A SEMI-BATCH REACTOR EXPERIMENT
for the Undergraduate Laboratory

MARIO DEREVJANIK, SOLMAZ BADRI, AND ROBERT BARAT
*New Jersey Institute of Technology • Newark, NJ 0102*

The advantages of the semi-batch reactor (SBR) are exploited in several industrial reactor applications. For example, in the reaction of a gas with a liquid (*e.g.*, ozonation of industrial wastewater to remove dyes[1]), the gas is continuously bubbled through the batch liquid. Conversely, a gaseous product can be continuously removed from a liquid system (*e.g.*, CO_2 in fermentation). The slow addition of one reactant into another assists in the control of a strong exotherm in the SBR, such as in polymerization reactors (*e.g.*, nylon[2] and polypropylene[3]). Polymer molecular weight distributions can be controlled by careful addition of the monomer (*e.g.*, styrene-butadiene rubber[4]). The SBR can be used to maximize selectivity, especially where byproducts or competing reactions are an issue (*e.g.*, substituted alkyl phenols[5]).

In spite of its industrial use, the SBR is often ignored in undergraduate reactor engineering classes. Still, the SBR offers a useful opportunity to combine both batch and flow concepts. Haji and Erkey[6] present an SBR experiment with the exothermic hydrolysis of acetic anhydride. In-situ Fourier transfer infrared spectroscopy is used for monitoring species of interest vs. time. Kinetic analyses are subsequently performed.

In this paper, an SBR is used to process the simple reaction between sodium hypochlorite and hydrogen peroxide. Inexpensive household bleach and pharmaceutical hydrogen peroxide solution serve as the convenient reactants. Product molecular oxygen is monitored through a rotameter. The overall change in solution conductivity is metered with a conductivity probe. The reaction exothermicity is monitored through a reactor thermocouple. The elegant model analyses combine reaction kinetics with species and energy balances.

REACTION AND KINETICS

The reaction used in this experiment is inspired by Shams El Din and Mohammed,[7] who studied the kinetics of this reaction as a means to remove residual bleach from water purification equipment.

$$H_2O_{2(aq)} + NaOCl_{(aq)} \rightarrow H_2O_{(l)} + NaCl_{(aq)} + O_{2(g)}$$

$$A + B \rightarrow R + S + T$$
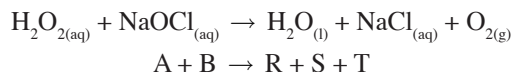
The letters representing the species are shown in corresponding order. The reported rate expression for the disappearance of A is second order:

$$-r_A = kC_A C_B = -r_B = r_S = r_T \qquad (1)$$

where r_i = reaction rate of species i, k = reaction rate constant, and C_i = molar concentration of i. Because the reaction evolves gaseous O_2 rather rapidly, it is preferable to run it in a semi-batch reactor. To start, a batch vessel contains hydrogen peroxide (H_2O_2 – species A) in a water solution. The aqueous solution of sodium hypochlorite (NaOCl – species B) is fed slowly over time at a constant rate. As shown above, species S and T are NaCl and O_2, respectively.

Mario Derevjanik graduated from NJIT with a B.S. in chemical engineering in 2008. During his undergraduate career, Mario assisted Dr. Barat in developing new student experiments. Mario is working as a chemical engineer for ConSerTech, a small environmental consulting company. His current responsibilities, including VOC monitoring, are at the Conoco-Phillips refinery in Linden, NJ.

Solmaz Badri was born in Tehran, Iran, and came to the United States after completing high school. She joined NJIT and graduated in 2009, majoring in chemical engineering. She is now living in New York City, married to a physician, and working as an individual contractor. She dedicates her work and research to her newborn son, Amin Zamanian.

Robert Barat is currently a professor of chemical engineering at NJIT, where he has been a member of the faculty since 1990. He completed his Ph.D. in chemical engineering at MIT in 1990. His research has been in combustion, reactor engineering, environmental monitoring, applied optics, and is currently in applied catalysis. He is also the faculty coordinator for the chemical engineering laboratories at NJIT.

