# The Devil's in the Delta

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#### Abstract

Students frequently confuse and incorrectly apply the several "deltas" that are used in chemical engineering. The deltas come in three different flavors: "out minus in", "big minus little" and "now versus then".

The first applies to a change in a stream property as the stream flows through a process. For example, the " $\Delta H$ " in an energy balance around a unit is the difference between the enthalpies of the streams leaving and the enthalpies of the streams entering.

The second delta is a driving force difference. In heat transfer, it is "hot temperature minus cold temperature." In mass transfer, it is "large chemical potential minus small chemical potential." The chemical potentials can be partial pressures, molar or mass concentrations, mole fractions or activities.

The third delta indicates the change in a variable with time. For example, in a batch reactor the  $\Delta C_A$  means the change in concentration of component A over some time period between  $t = t_1$  and  $t = t_2$ . The delta in time is  $\Delta t = t_2 - t_1$ .

Although the distinctions among these various deltas and their appropriate application should be obvious and fundamental, students frequently use the wrong delta. This note is intended to provide a friendly suggestion to professors that they remind their students of the need to be careful in applying deltas.

## Introduction

As I enter my 40<sup>th</sup> year of teaching, it seems appropriate to remind teachers and students of a fundamental error that occurs at a surprising frequency. This error is particularly evident in the courses that cover a wide variety of chemical engineering topics and serve to pull together the subjects supposedly learned in previous courses. The senior design course and a chemical engineering laboratory with a variety of experiments are this type of course. In teaching these courses I have frequently encountered quite bright students who misuse the deltas. Since the differences among the various deltas should be obvious and not at all confusing, it is remarkable that errors of this type crop up so frequently. But they do.

This paper will describe a particularly useful experiment in the undergraduate Lehigh University chemical processing laboratory that uses all three of the deltas and therefore helps to cement in the minds of the students the fundamental differences among the three kinds.

The title of this paper originates from the old expression "The devil is in the details." Some of you may also remember Flip Wilson's famous portrayal of Miss Geraldene with her "The devil made me do it."

## The Devil Deltas

A brief review might be useful to clarify the issues and applications addressed in this discussion.

#### A. "In Minus Out" Delta:

An "open" flow process has streams entering and streams leaving. Mass, component and energy balances can be applied under either steady-state or dynamic conditions. For example, a steady-state energy balance for a distillation column with a single feed and two products is

$$\Delta H = Q - W$$

The delta in this equation is

$$\Delta H = Bh_B + Dh_D - Fh_F$$

where the streams leaving the column are the distillate (with flowrate D and specific enthalpy  $h_D$ ) and the bottoms (with flowrate B and specific enthalpy  $h_B$ ) and the stream entering the column is the feed (with flowrate F and specific enthalpy  $h_F$ ). Of course appropriate and consistent units must be used for flowrates and specific enthalpies. If the flowrates are in moles per time, the specific enthalpies must be in energy units per mole (joule, kcal, Btu, etc).

In a heat exchanger, streams are heated or cooled. Under steady-state operations with no phase change, a stream enters at temperature  $T_{in}$  and leaves at temperature  $T_{out}$ . If the mass heat capacity  $c_p$  is constant and the mass flowrate is  $F_M$ , the  $\Delta H$  for the stream is

$$\Delta H = F_M c_p (T_{out} - T_{in})$$

If there is a phase change, for example if steam is entering as a vapor with specific enthalpy  $H_{in}$  and leaving as liquid condensate with specific enthalpy  $h_{out}$  through a steam trap, the  $\Delta H$  for the steam is

$$\Delta H = F_{steam} (h_{out} - H_{in})$$

In fluid flow systems, the appropriate deltas are differences in pressure, elevation, velocity and density between the inlet and the exit conditions.

## B. "Driving Force" Delta:

Transport processes occur because of differences in driving forces. In heat transfer, the difference is between hot and cold temperatures. In mass transfer, the difference is between large chemical potential and small chemical potential (partial pressure, concentration or activity). In momentum transfer, the difference is between high pressure or velocity and low pressure or velocity.

