

AN EXPERIMENT TO ILLUSTRATE THE HAZARDS OF EXOTHERMIC REACTION SCALE-UP

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Because the majority of industrial reactions are exothermic, it is important for chemical engineers and industrial chemists to understand heat generation and heat removal requirements for exothermic reactions.^[1-5] If heat removal is inadequate, the reaction temperature will increase

as the reaction proceeds. As temperature increases, the reaction rate will increase, resulting in increased heat generation. As shown in Figure 1, heat removal increases approximately linearly with increasing temperature while heat generation due to reaction increases exponentially. Consequently, in some cases, a condition known as thermal runaway may occur. Complications of runaway reactions include boiling over of reaction mixtures, unwanted and often dangerous side reactions at elevated temperatures, and rapid temperature and pressure increases that can lead to explosions.

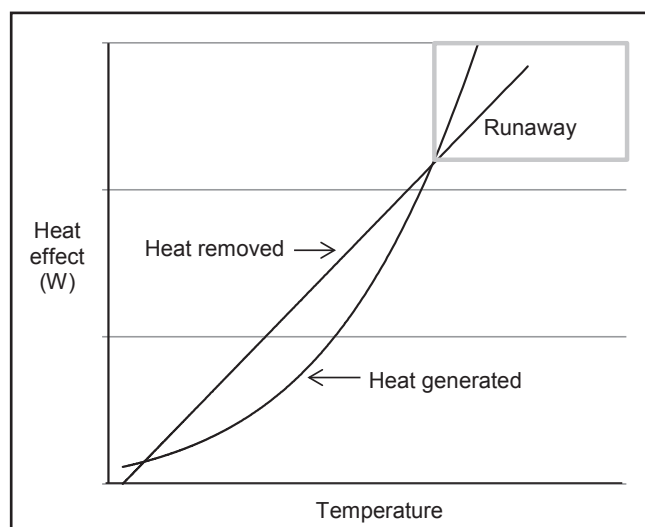


Figure 1. Heat effects as a function of temperature for an exothermic reaction.^[3]

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There are numerous examples in the literature of serious industrial accidents caused by thermal runaway.^[2-9] One such example is the explosion that occurred at T2 Laboratories in December 2007.^[6-8] The explosion was equivalent to 1,400 pounds of TNT, killed four people and injured 32, and resulted from a failure of an inadequate system designed to cool the exothermic reaction to produce methylcyclopentadienyl manganese tricarbonyl. This incident prompted the U.S. Chemical Safety and Hazard Investigation Board to recommend that reactive hazard awareness be added to undergraduate chemical engineering curricula requirements.^[6] Another example is the toxic vapor release that occurred at MFG Chemical in April 2004.^[9] A runaway chemical reaction rapidly pressurized the reactor, bursting a seal and opening a pressure relief valve during the production of triallyl cyanurate. Toxic vapors were released for 8 hours causing the evacuation of more than 200 families in the nearby community. This second example is representative of a frequent cause of thermal runaway: failure to account for the effect of reactor scale-up on heat removal. The cooling capacity of a 30 gallon test reactor was adequate to remove the heat of reaction, but scale-up to 4,000 gallons yielded a runaway reaction.

In an effort to reduce the number of costly and deadly industrial accidents, the ACS and AIChE have called for increased attention to chemical reaction hazards, especially thermal runaway, in the undergraduate curriculum. While the number of example problems and case studies available for students is growing,^[5,7,10] there do not appear to be many laboratory exercises devoted to this subject. We present a set of experiments and corresponding calculations to give students first-hand knowledge of the safety hazards encountered when scaling up an exothermic reaction. The reaction employed is the well-studied iodide-catalyzed decomposition of hydrogen peroxide into water and oxygen.^[11-15] Reaction conditions have been identified that provide a sharp contrast in reaction behavior in different-sized round-bottom flasks.

