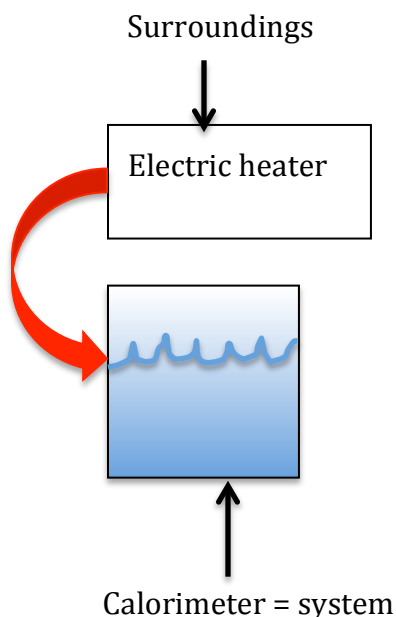


Calorimetry

→ Red arrows indicate the direction of heat flow

1. A calorimeter was calibrated with an electric heater, which supplied 22.5 kJ of energy to the calorimeter and increased the temperature of the calorimeter and its water from 22.45°C to 23.97°C. What is the heat capacity of the calorimeter?

- $q_{cal} = C_{cal}\Delta T$
 where q_{cal} is the heat absorbed by the calorimeter
 C_{cal} is the specific heat of the calorimeter
 ΔT is the change of temperature of the calorimeter
- $q_{cal} = +22.5 \text{ kJ}$ because heat was absorbed
 $\Delta T = T_f - T_i = 23.97 - 22.45 = 1.52^\circ\text{C}$
- So, $C_{cal} = \frac{q_{cal}}{\Delta T} = \frac{22.5 \text{ kJ}}{1.52^\circ\text{C}} = 14.8 \frac{\text{kJ}}{^\circ\text{C}}$



2. When 0.113 g of benzene, C_6H_6 , burns in excess oxygen in a calibrated constant-pressure calorimeter with a heat capacity of $551 \text{ J}/^\circ\text{C}$, the temperature of the calorimeter rises by 8.60°C . Write the thermochemical equation and calculate the reaction enthalpy for $2 \text{C}_6\text{H}_6(\text{l}) + 12 \text{O}_2(\text{g}) \rightarrow 12 \text{CO}_2(\text{g}) + 6 \text{H}_2\text{O}(\text{l})$.

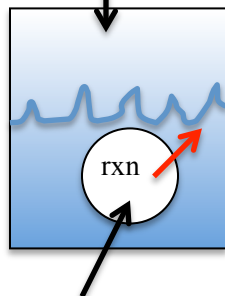
- $q_{rxn} = -q_{released} = -C_{cal}\Delta T = -551 \frac{\text{J}}{^\circ\text{C}} \times 8.60^\circ\text{C} = -4738.6 \text{ J} = -4.74 \text{ kJ}$
- the ΔH calculated above was for 0.113g of benzene, which is equal to

$$\frac{0.113\text{g}}{78 \frac{\text{g}}{\text{mol}}} = 0.00145 \text{ mol}$$
 because $MW(\text{benzene}) = (12 \times 6) + (1 \times 6) = 78 \frac{\text{g}}{\text{mol}}$

The underlined pieces of information make up the thermochemical equation.

- ΔH_{rxn} or enthalpy of reaction is ΔH for 1 mole reaction. Since this is a combustion reaction $\Delta H_{\text{rxn}} = \Delta H_{\text{combustion}}$, where $\Delta H_{\text{combustion}}$ is the enthalpy of combustion. $\Delta H_{\text{combustion}}$ is reported for 1 mole of fuel, in this case C_6H_6 . So the chemical equation will be $\text{C}_6\text{H}_6(\text{l}) + 6 \text{O}_2(\text{g}) \rightarrow 6 \text{CO}_2(\text{g}) + 3 \text{H}_2\text{O}(\text{l})$. ΔH_{rxn} for this equation is $-4.74 \text{ kJ} \times \frac{1 \text{ mol}}{0.00145 \text{ mol}} = -3269 \text{ kJ}$ because we want the ΔH for the combustion of 1 mole of benzene NOT 0.00145 moles.

Calorimeter = surroundings



System

3. A reaction known to release 2.00 kJ of heat takes place in a calorimeter containing 0.200 L of solution and the temperature rose by 4.46°C. When 100 mL of nitric acid and 100 mL of sodium hydroxide were mixed in the same calorimeter, the temperature rose by 2.01°C. What is the heat output for the neutralization reaction?

The chemical equation is $\text{HNO}_3 + \text{NaOH} \rightarrow \text{NaNO}_3 + \text{H}_2\text{O}$.

- First find the heat capacity of the calorimeter (like #1) for 0.2 L of solution.

$$C_{\text{calorimeter}} = \frac{q_{\text{cal}}}{\Delta T} = \frac{2.00 \text{ kJ}}{4.46^\circ\text{C}} = \frac{448 \text{ J}}{^\circ\text{C}}$$

- The $V_{\text{total}} = 0.2\text{L}$, so

$$q_{\text{neutralization reaction}} = -q_{\text{cal}} = -C_{\text{cal}}\Delta T = -\left(448 \frac{\text{J}}{^\circ\text{C}}\right)(2.01^\circ\text{C})$$

$$q_{\text{neutralization reaction}} = -900 \text{ J}$$

q_{rxn} is -, exothermic

4. When a solution of 1.691 g of silver nitrate is mixed with an excess of sodium chloride in a calorimeter of heat capacity 216 J/(°C) ¹, the temperature rises 3.03°C. What is the reaction enthalpy for $\text{NaCl}(\text{aq}) + \text{AgNO}_3(\text{aq}) \rightarrow \text{NaNO}_3(\text{aq}) + \text{AgCl}(\text{s})$?

