ENERGY BALANCES ON TRANSIENT PROCESSES

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This study proposes a set of experiments that will prove useful to students in understanding and putting into practice basic concepts involved in energy balances. These experiments, which form part of a course of Chemical Engineering Laboratory I, are very simple from the point of view of the required equipment and operations that students must carry out, as well as with regard to the concepts involved. The first part of the experiments consists of heating and later cooling a mass of water contained in a vessel by means of an electrical resistor of known power, which is first connected and then disconnected from a power source (batch process). The results of this experiment necessarily have to be interpreted in terms of an unsteady-state energy balance. In a second part, both heating and cooling of the water, by first connecting and then disconnecting the electrical resistor, are carried out while at the same time allowing water to flow at a constant rate through the vessel. Under these conditions the temperature is fixed at the inlet and obviously changing at the outlet. In this last case, a stationary state is eventually reached and the difference of the enthalpy between the incoming and exit water streams must appear in the energy balance.

These experiments, and others involving unsteady-state material balances, have been set up and tested in the laboratories of the chemical engineering department at the University of Alicante, where they are used as a practical complement, in the first year of the curriculum, to illustrate the concepts developed in Chapter 11, "Balance on Transient Processes," in the textbook by Felder and Rousseau.[1] The energy balances, along with the material balances, are essential tools for the study of any basic operation of chemical engineering, and therefore the fundamental concepts of material and energy balances are usually incorporated in the first year of all chemical engineering curricula. This is reflected in introductory chemical engineering textbooks (*e.g.*, Himmelblau,[2] Henley and Rosen,[3] and Reklaitis[4]), which have followed the guidelines established by the pioneer book by Hougen and Watson, *Material and Energy Balances*,[5] published in 1943. The journal *Chemical Engineering Education* has also shown

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its interest in this topic, *e.g.*, in the two-part article written by Bullard and Felder,[6,7] "A Student-Centered Approach to Teaching Material and Energy Balances."

The experiments relating to unsteady-state energy balances presented here have also been studied by other authors in *CEE*, such as Condoret[8] and Luyben.[9] Condoret, in his article "Teaching Transport Phenomena Around a Cup of Coffee," included in the category of ChE Class and Home Problems, presents the problem like this: *We put a cup of coffee on a table. Its initial temperature is around 80 °C. What is the temperature of the coffee after 10 min, for instance?* The paper solves the problem using a simulation model of the cooling process; the model takes into account the heat loss at vessel wall of the cup, the heat loss by heat transfer only at the surface of the liquid, and the heat loss resulting from evaporation. The paper also describes a simple lab experiment using porcelain cups filled with water, a numerical thermometer, a balance, and a stopwatch. The didactic value of the paper comes from showing how using heat transfer coefficients makes it possible to model and predict the simple experiment of cooling a cup of hot coffee. Another experiment relating to unsteady-state energy balances is described by Luyben[9] in the article "The Devil's in the Delta," included in the ChE Laboratory category. The process consists of a stirred vessel, 1 m diameter, containing 785 kg of water. The rpm's of the agitator can be varied to see the effect on the inside fluid coefficient. A spiral coil is wrapped around the outside of the vessel. The liquid in the vessel is initially at ambient temperature. It is heated by introducing steam at the top of the coil. When the water of the vessel reaches about 80 °C the steam is shut off and cooling water is introduced. The didactic value of this paper comes from providing a clear distinction of the three "deltas" as used in chemical engineering; the author refers to them as "In Minus Out" Delta, "Driving Force" Delta, and "Time" Delta. As the author mentions in the paper conclusions, although the distinction of the three deltas is obvious to the experienced engineer, they are often misapplied by young students.

EXPERIMENT

Apparatus

The experimental apparatus used is shown in Figure 1. It consists of a vessel with water inlet and outlet, equipped with an electrical resistor heater and a magnetic stirrer to ensure that the temperature is uniform throughout the vessel. The water, fed to the apparatus at a constant flow rate, comes from a tank that is kept at a constant water level. Water exits the vessel at the same flow rate as in the feed. In addition to the experimental apparatus just described, a stopwatch, beakers, and a balance will prove useful for measuring the flow rate properly.