THEORY

The iodide-catalyzed decomposition of hydrogen peroxide



is described by the rate equation

$$\text{rate} = \frac{-d[\text{H}_2\text{O}_2]}{dt} = k_o \exp\left(\frac{-E_a}{RT}\right) [\text{H}_2\text{O}_2] [\text{I}^-] \quad (2)$$

Conducting the reaction in a vessel surrounded by an ice bath provides heat removal given by

$$Q_r = U A (T_i - T) \quad (3)$$

where U is the overall heat transfer coefficient, A is the area available for heat transfer, and T_i is the temperature of the ice bath. The ice bath temperature can be assumed to be nearly constant at 0 °C as long as both ice and liquid water are

present and the bath is sufficiently stirred. The heat generated by the reaction is given by

$$Q_g = -V \Delta H^\circ (\text{rate}) \quad (4)$$

Q_g is positive because the heat of reaction is negative. On the other hand, Q_r is negative because T_i is less than the reaction temperature T . Any imbalance between the rate of heat generation and rate of heat removal will result in energy accumulation and a concomitant temperature change within the reactor given by

$$C m \frac{dT}{dt} = -V \Delta H^\circ (\text{rate}) + U A (T_i - T) \quad (5)$$

where C is the specific heat and m is the mass of the solution, both assumed to be constant here (we are neglecting any loss of mass due to water-saturated oxygen bubbles). Solving Eqs. (2) and (5) simultaneously provides information for T and $[\text{H}_2\text{O}_2]$ in the reactor as a function of time. The constants, C , ΔH° , and E_a can be found in the literature^[11] to be 4.18 J/g K (assuming the value for water), -98 kJ/mol, and 56 kJ/mol, respectively. The value of U can be estimated in a separate experiment by cooling, in an ice bath, a known mass of water at a known initial temperature, T_o . The rate term in Eq. (5) is zero in this case and rearranging and integrating the equation gives

$$\frac{(T_i - T_o)}{(T_i - T)} = \exp\left(\frac{U A t}{C m}\right) \quad (6)$$

Thus, a plot of $\ln[(T_i - T_o)/(T_i - T)]$ versus t yields a straight line with slope equal to $(U A)/(C m)$. To complete the solution of Eqs. (2) and (5), the pre-exponential constant, k_o , must be known or estimated. A Mathcad computer file that solves these equations is provided in the Appendix.

Note that Q_g depends on the reaction volume and Q_r depends on the surface area for heat transfer. For a round-bottom flask, half filled with reaction mixture, V is given by $2/3 \pi r^3$ and the surface area for heat transfer, A , is approximately $2 \pi (r + \delta/2)^2$, where δ is the wall thickness of the flask. Even if the heat transfer coefficient, U , is the same for all cases, as the reaction volume increases, the first term on the right-hand side of Eq. (5) increases faster than the second term causing a larger increase in reaction temperature, potentially resulting in runaway. In practice, U depends on mixing inside and outside of the reactor and on the material and thickness of the reactor walls and tends to decrease with increasing reactor size. In addition to reaction kinetics and thermochemistry, knowledge of mixing, heat transfer, process dynamics, and control system dynamics is required for safe scale-up of exothermic reactions.^[4] It is important to understand even small temperature changes that occur during reactions at lab scale and realize that these may be dramatically increased at industrial scale and lead to runaway if measures like increased cooling or dosing control are not implemented.

Flask Size	Volume of 30 % H ₂ O ₂ (cold water)	Volume of 0.1 M KI (hot water)
(ml)	(ml)	(ml)
100	30	15
250	75	37.5
500	150	75
1000	300	150

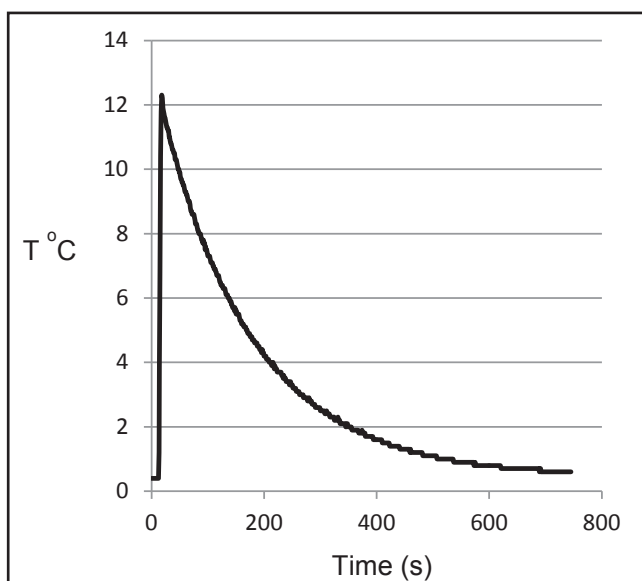


Figure 2. Temperature as a function of time for experiment to determine U for a 250 ml flask in an ice bath.

