The object of this column is to enhance our readers' collections of interesting and novel problems in chemical engineering. Problems of the type that can be used to motivate the student by presenting a particular principle in class, or in a new light, or that can be assigned as a novel home problem, are requested, as well as those that are more traditional in nature and that elucidate difficult concepts. Manuscripts should not exceed ten double-spaced pages if possible and should be accompanied by the originals of any figures or photographs. Please submit them to Professor James O. Wilkes (e-mail: wilkes@engin.umich.edu), Chemical Engineering Department, University of Michigan, Ann Arbor, MI 48109-2136.

NON-ADIABATIC CONTAINER FILLING AND EMPTYING

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All thermodynamics textbooks present container filling and container emptying (often called bottle filling and bottle emptying) as the simplest examples of unsteady-state, varying-inventory processes. If the process is adiabatic and the contents of the container are well mixed, then the differential mass and energy balances can be combined and integrated, leading to closed-form solutions. The classic problems are of the form:

Problem 1 • An evacuated, rigid, adiabatic container is connected to a compressed air line at a pressure of 738 kPa and a temperature of 22°C. The connecting valve is opened, and the air flows in until the container pressure is 738 kPa. What is the final temperature in the container?

Problem 2 • A rigid, adiabatic container contains air at 641 kPa and 29°C. Its valve is opened and it exhausts to the atmosphere at 86 kPa (at Salt Lake City, 1460 m above sea level). When the pressure in the container is the same as atmospheric pressure, what is the temperature in the container?

GENERAL THEORY FOR ADIABATIC FILLING AND EMPTYING

For a rigid container with flow of matter in or out, the energy balance on the contents, ignoring kinetic, gravitational, electrostatic, and magnetic energies,[1] is

$$d(mu)_{system} = h_{in} dm_{in} - h_{out} dm_{out} + dQ \qquad (1)$$

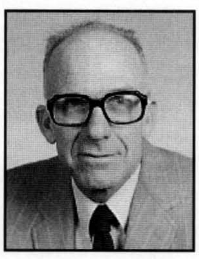
and the corresponding mass balance is

$$dm_{system} = dm_{in} - dm_{out} \qquad (2)$$

For a container filling from some reservoir (*e.g.*, the atmosphere into an evacuated container, or a large compressed-air or steam line into a container), we may assume perfect internal mixing and that h_{in} is a constant, combine Eqs. (1) and (2), and integrate to

$$(mu)_{system,final} - (mu)_{system,initial} = h_{in}(m_{final} - m_{initial}) + \Delta Q \qquad (3)$$

If the mixing is not perfect, then the specific properties shown in Eq. (3) and throughout this paper should be interpreted as mass-average values. For emptying (discharge, blowdown), the simple integration leading to Eq. (3) is not correct because the expansion work done by the fluid during the emptying process causes the temperature, and hence h_{out}, to decrease during the process. If one uses an average value of h_{out}, one can then use this integration.[2] If the material originally present in the system and flowing in or out is a



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perfect gas, we can substitute and change Eqs. (1) and (3) to

$$d\left(mC_V T\right)_{system} = C_p T_{in} dm_{in} - C_p T_{out} dm_{out} + dQ \tag{4}$$

For filling, we can integrate Eq. (4) to

$$\left(mC_V T\right)_{system,final} - \left(mC_V T\right)_{system,initial} = C_p T_{in}\left(m_{final} - m_{initial}\right) + \Delta Q \tag{5}$$

If $m_{initial}$ and dQ are both zero (initially empty container and adiabatic process), then for filling, Eq. (5) becomes

$$T_{system,final} = kT_{in} \tag{6}$$

If the container is not originally empty, but contains a gas with the same value of k as the gas that enters, $\Delta Q = 0$ and $T_{initial} = T_{in}$, then the solution is

$$T_{system,final} = kT_{in} - T_{initial}(k-1)\frac{m_{initial}}{m_{final}} \tag{7}$$

For adiabatic emptying, the perfect mixing assumption allows us to set the system temperature equal to the outflow temperature and integrate Eq. (4) to

$$\frac{T_{final}}{T_{initial}} = \left(\frac{m_{final}}{m_{initial}}\right)^{(k-1)} \tag{8}$$

Replacement of the m terms by their ideal-gas-law values produces

$$\frac{T_{final}}{T_{initial}} = \left(\frac{P_{final}}{P_{initial}}\right)^{\left(\frac{k-1}{k}\right)} \tag{9}$$

which is the relation for an isentropic expansion of an ideal gas.

