

# Model Experiment of Thermal Runaway Reactions Using the Aluminum–Hydrochloric Acid Reaction

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**S** Supporting Information

**ABSTRACT:** A laboratory exercise for the education of students about thermal runaway reactions based on the reaction between aluminum and hydrochloric acid as a model reaction is proposed. In the introductory part of the exercise, the induction period and subsequent thermal runaway behavior are evaluated via a simple observation of hydrogen gas evolution and measurement of the temperature, which also provide basic information on the mechanistic features of the thermal runaway reaction. The exercise also includes PC aided thermometric measurements of the reaction and kinetic analysis of the induction period. The initiation time of the thermal runaway behavior under certain reaction conditions is calculated using the kinetic parameters determined experimentally by the students. The laboratory exercise provides a fundamental understanding of the mechanistic features of a thermal runaway reaction, recognition of the need for adopting safety measures when performing chemical reactions, and experience of using kinetic analysis for safety assessment.

**KEYWORDS:** High School, Introductory Chemistry, First-Year Undergraduate, General, Second-Year Undergraduate, Upper-Division Undergraduate, Laboratory Instruction, Hands-On Learning, Manipulatives, Safety, Hazards, Kinetics, Laboratory Computing, Interfacing

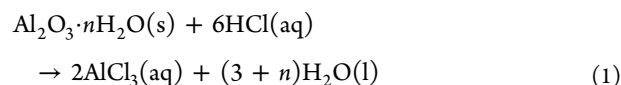


It is important to include safety education regarding chemical reactions that cause explosions and fires in the curriculum of students studying chemical sciences. These students must acquire the fundamental knowledge that will help prevent serious accidents potentially encountered in the chemistry laboratory, in chemical plants, and in their daily lives.

Thermal runaway reactions are characterized as those reactions having an induction period (an initial slow phase) followed by a rapid increase in the rate of heat production.<sup>1</sup> If the heat from the feedback cycle of an exothermic reaction and the subsequent acceleration of the reaction is not controlled, the reaction will become dangerous very quickly. To avoid this hazard, the reaction rate must be controlled by promptly releasing the self-generated heat to the exterior of the reaction system. Thermal runaway reactions have been the cause of many of the most serious chemical accidents.<sup>2,3</sup> For example, these dangerous phenomena are observed during the synthesis of Grignard reagents, the spontaneous ignition of ammonium nitrate, and the ignition of lithium ion batteries.<sup>2–6</sup>

Although learning about the mechanism of thermal runaway reactions and their prevention through laboratory exercises would be effective for safety education, it is not possible to employ such hazardous reactions as experiments in student laboratories. In this study, a laboratory exercise designed to teach students about thermal runaway reactions is proposed using a reaction between an aluminum (Al) and hydrochloric acid (HCl(aq)) that is widely used in chemistry education.<sup>7,8</sup> The serious accident due to thermal runaway in an Al–AlCl<sub>3</sub>–

HCl(aq) system has also been reported.<sup>9</sup> In an open system, however, this reaction can act as a pseudothermal runaway reaction for which explosion and ignition are not a concern. An induction period is clearly observed for the reaction due to the presence of a surface layer of Al-oxides and hydroxides involving Al<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O, Al(OH)<sub>3</sub>, and AlO(OH) on the Al plate, which initially inhibits the reaction between Al(s) and HCl(aq).<sup>8–10</sup> It has been reported that the thickness of the surface Al-oxide layer on Al plate is approximately 4–5 nm.<sup>10–12</sup> During the induction period, the Al-oxide coating such as Al<sub>2</sub>O<sub>3</sub>·nH<sub>2</sub>O is removed according to eq 1.

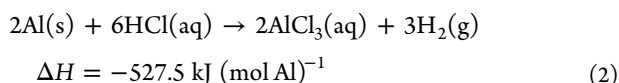


Although the surface reaction is an exothermic reaction, the reaction does not contribute significantly to the temperature increase of the reaction system because of the slow reaction rate and the limited amount of Al-oxides. Once the surface layer is removed due to the surface reaction (for example, eq 1), the internal Al(s) directly reacts with HCl(aq), producing a significant exothermic effect. The reaction (majorly expressed by eq 2 among many possible consecutive and concurrent

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reactions<sup>9</sup>) is accelerated by the subsequent increase in temperature



In concentrated HCl(aq), AlCl<sub>3</sub>(aq) produced by eqs 1 and 2 would form AlCl<sub>4</sub><sup>-</sup>(aq). The acceleration of Al(s)–HCl(aq) reaction is also due to the increase in the surface area of Al plate by corrosion and dispersion of Al powders in HCl(aq).