EXPERIMENTAL DETAILS

These experiments can be conducted by student teams in a laboratory course or can be demonstrated in a classroom setting by an instructor. For the laboratory course, each team of students should be able to measure the heat transfer coefficient and conduct the reaction in two different-sized flasks in a 3-hour lab session. Performing the reaction in a 100 ml flask followed by a 1000 ml flask provides the most dramatic effect. Two-necked round-bottom flasks are recommended to allow clamping and thermometer/thermocouple insertion via one neck and chemical addition via the other. It is best if a large clear glass or plastic bowl is used for the ice bath to facilitate observation of the reaction. We used the same 5 L capacity plastic bowl (Target, Room Essentials No. 200-05-0333) for all of our studies. Place the ice bath on a magnetic stir plate and insert a 2 inch or larger stir bar. Suspend the flask in the ice water using a ring stand and clamp. Insert a 1 to 1 ¼ inch egg-shaped stir bar in the flask.

Measure the heat transfer coefficient for each flask by adding hot water to cold water and following the temperature with time. First add water to the flask in an amount equal to the amount of H₂O₂ to be used in the reaction and cool that with stirring in the ice bath. Position a thermometer or thermocouple to be below the liquid level but above the stir bar in the flask. Once the temperature in the reactor reaches a steady value close to 0 °C, add hot tap water in the amount to be used for the KI solution in the reaction and record the temperature as often as is practical. We recorded the temperature every second with a National Instruments USB-TC01 temperature logger equipped with a type J thermocouple and connected to a Windows-based personal computer. Alternatively, a thermometer could be read and recorded about every 20 seconds. The amounts of reactants and water used for each flask size are shown in Table 1.

For the peroxide decomposition reaction, modify the above procedure to add room temperature 0.1 M KI in water to pre-cooled 30 % hydrogen peroxide in the amounts shown in Table 1. The temperature will immediately jump to about 8 °C due to the two solutions reaching thermal equilibrium. The temperature will either increase or decrease from there depending on which term of Eq. (5) is larger for a particular reactor.

SAFETY PRECAUTIONS

The popular “elephant’s toothpaste” experiment (see, for example, Reference 16) illustrates that hydrogen peroxide decomposition can yield a dramatic and potentially dangerous rapid exothermic reaction. The runaway condition we suggest can be done safely as shown at <<https://youtu.be/6m-ZGB-qIU>> provided the following safety precautions are observed. Hydrogen peroxide and potassium iodide are toxic and skin irritants. Peroxide is also a strong oxidant. Gloves and safety glasses should be worn when handling these materials. Round-bottom flask reactors need to be open to the atmosphere to avoid pressure build-up from the oxygen produced. No flammable materials or ignition sources should be present during the production of oxygen via the reaction. Temperatures at or near the boiling point of the mixture^[17] may be reached in the larger flask and/or in any flask that is removed from the ice bath before the reaction is complete. Care should be taken when handling these mixtures and especially in avoiding contact with escaping steam from the flasks. Personal protective equipment for boiling liquids should be worn.

RESULTS

Figure 2 shows typical temperature versus time results for adding hot water to cold water in the 250 ml flask. Figure 3 (next page) shows a plot of $\ln((T_i - T_o)/(T_i - T))$ versus time for the first 200 seconds after the temperature reached its highest point as a result of mixing the hot and cold water. Determination of the slopes from similar plots for each reactor resulted

in the heat transfer coefficients reported in Table 2. The uncertainties reported in the U values were based on averaging two or three experiments on each flask and the observation that the U values obtained were slightly dependent on the

