delta t}}$ $\quad$ $s = q/m\,\Delta t = -2300\ \text{J}/(85\ \text{g} \times (26.8-92.5)\ ^{o}\text{C})$

$s = \boxed{0.412\ \text{J/g}\ ^{o}\text{C}}$

Another way to do this would be $-q_{pellet} = +q_{water}$

$-m\mathbf{s}\Delta T\ (\text{pellet}) \quad = \quad ms\Delta T\ (\text{water})$

$-85.0\ \text{g} \times \mathbf{s} \times (26.8-92.5)\ ^{o}\text{C} = 150\ \text{g} \times 4.184\ \text{J/g}^{o}\text{C} \times (26.8 - 23.1)\ ^{o}\text{C}$

EXAMPLE 4: WRITING THERMOCHEMICAL EQUATION

Nitromethane, CH_3NO_2, an organic solvent burns in oxygen according to the following reaction:

$$CH_3NO_{2(g)} + {}^3/_4O_{2(g)} \longrightarrow CO_{2(g)} + {}^3/_2H_2O_{(l)} + {}^1/_2N_{2(g)}$$

You place 1.724 g of nitromethane in a calorimeter with oxygen and ignite it. The temperature of the calorimeter increases from 22.23 °C to 28.81 °C. The heat capacity of the calorimeter is 3.044 kJ/°C. Write the thermochemical equation for the reaction.

Answer: First calculate the heat evolved in calorimeter:

Step 1 $\boxed{q = C_{cal}\Delta t}$

$$q_{rxn} = -\left(\frac{3.044\ \text{kJ}}{°\text{C}}\right)(28.81°\text{C} - 22.23°\text{C}) = \boldsymbol{-20.03\ kJ}$$

Step 2 Convert the heat evolved to per mol.

$$q_{rxn} = \frac{-20.03\ \text{kJ}}{1.724\ \text{g}\ CH_3NO_2} \times \frac{61.04\ \text{g}\ CH_3NO_2}{1\ \text{mol}\ CH_3NO_2} = \boxed{-709\ \text{kJ/mol}}$$

Step 3 Now write the equation:

$$\boxed{CH_3NO_{2(l)} + {}^3\!/_4O_{2(g)} \longrightarrow CO_{2(g)} + {}^3/_2H_2O_{(l)} + {}^1\!/_2N_{2(g)};\ \Delta H = -709\ \text{kJ}}$$

EXAMPLE 5: CALCULATING FINAL TEMP.

A student mixes 22.8 g water at 69.3 ^oC with 32.6 g water at 25.2 ^oC in an insulated flask. What is the final temperature of the water?

Answer: heat absorbed (+q) = heat lost (-q)

$$+q_{\text{cold water}} = -q_{\text{hot water}} \quad \text{OR} \quad q_{\text{cold water}} + q_{\text{hot water}} = 0$$

$$q_{\text{cold water}} \qquad + \qquad q_{\text{hot water}} \qquad = 0$$

$$[\underbrace{32.6\text{ g} \times 4.184}_{136.3984}\ \text{J/g}^o\text{C} \times (T_f - 25.2)^o\text{C}] + [\underbrace{22.8\text{ g} \times 4.184}_{95.3952}\ \text{J/g}^o\text{C} \times (T_f - 69.3)^o\text{C}] = 0$$

$$[136.3984\ T_f - 3437.24] \quad + \quad [95.3952\ T_f - 6610.8874] \quad = 0$$

$$231.7936\ T_f = 10048.127$$

$$T_f = \boxed{43.3\ ^oC}$$

EXAMPLE 6: HEAT OF NEUTRALIZATION

When 30.0 mL of 0.250 M NaOH is mixed with 30.0 mL of 0.350 M HCl, both initially at 25.0 ^oC , the final temperature is 28.9 ^oC. Calculate the heat of reaction and the enthalpy of the reaction.

Answer: To answer this, we have to assume:

1) Volumes are additive – so 30 mL + 30 mL = 60 mL.
2) Density of solutions is equivalent to water (1g/mL). So 60 mL = 60 g
3) Specific heat of the solution is same as water = 4.184 J/g ^oC.

Using specific heat equation $\boxed{\mathbf{q = ms\Delta t}}$

Step 1
Step 2

(heat released) -q = 60 g × 4.184 J/g ^oC × (28.9 – 25) ^oC = 979.056 = -979 J

To find enthalpy: a) write balanced equation; 2) find mols of each reactant; c) find limiting reagent if different mols; d) divide energy by mols.

$$NaOH + HCl \longrightarrow NaCl + H_2O$$

(0.250 mol/L x 0.03L) (0.350 mol/L x 0.03 L)

0.0075 mol NaOH 0.0105 mol HCl ***(NaOH is limiting reagent)***

ΔH = kJ/mol

$$-979\ \mathrm{J}\,\frac{1\ \mathrm{kJ}}{1000\mathrm{J}} \times \frac{1}{0.0075\ \mathrm{mol}} = \boxed{130.5\ \mathrm{kJ/mol}}$$

EXAMPLE 7: BOMB CALORIMETER CALC.

0.5763 g of glucose, a simple sugar, is combusted in a bomb calorimeter (C_{cal} = 0.620 kJ/^{o}C). It raises the temperature of the calorimeter by 1.45 ^{o}C. What is the food caloric value of glucose?

Answer: Food caloric value is also the specific heat. To find this; find the qcal first and then divide it by gram of food to get the caloric value.

$$\boxed{q = -C_{cal}\Delta t}$$

$$q = 0.620\ kJ/^{o}C \times 1.45\ ^{o}C = -8.99\ kJ$$

$$-8.99\ kJ/0.5763\ g = \boxed{-15.6\ kJ/g}$$

KEY CONCEPTS

- Measuring heats of reaction – calorimetry
- Bomb calorimetry
- Heat of reactions