The induction period and the thermal runaway behavior attributed to the reactions of surface Al-oxide layer and Al metal, respectively, can be visually distinguished by observing the evolution of H<sub>2</sub>(g). In the laboratory exercise, the students discuss the mechanistic features of the thermal runaway reaction on the basis of the results of the thermometric measurements of the reaction, which is performed in an insulating container.<sup>13,14</sup> Additionally, students calculate the initiation time of the thermal runaway behavior under different reaction conditions from the kinetic analysis for the experimentally determined induction periods. On the basis of the laboratory exercise, the students then discuss the most suitable procedures for managing the reaction in an effective and safe manner. To demonstrate the usefulness of the new educational laboratory protocol, a 5-h practice using the laboratory exercise was presented as part of an undergraduate laboratory course for postgeneral chemistry students (five three-member groups).

## EXPERIMENTAL OVERVIEW

### Materials

Al plates (30 × 15 mm, thickness 0.3 mm, AL-013426, Nilaco, Japan) were treated in boiling water for 20 min to obtain a uniform thickness of the oxide layers on the surfaces. Stock solutions of HCl(aq) with different molar concentrations were prepared by diluting concentrated HCl (Chemical reagent, Nacalai Tesque, Japan).

### Demonstration of the Aluminum–Hydrochloric Acid Reaction

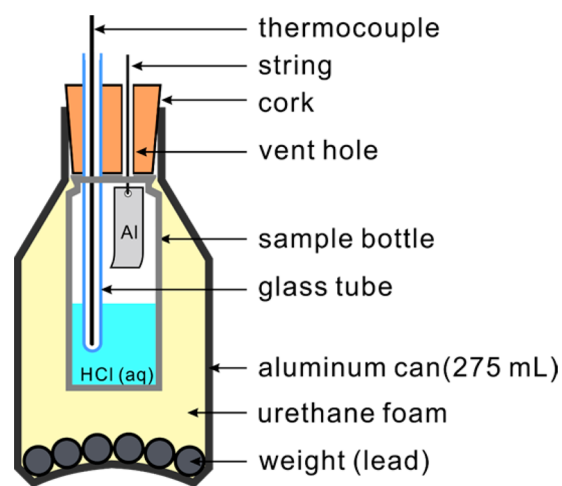
Students are introduced to the concept of thermal runaway reactions and the accidents that they can cause. For example, the explosion of a reaction system during preparation of a Grignard reagent,<sup>2,4</sup> was presented to the students, for which videos available on web are helpful.<sup>3</sup> The reaction of an Al plate and 3.0 M HCl(aq) was demonstrated using a test tube. During the demonstration, the students could observe the evolution of H<sub>2</sub>(g) after a significant induction period. Once the gas evolution was observed a temperature increase was also noted. This reaction was compared with the reaction behavior using a surface-polished Al plate. Students learned that the presence of the oxide layer on the Al surface and the need for it to react first with HCl(aq) is the origin of the significant induction period. Using these observations, the students discussed the similarities of the Al plate–HCl(aq) reaction and the thermal runaway reaction and the mechanism of the thermal runaway reaction. At this point, it is also important to call students' attention to hazardous natures of uncoated aluminum powder and hydrochloric acid and the reactivity between these two materials. The Materials Safety Data Sheet (MSDS) and the Globally Harmonized System (GHS) of Classification and Labeling of Chemicals provides reliable information on the chemicals, for which students can easily access through Internet using mobile

phone. Further, some Web sites provide program to predict the reactivity when different chemicals are mixed, for example, National Oceanic and Atmospheric Administration (NOAA) site "CAMEO Chemicals".<sup>15</sup> Such information seeking task introduced in each laboratory exercise may bring up students' information literacy of chemical safety.

