Heats of Ionic reactions

Calorimetry

The reactions investigated are:

1. The heat of ionization of water H_2O (l)
2. The heat of ionization of Na^+ $^-OOC\text{-}CH_2\text{-}COOH$ (aq), say Na^+HR^-

$$H_2O(l) = H^+(aq) + OH^-(aq) \quad \Delta H_1$$
$$HR^{-1}(aq) = H^+(aq) + R^{-2}(aq) \quad \Delta H_2$$

The approach taken here is to determine the enthalpy change for the reverse reactions. The reactions are in solution thus both p and V would not change in these reactions.

$$H^+(aq) + OH^-(aq) = \qquad \Delta H_3 = -\Delta H_1$$
$$HR^{-1}(aq) + OH^-(aq) = R^{-2}(aq) + H_2O(l) \quad \Delta H_4$$

$$H^+(aq) + OH^-(aq) = \; + H_2O(l) \qquad \Delta H_3 = -\Delta H_1$$
$$HR^{-1}(aq) + OH^-(aq) = R^{-2}(aq) + H_2O(l) \quad \Delta H_4$$

Energy Changes of Ionic Reactions

Reactions are associated with energy exchanges. The reaction energy changes can be expressed as ΔH and ΔE. The heat and work associated with the above mentioned quantities can be stated.

Internal energy change; $\Delta E = q + w = q - p\Delta V$

For reactions performed at constant volume, $\Delta E = q_v$

By definition $H = E + pV$

Enthalpy energy change; $\Delta H = \Delta E + \Delta(pV)$

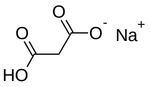
For reactions where the neither *p* nor *V* changes,

Enthalpy energy change; $\Delta H = \Delta E = q_v$

$$H^+(aq) + OH^-(aq) = H_2O(l) \qquad \Delta H_3$$
$$Na^+(aq) + OH^-(aq) + H^+(aq) + Cl^-(aq) = H_2O(l) + Na^+(aq) + Cl^-(aq)$$

$$OH^-(aq) + HR^{-1}(aq) = R^{-2}(aq) + H_2O(l) \qquad \Delta H_4$$
$$2Na^+(aq) + OH^-(aq) + HR^{-1}(aq) = R^{-2}(aq) + 2Na^+(aq) + H_2O(l)(aq)$$

HR^- →



Definition symbols q_v = heat per mole
q_e = heat generated in the experiment

The experiment measures the energy/heat *lost* during the reaction by measuring the heat q_e *gained* by the calorimeter and its contents (water).

Procedural steps in brief:

1 Determining the heat capacity of the calorimeter, C_S, using a reaction of standard compound where energy/heat q_e (heat involved with m_{std} involved is known (triplicate runs).

2. Use the C_S to calculate the energy/heat q_e involved in the 'test' reaction (triplicate runs).

3. Calculate the ΔH of the test reaction using the q_e from the step above.

Solution Calorimetry Solutions

0.1 M HCl (provided)
0.25 M HCl (provided)
2.5 M NaOH (provided)

Prepare 0.25M Sodium Malonate Solution:

Prepare 0.5 M NaOH: Mix 40 mL 2.5M NaOH and 160 mL of DI water in a 250 mL Erlenmeyer flask.
Prepare 0.5 M malonic acid: Dissolve 10.4011g of malonic acid in a 200 mL volumetric flask.

Prepare 0.25M Sodium Malonate Solution: Prepare a total of 400 mL of the solution by mixing 200 mL of 0.5 M NaOH and 200 mL of 0.5 M malonic acid.

Reactions performed in the Experiment

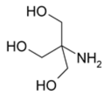
Rxn 1 - TRIS Base (standard)
0.5g (m_{std}) Tris (accurate actual mass recorded) (LR) + 100 mL 0.1 M HCl.

Rxn 2
10 mL of 2.5 M NaOH + 100 mL of 0.25 M HCl (LR).

Rxn 3
10 mL of 2.5 M NaOH + 100 mL of 0.25 M sodium malonate* (LR).