For example, consider a perfectly mixed vessel that is surrounded by a jacket. The temperature of the liquid in the vessel is  $T_{vessel}$ . Suppose the jacket is completely filled with condensing steam at temperature  $T_{steam}$ . The driving force for heat transfer is

$$\Delta T = T_{steam} - T_{vessel}$$

The heat-transfer rate Q that results from the driving force DT is

$$Q = UA_{H} \Delta T = UA_{H} (T_{steam} - T_{vessel})$$

where U is the overall heat-transfer coefficient and  $A_H$  is the heat-transfer area of the vessel wall. In this example the jacket temperature is the same at all positions in the jacket.

If the vessel is cooled or heated by a fluid flowing through the jacket or through an internal or external coil in plug flow, the temperature of this fluid changes with position. Therefore the temperature driving force changes, and a log-mean temperature difference must be used.

$$\Delta T_{LM} = \frac{\Delta T_1 - \Delta T_2}{\ln\!\left(\frac{\Delta T_1}{\Delta T_2}\right)}$$

where the two deltas are the temperature differences at the inlet and outlet ends of the jacket or coil.

$$\Delta T_1 = T_{vessel} - T_{Cin}$$
$$\Delta T_2 = T_{vessel} - T_{Cout}$$

Now the heat-transfer rate is

$$Q = UA_{H} \left(\Delta T\right)_{LM} = UA_{H} \frac{\Delta T_{1} - \Delta T_{2}}{\ln\left(\frac{\Delta T_{1}}{\Delta T_{2}}\right)}$$

If a circulating cooling water system is used with a high rate of circulation, the temperature in the jacket is essentially constant at some temperature  $T_J$ . The heat-transfer rate is

$$Q = UA_H \Delta T = UA_H (T_{vessel} - T_J)$$

In this type of system, a cold makeup water stream at  $T_{Cin}$  is added to the circulating loop, and water is removed at the jacket temperature  $T_J$ . A circulating cooling water system has superior dynamics compared to the once-through system. The high circulation rate maintains a high coolant-side film coefficient that does not change with the load on the system (the makeup water flowrate), so time constants are less variable.

### C. "Time" Delta:

The variables in a dynamic process change with time, so we can talk about changes in time  $\Delta t$  and changes in properties  $\Delta x$  between their value at one point in time and their value at a later point in time. For example, when the liquid in a vessel is heated up at startup, the temperature changes with time.

$$\Delta T = T_{(t_2)} - T_{(t_1)}$$

At any point in time the rate of change of temperature is

$$\frac{dT}{dt} \approx \frac{\Delta T}{\Delta t} \approx \frac{T_{(t_2)} - T_{(t_1)}}{t_2 - t_1}$$

if the time increment between  $t_2$  and  $t_1$  is small.

## **Laboratory Experiment Utilizing All Three Deltas**

## A. Apparatus:

The process consists of a stirred vessel, 1 m in diameter containing 785 kg of water. The rpm's of the agitator can be varied to see the effect on

the inside film coefficient. A spiral coil is wrapped around the outside of the vessel, making 9 wraps around the circumference. Figure 1 gives a sketch of the apparatus. The tank is equipped with a 0.3 m 6-blade impeller with four baffles. The heat-transfer area is 3.14 m<sup>2</sup>.

The liquid in the vessel is initially at ambient temperature. It is heated by introducing steam at the top of the coil. Condensate leaves at the bottom through a steam trap. Temperature inside the vessel and at the inlet and outlet of the coil are monitored by a data acquisition system.

When the temperature of the vessel reaches about 90 °C, the steam is shut off and cooling water is introduced. The water enters at the bottom of the coil and leaves at the top.

#### B. Data and Analysis:

Figure 2 shows typical temperature versus time trajectories for the batch heat up and cool down. The temperature in the coil during heat up is shown as being constant at the steam temperature. This is actually not the case because it takes some time for the coil to become completely full of steam. This complicates the analysis of the heat up because the temperature profile along the coil is not known until it is full of steam. We consider this later in this paper.

The analysis of the cool down is much more straight-forward, and our discussion for the purpose of illustrating the "devil deltas" will concentrate on this part of the batch cycle.

The flowrate of cooling water is constant and can be measured by the old fashioned "bucket and stop watch" method. The inlet and outlet cooling water temperatures are measured as is the vessel temperature.

