A Thermodynamic Investigation of the Reaction Between Hypochlorite and Iodide

Abstract[1]

The method of continuous variations and a calorimetric determination of enthalpy are used to verify the stoichiometry for the reaction between hypochlorite, OCl^-, and iodide, I^-. Stoichiometric mixing occurred with a 3:1 mole ratio between OCl^- and I^-, suggesting that the reaction is

$$3OCl^-(aq) + I^-(aq) \rightarrow IO_3^-(aq) + 3Cl^-(aq)$$

The experimentally determined value of –341 kJ/mol_{rxn} for ΔH compares favorably with the expected value of –346.4 kJ/mol_{rxn}, providing further evidence that the proposed stoichiometry is correct.

Introduction[2]

Hypochlorite ion, OCl^-, is a potent oxidizing agent used in many household bleaches. Although hypochlorite's reactivity with a wide variety of organic molecules is well known (*1*), particularly for organic dyes, its reactivity with inorganic ions has been studied less frequently. This is somewhat surprising given the significant release of OCl^- into the environment from household use (*2*).

One of the challenges in studying any reaction is determining the products. This is a particular problem for an oxidation-reduction reaction when many oxidation states are available to the oxidizing agent or to the reducing agent. For example, the chlorine in OCl^-, which has an oxidation state of +1, can be reduced to an oxidation state of 0 in Cl_2 or to an oxidation state of –1 in Cl^-, or it can be oxidized to an oxidation state of +3 in ClO_2^-, to an oxidation state of +5 in ClO_3^-, or to an oxidation state of +7 in ClO_4^-. Although it is possible to identify the products by using a standard qualitative analysis scheme, this often requires that we first isolate an individual species before we use an identifying chemical test.

The method of continuous variations (MCV), first described by Job (*3*) for the stoichiometric analysis of metal–ligand complexes, provides a simple method for determining the stoichiometry of an oxidation-reduction reaction. The basis of MCV involves combining solutions of two reactants, A and B, such that their combined moles, n_{tot}, remains constant in all experiments; thus

$$n_A + n_B = n_{tot} \tag{1}$$

where n_A and n_B are, respectively, the moles of A and B. The relative amount of each reactant is expressed as its mole fraction, X_A or X_B

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[1] There are four things to note about this abstract: it states the experiment's purpose; it summarizes the experiment's two main conclusions; it compares one of the experiment's results to a theoretical value; and, at just three sentences in length, it is concise. As you prepare your abstract, try to accomplish these four things.

[2] An introduction places your work within a context that defines the experiment's goals. For this fictitious report, assume that students are told that OCl^- is the active ingredient in bleach, that it is an oxidizing agent, and that its release into the environment poses a concern. Assume, as well, that the goal of the experiment is to determine the stoichiometry of the reaction between OCl^- and I^-. To help students in their planning, they are provided with a copy of Job's paper on the method of continuous variations for metal–ligand complexes and asked to adapt that procedure to this experiment. In addition, because they had just studied calorimetry, the students are asked to use calorimetry in this experiment. Note that this introduction accomplishes three things: it provides additional context for the experiment by citing references to the chemistry of OCl^- and by discussing the difficulty of determining the stoichiometry of oxidation-reduction reactions; it explains Job's method; and it clearly states the experiment's goals. Note that the introduction's first paragraph begins with a "hook" that tells the reader why s/he should be interested in this research, and note, as well, that the introduction's final paragraph provides a transition to the rest of the report, telling the reader what is to come.

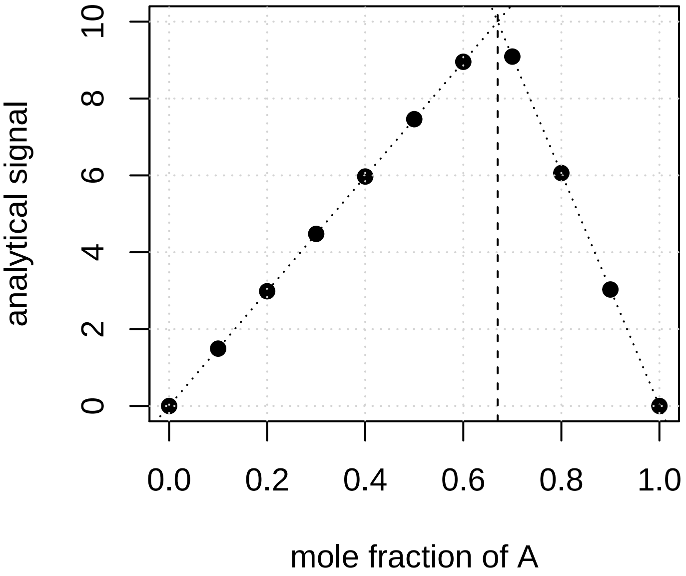

Figure 1: Hypothetical MCV plot for the reaction of A and B showing a stoichiometric mixing when the mole ratio of A to B is 2:1. The vertical dashed line shows the stoichiometric mixture.