REACTOR SPECIES BALANCES

A semi-batch design equation applies for B:

$$F_B + r_B V = \frac{dN_B}{dt} \qquad (2)$$

where F_B = molar flow rate inlet to the batch, V = batch liquid volume, and N_i = moles of i in the batch. A simple batch design equation applies for A:

$$r_A V = \frac{dN_A}{dt} \qquad (3)$$

The inlet molar flow rate of B can be written in more convenient volumetric terms:

$$F_B = \frac{v_B \rho_B f_B}{W_B} \qquad (4)$$

where v_B = volumetric feed rate of B, ρ_B = bleach mass density, f_B = mass fraction of species B in the feed bleach solution, and W_B = molecular weight of B. Since $N_i = C_i V$, and V = f(t) in the most general semi-batch case, Eq. (3) becomes:

$$r_A - \frac{C_A}{V}\frac{dV}{dt} = \frac{dC_A}{dt} \qquad (5)$$

and Eq. (2) becomes:

$$\frac{F_B}{V} + r_B - \frac{C_B}{V}\frac{dV}{dt} = \frac{dC_B}{dt} \qquad (6)$$

The rate of change of the volume is accounted for with a transient mass balance:

$$v_B \rho_B = \frac{d(\bar{\rho}V)}{dt} \qquad (7)$$

where $\bar{\rho}$ = mass density of batch solution. It can be reasonably assumed $\bar{\rho}$ is constant; then, Eq. (7) reduces to:

$$v_B \frac{\rho_B}{\bar{\rho}} = \frac{dV}{dt} \qquad (8)$$

The volumetric feed rate of B is set at a constant value by the user in the experiment.

Eqs. (1), (4)-(6), and (8) form a partial system that will be solved simultaneously. The system is integrated from t = 0 (when the reactant B solution flow begins) to whenever the peroxide feed is ended by the user.

EVOLUTION OF O$_2$

Assuming that the bleach solution mixes thoroughly into the peroxide solution, the reaction mixture will likely saturate with O$_2$ very rapidly. We can assume that the O$_2$ evolution rate is approximately the same as the reaction rate, and is given by:

$$F_T \approx r_T V \qquad (9)$$

The Ideal Gas Law can be used to convert F_T to a volumetric rate.

$$\frac{r_T V R T_s}{P_s} \approx v_T \qquad (10)$$

where T_s, P_s represent standard temperature and pressure conditions (298 K, 1 atm), respectively, and R = ideal gas constant (0.0821 liter-atm/mole-K). Eq. (10) can be added to the set of equations to be solved. The volumetric rate of evolved O$_2$ is one of three possible sources of data in this experiment. The rate r_T is obtained from Eq. (1).

CONDUCTIVITY CHANGE AND CHLORIDE ION

The conductivity of the solution is a weighted sum of the contributions of the ionic species, including NaOCl as the active ingredient, a small amount of NaOH to help prevent degradation of NaOCl to release Cl$_2$, and residual NaCl from the bleach manufacturing process. We assume that C_{NaOCl} in the SBR is very small, and insignificantly contributes to the solution conductivity. Subsequent SBR modeling supports this claim. The batch solution conductivity can be estimated as:

$$C \approx \sum_i \bar{c}_i C_i = \bar{c}_{NaCl} C_{NaCl} + \bar{c}_{NaOH} C_{NaOH} \equiv Cond_{NaCl} + Cond_{NaOH} \qquad (11)$$

where C = solution conductivity, $\bar{c}_i$ = effective molar conductivity of species i, C_i = molar concentration of i, and $Cond_i$ = contribution of i to the total conductivity.

Accounting for the contribution of NaCl to the solution conductivity requires a species balance, including the presence of NaCl in the bleach feed:

$$\frac{F_s}{V} + r_s - \frac{C_s}{V}\frac{dV}{dt} = \frac{dC_s}{dt} \qquad (12)$$

The inlet molar flow rate of S can be written in more convenient volumetric terms:

$$F_S = \frac{v_B \rho_B f_S}{W_S} \qquad (13)$$

where f_S = mass fraction of NaCl in the feed bleach solution. Molar conductivity data for NaCl aqueous solutions are available[8] over the temperature range of interest to yield a relationship valid up to 0.85 molar concentration:

$$\Lambda_S^O = 0.0117 T_c^2 + 1.3737 T_c + 51.665$$

(Λ_S^O in mS/cm/molar, temperature T_c in °C)