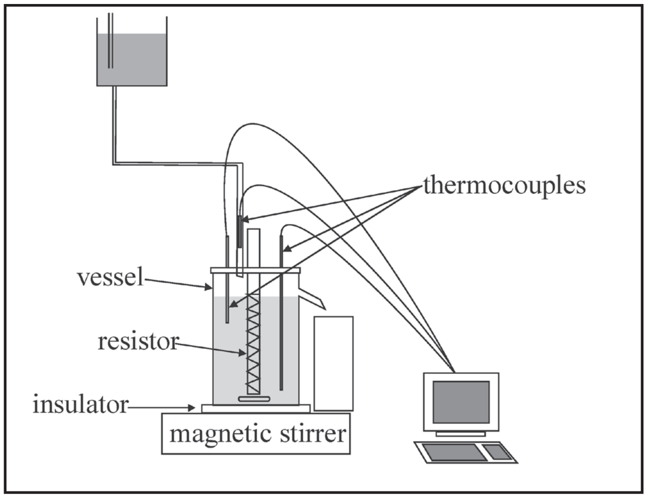

Figure 1. *Experimental apparatus.*

TABLE 1
Details of the Experimental Apparatus

Parameter	Value
P (W)	110
M_w (kg)	1.75
M_v (kg)	1.63
M_r (kg)	0.10
Cp_w (J/kg °C)	4180
Cp_v (J/kg °C)	460
Cp_r (J/kg °C)	836
m (kg/s)	$4.0\cdot10^{-3}$

The vessel consists of a stainless steel cylinder of 10 cm internal diameter, 23 cm length, and 1.63 kg weight. It is also insulated at the base to isolate it from the magnetic stirrer, and in addition, has a methacrylate cover that blocks evaporation. Therefore, water mass remains constant and evaporative cooling is avoided. Table 1 shows the power of the resistor (P), the overflow capacity of the vessel (mass of water, M_w), the mass of the vessel (M_v) and the resistor (M_r), as well as the heat capacities Cp_w, Cp_v, and Cp_r, of the water, vessel, and resistor, respectively. It also contains the value of constant flow rate of water that enters the vessel (m). Three thermocouples interfaced with a PC measure and record the temperature of the water in the inlet (T_{in}) and at two other points in the vessel (T_1 in the uppermost part of the vessel and T_2 in the lowermost). The extent to which the vessel is well stirred depends upon how close T_1 and T_2 are. The continuous monitoring and recording of temperatures by the thermocouples interfaced with the PC makes it possible to extract numerous experimental data points.

The experimental method consists of the following steps.

Without water circulation:

Experiment A1: The vessel, full of water, is warmed up to 45 °C by connection of the resistor to the power source (nonstationary regime).

Figure 2 shows the experimental data obtained in the form of temperature T of the water in the vessel vs. time t. The measured values of temperatures T_1 and T_2 are practically equal, with less than two-tenths of a degree difference between them, which indicates that the vessel is perfectly stirred. These circumstances—equal temperatures and good stirring—together with the fact that water has a high heat capacity, ensure that the heat generated by the resistor is quickly transferred to the mass of water, preventing the resistor surface temperature from reaching higher than 100 ˚C, thus avoiding local boiling.

The average value of T_1 and T_2 has been used to represent the experimental data graphically, and is shown as the dashed line in Figure 2.

Experiment A2: When the temperature reaches 45 ˚C, the resistor is disconnected from the power source and the evolution of temperature with time is studied as an experiment of water cooling under nonstationary conditions.

Figure 3 shows (dashed line) the experimental data obtained in the form of temperature T of the water in the vessel vs. time t.

With water circulation:

Experiment B1: The water in the vessel is pre-heated to 45 ˚C. The experiment begins when a valve is opened to allow water to flow through the vessel at a constant rate without disconnecting the resistor from the power source. This implies a cooling experiment, and the time and temperatures are recorded until a steady state temperature (constant temperature) is reached. The flow rate of water that enters the vessel is measured when it exits by means of the "bucket and stopwatch" method.

Experiment B2: While maintaining water circulation the resistor is disconnected. The temperature then decreases until a different stationary state is reached.

Experiment B3: The resistor is connected without varying the water flow rate, thus raising the temperature to the stationary state temperature that was reached at the end of experiment B1.