PROBLEM SOLUTION

Using Eqs. (6) and (9), with the adiabatic assumption and the further assumption that air is an ideal gas with k = 1.40, we can solve Problems 1 and 2, finding

$$T_{system,final} = kT_{in} = (1.40)(295\,K) = 413\,K = 140°C$$

and

$$\frac{T_{final}}{T_{initial}} = \left(\frac{P_{final}}{P_{initial}}\right)^{\left(\frac{k-1}{k}\right)} = \left(\frac{86\text{ kpa}}{641\text{ kpa}}\right)^{\left(\frac{0.4}{1.4}\right)} = 0.563$$

$$T_{final} = 0.563\,T_{initial} = (0.563)(302\,K) = 170\,K = -103°C$$

But experimental results[3] do not agree, even approximately, with these simple theories. This disagreement is explained[3] as being due to significant heat transfer. This appears startling, because the filling and emptying experiments are normally finished in a few seconds. But, as shown below, it is correct.

General Theory for Non-Adiabatic filling • If we now allow for heat transfer, and replace dQ by $hA(T-T_{surroundings})dt$ and keep the ideal gas assumption, then Eq. (4) becomes

$$d\left(mC_V T\right)_{system} = C_p T_{in} dm_{in} - C_p T_{out} dm_{out} + hA\left(T_{system} - T_{surroundings}\right)dt \tag{10}$$

For filling, we drop the outflow term and rearrange to

$$\frac{d(mT)_{system}}{dt} = \dot{m}_{in} kT_{in} - \frac{hA}{C_V}\left(T_{system} - T_{surroundings}\right) \tag{11}$$

To save writing, we define $\alpha = hA/C_V$ and drop the subscript on T_{system}. If we assume a constant filling rate, we can replace the instantaneous system mass with

$$m = m_{initial} + \dot{m}_{in} t \tag{12}$$

and rearrange to

$$\left(m_{initial} + \dot{m}_{in} t\right)\frac{dT}{dt} = \dot{m}_{in}\left(kT_{in} - T\right) - \alpha\left(T - T_{surroundings}\right) \tag{13}$$

Separating variables, integrating from start to finish, and assuming that the $T_{surroundings}$ is constant and equal to the initial temperature of the gas in the container, we find

$$\frac{-T + \left(\frac{\dot{m}_{in}}{\dot{m}_{in} + \alpha}\right)kT_{in} + \left(\frac{\alpha}{\dot{m}_{in} + \alpha}\right)T_{surroundings}}{\left(\frac{\dot{m}_{in}}{\dot{m}_{in} + \alpha}\right)kT_{in} + \left(\frac{\alpha}{\dot{m}_{in} + \alpha} - 1\right)T_{surroundings}} = \left(\frac{m_{initial} + \dot{m}_{in} t}{m_{initial}}\right)^{-\left(1 + \frac{\alpha}{\dot{m}_{in}}\right)} \tag{14}$$

If, instead of assuming a constant inflow rate, we assume an inflow rate that declines linearly with time, we can write

$$m_{system} = m_{initial} + \int (a - bt)dt = m_{initial} + at - 0.5\,bt^2 \tag{15}$$

where a and b are data-fitting constants. Substituting this for m_{system} in Eq. (11) and rearranging, we find

$$\frac{dT}{dt} = \frac{(a - bt)(kT_{in} - T) - \alpha\left(T - T_{surroundings}\right)}{m_{initial} + at - 0.5bt^2} \tag{16}$$

which can be integrated numerically.