At any point in time, there are two ways to estimate the instantaneous heat-transfer rate. From the measurement of the cooling water flowrate and inlet and outlet temperature, the heat-transfer rate at that point in time is

$$Q_{CW} = F_{CW} c_p (T_{C,out} - T_{C,in})$$

This is the "out minus in" delta. At time equal 30 minute in Figure 2, this "in-minus-out" delta is

$$\Delta T_{out-in} = T_{C,out} - T_{C,in} = 38 - 15 = 23 C^{\circ}$$

The heat-transfer rate can also be estimated by the time rate of change of the vessel temperature. This uses the "time" delta. At time equal  $t_n$ , the instantaneous rate of heat transfer to the fluid in the vessel is

$$Q_{vessel(t=t_n)} = M_{vessel} c_p \frac{(T_{vessel})_{(t=t_n)} - (T_{vessel})_{(t=t_{n-1})}}{t_n - t_{n-1}}$$

Since the heat-transfer rate varies with time, the slope of the temperature versus time curve varies during the batch cool down. Having two independent ways to estimate the rate of heat transfer improves reliability of the estimated film coefficients. Figure 2 shows that this delta at a 30 minutes is about 3.5 °C per minute (the slope of the vessel temperature line).

$$\Delta T_{time} = 3.5 \, C^{\circ} / \text{minute}$$

Using this value, the instantaneous heat-transfer rate is calculated to be 192 kW. The heat-transfer rate from the flowrate of cooling water (2 kg/sec) and the inlet and outlet cooling water temperatures is very close to this number.

The temperature of the cooling water in the coil varies along its length, so a log-mean temperature difference is used. This is the "driving force" delta.

$$\Delta T_{LM} = \frac{\Delta T_1 - \Delta T_2}{\ln\!\left(\frac{\Delta T_1}{\Delta T_2}\right)}$$

where the two deltas are the temperature differences at the inlet and outlet ends of the coil.

$$\Delta T_1 = T_{vessel} - T_{Cin}$$
$$\Delta T_2 = T_{vessel} - T_{Cout}$$

The log-mean temperature difference at this point in time is

$$\Delta T_{LM} = \frac{\Delta T_1 - \Delta T_2}{\ln\left(\frac{\Delta T_1}{\Delta T_2}\right)} = \frac{(70 - 38) - (70 - 15)}{\ln\left(\frac{70 - 38}{70 - 15}\right)} = 42.5^{\circ} C$$

With a heat-transfer area of 3.14 m<sup>2</sup>, the overall heat-transfer coefficient is

$$U == \frac{Q}{A_H \Delta T_{IM}} = \frac{192}{(3.14)(42.5)} = 1.44 \text{ kW m}^{-2} \text{ K}^{-1}$$

The vessel inside film coefficient can then be calculated by accounting for heat conduction through the vessel wall and by estimating the

film coefficient inside the coil using the Dittus-Boelter equation and an appropriate equivalent diameter.

Even with a constant agitator speed, there is some variation of the overall heat-transfer coefficient and the inside film coefficient with time. This occurs because the varying temperature in the vessel affects the viscosity of the water.

## C. Approximate Analysis for Heatup:

If the temperature in the coil were constant during the heatup period and if the overall heat-transfer coefficient were also constant with time, the analysis would be quite simple. It would use "time" deltas in a way that may not be obvious. The situation is analogous to the steady-state flow of fluid down the length of a heated tube. In that situation, the appropriate driving force for calculating the heat-transfer rate is a log-mean temperature difference using the temperature differentials at the inlet and exit ends of the tube. The log-mean temperature difference assumes a constant heat-transfer coefficient. The independent variable is length.

In the batch heatup situation, the independent variable is time, but the heat-transfer equations are the same. Therefore the total heat transfer can be calculated by the change in vessel temperature from some point in time to another point in time. The driving force can be calculated using a log-mean temperature difference based on the difference between the constant steam temperature and the temperature of the vessel at the two points in time.

The similarity between length and time coordinates is understood if you visualize a little particle of fluid flowing down the tube in steady-state flow. It sees a constant steam temperature and is heated as it flows along. This is exactly the same as the batch heatup of a vessel.

It should be emphasized that the analysis discussed in this section makes two important assumptions. First, the steam temperature is constant. Second, the overall heat-transfer coefficient is constant.