Figure 4 represents the data obtained in experiments B1, B2, and B3 as three different but connected portions of a dashed line.

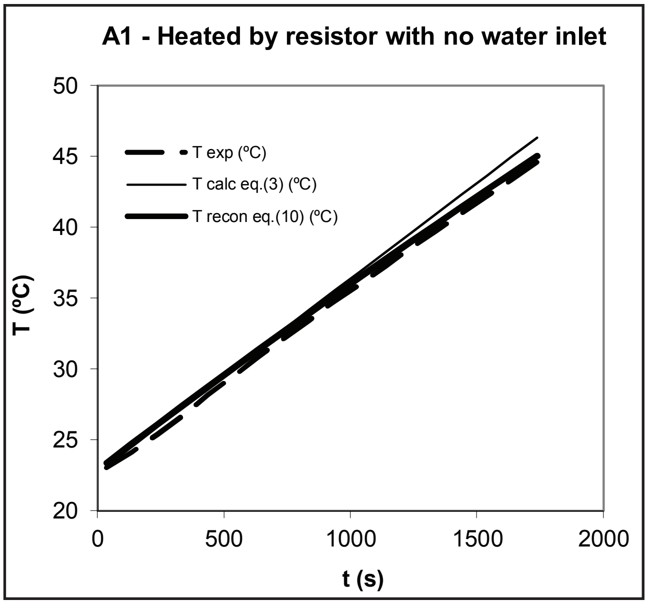

Figure 2. *Experiment A1. Water heating to 45 °C.*

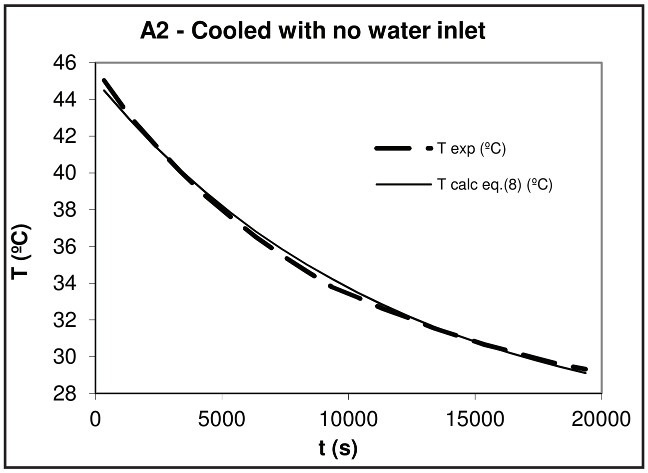

Figure 3. *Water cooling with resistor switched off.*

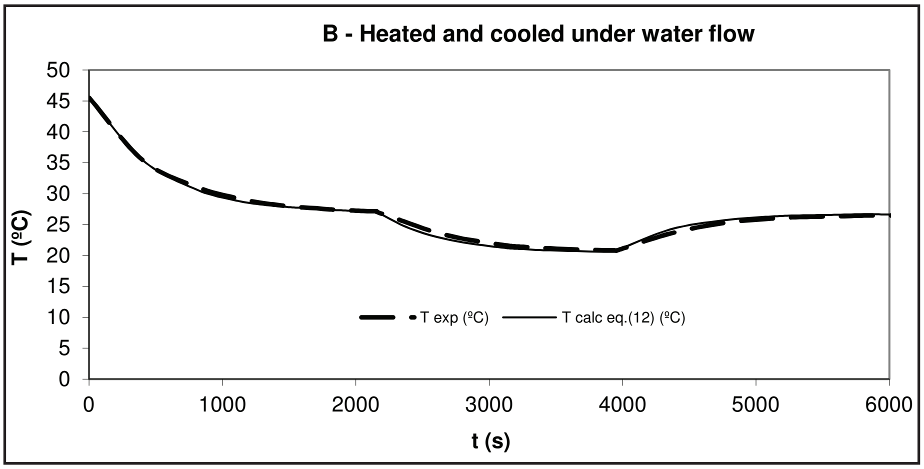

Figure 4. *Experiments B1-3. Cooling and heating with flow.*

DISCUSSION

Without water circulation:

Experiment A1 is a process of heating in the nonstationary regime where the temperature of the mass of water M_w, the mass of the vessel M_v, and the mass of the electrical resistor M_r are raised thanks to the difference between the heat received from the electrical resistor of power P and the heat lost by convection Q_l through the walls of the vessel.

