At this point in the course, we have covered the topics of thermodynamics and chemical kinetics— which are both fairly distinct topics (i.e., one is not derived from the other). Our next item of business will be to couple these two topics together to predict the performance of reactors.

In a sense, what we will do here is analogous to one of the first topics introduced in heat transfer, e.g., the "lumped capacity solution" for transient cooling of an object. To review, say we have a control mass subject to transient heat transfer. The first law, written on a rate basis, would be

$$\frac{dU}{dt} = _Q$$

We can, however, develop a more descriptive prediction of the system by making some assumptions, in particular:

1. The temperature of the system is uniform, at least at any point in time, i.e., near any position of the system.

    $$\frac{dU}{dt} = _Q$$

2. The rate of heat transfer is given by the convective rate law: $$_Q = ha(T_s - T_1)$$

Putting these two assumptions together gives the familiar first-order cooling law,

$$c_v V \frac{dT}{dt} = ha(A)(T_s - T_1)$$

which we can solve easily for the temperature as a function of time.

What was the rationale for assuming that the temperature was uniform throughout the system? You might recall that this assumption implies that the resistance to heat transfer within the system is significantly smaller than the resistance to heat transfer from the system to the environment. This assumption is analogous to the assumption of a well-stirred reactor.

We want to something similar here— except expanded to include

1. **The Constant Volume, Stirred Reactor**

Say we have a control mass with a fixed volume, within which a chemical reaction is progressing. This could represent, for example, a cylinder at the top of the compression stroke, immediately following ignition. We want to predict the rate at which the total, chemical, temperature and pressure of the system changes. We can define a control volume, within which we have a control mass with a fixed volume, within which the temperature is uniform throughout the system.

As was the case with the Biot number, there is a dimensionless number

$$\frac{\text{constant volume, stirred reactor}}{\text{well-stirred reactor}}$$

which we will define as the well-stirred ratio (or well-mixed ratio).

We are assuming that the well-stirred assumption is valid.

The first law for this system is not different than that already presented here, and the assumption of uniform temperature throughout the system still needs to be made, but there is another new aspect to this new system: the rate of the reaction. In the simple heat transfer problem, the rate of the reaction is presumed to be zero. The heat transfer coefficient, the fluid temperature, and the fluid properties are the same for every point in the control volume. The distinction here is that the reaction is presumed to be non-zero. The heat transfer coefficient and the fluid properties may vary throughout the control volume, but the reaction is still presumed to be non-zero.

We want to something similar here— except expanded to include

1. **The Constant Volume, Stirred Reactor**

Say we have a control mass with a fixed volume, within which a chemical reaction is progressing. This could represent, for example, a cylinder at the top of the compression stroke, immediately following ignition. We want to predict the rate at which the fuel, oxidizer, temperature and pressure change in the system.

The first law for this system is no different than that already presented,

$$\frac{dU}{dt} = _Q$$

Notethat the heat transfer _Q is the heat transferred across the boundary of the system (by a temperature gradient) — it is not the heat released by combustion. The effect of the heat due to combustion is contained within the _Q term, i.e., the change in chemical internal energy. Redistribution to complete the solution would be valid provided that the

$$\frac{\text{fuel}}{\text{oxidizer}}$$
To elaborate further, consider the fact that our system at any point in time consists of a mixture of $N$ species, so that

$$U = \sum_{i=1}^{N} u_i N_i$$

where $N_i$ is the molen number of species $i$ and $u_i$ is the internal energy per unit mole of $i$.

So

$$dU = \sum_{i=1}^{N} u_i dN_i$$

and

$$dN_i = \frac{dN}{V} = \frac{dN_i}{\nu_i}$$

where $\nu_i$ is the reaction rate of species $i$, with units of kmol/m$^3$s.

Now, putting everything back into the first law, Eq. (3), we get

$$\frac{d}{dt} \left( \sum_{i=1}^{N} N_i u_i \right) = \sum_{i=1}^{N} \nu_i \frac{dN_i}{dt}$$

In general, change with time.