Next, the students considered the possible methods for measuring the initiation time of the thermal runaway for the Al plate–HCl(aq) reaction. Measurement of the temperature of the reaction solution during the reaction was proposed by the students with the suggestion that the increase in temperature promotes the thermal runaway behavior. Determination of the time from the start of the experiment to the initiation of the temperature increase was used as a measure of the induction period for the thermal runaway reaction. The students were also asked about possible factors affecting the induction period, and their answers included the HCl(aq) concentration, the surface properties of the Al plate, the temperature of HCl(aq), and the adiabaticity of the reaction vessel. The final experimental approach for evaluating the induction period was based on these student discussions and the instructor chose to determine the effects of the HCl(aq) concentration and temperature on the induction period. A complete manual of the experimental procedures in line with the students' discussion is provided by the instructor at the beginning of the experimental work, as the second part of student handout (see [Supporting Information](#)). The above introductory part can be used for designing a laboratory exercise in high school chemistry courses for introducing the thermal runaway phenomena qualitatively.

### Instrumental Setup and Measurements

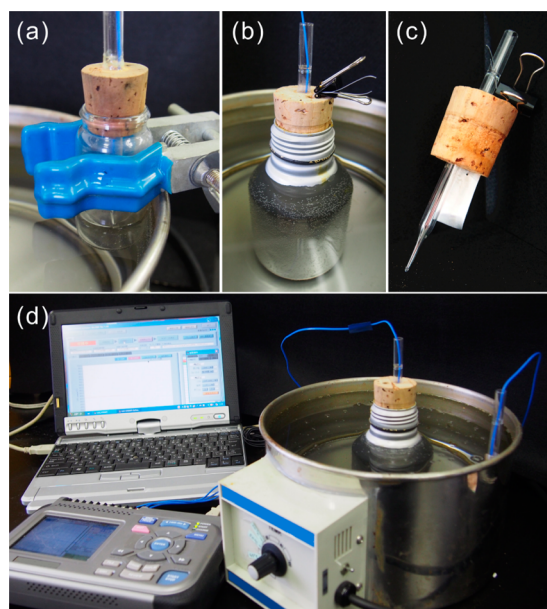
A reaction vessel with minimized thermal leakage was developed for determining the induction period of the Al plate–HCl(aq) reaction as shown in [Figure 1](#). The reaction



**Figure 1.** Reaction vessel for the Al plate–HCl(aq) reaction.

vessel is maintained at a constant temperature during the induction period using an electric water bath. This makes it easier to detect the increase in temperature at the end of the induction period. Details of the reaction vessel setup are described in the Instructor Information in the [Supporting Information](#) with a possible alternative for a twin-type reaction vessel that enables differential measurement of the temperature change.

Figure 2 shows the experimental setup and measurement procedures for measuring the induction period: warming up of



**Figure 2.** Experimental setup and measurement procedures: (a) warm-up of HCl(aq), (b) adiabatic reaction vessel placed at the center of the water bath, (c) construction of the cork stopper equipped with the thermocouple and Al plate, and (d) overview of the experimental setup.

hydrochloric acid in a sample bottle (Figure 2a), setting up of the reaction vessel (Figure 2b,c), and overall view of the experimental setup (Figure 2d).

Step 1: Hydrochloric acid of a known molar concentration (10 mL) is transferred to a 30 mL glass sample bottle which is heated to the desired temperature in the water bath (30 °C–60 °C) (Figure 2a).

Step 2: Once thermal equilibrium has been established between the water bath and HCl(aq), the glass sample bottle is placed in the fabricated reaction vessel (see [Instructor Information](#)) that has been placed at the center of the water bath (Figure 2b). The opening of the reaction vessel is capped with a cork equipped with a thermocouple and an Al plate suspended by a string (Figure 2c).

Step 3: Once the temperature of HCl(aq) is stabilized, the Al plate is dropped into HCl(aq) by pulling the string. Measurement of the temperature of HCl(aq) begins at this time. The temperature data are recorded continuously using a data logger (midi LOGGER GL220, Graphtec) connected to a PC until a temperature increase of 10 °C is observed.