General Theory for Non-Adiabatic Emptying • For container emptying, Eq. (11) becomes

$$\frac{d(mT)_{system}}{dt} = -\dot{m}_{out} kT - \alpha\left(T - T_{surroundings}\right) \tag{17}$$

For an assumed constant flow rate, the equivalent of Eq. (13) is

$$\left(m_{\text{initial}} - \dot{m}_{\text{out}}t\right)\frac{dT}{dt} = -\dot{m}_{\text{out}}T(k-1) - \alpha\left(T - T_{\text{surroundings}}\right) \tag{18}$$

and the equivalent of Eq. (14) is

$$\frac{\left[-\dot{m}_{\text{out}}(k-1)-\alpha\right]T + \alpha T_{\text{surroundings}}}{\left[-\dot{m}_{\text{out}}(k-1)-\alpha\right]T_{\text{initial}} + \alpha T_{\text{surroundings}}} = \left(\frac{m_{\text{initial}} - \dot{m}_{\text{out}}t}{m_{\text{initial}}}\right)^{\left[(k-1)+\frac{\alpha}{\dot{m}_{\text{out}}}\right]} \tag{19}$$

For the assumed linearly decreasing mass flow rate out, the equivalent of Eq. (16) is

$$\frac{dT}{dt} = \frac{-(a-bt)(k-1)T - \alpha\left(T - T_{\text{surroundings}}\right)}{m_{\text{initial}} - at + 0.5bt^2} \tag{20}$$

which is also suitable for numerical integration.

EXPERIMENTAL TESTS

The experimental apparatus,[4] sketched in Figure 1, consisted of an ordinary 0.027 m^3 propane storage container, a pressure transducer, thermocouples, and a data logger. The container was evacuated, filled from a compressed air main, and then emptied to the atmosphere several times, with several sizes of thermocouples (see discussion of thermocouple measuring lag below), and with inlet and outlet flow restrictors, in some cases, to slow the flow. Figures 2 and 3 show the temperature measurements for typical filling and emptying experiments. The measured maximum and minimum temperatures are far from those computed above.

We can estimate the heat transfer coefficient between the

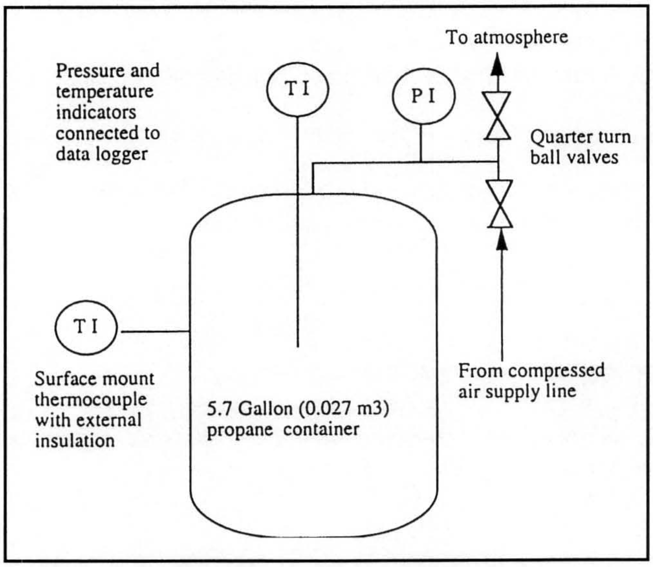

Figure 1. *Flow and instrumentation diagram of the experimental apparatus. The data logger records temperatures and pressures at 1/3-second intervals.*

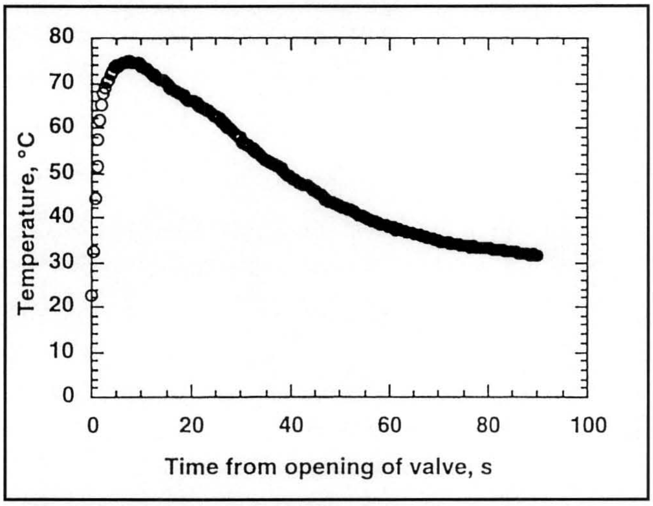

Figure 2. *Temperature-time plot for filling the container from the laboratory compressed air main at 738 kPa. The pressure reached that value in ≈ 5.3 s. The temperature rose from 22 to 74.5°C, reaching the peak at 6 s. The air inlet valve was closed at 5 s, and the pressure allowed to decrease as the air in the container cooled. The metal walls of the tank rose in temperature from 26 to 29.3°C. After the peak temperature, the gas cooled slowly toward room temperature. For the adiabatic assumption, the peak temperature, calculated in the text, was 140°C.*