The contribution of the NaOH to the solution conductivity is:

$$Cond_S = \Lambda_S^O C_S \qquad (14)$$

Accounting for the contribution of NaOH to the solution

conductivity requires a non-reactive species balance. Representing NaOH as the inert I, the balance is:

$$\frac{F_I}{V} - \frac{C_I}{V}\frac{dV}{dt} = \frac{dC_I}{dt} \qquad (15)$$

The inlet molar flow rate of I can be written in more convenient volumetric terms:

$$F_I = \frac{v_B \rho_B f_I}{W_I} \qquad (16)$$

where f_I = mass fraction of NaOH in the feed bleach solution. Molar conductivity Λ_I^O data for NaOH aqueous solutions are available[11] over the temperature range of interest to yield a relationship valid up to 0.3 molar concentration:

$$\Lambda_I^O = -0.0241 T_c^2 + 5.0658 T_c + 111.13$$
(Λ_I^O in mS/cm/molar, temperature T_c in °C)

The contribution of the NaOH to the solution conductivity is:

$$\text{Cond}_I = \Lambda_I^O C_I \qquad (17)$$

ENERGY BALANCE

The energy balance should reflect the configuration of the reactor vessel. In a typical experiment, the liquid is in contact with stainless steel walls and internal components (*e.g.*, agitator, probes). An air-filled jacket surrounds the walls. Heat losses to this metal must be considered. A simple heat loss calibration was performed wherein an electric immersion heater of known wattage was placed into the vessel filled with water covering the metal parts. A simple heat balance of this calibration is:

$$\frac{dT}{dt} = \frac{Q_h}{m_w c_{pw} + m_m c_{pm}} \qquad (18a)$$

where Q_h = electrical heating rate; m_w and m_m = masses of water and metal parts, respectively; and c_{pw} and c_{pm} = mass-based specific heats of water and metal, respectively. A successful linear regression of the measured temperature vs. time, according to the integrated form of Eq. (18a), yielded a heat loss calibration of $m_m c_{pm}$ = 1284 cal/°C.

It can be shown, consistent with Fogler and Gurmen,[9] that the reactor energy balance is:

$$\frac{dT}{dt} = \left(\frac{-\sum_i F_{j_0} \int_{T_f}^{T} c_{p_j} dT + V(-r_A)(-\Delta H_{r_A}) + P\frac{dV}{dt}}{m_m c_{pm} + V\sum_j c_{p_j} C_j} \right) \qquad (18b)$$

where T = reactor temperature, c_{pj} = molar heat capacity of

species j, C_j = molar concentration of j inside the reactor, F_{jo} = molar feed rate of j, T_f = feed temperature, ΔH_{rA} = heat of reaction per mole of A, and P = system pressure. The final term in the numerator is included since the fluid volume is not constant. It is small compared to the other terms, however, and can be neglected. Selected terms are now examined.

$$\sum_j c_{p_j} C_j = \frac{\overline{c}_p \overline{\rho}}{\overline{M}} \qquad (19)$$

where $\overline{c}_p$ and $\overline{M}$ are the mean molar heat capacity and molecular weight, respectively, of the solution. As an approximation due to the high degree of dilution, the properties of the solvent water can be used. If the mass-based value is used for $\overline{c}_p$, $\overline{M}$ is not needed.

$$\sum_j F_{j_0} \int_{T_f}^{T} c_{p_j} dT \approx \frac{v_B \rho_B c_{p_B}}{M_B} \left(T - T_B \right) \qquad (20)$$

where T_B, M_B, and c_{pB} = temperature, average molecular weight, and mean heat capacity (mole-based), respectively, of the feed bleach. If the mass-based value is used for c_{pB}, M_B is not needed.

The standard heat of reaction (-37.2 kcal/mole at 25 °C for the reaction as written earlier) is assumed to be independent of temperature, especially in consideration of the limited temperature range of the experiment.