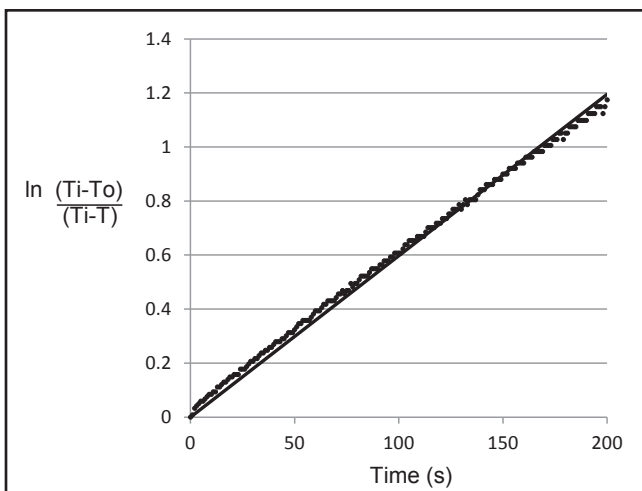


Figure 3. Plot to determine $U = (\text{slope})(C)(m)/A$ from data in Figure 2.

TABLE 2
Dimensions, heat transfer coefficients, and surface area for different flasks.

Flask Size	r	U	A
(ml)	(cm)	(W/m ² K)	(m ²)
100	2.879	320 ± 20	0.00558
250	3.908	281 ± 20	0.01009
500	4.924	279 ± 20	0.01586
1000	6.204	230 ± 20	0.02497

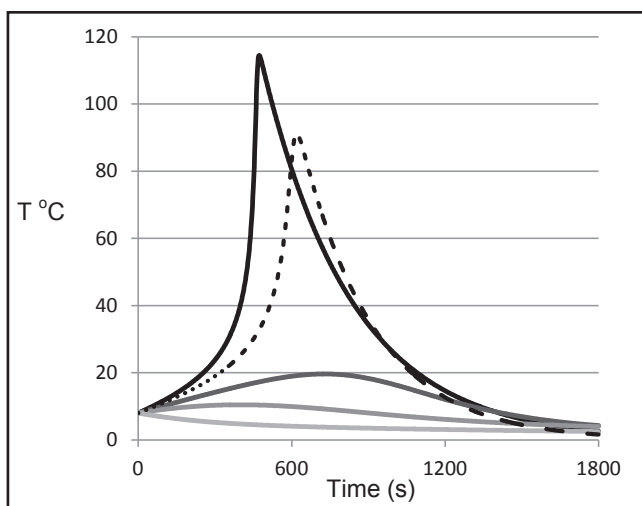


Figure 4. Temperature profiles predicted from solving Eqs. (2) and (5). Upper curve = 1000 ml flask, lower curve = 100 ml flask, dashed curve = 1000 ml flask with $U = 280 \text{ W/m}^2\text{K}$.

stirring rate, the placement of the flask in the ice bath, and the amount of ice and water in the bath for each experiment. Using the same stir bars and the same stirrer plate setting for all flasks resulted in noticeably better mixing in the 100 ml flask and worse mixing in the 1000 ml flask. Even though the flasks were filled to 45% of their volume, the areas for heat transfer reported in Table 2 and used in subsequent calculations were based on 50% of the reactor volume due to a rise in liquid level resulting from the stirring vortex.

Eqs. (2) and (5) were solved using the U and A values in Table 2, the heat capacity, heat of reaction, and activation energy values noted previously and an estimated k_0 value of $3.083 \times 10^8 \text{ L}/(\text{mol s})$. The calculated results for temperature as a function of time for the decomposition reaction in the four flasks are shown in Figure 4. These calculations predict a runaway reaction in the largest flask only. The upper, solid line in Figure 4 was obtained using our measured $U = 230 \text{ W/m}^2\text{K}$ value for the 1000 ml flask. The dashed line was obtained using our average value for all reactors of $U = 280 \text{ W/m}^2\text{K}$. Thus, thermal runaway would be predicted even if we had better stirring than we were able to obtain in the 1000 ml flask.

Experimental results for temperature as a function of time for reacting 6.529 mol/L H_2O_2 and 0.033 mol/L KI in an ice bath in the four flasks are shown in Figure 5. Although the initial temperature, bath temperature, and initial concentrations were the same and the volume of liquid in each flask was established at 45% of the flask volume in each case, it is clear that there was sufficient heat removal to control the reaction in the smaller flasks but not in the largest flask. The generation of oxygen bubbles was observed in each flask, but increased bubbles and escaping steam observed in the 1000 ml flask may have indicated some local boiling in that flask.