$$X_A = \frac{n_A}{n_{tot}} \tag{2}$$

$$X_B = 1 - X_A = \frac{n_B}{n_{tot}} \tag{3}$$

In a reaction between A and B, the extent of the reaction is determined by the limiting reagent. If an analytical signal is proportional to the limiting reagent, then a plot of that signal as a function of X_A consists of two straight lines that intersect at a mole fraction for A that corresponds to the stoichiometric mixing of A and B. The mole ratio of A and B at this point is given by

$$\frac{n_A}{n_B} = \frac{X_A}{X_B} = \frac{X_A}{1 - X_A} \tag{4}$$

Figure 1 shows an MCV plot for a hypothetical reaction between the reactants A and B. The intersection at $X_A = 0.67$ indicates that two moles of A react stoichiometrically with one mole of B, from which we conclude that the reaction is

$$\text{2A} + \text{B} \rightarrow \text{Products}$$

As noted by Job (*3*), there are three important limitations to the MCV: the reaction must involve only two reactants, there must be only one possible reaction, and the free energy for the reaction must be highly favorable.

To evaluate the utility of the MCV as a method for studying oxidation-reduction chemistry, we present results for an analysis of the reaction between hypochlorite and iodide. A determination of the reaction's enthalpy provides further confirmation of the MCV results.

Procedure[3]

All reactions were carried out in a locally-designed cup calorimeter. Two small 8 oz. Styrofoam cups were nestled together and trimmed such that the inner cup did not protrude above the outer cup. The bottom of a 20 oz. Styrofoam cup was removed and used to fashion a top. Small holes were punched in the top to accommodate a digital thermometer, which was connected to a LabQuest data interface (Vernier), and to accommodate a small glass funnel for adding reagents. Data were analyzed using LoggerPro (Vernier).

The calorimeter's suitability for calorimetry experiments was tested by measuring the change in temperature when reacting 1.00 M solutions of HCl (Fisher Scientific) and NaOH (Fisher Scientific). The calorimeter's constant was determined using the method of Joule (*4*), which is based on the thermal transfer of heat from hot water to cold water. In all calorimetry experiments, the temperature was monitored for several minutes both before and after adding the second solution to ensure that ΔT could be determined accurately by extrapolation.

Solutions of 0.213 M OCl^- and 0.213 M I^- were prepared from a commercial bleach (Kroger Brand) and reagent-grade KI (Fisher Scientific), respectively. The solution of KI was 0.1 M in NaOH (Fisher Scientific). Calorimetry experiments for reactions involving OCl^- and I^- were limited to a combined volume of 80 mL. The reagent with the larger volume was placed in the calorimeter and the reagent with the smaller volume was then added. For those experiments used to establish the reaction's stoichiometry only the solution volumes are reported; the mass of each solution was measured in experiments used to determine ΔH.

Results and Conclusions[4]

When an object with a known mass, m, and a known specific heat, S, experiences a change in temperature, ΔT, the heat, q, absorbed or released is given by

$$q = mS\Delta T \tag{5}$$

where q is negative when the object loses heat and is positive when the object gains heat. Equation 5 is the fundamental equation of calorimetry.

Evaluating the Calorimeter. An ideal calorimeter is a perfect insulator that allows a reaction to take place without exchanging energy with either the calorimeter itself or with the external environment. To evaluate the suitability of our calorimeter, we measured the change in temperature upon mixing 40.0 mL of 1.00 M HCl with 40.0 mL of 1.00 M NaOH. As seen in Figure 2, the calorimeter maintains a relatively constant temperature once the reaction is complete, suggesting that there is a minimal loss of heat to the laboratory environment.

To determine whether the calorimeter absorbs heat, we note that the theoretical ΔH° for the reaction

$$\mathrm{H_3O^+}(aq) + \mathrm{OH^-}(aq) \rightleftharpoons 2\mathrm{H_2O}(l)$$

is –55.836 $\mathrm{kJ/mol_{rxn}}$, which gives an expected change in temperature for the data in Figure 2 of approximately 6.7°C (Note 1). As the actual change in temperature is 6.3°C, the calorimeter itself clearly absorbs some of the energy released by the reaction, a contribution that we can correct for by measuring the calorimeter's heat capacity.