Experiment A1 can be modeled by means of the following energy balance

$$\left(M_W C_{p_W} + M_V C_{p_v} + M_r C_{pr}\right)\frac{dT}{dt} = P - Q_l \tag{1}$$

The mechanical work is not included in this energy balance because in the present case it arises only from the magnetic stirrer and it can be considered negligible.

Neglecting the losses of heat through the walls, Eq. (1) simplifies to

$$\left(M_W C_{p_W} + M_V C_{p_v} + M_r C_{pr}\right)\frac{dT}{dt} = P \tag{2}$$

Integration then leads to

$$T = T_0 + \frac{P}{\left(M_W C_{p_W} + M_V C_{p_v} + M_r C_{pr}\right)} t \tag{3}$$

where T_0 is the initial temperature of the water in the vessel at the beginning of experiment A1, 22.9 °C in this case.

Notice that Figure 2 contains the plot of the simplified model embodied in Eq. (3) (equation of a straight line). It can be observed that the calculated temperatures (represented by the thin continuous line) are a little higher than the experimental ones (dashed line), but the difference does not become greater than 2 °C until only after 500s. A small improvement can be obtained if Eq. (1) is used instead, *i.e.*, by taking into account the heat lost by convection Q_l through the walls of the vessel. This lost heat can be expressed as

$$Q_l = UA\left(T - T_{amb}\right) \tag{4}$$

where

A= External surface of the vessel (m^2)

U= Global coefficient of heat transfer (W/m^2 °C)

T= Water temperature (°C)

T_{amb}= Ambient temperature (°C)

The experimental value of product UA can be determined from the data of experiment A2, where the vessel is cooled. Applying an energy balance in this case, in which electrical energy P is not supplied, yields

$$\left(M_W C_{pw} + M_V C_{p_v} + M_r C_{pr}\right)\frac{dT}{dt} = -Q1 \tag{5}$$

which combined with Eq. (4) results in

$$\left(M_W C_{pw} + M_V C_{p_v} + M_r C_{pr}\right)\frac{dT}{dt} = -UA\left(T - Tamb\right) \tag{6}$$

and the integration leads to

$$\ln\frac{T - T_{amb}}{T_0 - T_{amb}} = -\frac{UA}{\left(M_W C_{pw} + M_V C_{p_v} + M_r C_{pr}\right)} t \tag{7}$$

Here, T_0 is the initial temperature of the water at the beginning of experiment A2, and corresponds to the final temperature at the end of experiment A1, 45.1 °C, while the ambient temperature is 25.3 °C.

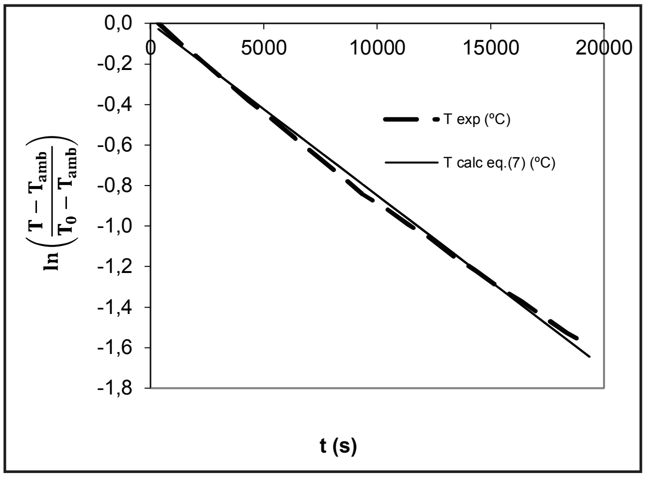

Figure 5. *The slope of the straight line allows calculation of the parameter UA.*

Figure 5 is another plot of the experimental data of the cooling process but of the form

$$\ln\frac{T - T_{amb}}{T_0 - T_{amb}}$$

as a function of time t.