The energy balance in the form used for data modeling is now written as:

$$\frac{dT}{dt} = \left(\frac{-v_B \rho_B c_{p_B}(T - T_B) + V(-r_A)(-\Delta H_{r_A})}{m_m c_{pm} + V\overline{c}_p \overline{\rho}} \right) \qquad (21)$$

EXPERIMENTAL CONSIDERATIONS

Figure 1 illustrates the basic configuration of the current experimental system. An agitated reactor vessel is used. The
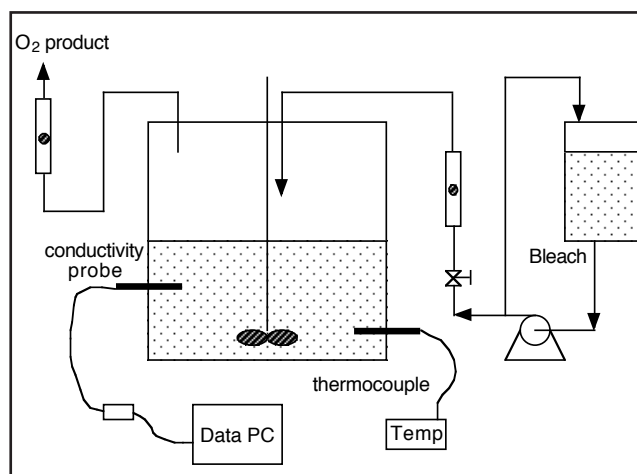

Figure 1. *Schematic of the semi-batch reactor experiment.*

bleach solution, held in an external reservoir, is pumped through a calibrated flow meter, and into the reactor. A bypass is used since the pump capacity is too large. A magnetic-drive centrifugal pump is useful since all wetted parts are plastic-coated to avoid corrosion. The vessel has access ports for a stainless steel thermocouple and a conductivity probe. The probe is inserted through a side port to ensure immersion. The vessel is sealed since product O_2 gas is vented through a calibrated flow meter. A differential pressure gauge (not shown in the figure) is used in the current system to measure the pressure in the vapor space in the vessel during a run. Variations on this setup should be considered depending on available equipment.

In the present system, a Vernier® conductivity probe with GoLink® interface and Logger Lite® data collection and plotting software are used. A data collection PC is accessed via the USB interface. The probe is calibrated with two conductivity standard solutions available from Vernier®.

A Vernier® chloride ion specific electrode (ISE) is an alternative to the conductivity probe. Its membrane requires more care, however, making the ISE not as robust as the all-metal conductivity probe. Hence, the ISE was limited to determination of the chloride content of the bleach, and not inserted into the reactor.

Finally, the most likely experimental parameter to vary is the bleach feed rate. Alternative experiments include dilution of either the peroxide or bleach solutions. In either case, care should be taken such that the O_2 evolution rate remains within the useful range of the flow meter.

In a typical run of the present system, a 5 liter agitated (200 rpm) vessel is filled with 3 liters of over-the-counter hydrogen peroxide solution (3%) that had been stored in a laboratory refrigerator to improve shelf life. The initial conductivity reading is ≈ 0 and the initial temperature is ≈ 13 °C. About one liter of laundry bleach is stored in the reservoir. At time t = 0, the bleach is flowed into the batch at a constant 4 gallons/hour rate. The O_2 evolution begins almost immediately, and continues until the available bleach is exhausted (~ 350 seconds). The batch solution conductivity rises monotonically until the maximum value measurable by the probe ($\sim 28,000$ μS/cm) is reached. A larger or second bleach reservoir can be used to feed more bleach so as to exhaust the remaining peroxide. Consuming ≈ 1 liter of bleach in this system causes the batch temperature to rise to ≈ 8 centigrade degrees. Current runs show reactor pressures of only a few inches of water above atmospheric. The data from this run are shown in Figures 2 and 3 (page 124).

The Clorox® bleach contains ~ 6 wt. % NaOCl as the active ingredient. In addition,[10] it contains NaOH added to prevent degradation of the NaOCl to Cl_2. The MSDS also quotes a specific gravity of 1.1 and pH of ~ 11.4 for the bleach. A sample of the bleach revealed a pH of 12, corresponding to an NaOH concentration of 0.01 molar or 0.36 wt. %. It also contains residual NaCl from the manufacturing process.[11] The NaCl concentration in the bleach, determined from an ISE measurement, is 32 grams/liter or 2.9 wt. %. For bleach, $\rho_B = 1.1$ g/cm^3, and $c_{pB} = 0.9$ cal/g- °C (estimated).