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[3] The most striking observation about this procedure is the relative absence of numerical information. Note that the procedure makes no attempt to describe in detail each individual experiment. For example, examine carefully the first two sentences in the procedure's second paragraph and contrast the general information provided there with the more specific details included in the results and conclusions section.

[4] There are five things to note here. First, the results and conclusions are organized so that the reader can follow the logic of the data analysis; note, in particular, the use of subheadings to focus the reader's attention. Second, figures are used to present representative data and tables are used to present results across a range of conditions. Third, where appropriate, results are summarized using means and standard deviations. Fourth, the main conclusions for each part of the experiment are stated clearly. Fifth, and finally, an analysis of error in included.

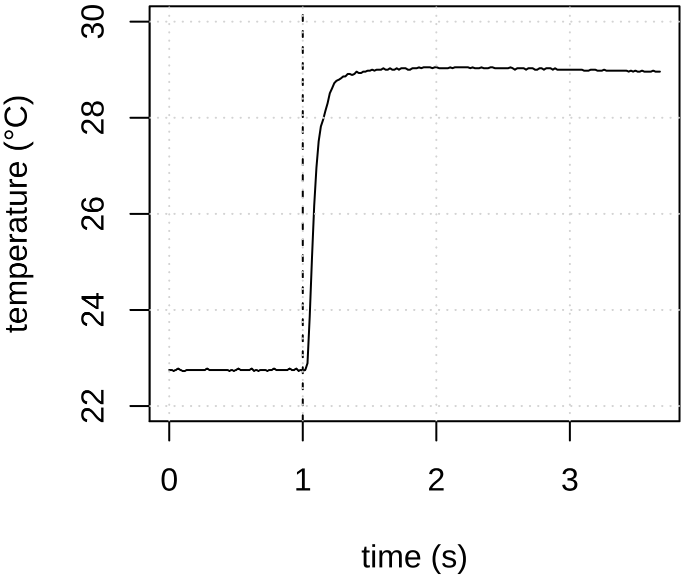

Figure 2: Temperature vs. time curve for the reaction of 40.0 mL of 1.00 M HCl with 40.0 mL of 1.00 M NaOH. The sample of HCl was added to the calorimeter first with the NaOH added at the time indicated by the dashded vertical line. The nearly constant temperature after the reaction is complete indicates that the rate at which heat is lost to the external environment is minimal.

Determining the Calorimeter's Heat Capacity. To accurately measure an exothermic reaction's ΔH by calorimetry we must know how much heat the calorimeter absorbs, q_{cal}, which is equivalent to

$$q_{cal} = C_{cal} \Delta T_{cal} \tag{6}$$

where C_{cal}, which is equivalent to mS, is the calorimeter's heat capacity and ΔT is the calorimeter's change in temperature. In Joule's method for determining a calorimeter's constant we combine a known mass of hot water, m_h, with a known mass of room temperature water, m_{rt}, and observe the change in temperature for both (*4*). A conservation of energy requires that the heat lost by the hot water is absorbed by the room temperature water and by the calorimeter; thus

$$-q_h = q_{rt} + q_{cal} \tag{7}$$

Substituting equation 5 and equation 6 into equation 7 gives

$$-m_h S \Delta T_h = m_{rt} S \Delta T_{rt} + C_{cal} \Delta T_{cal} \tag{8}$$

where m is the mass of water and S is the specific heat of water (4.184 J/g°C). In a typical experiment, a final temperature of 41.3°C was achieved upon mixing 40.133 g of room temperature water at an initial temperature of 24.7°C with 39.168 g of hot water at an initial temperature of 61.5°C, which gives a C_{cal} of 31.5 J/°C (Note 2). The average C_{cal} for three trials was 31.4 J/°C with a standard deviation of 0.56 J/°C.

Establishing Stoichiometry by the Method of Continuous Variations. To establish the reaction's stoichiometry by the method of continuous variations, we carried out a series of calorimetry experiments in which we changed the relative amounts of OCl^- and of I^- while maintaining a constant combined volume of 80.0 mL. Temperature-time curves for these experiments were similar to that shown in Figure 2 and are not included here. Figure 3, which is a variation of the traditional MCV plot, shows that a stoichiometric mixing occurs for the reaction of 60.0 mL of 0.213 M OCl^- with 20.0 mL of 0.213 M I^-. This corresponds to 1.28×10^{-2} mol OCl^- and 4.26×10^{-3} mol I^-, or a 3:1 molar ratio.