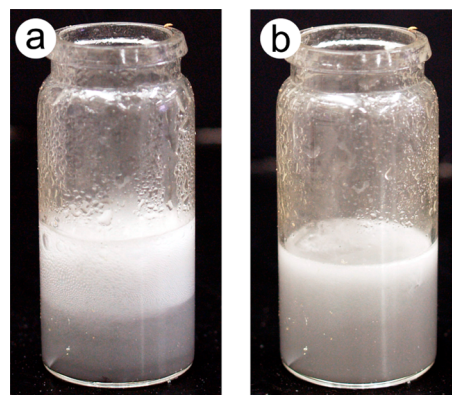
Step 4: As soon as the data is halted, the cap of the reaction vessel should be removed so that crushed ice may be added to the glass sample bottle inside the reaction vessel to decelerate the reaction.

In our educational practice, the students measured the induction period for the reaction at a constant temperature (40 °C) using HCl(aq) solutions with five different molar concentrations (1.5–3.5 M). The temperature dependent change in the induction period was also investigated using 3.0 M HCl(aq) at four different temperatures (30 °C–60 °C). When laboratory time is limited, different student groups can perform the measurements using different HCl(aq) concentrations and at different temperatures, and the data obtained by

each group can be shared within the class for analysis. This style is also useful to increase data points for kinetic analyses.

## HAZARDS

At the concentration used in this experiment, hydrochloric acid is corrosive to eyes and skin and thus instructors and students should be required to wear chemical splash goggles and protective gloves (polyethylene gloves protect well for HCl(aq) and are inexpensive) throughout the experiment. The temperature of the reaction system rapidly increases after the induction period. If the reaction system is left unattended after completing the required measurements, the temperature can reach 100 °C and care must be taken when handling the reaction system once the measurements have been completed. The reaction system must be cooled down immediately using crushed ice once the data have been obtained. Figure 3



**Figure 3.** Comparison of the appearances of the reaction system (removed from the reaction vessel) (a) just after the measurement was terminated ([HCl] = 3.0 M; 70 °C) and (b) after the reaction was decelerated by adding crushed ice.

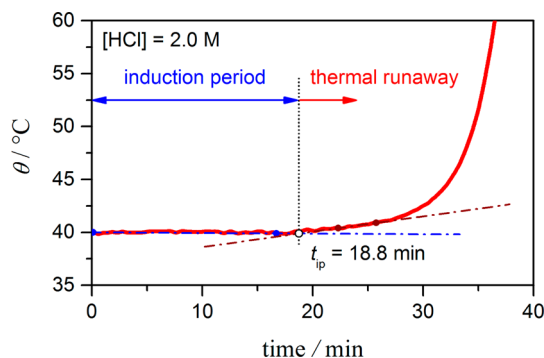
compares the appearances of the reaction system just after the measurement was terminated (70 °C) and after the reaction was decelerated by adding crushed ice. Hydrogen gas is rapidly generated and released during the thermal runaway reaction. The experiment should be performed in a lab with sufficient ventilation (table top hoods can add additional ventilation) and all ignition sources should be removed from the work area to avoid the possibility of fire or explosion. The acidic waste should be collected in an appropriately labeled waste container and disposed of according to local regulations.

## EXPERIMENTAL RESULTS AND DATA ANALYSIS

### Analysis of the Thermometric Data

Typical student data for the reaction between the Al plate and HCl(aq) are shown in Figure 4. The temperature of HCl(aq) was nearly constant during the induction period and then rapidly increased due to the reaction between the Al metal and HCl(aq) (thermal runaway). The induction period can be empirically determined from the extrapolated onset of the temperature increase, for which a graphical method was employed for the student exercise (see [Instructor information](#)). From the data, the students can obtain the length of the induction period,  $t_{ip}$ , and the average temperature during the induction period,  $\theta_{avg}$ .