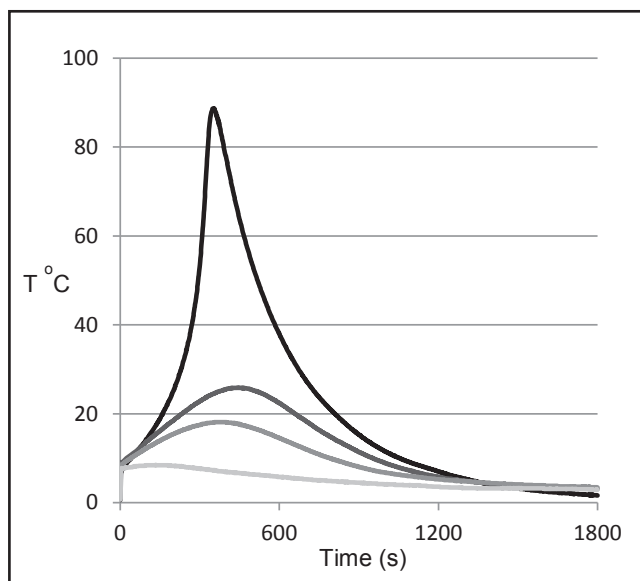


Figure 5. Experimentally measured temperature profiles. Upper curve = 1000 ml flask, lower curve = 100 ml flask.

The boiling point of the mixture was initially about 104 °C^[17] and decreased to slightly above 100 °C as the H₂O₂ reacted. These temperatures were not observed at the thermocouple but may have been reached locally within the 1000 ml flask. The reaction mixture went from clear to brown to yellow due to the appearance and disappearance of free iodide. In the 1000 ml flask, the mixture became clear again indicating that the reaction was complete in less than 10 minutes while it remained yellow for the duration of the experiment in the other flasks.

The predicted and measured results are in reasonable qualitative agreement considering the uncertainties in the model parameters. The discrepancy in the maximum temperature can be attributed to uncertainty in the U value, heat losses, and local boiling of the solution in the largest flask. A higher U value might be expected under reacting conditions than was measured using hot and cold water due to better mixing via bubbling oxygen during reaction. Some of the generated heat went to vaporize the water and escaped with the steam. These and other heat loss effects were not accounted for in Eq. (5).

STUDENT EXPERIENCE

We introduced the hydrogen peroxide decomposition experiment in the latest edition of our unit operations laboratory class. Groups of three or four students were asked to do the following as a pre-lab exercise before conducting the heat transfer coefficient measurements and decomposition experiments in 100 ml and 1000 ml flasks:

1. Study an experiment description that included the first paragraph of the Theory section, portions of the Experimental Details and Safety Precautions sections, a data file with the raw data from Figure 2, and the Appendix file of this paper, solving Eqs. (2) and (5) for a 250 ml reactor that did not exhibit runaway behavior.
2. Find on the web or elsewhere a report of an industrial accident involving problems with an exothermic chemical reaction and briefly explain what happened and what could have been done to prevent the accident.
3. Using the temperature versus time data from Figure 2, estimate the overall heat transfer coefficient of the 250 ml flask.
4. Research the term “thermal runaway” and briefly explain it.
5. Give the experimental procedure you will use to (1) evaluate the overall heat transfer coefficients for two round-bottom flask reactors in an ice bath, and (2) record and explain the temperature versus time behavior during hydrogen peroxide decomposition reactions in the same two reactors.
6. Sketch four qualitative graphs of the expected T versus time results for four experiments: (1) measuring U in a small reactor, (2) H₂O₂ decomposition in the small reactor, (3) measuring \dot{U} in a larger reactor, and (4) H₂O₂

decomposition in the larger reactor. Indicate your best guess for the maximum expected T in each experiment.

7. List the safety precautions you will take for this experiment.

Requirements for final reports, due one week after completing the laboratory experimentation, included:

1. Report the overall heat transfer coefficient results for the reactors.
2. Compare experimental and calculated temperature versus time results for peroxide decomposition in the two reactors.
3. Explain the differences in behavior between the 100 ml and 1000 ml reactors.
4. Discuss how the observed differences illustrate some of the hazards that can occur when scaling-up exothermic reactions.
5. Discuss what could be done to prevent these hazards.