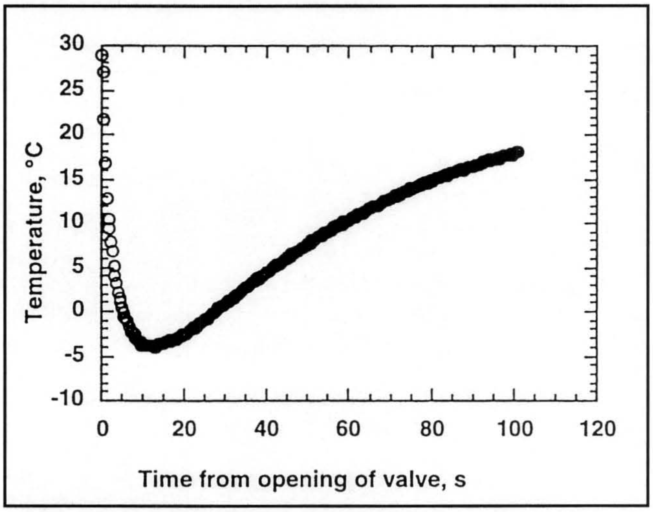

Figure 3. *Temperature-time plot for emptying the container to the atmosphere (at 86 kPa) from an initial pressure of 641 kPa. The pressure reached atmospheric in ≈ 1.7 s. The temperature fell from 29 to -4°C, reaching its minimum at 9.7 s. The metal walls of the tank fell in temperature from 28.8 to 27.5°C. After the minimum temperature, the gas warmed slowly toward room temperature with the exit valve open. For the adiabatic assumption, the minimum temperature, calculated in the text, was -103°C.*

air in the containers and the container walls if we assume that the thermocouple lag was small compared to 100 s and that in each process the gas underwent a step change in temperature and was then cooled or heated by simple convective heat transfer with a constant-temperature container wall. With these assumptions, the gas temperature is given by

$$\frac{T - T_{wall}}{T_{after\ step} - T_{wall}} = \exp\left(-\frac{hA}{mC}t\right) \tag{21}$$

suggesting that a plot of the ln of the temperature ratio at the left of Eq. (21) vs. t should form a straight line, from which h could be estimated. Figures 4 and 5 show such plots; from the slopes, one may infer the values of the heat-transfer coefficients. The choice of $T_{after\ step}$ is arbitrary, made to force the straight lines through 1.0 on the ordinate. Changing these values moves the curves up and down without changing their slopes.

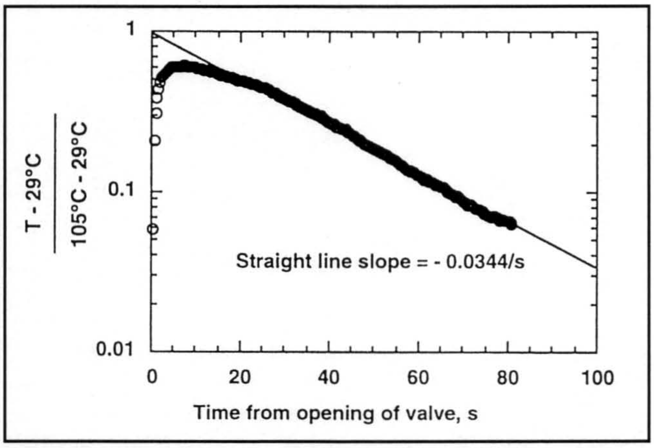

Figure 4. *Replot of temperature-time data from Figure 2, in the form suggested by Eq. (21).*