DATA, ANALYSIS, AND DISCUSSION

The rate constant used in Eq. (1) is estimated from the data of Shams and Mohammed.[7]

$$ k \approx 2 \cdot 10^{12} \exp\left(\frac{-11800}{RT}\right) liter/mole-sec \qquad (22) $$

where R = 1.987 cal/mole-K, and T = absolute temperature (K).

The analysis approaches the simulation of the experiment as a design problem. In this approach, the model defined by Eqs. (1), (4)-(6), (8), (10)-(17), (21), and (22) is solved with a numerical ordinary differential equation solver package.

Figures 2 and 3 show experimental and corresponding model results for batch solution conductivity, batch temperature, and evolved O_2 rate. The uncertainty bars are based on estimated precisions of the measuring devices. Relative fits are reasonable for temperature and O_2. In fact, the heat loss term in the energy balance accounts for ~ 2-3 degree reduction in the observed temperature rise. The model under-prediction of the conductivity suggests that the bleach might contain an additional inert ionic species not accounted for. In addition, modeling results are most sensitive to the bleach rate. An accurate measure of the bleach flow rate is critical.

As a point of discussion, and lacking direct concentration measurements, the model profiles for C_A and C_B are shown in Figure 4 (page 125). The peroxide concentration drops monotonically as the bleach is added. The batch concentration of the bleach jumps initially as the bleach is first added, and then rises slowly, but all at a very low value. These values are consistent with the

$$ C_{H_2O_2} \gg C_{NaOCl} $$

assumption made earlier. It also is consistent with the claim that NaOCl does not appreciably contribute to the batch conductivity.

CONCLUSIONS

The reaction $H_2O_{2(aq)} + NaOCl_{(aq)} \rightarrow H_2O_{(l)} + NaCl_{(aq)} + O_{2(g)}$ is a useful system to study in a semi-batch reactor. Generation of a gaseous product offers an opportunity for additional data beyond that of probes. The availability of published conductivity data provides a direct means to convert data to concentration of a product. Therefore, unlike most experiments, products are monitored instead of reactants. The multiple species balances required for modeling will challenge the student, but not be out of the realm of undergraduate reactor engineering. This is especially true with the inclusion of an energy balance.