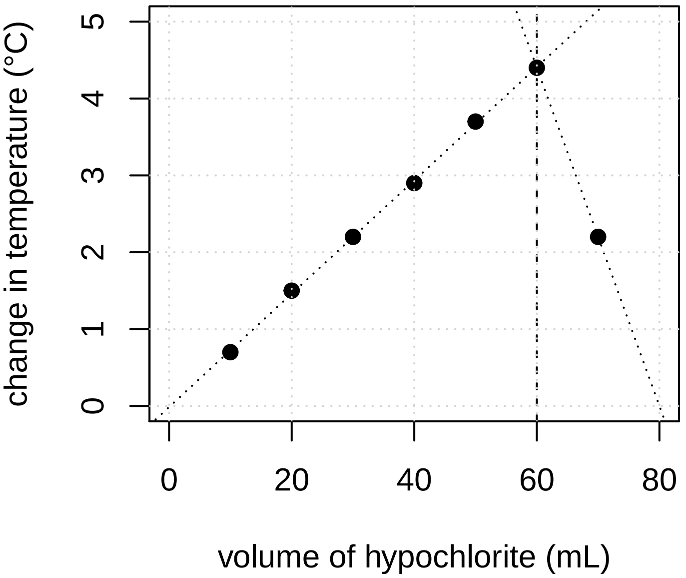

Figure 3: MCV plot showing that stoichiometric mixing occurs when 60.0 mL of 0.213 M hypochlorite react with 20.0 mL of 0.213 M iodide.

Because iodine in I^- is in its most negative oxidation state, it must undergo oxidation. The chlorine in OCl^- must be reduced to either Cl_2 or to Cl^-. If Cl_2 is the product, then a total of three electrons are needed to reduce the chlorine in three OCl^- ions from oxidation states of +1 to 0. This requires the single iodine in I^- to experience a three electron oxidation from its initial oxidation state of –1 to a final oxidation state of +2; however, no such oxidation state exists for iodine. If Cl^- is the reduction product, then a total of six electrons are needed to reduce the chlorine in three OCl^- ions from oxidation states of +1 to –1. Oxidation of I^- to IO_3^- provides the necessary electrons. The proposed balanced reaction for this system is

$$3\mathrm{OCl}^-(aq) + \mathrm{I}^-(aq) \rightarrow \mathrm{IO}_3^-(aq) + 3\mathrm{Cl}^-(aq)$$

Determining ΔH for the Reaction. To determine ΔH for the reaction between OCl^- and I^- we completed additional calorimetry experiments using 60.00 mL of 0.213 M OCl^- and 20.00 mL of 0.213 M I^-. Table 1 summarizes the results of these experiments where

$$\Delta H = \frac{q_{rxn}}{n_{LR}} \times \frac{\nu_{LR}}{\mathrm{mol_{rxn}}} = \frac{-(q_{soln} + q_{cal})}{n_{LR}} \times \frac{\nu_{LR}}{\mathrm{mol_{rxn}}} = \frac{-(mS\Delta T + C\Delta T)}{n_{LR}} \times \frac{\nu_{LR}}{\mathrm{mol_{rxn}}} \tag{9}$$

and where q_{rxn} is the heat released by the reaction, q_{soln} is the heat absorbed by the reaction mixture, q_{cal}, is the heat absorbed by the calorimeter, m is the total mass of the reaction mixture, S is the reaction mixture's specific heat (which we assume is equivalent to that for water), C, is the calorimeter's constant, n_{LR} is the moles of the limiting reagent, and ν_{LR} is the limiting reagent's stoichiometric coefficient in the balanced reaction (Note 3).

Table 1: Calorimetry Results for the Reaction of OCl^- with I^-

	total mass (g)	ΔT (^oC)	ΔH (kJ/$\mathrm{mol_{rxn}}$)
1	82.409	3.9	-344
2	82.616	3.8	-336
3	82.195	3.9	-344

The mean and the standard deviation for the results in Table 1 are –341 kJ/$\mathrm{mol_{rxn}}$ and 4.62 kJ/$\mathrm{mol_{rxn}}$, respectively. The theoretical value for ΔH is –346.4 kJ/$\mathrm{mol_{rxn}}$, which gives an error of –1.8%. Because ΔT

is known to just two significant figures, the expected uncertainty in ΔH is ±10 kJ/mol$_{\text{rxn}}$, or a relative uncertainty of ±2.8%. Our experimental uncertainty of –1.8%, therefore, is reasonable and suggests that there are no significant problems with the experiment.