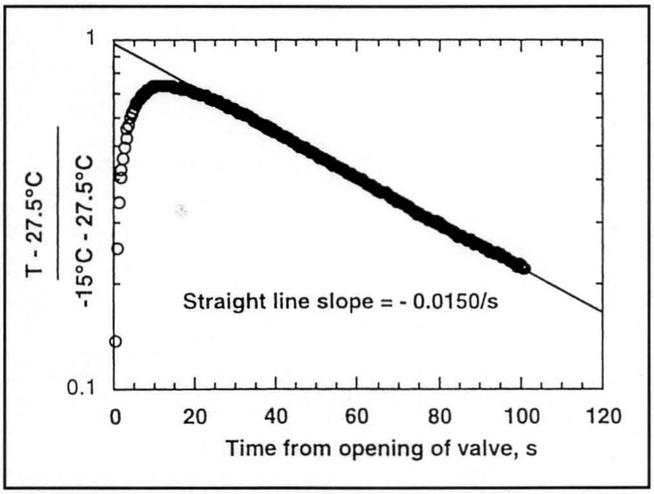

Figure 5. *Replot of temperature-time data from Figure 3 in the form suggested by Eq. (21).*

From these tests, one can estimate the heat-transfer coefficients. For example, for the filling test (Figures 2 and 4), with $C = C_V = 2.5R$

$$h = \frac{(166\,g)(2.5)(8.314)\left(\frac{J}{mol\,K}\right)\left(\frac{0.0344}{s}\right)}{0.390\,m^2}\frac{mol}{29\,g} = 10.49\frac{W}{m^2K}$$

and for emptying (Figures 3 and 5), with $C = C_p = 3.5\ R$

$$h = 0.91\frac{W}{m^2K}$$

The surprisingly large difference is largely due to the difference in air densities (due to differing pressures) for the two cases. The heat-transfer coefficients, estimated from a flat-wall natural convection correlation[5]

$$Nu = 0.0210(Gr\,Pr)^{0.4} \tag{22}$$

using average values of the gas density and the temperature differences, are 11.9 and 1.7 W/(m^{2}K). The first is close to the value calculated from the cooling curve and the second about twice the value calculated from the warming curve.

If we assume that the processes were practically two-step, with a quick adiabatic process followed by a slow transfer of heat to or from the walls of the container, then by energy balance, we can compute that

$$\Delta T_{container\ walls} = \frac{\left[mC\left(T_{adiabatic} - T_{final}\right)\right]_{gas\ in\ container}}{(mC)_{container\ walls}} \tag{23}$$

For the filling experiment, with $C = C_V$, the value are

$$\Delta T_{container\ walls} = \frac{\left\{182\,g\left[\frac{(2.5)(8.314)}{29}\frac{J}{gK}\right](140°C - 29°C)\right\}}{\left[(7.03\,kg)(0.46)\frac{kJ}{kg\,K}\right]} = 4.48°C$$

and the corresponding value for emptying, with $C = C_p$, is -0.94°C. The measured values are 3.3 and -1.3°C.

THERMOCOUPLE LAG

A major part of the difference between the steep parts of the temperature curves on Figures 2 and 4 and the values calculated from adiabatic behavior, or those computed by Eqs. (14), (16), (19), and (20), is due to thermocouple lag. This is normally characterized[6] in terms of the first-order time constant of the thermocouple. If we assume that the gas in the container undergoes a step increase or decrease in temperature, followed by a first-order decay toward the surrounding temperature, and that the thermocouple responds as described in Reference 6, then the equation for the thermocouple reading will be

$$\frac{dT_{thermocouple}}{dt} = b\left\{\left[T_{wall} + \left(T_{end\ of\ step} - T_{wall}\right)\exp(-at)\right] - T\right\} \quad (24)$$

where a and b are the time constants of the cooling or heating air in the container and of the thermocouple. The integrated form is

$$\frac{T_{thermocouple} - T_{wall}}{T_{end of step} - T_{wall}} = \frac{a}{b-a}\left[\exp(-at) - \exp(-bt)\right] \quad (25)$$

with the peak value of $T_{thermocouple}$ occurring at

$$t = \frac{\ln(b/a)}{b-a} \quad (26)$$

with maximum value

$$\left(\frac{T_{thermocouple} - T_{wall}}{T_{end of step} - T_{wall}}\right)_{maximum} = \left(\frac{a}{b}\right)^{\left(\frac{b}{b-a}\right)} \quad (27)$$

Figure 6 shows a comparison of the reported temperatures for two sizes of thermocouple for identical filling experiments. As expected, the smaller thermocouple reports a higher peak temperature and reaches it sooner. Table 1 shows the comparison of the time-to-peak reported T and the estimated value of $T_{end\ of\ step}$ calculated from Eqs. (26) and (27). The computed and observed times-to-peak reported temperature are in good agreement, but the computed maximum temperatures are far too high, indicating that after a few seconds, the two-first-order-processes-in-series model works well, but its extrapolation to t=0 does not. If the contained gas temperatures were not changing rapidly due to heat transfer, this thermocouple lag would pose no problem.