Figure 2. (right) Observed and predicted batch solution conductivity for bleach / hydrogen peroxide semi-batch run.
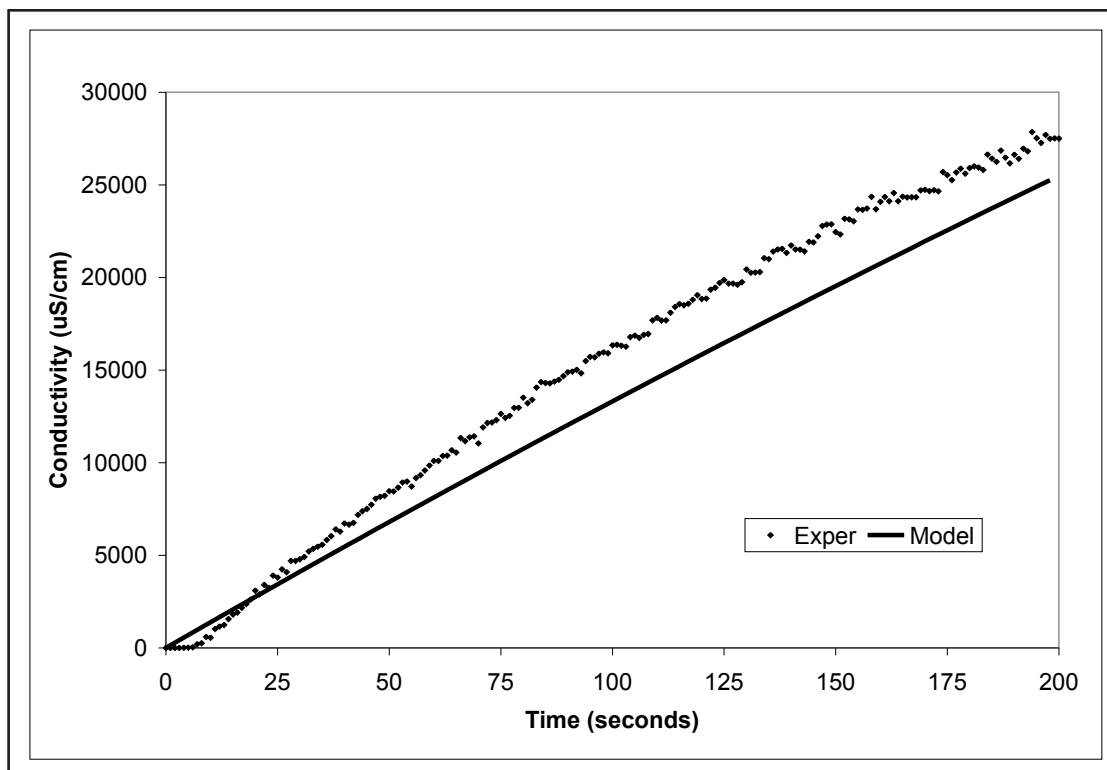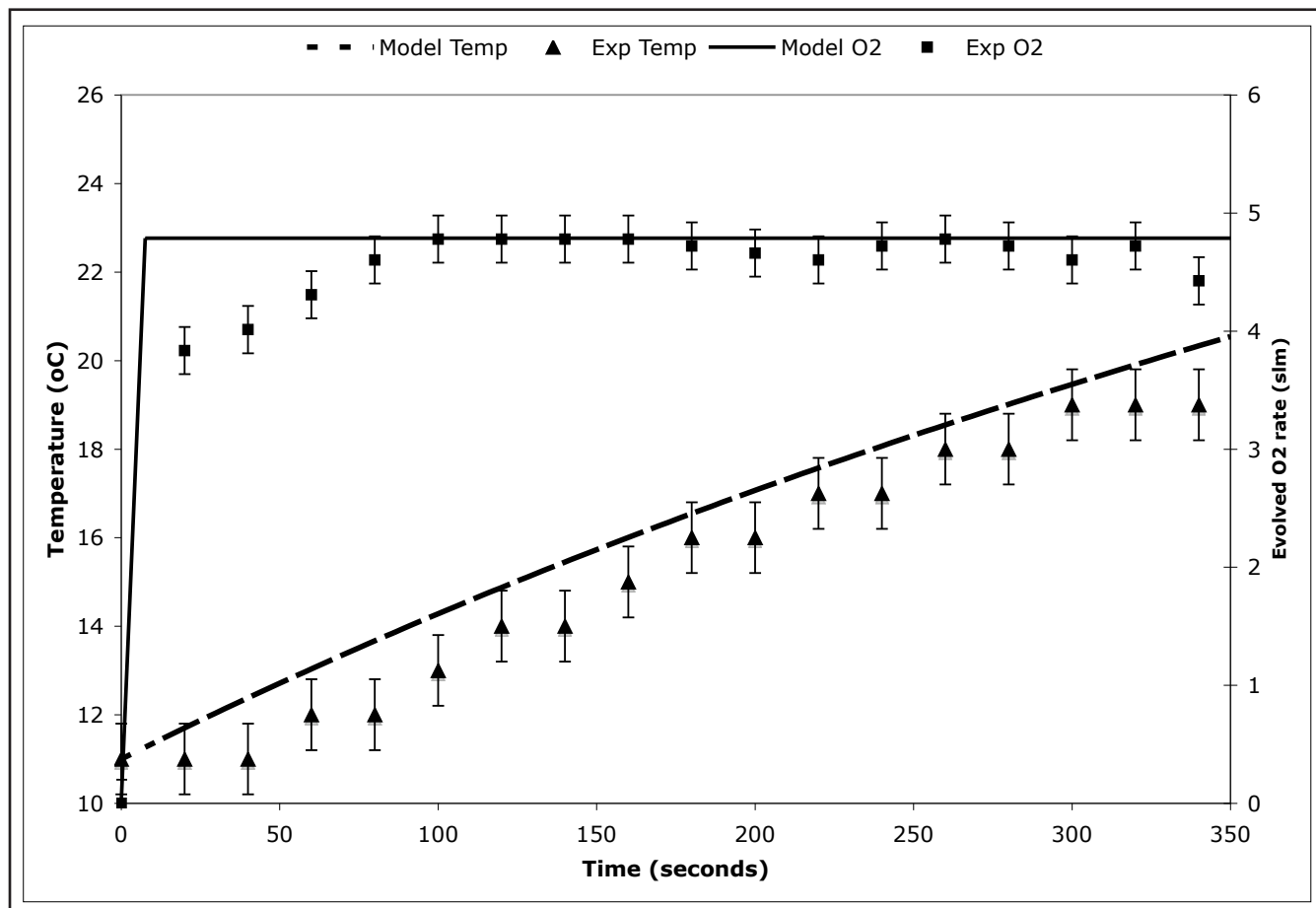
Figure 3. (below) Observed and predicted batch solution temperature and evolved oxygen rate.