* Prepare by mixing reactants (previous page).

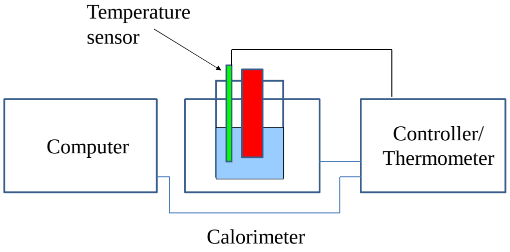
Procedure in brief:



= TRIS

1. Determining the heat capacity of the calorimeter, C, using a reaction of known standard reaction where energy/heat q involved (triplicate). 0.5g TRIS (accurate mass recorded, m_{std}) + 100 mL 0.1 M HCl
2. Run the reaction (Rxn 2) of which enthalpy change to be determined (triplicate). 10 ml of 2.5 M NaOH combined with 100 ml of 0.25 M HCl ($moles_{H^+}$).
3. Run the reaction (Rxn 3) of which enthalpy change to be determined (triplicate). 10 mL of 2.5 M NaOH combined with 100 mL of 0.25 M sodium malonate* ($moles_{H^+}$).

Operation of the solution calorimeter.



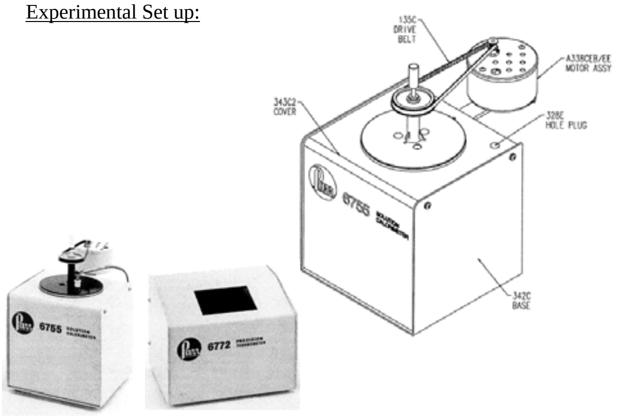
Temperature sensor

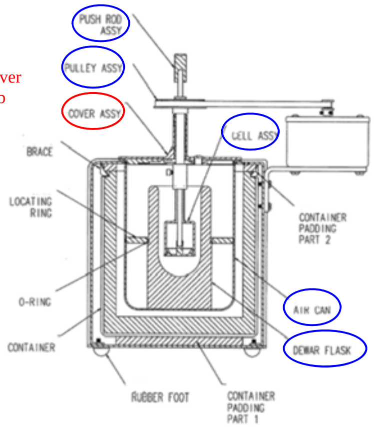
Computer

Controller/ Thermometer

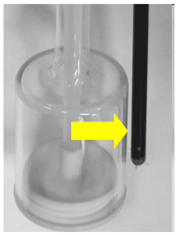
Calorimeter

Experimental Set up:

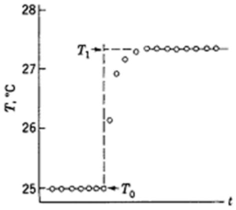




Calorimeter Cover with Stirrer Hub & Bearing Assembly



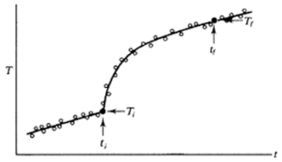
The heat generated from the reaction is absorbed by the calorimeter (container + stirrer + water (solutions) + temperature detectors), raising its temperature by ΔT;



Thermogram

$$q_v = C_S(T_1 - T_0) = C_S \Delta T$$
$$C_S = \text{heat capacity of calorimeter}$$

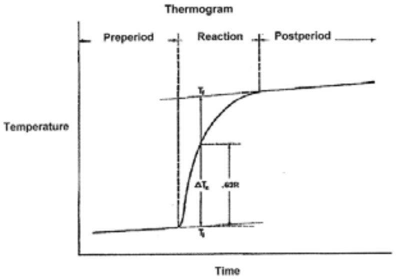
The stirrer does mechanical work thus would raise the temperature of the system slowly before (and after) the reaction. Any object at a higher temperature that its environment would lose heat (Law of Cooling). A corrected temperature change is used for calculations.