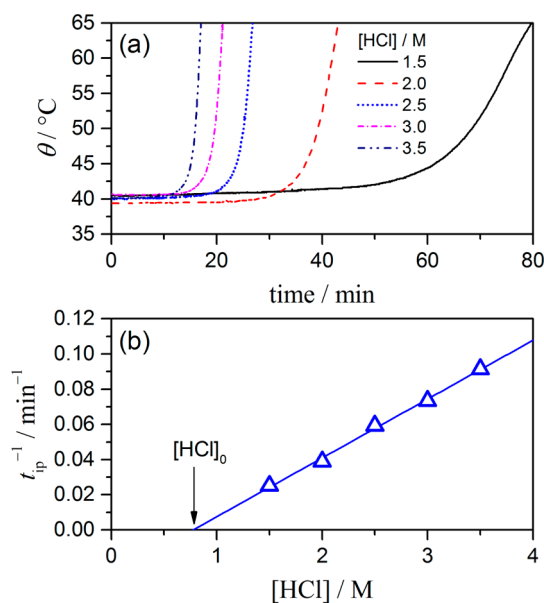




**Figure 4.** Typical thermometric data for the reaction of an Al plate and 2.0 M HCl(aq) at 40 °C.

### Effect of the HCl(aq) Concentration

Figure 5 shows the effect of the acid molarity, [HCl], on the thermometric curve for the reaction between an Al plate and



**Figure 5.** Effect of [HCl] on the reaction between an Al plate and HCl(aq) at 40 °C: (a) typical thermograms recorded at different [HCl] and (b) relationship between  $t_{ip}^{-1}$  and [HCl] and determination of  $[HCl]_0$ .

HCl(aq) at 40 °C, which was reported by a students' group. With increasing acid molarity, a significant decrease in  $t_{ip}$  and an increase in the self-heating rate during the thermal runaway reaction are clearly observed (Figure 5a). The students discussed the effect of the acid molarity on  $t_{ip}$  and the relationship between the reciprocal of  $t_{ip}$  and [HCl] (Figure 5b). In particular, a linear correlation between the reciprocal of  $t_{ip}$  and the [HCl] was found ( $R^2 = 0.9959$  for the students' data in Figure 5b). The reciprocal  $t_{ip}$  means the average reaction rate during the induction period when the advancement of the surface reaction was expressed using the fraction reacted by setting the overall reaction to be unity.<sup>16–18</sup> The intersection point on the concentration axis at  $t_{ip}^{-1} = 0$  is interpreted as a reaction limit concentration,  $[HCl]_0$  ( $= 0.78 \pm 0.06$  M for the data in Figure 5b). Actually, in our preliminary experiments for designing the student exercise, no detectable temperature change was observed for a night when using  $[HCl] = 0.5$  M.

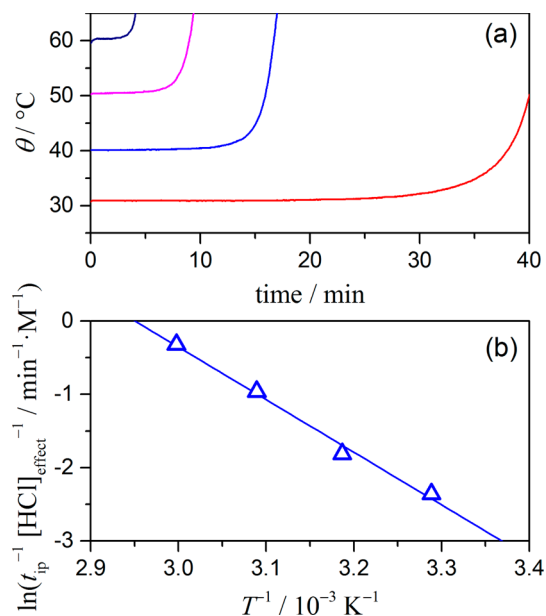
The experimental data of  $t_{ip}$  at different [HCl] in a range from 1.0 to 4.0 M were provided in the Instructor Information in the Supporting Information for discussing the practical utility of the empirical linear relationship between  $t_{ip}^{-1}$  and [HCl]. Using the effective acid molarity,  $[HCl]_{\text{effect}}$  obtained by subtracting  $[HCl]_0$  from the actual concentration, students were able to empirically express the rate behavior at a constant temperature using the first-order rate equation with respect to  $[HCl]_{\text{effect}}$

$$\frac{1}{t_{ip}} = k[HCl]_{\text{effect}} \quad (3)$$

where  $k$  is the rate constant at a temperature  $\theta_{\text{avg}}$ . This empirical kinetic expression is applicable only within a limited range of acid molarity, but was employed in this laboratory exercise for making the kinetic analysis accessible to students.