Figure 3 shows how the vessel temperature changes during the heatup. It starts at  $T_1$  when time is  $t_1$  and ends at  $T_2$  when time is  $t_2$ . The total amount of energy added during this period is

$$Energy = M_{vessel} c_p (T_2 - T_1)$$

The average heat-transfer rate over this period is

$$Q = \frac{Energy}{t_2 - t_1} = \frac{M_{vessel}c_p(T_2 - T_1)}{t_2 - t_1}$$

The instantaneous energy balance on the fluid in the vessel is

$$M_{vessel}c_p \frac{dT_{vessel}}{dt} = A_H U(T_{steam} - T_{vessel})$$

This linear ordinary differential equation can be integrated to give

$$T_{vessel(t)} = T_{steam} + c_1 e^{-\left(\frac{A_h U}{M_{vessel} c_p}\right)^t}$$

The constant of integration  $c_I$  is evaluated at the initial condition where  $T_{vessel} = T_I$ .

$$c_1 = (T_1 - T_{steam})e^{\left(\frac{A_h U}{M_{vessel} c_p}\right)t_1}$$

The time dependent vessel temperature is

$$T_{vessel(t)} = T_{steam} + (T_1 - T_{steam})e^{-\left(\frac{A_H U}{M_{vessel}c_p}\right)(t - t_1)}$$

Now evaluating this equation at time equal  $t_2$  where  $T_{vessel} = T_2$  gives

$$T_2 = T_{steam} + (T_1 - T_{steam})e^{-\left(\frac{A_H U}{M_{vessel} c_p}\right)(t_2 - t_1)}$$

Rearranging gives

$$\frac{T_2 - T_{steam}}{T_1 - T_{steam}} = e^{-\left(\frac{A_H U}{M_{vessel} c_p}\right)(t_2 - t_1)}$$

Taking the natural log of both side of this equation gives

$$\ln\left[\frac{T_{steam} - T_2}{T_{steam} - T_1}\right] = -\left(\frac{A_H U}{M_{vessel} c_p}\right) (t_2 - t_1)$$

Rearranging and substituting the previously defined equation for Q give

$$\ln \left[ \frac{T_{steam} - T_2}{T_{steam} - T_1} \right] = -\left[ \frac{A_H U (T_2 - T_1)}{M_{vessel} c_p (T_2 - T_1)} \right]$$

$$\ln \left[ \frac{T_{steam} - T_2}{T_{steam} - T_1} \right] = \left( \frac{A_H U (T_1 - T_2)}{Q} \right)$$

$$Q = UA_{H} \frac{(T_{1} - T_{2})}{\ln \left[ \frac{T_{steam} - T_{2}}{T_{steam} - T_{1}} \right]} = UA_{H} \frac{(T_{steam} - T_{2}) - (T_{steam} - T_{1})}{\ln \left[ \frac{T_{steam} - T_{2}}{T_{steam} - T_{1}} \right]}$$

$$Q = UA_{H} (\Delta T)_{IM}$$

In our experimental apparatus, the temperature through the entire coil is not equal to the steam temperature for about half of the heatup period. In addition, the change in viscosity due to changes in temperature results in variations in the heat-transfer coefficient. So the simple analysis described above can only be applied for the period towards the end of the heatup.

During the initial part of the heatup when the temperature of the exit stream from the coil is not equal to the inlet temperature, the full heat-transfer area is not being used for steam condensation. Thus it is uncertain how to calculate an internal heat-transfer coefficient. One approximate method is to assume that the active heat-transfer area varies linearly with time during this period.

Once the temperature of the exit stream from the coil becomes equal to the inlet temperature, either the approximate method discussed in this section or a rigorous approach can be applied. The rigorous method evaluates the inside film coefficient at each point in time by getting the heat-transfer rate from the rate of change of the vessel temperature and using the differential temperature driving force of  $T_{steam}$  minus  $T_{vessel}$  and the full heat-transfer area.

For example, in Figure 2 at time equal 20 minute, the differential temperature driving force is  $100 - 85 \text{ C}^{\circ}$  and the slope of the  $T_{vessel}$  curve is about 1.3  $\text{C}^{\circ}$  per minute.

## **Conclusion**

This paper has attempted to provide a clear distinction among the three deltas that are used in chemical engineering. Although they are obvious to the experienced engineer, they are often misapplied by young students.

## Acknowledgement

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## **Figure Captions**

- Figure 1- Heated or Cooled Agitated Vessel
- Figure 2 Temperature Profiles and Temperature Deltas during Cooling
- Figure 3- Using Time Delta for Heatup with Constant U and T<sub>steam</sub>