ESTIMATING MAXIMUM TEMPERATURES

To estimate the maximum temperatures from Eqs. (14), (16), (19), and (20), the mass flow rates were computed by

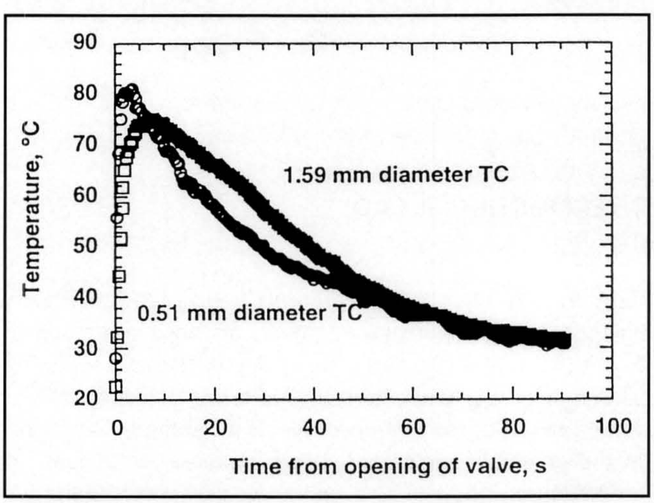

Figure 6. Reported temperatures for two identical filling experiments with different size thermocouples. The 0.51 -mm diameter thermocouple reached its peak reading at 3.3 s; the 1.59-mm diameter thermocouple reached its at 7.67 s.

TABLE 1
Applications of Eqs. (26) and (27) with the Time Constant of Cooling the Container Assumed = 0.034/s (See Figure 4)

	0.51-mm diameter Thermocouple	1.59-mm diameter Thermocouple
Reported time constant,[6] s	1/4 = 0.25	1/9 = 1.11
Observed time to peak reported T,s	3.3	7.67
Calculated time to peak T, by Eq. (26), s	3.2	9.3
Right-hand side of Eq. (27)	0.027	0.099
Calculated $T_{end\ of\ step}$ from Eq. (27), °C	2000	500

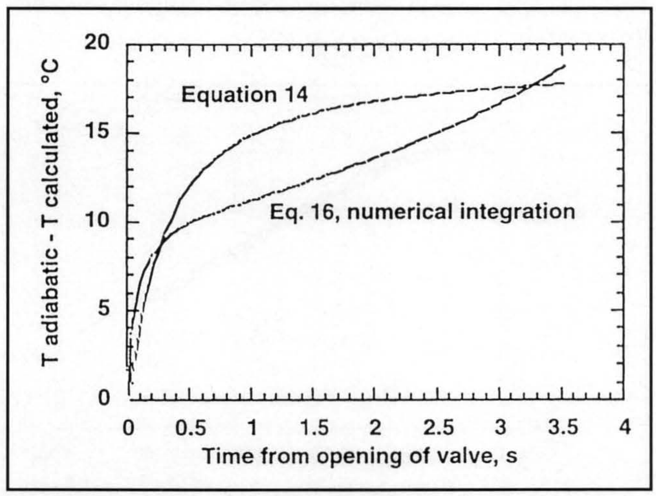

Figure 7. Computed departure of the tank temperature for tank filling from the calculated adiabatic temperature for the same conditions. Here, $m_{initial}$=3.5 g.