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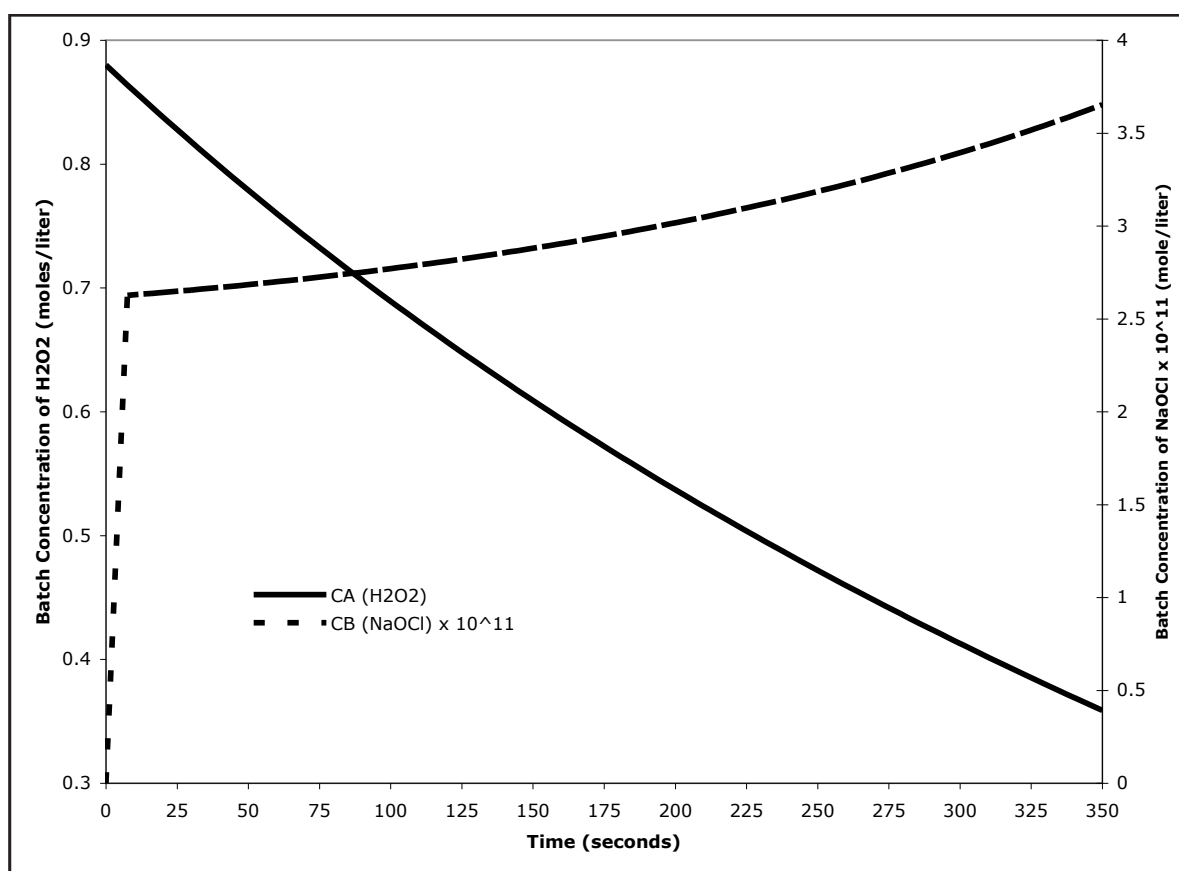
11. Clorox® MSDS: <http://www.thecloroxcompany.com/products/msds/> ❑

Figure 4. *Model-based predicted concentrations of species A (H_2O_2) and B (NaOCl) in the batch.*