According to Eq. (7), the slope of the straight line in Figure 5 is -8.50·10^{-5} s^{-1}, that leads to a value for the parameter UA of 0.693 W/°C. Since the external surface of the vessel A is known, 0.07235 (m^2), the value for the global coefficient of heat transfer U can be calculated (9.59 W/m^2 °C). In this cooling experiment A2, there are different heat transfer mechanisms, namely: internal liquid convection in series with conduction in the stainless steel wall and external transfer to ambient air. The internal individual coefficient of heat transfer is high (forced convection since the water is stirred). Also the heat transfer by conduction in the stainless steel wall is high. The external coefficient (free convection to air) is low, however, and therefore this last mechanism is probably the limiting one. In fact, the value of the overall coefficient computed, U= 9.59 W/m^2 °C, is close to the value of a usual external heat transfer coefficient.

Eq. (7) written in the following format

$$\frac{T - T_{amb}}{T_0 - T_{amb}} = e^{-\frac{UA}{\left(M_W C_{Pw} + M_V C_{Pv} + M_r C_{Pr}\right)} t} \tag{8}$$

permits comparison using Figure 3 of the calculated (continuous line) and experimental (dotted line) values of the cooling experiment A2. It can be observed that there is good agreement between the experimental and calculated data.

In the same way, once the value of UA is known, the variation of temperature with time in experiment A1 can be recalculated by means of Eq. (9), which includes the losses of heat through the walls.

$$\left(M_W C_{p_W} + M_V C_{p_v} + M_r C_{p_r}\right)\frac{dT}{dt} = P - UA\left(T - T_{amb}\right) \qquad (9)$$

An expression that once integrated leads to

$$\ln\frac{P - UA\left(T - T_{amb}\right)}{P - UA\left(T_0 - T_{amb}\right)} = -\frac{UA}{\left(M_W C_{p_W} + M_V C_{p_v} + M_r C_{p_r}\right)} t \qquad (10)$$

Figure 2 shows the variation of water temperature with time calculated using Eq. (10). It can be observed that this simulation with Eq. (10) (bold solid line), which does take into account the losses of heat through the walls of the vessel, represents a very slight improvement on the simulation done using Eq. (3) (thin continuous line), which neglected those heat losses. This small improvement suggests that the Q_1 term in Eq. (1) can be neglected to a first approximation to give Eq. (2). Indeed, the effect of heat losses on the temperature is greatest toward the end of the experiment when ΔT reaches its highest value, around 10 W, which compared to a power of 110 W of the electrical resistor means a deviation of around 10% when neglecting heat losses through the walls.

With water circulation

The process that takes place in experiment B1 can be modeled by means of Eq. (1) extended to include the term $mC_{pw}(T_{in} - T)$. This term represents the change in enthalpy of the water flowing through the vessel between the inlet and outlet. In the experiments where water is circulating through the vessel, T corresponds to the outlet water temperature if the vessel is well stirred.

$$\left(M_W C_{p_W} + M_V C_{p_v} + M_r C_{pr}\right)\frac{dT}{dt} = mC_{p_W}\left(T_{in} - T\right) + P - UA\left(T - T_{amb}\right) \qquad (11)$$

which after integration leads to:

$$\ln\frac{mC_{p_W}T_{en} + P + UAT_{amb} - \left(mC_{p_W} + UA\right)T}{mC_{p_W}T_{en} + P + UAT_{amb} - \left(mC_{p_W} + UA\right)T_o} = -\frac{\left(mC_{p_W} + UA\right)}{\left(M_W C_{p_W} + M_V C_{p_v} + M_r C_{pr}\right)} t \qquad (12)$$

In this case, T_0, the initial temperature of water at the beginning of experiment B1, has a value of 45.5 °C. The temperature inside the vessel decreases to a constant value (stationary state).

Once a stationary state has been achieved, the temperature will not vary with time and therefore $dT/dt = 0$. Upon substitution of this into Eq. (11), the temperature of the stationary state is easily obtained:

$$0 = mC_{p_W}\left(T_{en} - T\right) + P - UA\left(T - T_{amb}\right) \qquad (13)$$

Putting known data values into Eq. (12), the variation of temperature T with time t is obtained. These calculated values for experiment B1 are plotted alongside the experimental ones in Figure 4. The good agreement between the experimental (dashed line) and calculated (continuous line) data is evident.