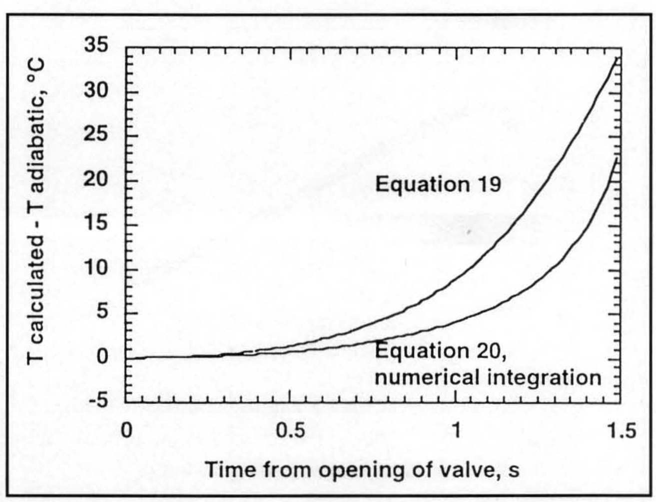

Figure 8. Computed departure of the tank temperature for tank emptying from the calculated adiabatic temperature for the same conditions.

differencing the calculated mass in the container at each 1/3-second measuring interval. This has the drawback that it relies on the thermocouple reading, which is known to lag the true temperature. With this caveat, the flow rates corresponding to Figures 2 and 3 were estimated as

$$\dot{m} = 100\frac{g}{s} - 28.6\frac{g}{s^2}t; \quad 0 \le t \le 3.5s$$

and

$$\dot{m} = 239\frac{g}{s} - 171\frac{g}{s^2}t; \quad 0 \le t \le 1.5s$$

For both filling and emptying, the heat-transfer coefficient was estimated from Eq. (22) and assumed constant. At the average density and temperature difference between wall and gas, the estimated values were 8.9 and 9.0 $W/(m^2K)$ for filling and emptying. Figures 7 and 8 show the calculated departures from the corresponding adiabatic solutions (Eqs. 7 and 8). From them we see that in both cases the major departure occurs at the boundary of the process at which the mass of air in the container is least (the start for filling, the finish for emptying); this is the natural consequence of dividing a calculated heat flow that is assumed independent of the mass by a small mass rather than a large one. Because of the strength of the assumptions and the thermocouple lag problem, these figures should be seen as order-of-magnitude. Nonetheless, they make clear that even for these fast processes, with plausible heat-transfer coefficients, the calculated temperatures are substantially different from the computed adiabatic temperatures.

APPLICATION TO LARGER TANKS

Equations (14) and (19) show that for the constant mass-flow-rate in or out simplification, and for $T_{in}=T_{initial}=T_{surroundings}$, the T-t behavior depends only on the two dimensionless groups m/m_o and $\alpha/\dot{m}$. Thus the experimental results shown here should also be observed in any container for which these parameters have the same values. The first can take on any value, but the second is a function of container geometry. If the initial conditions in the container and the reservoir conditions for filling and emptying are the same for two tanks, then $\dot{m}$ should be proportional to the cross-sectional area of the inlet pipe. If the heat-transfer coefficient does not change, then α is proportional to the surface area of the container. If the ratio of the inlet pipe cross-sectional area to the surface area of the container does not change, then the second of these dimensionless groups should also not change (or change much with changes in the heat-transfer coefficient). Thus, while the experiments reported here were all performed in a 0.027 m^3 container, they should be directly applicable to larger tanks with the same dimension ratios.

CONCLUSIONS

The adiabatic, ideal-gas container filling and emptying solutions have a traditional place in thermodynamics textbooks because they are the simplest unsteady-state, varying-inventory problems that can be solved in closed form. In practice, it is impossible to conduct these processes without heat-transfer-producing gas temperatures far different from the adiabatic flow solutions, mostly because while the amount of heat transferred is small, the mass of gas into which it is transferred is also small. The effects of such heat transfer on the temperature-time behavior of such processes can be estimated with at least order-of-magnitude accuracy.

Thermocouple lag adds to the effect of the heat transfer, further increasing the difference between the observed temperature extremes and the values calculated for adiabatic filling and emptying.

A different version of this problem and experiment appeared while this paper was in press.[7]

NOMENCLATURE

A	area
a	time constant of cooling or heating air in the container
a,b	constants in data-fitting equations
b	time constant of thermocouple
C	heat capacity
C_p	heat capacity at constant pressure
C_V	heat capacity at constant volume
Gr	Grashof Number
h	heat-transfer coefficient
h	specific enthalpy
k	C_p/C_V
m	mass
$\dot{m}$	mass flow rate
Nu	Nusselt number
P	pressure
Pr	Prandtl number
Q	heat quantity
R	universal gas constant
T	temperature
t	time
u	specific internal energy
α	hA/C_V

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