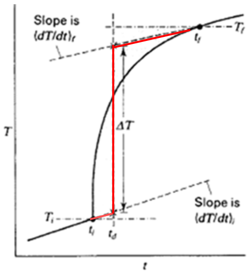


$$\Delta T_c = \left(T_f - T_i\right) - \int_{t_i}^{t_f} \left(\frac{dT}{dt}\right)_{leak+stir} dt$$

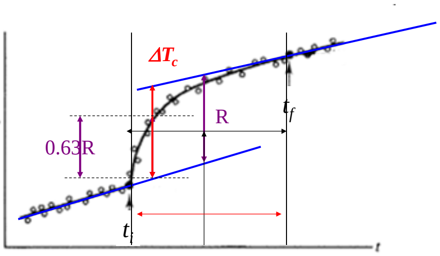
$$\Delta T_c = \left(T_f - T_i\right) - \int_{t_i}^{t_f} \left[\frac{\left[P - k(T - T_s)\right]}{C_S}\right] dt$$

$$\Delta T_c = determined\ graphicaly$$





Determine the $\Delta T_C = \Delta T$ (height) between the extrapolated lines where the areas confined by extrapolated lines and rising part of the thermogram (dotted lines and curve) are equal.



$time\ of\ start\ of\ reaction = t_i$

$time\ of\ end\ of\ reaction = t_f$ reaction period = $t_f - t_i$

T_f, T_i are 'initial' and 'final' temperatures of the reaction mixture

Corrected temperature rise ΔT_c found graphically.

Measure the time for the 50% completion of reaction =

$$time_{@half} = \frac{t_i + t_f}{2}$$

Measure the distance between the two extrapolated lines at $time_{@half}$ = R

Calculate 0.63R.

Find the point on the T vs t curve (thermogram) which is 0.63R above the extrapolated pre-period line.

Draw a vertical line thro' the above mentioned point; find the intersection temperatures of the vertical line with the extrapolated lines, determine ΔT_C. (there is an alternate accurate way to get it)

Calculations:

Use the data from the standard run.

1. Determination of the heat capacity of the calorimeter C and it's contents (water) using the corrected temperature change $\Delta T_{c,std}$ for the NaOH and TRIS standard sample of known mass m_{std} for which heat generated $q_e = q_{std}$ and therefore,

$$C_S = \frac{q_{std}}{\Delta T_{c,std}}$$

$$q_{std} = m_{TRIS}[58.738 + 0.3433(25 - T_{0.63R})]$$

$$m_{TRIS} = mass\ of\ TRIS\ (g)$$

$$T(0.63R) = temperature\ at\ 0.63R\ on\ thermogram$$

$$Heat\ evolved\ per\ gram\ of\ TRIS = 58.738\ \frac{cal}{g}(given)$$

$0.3433(25 - T_{0.63R})$ corrects q so that value is for 25^oC

$$C_S = \frac{q_{std}}{\Delta T_{c,std}} \quad cal$$

Calculations:

Use the data from the standard runs.

2. Determination of the q_{test} (= q_e) for the test reactions by measuring $\Delta T_{test,c}$ values for each test reaction where the moles of the limiting reagent is $moles_{test}$, $=q_{test}$

$$q_{test} = C_S \times \Delta T_{c,test}$$

$$\Delta H = -\frac{q_{test}}{moles_{test}}$$

$$\nearrow$$

$$\Delta H_3, \Delta H_4$$

$$\Delta H_1 = -\Delta H_3, \quad \Delta H_2 = -\Delta H_3 + \Delta H_4$$

Transfer data

Importing logged data to the computer (for graphing) and data manipulation.

Keep the data logger turned on during each run.

DO NOT leave of the data collection screen before saving the raw data as an Excel spreadsheet.

Import the data an Excel spreadsheet installed in a PC via FTP.

SAVE the raw data with a descriptive title and make a working copy of it. Preserve the raw data (for each run).