In the experiments involving water circulation the ambient temperature is 21.0 °C. The temperature at the water inlet is 20.4 °C in this case.

On the other hand, Eq. (13) produces a calculated temperature for the stationary state, 26.8 °C, that is very close to the experimental one.

In cooling experiment B2, the resistor is disconnected while maintaining water flow. Therefore, this can be modeled by a modified Eq. (11), in which the term P, the power of the electrical resistor, does not appear:

$$\left(M_W C_{p_W} + M_V C_{p_v} + M_r C_{pr}\right)\frac{dT}{dt} = mC_{p_W}\left(T_{in} - T\right) - UA\left(T - T_{amb}\right) \qquad (14)$$

In the same way, integration of Eq. (14) leads to an equation similar to Eq. (12) in which P is absent and in which T_0 must be the initial temperature of water when experiment B2 begins. Therefore, the final temperature of the stationary state at the end of experiment B1 must be used. Figure 4 shows the calculated values (continuous line) of experiment B2, which exhibit good agreement with the experimental ones (dashed line). For longer time periods, when the stationary state is reached and $dT/dt = 0$, the following equation will hold true

$$0 = mC_{pw}\left(T_{in} - T\right) - UA\left(T - T_{amb}\right) \qquad (15)$$

and allows calculation of the final temperature of experiment B2.

Since in this experiment $T_{in} = T_{amb}$, according to Eq. (15) the final temperature should be equal or close to T_{amb}. In the present case, this corresponds to a final temperature of 20.5 °C. (T_{amb}=21.0 °C)

In experiment B3 the resistor is reconnected while maintaining water circulation. Therefore, the same differential Eq. (11) and the same integrated Eq. (12) are valid, the only difference being that T_0 now corresponds to the final temperature of experiment B2. Figure 4 shows the calculated values and the experimental ones plotted on the same graph. The good agreement of the data is again evident. The final temperature of the stationary state will be the same in experiment B3 as in B1, which is given by Eq. (13). In experiment B3 the temperature of the stationary state is 26.8 °C, very similar to the 26.9 °C reached in B1.

It should be pointed out that in the beginning of each experiment a small period of time passes where there is some inertia due to the initial connection or disconnection of the resistor. What happens during this time has not been taken into account because the energy balances in this case would not correspond exactly to those (the equations) presented here.

EXPERIENCES GAINED BY THE STUDENTS

The entire experiment, consisting of two sessions lasting three hours each, is conducted in pairs by the students. During the first session, the students observe the process without water circulation, whereas during the second one, the process with water circulation is studied. Students gain ample practical experience, *e.g.*, on measuring temperatures by thermocouples interfaced with a PC, on control and measurement of flow rates. Most students find the module effective as an introduction to the concept of unsteady-state process, of which most of them have only theoretical background knowledge. In addition to this, the concept of overall heat transfer coefficient (U) is introduced and its experimental value is obtained during the experiments.

After the experimental part, the students, still working in pairs, are expected to submit a report containing all the results obtained including a discussion that compares experimental data with those calculated using the theoretical equations. In this way they test the potential of theoretical models to predict experimental results. Occasionally something is bound to go wrong during experimentation (random fluctuations in the flow rate that is not constant during the experiment, erroneous measurement of the flow rate by the student, erroneous temperature readings caused by improper positioning of the thermocouples or by the magnetic stirrer that is not working properly, etc.) and therefore the experimental data end up not fitting the theoretical models perfectly. In this case, students also learn the importance of handling and taking care of the experimental details in order to obtain valid and reliable experimental results that are predicted by theoretical models. Regarding safety aspects, the experimental set-up is very simple and safe, without apparent danger in operation for students. The product flowing is water and temperatures are low. The trickiest part of the apparatus is the electric resistance heater, which must be connected and disconnected at the right time. In order to prevent this part being broken due to forgetfulness, an electrical safety switch must be installed. In their reports, students are asked to give an assessment of the experimental module both in terms of its pedagogical value and the operation of the equipment. Most students give very positive feedback. Finally, at the end of the course, each student is expected to make an oral presentation of the experiment on his/her own in front of lecturers and other students.

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