### Effect of Temperature

As shown in Figure 6, there is a distinct decrease in the value of  $t_{ip}$  and an increase in the self-heating rate during the thermal



**Figure 6.** Effect of initial temperature on the reaction between an Al plate and 3.0 M HCl(aq) ( $[HCl]_{\text{effect}} = 2.2$  M) (reported by a students' group): (a) typical thermograms and (b) Arrhenius plot for the induction period.

runaway reaction observed by raising the initial temperature of the reaction. Using the series of thermograms obtained at different temperatures (Figure 6a), the students were able to discuss the temperature-dependent change in  $t_{ip}$ . Students were also able to create an Arrhenius plot of the logarithm of the reciprocal of  $t_{ip} \cdot [HCl]_{\text{effect}}$  versus the reciprocal of the absolute temperature  $T$  and used the results to discuss the kinetic behavior during the induction period (Figure 6b) according to eq 4<sup>16–18</sup>

$$\ln \frac{1}{t_{ip}[HCl]_{\text{effect}}} = \ln A - \frac{E_a}{RT} \quad (4)$$

where  $A$ ,  $E_a$ , and  $R$  are the Arrhenius pre-exponential factor, the apparent activation energy, and the gas constant, respectively. Assuming  $[HCl]_{\text{effect}}$  is constant during the induction period, the plot of  $\ln(t_{ip}^{-1} \cdot [HCl]_{\text{effect}}^{-1})$  against  $T^{-1}$  should be a

straight line with the slope  $-E_a/R$ . From a plot using typical data reported by a student group (Figure 6b), the values for  $E_a$  ( $\text{kJ mol}^{-1}$ ) and  $\ln [A (\text{min}^{-1}\cdot\text{M}^{-1})]$  were determined to be  $59.6 \pm 3.8$  and  $21.2 \pm 1.5$ , respectively, with a correlation coefficient  $R^2$  of 0.9922. The  $E_a$  values reported by the different student groups ranged from 55 to 65  $\text{kJ mol}^{-1}$ . Although the Arrhenius parameters determined experimentally have only empirical meanings because of the complexity of the reaction during the induction period,<sup>11</sup> these values are practically useful for predicting the length of the induction period to the subsequent thermal runaway as is widely used for safety assessments and lifetime predictions of materials.

## POST-LABORATORY LEARNING EXERCISE

Students were asked to predict the duration of the induction period at a given temperature and  $\text{HCl(aq)}$  concentration using the results of the kinetic analysis for the induction period. The duration of the induction period was calculated according to eq 4 using the experimentally determined values for  $E_a$ ,  $A$ , and  $[\text{HCl}]_0$ . To summarize the experimental study of this thermal runaway reaction, students were also required to discuss appropriate procedures for controlling this type of reaction in a safe and efficient manner. Many students suggested cooling the reaction system just prior to the completion of the induction period.

## CONCLUSIONS

The reaction between Al plate and  $\text{HCl(aq)}$  can be used as a model system for thermal runaway reactions. The mechanism of the thermal runaway reaction is deduced from the simple observation of hydrogen gas evolution and measurement of the temperature of the reaction system in a test tube. With close supervision, this experiment could be applicable for high school chemistry courses. For undergraduate chemistry courses a kinetic analysis of the induction period is included. This involves determining the length of the induction period at different acid molarities and temperatures using the simplified calorimetric vessel and thermometric methods. The kinetic parameters determined from the simple kinetic analysis can then be used by students to calculate the duration of the induction period at a given acid concentration and temperature. Through this laboratory exercise, students experience the potentially hazardous nature of a thermal runaway reaction and learn to recognize the need to implement appropriate safety measures to reduce the risk presented by such reactions. The laboratory exercise is concluded by having students suggest the most appropriate procedures for managing the reaction in an effective and safe manner.

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.6b00150.

Instructor information, student handout. (PDF)  
Instructor information, student handout. (DOCX)  
MS Excel spreadsheet for data analysis with experimental data. (XLSX)

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## Notes

The authors declare no competing financial interest.

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