Notes[5]

Note 1. The value of 6.7°C was determined as follows:

- Because equal moles of HCl and of NaOH are mixed—in this case, 0.0400 mol of HCl or NaOH—we can assign either reagent as the limiting reagent.
- The amount of heat released, q_{rxn}, is

$$q_{rxn} = \frac{-55.836 \text{ kJ}}{\text{mol}_{\text{rxn}}} \times 0.0400 \text{ mol HCl} \times \frac{1000 \text{ J}}{\text{kJ}} = -2233 \text{ J}$$

- The amount of heat absorbed by the calorimeter, q_{cal}, is $-q_{rxn}$, or +2233 J.
- The change in temperature is determined using the equation $q_{cal} = mS\Delta T$. Assuming the combined solution has a density of 1.0 g/mL, gives the solution's mass as 80 g; thus

$$+2233 \text{ J} = (80 \text{ g})(4.184 \text{ J/g°C})\Delta T$$

or a ΔT of 6.7°C.

Note 2. Substituting into equation 7 the results for this trial

$$-(39.168 \text{ g})(4.184 \text{ J/g°C})(41.3 - 61.5 \text{ °C}) = (40.133 \text{ g})(4.184 \text{ J/g°C})(41.3 - 24.7 \text{ °C}) + C_{cal}(41.3 - 24.7 \text{ °C})$$

and solving for C_{cal} gives a result of 31.5 J/°C.

Note 3. Outlined here is the calculation for the first row in Table 1. Applying a conservation of energy requires that

$$-q_{rxn} = q_{soln} + q_{cal}$$

where q_{rxn} is the heat released by the exothermic reaction, q_{soln} is the heat absorbed by the reaction mixture, and q_{cal} is the heat absorbed by the calorimeter. Substituting in equation 5 and equation 6 gives

$$-q_{rxn} = m_{soln}S_{soln}\Delta T_{soln} + C_{cal}\Delta T_{cal}$$

$$-q_{rxn} = (82.409 \text{ g})(4.184 \text{ J/g°C})(3.9 \text{ °C}) + (31.4 \text{ J/°C})(3.9 \text{ °C}) = -1467 \text{ J}$$

Because this is a stoichiometric mixture, we can calculate ΔH using either OCl^- or I^-; here we use I^- as the limiting reagent

$$\Delta H = \frac{q_{rxn}}{n_{LR}} \times \frac{\nu_{LR}}{\text{mol}_{\text{rxn}}} = \frac{-1467 \text{ J}}{(0.213 \text{ M})(0.02000 \text{ L})} \times \frac{1 \text{ mol I}^-}{\text{mol}_{\text{rxn}}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -344 \text{ kJ/mol}_{\text{rxn}}$$

References[6]

1. Ajax, V. *The Chemistry of Bleach*, Comet Press: New York, 1999.
2. "The Effects of Chlorine Bleach on the Environment", http://www.livestrong.com/article/217675-the-effects-of-chlorine-bleach-on-the-environment/ (accessed January 2017)

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[5] Use notes to present sample calculations or to include additional explanations. The purpose of this section is to present important material whose presence in the main body of the report might disrupt your reader's ability to engage with your report's narrative.

[6] The second and the third references are real; the first and the last references are fictitious entries created for this sample report. Note that books are identified by their title, information about the publisher, and the date of publication; journal articles are identified by their title, the journal, the year of publication, the volume, and the page; websites are identified by their title, the url, and the date the url was accessed.

3. Job, P. "The Method of Continuous Variations for Studying Metal-Ligand Complexation," *Ann. Chim.* **1928**, *9*, 113.
4. Joule, K. J. "Establishing the Calorimeter Constant by the Thermal Transfer of Energy from Hot to Cold Water," *J. Therm.* **1945**, *8*, 134.

Supporting Materials[7]

The following supplemental information is available on Dropbox:

- two additional temperature-time curves used to validate the calorimeter's performance
- the three temperature-time curves used to determine the calorimeter's heat capacity
- the three temperature-time curves used to determine the reaction's ΔH value

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[7] Use the appendix to summarize the data files available to the reader. All data that appears in your report—whether directly in the form of a figure or a table—or indirectly in the discussion of your results must be accessible to your reader.