$$q_{\text{rxn}} = -q_{\text{cal}} = -C_{\text{cal}}\Delta T = -\left(216 \frac{\text{J}}{^\circ\text{C}}\right)(3.03^\circ\text{C}) = -655 \text{ J}$$

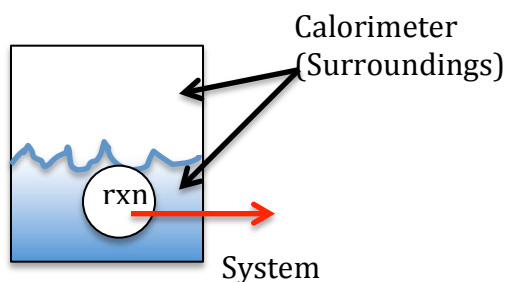
655 J is the heat released if 1.691 g of silver nitrate is reacted with excess NaOH.

Reaction enthalpies (ΔH_{rxn}) are always given in units of $\frac{\text{energy (J or kJ)}}{\text{mol of reaction}}$.

Therefore $1.691 \text{ g AgNO}_3 \times \left(\frac{1 \text{ mol AgNO}_3}{169.9 \text{ g AgNO}_3}\right) = 0.00995 \text{ mol AgNO}_3$

$$\Delta H_{rxn} = \frac{-0.654 \text{ kJ}}{0.00995 \text{ mol AgNO}_3} = -65.7 \text{ kJ} = \Delta H_{rxn} \text{ exothermic}$$

since 1 mole of reaction corresponds to 1 mole of AgNO₃



*** The next two problems deal with combustion reactions. When reporting the molar heat or enthalpy of combustion for a certain fuel, one assumes the value of the heat of combustion or enthalpy of combustion is per 1 mole of the fuel. ***

5. If we set up a bomb calorimetry experiment to determine the molar enthalpy of combustion of ethane (C₂H₆) using 1 L of water as our heat sink, 2.805 g of ethane, and measure an initial and final temperature of 25.20°C and 58.92°C, respectively, what will be the experimentally determined molar enthalpy of combustion of ethane? The chemical equation is 2 C₂H₆ + 7 O₂ → 4 CO₂ + 6 H₂O? Assume the density of the water is 1.00 g/mL. Assume the calorimeter itself absorbs no heat. The specific heat capacity of water is 4.184 J/(g·K).

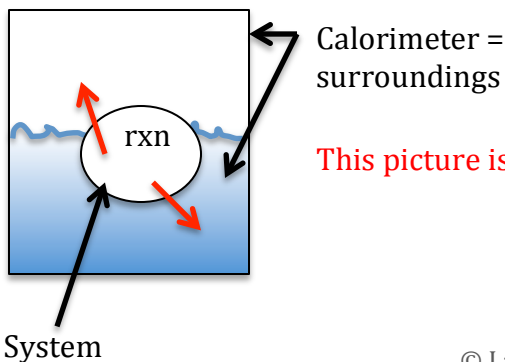
- Fuel = C₂H₆
- 2.805 g of ethane is $\frac{2.805 \text{ g}}{((12 \times 2) + (1 \times 6)) \frac{\text{g}}{\text{mol}}} = 0.0935 \text{ mol}$
- $q_{rxn} = -q_{cal} = -C_{cal} \Delta T = - (C_{s, H_2O} \times M_{H_2O}) \Delta T$ because we assume $C_{hardware} = 0$

$$= - \left(4.184 \frac{\text{J}}{\text{g} \cdot \text{L}} \right) \left(1 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ g}}{\text{mL}} \right) (58.92 - 25.20)$$

$$= -141084 \text{ J} = -141.08 \text{ kJ}$$

So, 141.08 kJ of heat is released by the combustion of 0.0935 moles of ethane.

- $\Delta H_{comb} = -141.08 \text{ kJ} \times \frac{1 \text{ mol}}{0.0935 \text{ mol}} = -1508.9 \text{ kJ}$ since ΔH_{comb} is for 1 mole of fuel.



This picture is the same for #5 and #6.



6. 1.14 g of octane (C_8H_{18}) is combusted in a bomb calorimeter surrounded by 1 L of water. The initial and final temperatures of the water are $25^\circ C$ and $33^\circ C$ respectively. The heat capacity of the calorimeter hardware (all of the calorimeter except for the water) is $456 J/^\circ C$.

The chemical equation is $2 C_8H_{18} + 25 O_2 = 16 CO_2 + 18 H_2O$.

Determine the molar enthalpy of combustion of octane.

- Fuel = C_8H_{18}

- 1.14 g octane is $\frac{1.14 g}{(12 \times 8) + (1 \times 18) g/mol} = 0.01 mol$

- $q_{rxn} = -q_{cal} = -C_{cal}\Delta T = -(C_{H_2O} + C_{hardware})\Delta T =$
 $- (C_{S \cdot H_2O} \times M_{H_2O}) (C_{hardware})\Delta T$
 $= - \left[\left(4.184 \frac{J}{g \cdot L} \right) (1000g) + \left(456 \frac{J}{^\circ C} \right) \right] (33 - 25^\circ C)$
 $= -(4640 J)(8) = 37120 J = -37.12 kJ$

So, $-37.12 kJ$ of heat is released by the combustion of 0.01 moles of octane.

- $\Delta H_{combustion} = (-37.12 kJ) \left(\frac{1 mol}{0.01 mol} \right) = -3712 kJ$ because $\Delta H_{combustion}$ is reported for 1 mole of fuel.