The experiment was well received by the students and all 11 groups completed it without mishap within 3 to 4 hours. The main point that thermal runaway can occur upon scale-up was ultimately understood by all participants—especially the one group who sent a student running to the instructor exclaiming that something had gone wrong with the 1000 ml experiment because the temperature was rising alarmingly fast. Some groups fully understood that the heat generation term will exceed the heat removal term due to decreasing surface-to-volume ratio, even if the heat transfer coefficient was constant for all reactors. Unfortunately, some groups focused on the observed lower overall heat transfer coefficient in the larger flask as the reason for the runaway in that flask and did not appreciate the main effect of the decreasing surface to volume ratio until after the final report was graded. In future implementations of the experiment we will explicitly prompt the students to consider the implications of changes in the V and A terms of Eq. (5) during scale-up.

CONCLUSION

Conditions have been identified for conducting a relatively safe experiment that provides a dramatic illustration of the need to account for heat removal when scaling up an exothermic reaction. Students in a lab setting, or an instructor in a classroom demonstration, can monitor the temperature change during the decomposition of hydrogen peroxide in different-sized round-bottom flasks in an ice bath. Beginning with the same initial conditions, the reaction proceeds slowly with minimal change in temperature in a 100 ml flask and exhibits thermal runaway when scaled up to a 1000 ml flask. Witnessing this concrete example for themselves should impress upon students the potential hazards of exothermic reactions and could help prevent accidents due to thermal runaway in the future.

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APPENDIX

H₂O₂ decomposition calculations with Mathcad

250 ml flask 75 ml 30 % H₂O₂ in water + 37.5 ml 0.1 M KI in water

Density of 30 % H₂O₂ is 1.11 g/ml Density of 0.1 M KI is 1.0 g/ml

C_p is peroxide concentration, C_i is iodide concentration

$$\begin{aligned} R &:= 8.314 \quad \text{J / mol K} & T_i &:= 273.15 \quad \text{K} \\ E &:= 56000 \quad \text{DHr} & &:= -98000 \quad \text{J / mol} \\ V &:= 0.1125 \quad \text{L} & m &:= 75 \cdot 1.11 + 37.5 = 120.75 \quad \text{g} \\ A &:= 0.01009 \quad \text{m}^2 & k_o &:= 3.083 \cdot 10^8 \quad \text{L / mol s} \end{aligned}$$

$$U := 280 \quad \text{W / m}^2 \text{ K} \quad U \cdot A = 2.825 \quad \text{W / K}$$

$$C := 4.18 \quad \text{J / g K}$$

$$C_{po} := 6.53 \quad C_{io} := 0.033 \quad \text{mol / L}$$

$$t_e := 1800 \quad \text{Endpoint of solution interval (s)}$$

Given

$$\frac{d}{dt} T(t) = \frac{V \cdot -DHR \cdot \left(k_o \cdot \exp\left(\frac{-E}{R \cdot T(t)}\right) \right) \cdot C_p(t) \cdot C_{io} + U \cdot A \cdot (T_i - T(t))}{C \cdot m}$$

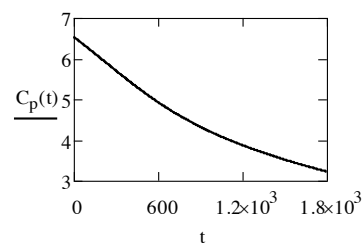
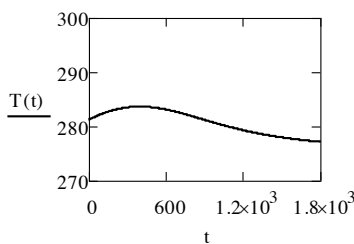
$$T(0) = 8 + 273.15$$

$$\frac{d}{dt} C_p(t) = \left(-k_o \cdot \exp\left(\frac{-E}{R \cdot T(t)}\right) \right) \cdot C_p(t) \cdot C_{ic}$$

$$C_p(0) = C_{po}$$

$$\begin{pmatrix} T \\ C_p \end{pmatrix} := \text{Odesolve} \left[\begin{pmatrix} T \\ C_p \end{pmatrix}, t, t_e, 1 \times 10^3 \right]$$

$$t := 0, \frac{t_e}{1 \times 10^3} .. t_e$$



□