Aqueous Calorimetry

Many calorimetry labs involve adding a solid (say, perhaps, an unknown metal) to a water bath and determining the temperature change of the water bath. However, there are multiple times when you will need to determine the energy change of an aqueous reaction: for example, to determine ΔH_{neut} for an acid-base neutralization, or ΔH_{soln} when dissolving a salt.

There are 4 important assumptions made during aqueous calorimetry labs*

1. It is assumed that the density of the aqueous solution is the _Same_ as for water, 1 g/mL. (100 mL of solution is said to have a mass of 100 g).

2. It is assumed that the volumes of reactants are _additive_. (100 mL of reactant A + 200 mL of reactant B = 300 mL of reaction mixture)

3. It is assumed that the specific heat capacity of an aqueous reaction mixture is the same as water, 4.18 J/g °C.

4. It is assumed that heat is _not_ lost to, or absorbed by, the surroundings.

   *If these assumptions are not correct, the problem should specifically tell you otherwise.

Normal calorimetry math still applies! But (yay!) no double mCAT problems: you must _add_ the masses of all chemicals reacting (including water if something is being dissolved), because the heat absorbed or released is being shared by all the chemicals present in the system.   _mass of everything inside the calorimeter!_

$$+q_{rxn} = -[mC\Delta T]_{calorimeter}$$

To calculate the enthalpy of reaction (or phase change), you will need to divide q_{rxn} by the moles of reaction.

$$\Delta H_{rxn} = \frac{q_{rxn}}{mol_{rxn}}$$

<u>Reminder:</u> Experimental Error with Calorimetry! (i.e. the flaws of assumption #4)

- We assume in the above equation that **ALL** energy lost by the system is gained *only* by the water, but that's not true! The calorimeter can also absorb heat, or heat can be lost to the surrounding air.

- Both of these errors would lead to a calculated heat (q) that was SMALLER than the actual heat exchange, and thus the calculated ΔH would be ___↓___ than the actual ΔH.

1. An experiment was conducted in which 5.19 g of Na_2CO_3 was dissolved in 75.0 g of distilled water. A temperature increase of the system of 3.8°C was observed. Calculate the enthalpy of dissolution for sodium carbonate. (Assume that the solution has a density of 1.00 g/mL and a specific heat of 4.18 J/g °C.)

$$q_{Sol'n} = -q_{cal} = -\underbrace{(5.19 + 75.0g)}_{80.19g}(4.18\,^{J}\!/_{g\cdot c})(3.8°c) = \underbrace{-1,273.7\,J}_{2\,s.f.}$$

$$5.19\,g\,Na_2CO_3 \times \frac{1\,mol}{105.99\,g\,Na_2CO_3} = 0.0490\,mol\,rxn$$

$$\Rightarrow \Delta H_{Sol'n} = \frac{kJ}{mol_{rxn}} = \frac{-1.2737\,kJ}{0.0490\,mol_{rxn}} = \boxed{-26\,kJ/_{mol_{rxn}}}$$

2. A 100.0 mL sample of 0.300 M NaOH is mixed with a 100.0 mL sample of 0.300 M HCl in a coffee cup calorimeter. If both solutions were initially at 35.00°C and the temperature of the resulting solution was recorded as 37.00°C, determine the heat absorbed or released in kJ/mol$_{rxn}$ for the neutralization reaction between aqueous NaOH and HCl. Assume that no heat is lost to the calorimeter or the surrounding, and that the density and the heat capacity of the resulting solution are the same as water.

$$q_{rxn} = -q_{cal} = -\underbrace{(200.0\,g)}_{(100.0+100.0)mL \times 1.0\,g/mL}(4.18\tfrac{J}{g\cdot c})(\overbrace{37.00-35.00}^{2.00°C}) = -1{,}672\,J$$

*Neither reactant is limiting, so pick either!

$$0.300\,M \times 0.10000\,L = 0.0300\,mol\,NaOH \times \frac{1\,mol\,rxn}{1\,mol\,NaOH} = 0.0300\ mol\,rxn$$

$$\Rightarrow \Delta H = \frac{kJ}{mol_{rxn}} = \frac{-1.672\,kJ}{0.0300\,mol\,rxn} = \boxed{-55.7\ kJ/mol_{rxn}}$$

3. A student conducts an experiment to determine the enthalpy of neutralization for sodium hydroxide reacting with phosphoric acid in the reaction shown below. The student combines 25.0 mL of equimolar solutions of acid and base, both having an initial temperature of 22.50°C, in a coffee cup calorimeter. Each solution has a density of 1.00 g/mL and a specific heat of 4.18 J/g °C. The student collects data until a maximum temperature of 26.40°C is reached. *each!*

$$3\,NaOH(aq) + H_3PO_4(aq) \rightarrow 3\,H_2O(l) + Na_3PO_4(aq)$$
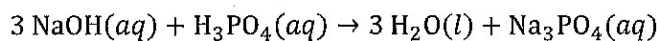
a. Calculate q$_{rxn}$ for this neutralization reaction.

$$q_{rxn} = -q_{cal} = -\underbrace{(50.0\,g)}_{(25.0+25.0)mL \times 1\,g/mL}(4.18\,J/g°c)(\overbrace{26.40-22.50}^{3.90°C}) = \boxed{-815\,J}$$

b. Calculate the ΔH$_{neut}$ if the initial molarity of both solutions is equal to 0.80 M. Report your answer in kJ/mol.

Base is limiting! $$0.80M \times 0.0250\,L = 0.020\,mol\,NaOH \times \frac{1\,mol\,rxn}{3\,mol\,NaOH} = 0.0067\,mol\,rxn$$

$$\Delta H_{neut} = \frac{kJ}{mol_{rxn}} = \frac{-0.815\,kJ}{0.0067\,mol\,rxn} = \boxed{-120\,kJ/mol_{rxn}}$$