Let $A$ be the molen number of moles in the system and $c_v$ be the molar heat capacity of the system.

$$\frac{d}{dt} (A c_v) = \sum_{i=1}^{N} \nu_i \frac{dN_i}{dt}$$

where $A$ is the total number of moles in the system and $c_v$ is the total molar heat capacity of the system.

Now, putting everything back into the first law, Eq. (2), we get

$$\frac{d}{dt} (A c_v) = \sum_{i=1}^{N} \nu_i \frac{dN_i}{dt}$$

In general, change with time.

The quantity $\nu_i$ is the reaction rate of species $i$, with units of kmol/m$^3$s.

In the previous notes I used the symbol $R_i$ to denote this quantity. Here I'm being consistent with Turn's. We would predict $\nu_i$ from kinetic theory—either using the law of mass action applied to the detailed chemical mechanism of the reaction, or (as will be done here) by using a global reaction mechanism and approximating it by the law of mass action applied to the global reaction. The global reaction is the sum of all the reactions that make up the global reaction.

In the previous notes I used the symbol $A_0$ to denote the total number of moles of $i$.

The total molar heat capacity of the system is the sum of the molar heat capacities of all the species.

$$c_v = \sum_{i=1}^{N} c_{v,i}$$

where $c_{v,i}$ is the molar heat capacity of species $i$.

Now

$$\frac{d}{dt} (A c_v) = \sum_{i=1}^{N} \nu_i \frac{dN_i}{dt}$$

In general, change with time.

The specific heat of a species in a mole basis is the total molar heat capacity of the species divided by the number of moles of the species. Both of these quantities will change with time.

$$c_v = \frac{A c_v}{A} = \sum_{i=1}^{N} c_{v,i}$$

where $A$ is the total number of moles in the system and $c_v$ is the molar heat capacity of the system.

Now

$$\frac{d}{dt} (A c_v) = \sum_{i=1}^{N} \nu_i \frac{dN_i}{dt}$$

In general, change with time.
Numerical Solution

Example

result. The last lines use the facts that

\[ y' = \frac{dy}{dx} \]

and by assuming moles are all equal, the last line

\[ \Delta V = \frac{dV}{dx} \]

provide a coupled set of nonlinear first-order ordinary differential equations.

Equations (15), for the temperature, and (10), for the mole numbers, are:

\[ \frac{dN_i}{dt} = \sum_j \left( \Delta H_{ij} \right) \frac{dy_j}{dt} \]

result. From the mole balance of the reaction, the reaction rates would be

\[ CH_4 + O_2 \rightarrow CO_2 + H_2O \]

so, for this case:

\[ 0 = \frac{dQ}{dt} = \Delta H_T \sum_i \Delta N_i \]

The result is:

\[ \Delta H_T \sum_i \Delta N_i = \Delta H_T \sum_i \Delta N_i \]

The last line uses the same and consistent, i.e., \( \sum_i \Delta N_i \) is equaled to zero. This is because the change in mass is constant and in 1 sec.

The system is closed, then

\[ \frac{dQ}{dt} = \Delta H_T \sum_i \Delta N_i \]

Putting all of the above into Eq. (9), and using the fact that \( \Delta H_T \) is the overall enthalpy of formation of the fuel, this becomes

\[ \Delta H_T \sum_i \Delta N_i = \Delta H_T \sum_i \Delta N_i \]

Then

\[ \Delta H_T \sum_i \Delta N_i = \frac{1}{16} \Delta H_T \sum_i \Delta N_i \]

the overall result is:

\[ \Delta H_T \sum_i \Delta N_i = \Delta H_T \sum_i \Delta N_i \]
\[ \frac{d}{dt} P = \frac{d}{dt} L \left( \frac{\Delta H}{\Delta n} \right) - \frac{d}{dt} N \]

Integrate this to get

\[ \frac{dP}{dN} = \frac{dL}{dN} \left( \frac{\Delta H}{\Delta n} \right) \]

Note that in our first example, \( \Delta A/N = \text{const.} \) and put everything into Eq. (18)

\[ \frac{d}{dt} P = \frac{d}{dt} L \left( \frac{\Delta H}{\Delta n} \right) - \frac{d}{dt} N \]

Integrate this to get

\[ \frac{dP}{dN} = \frac{dL}{dN} \left( \frac{\Delta H}{\Delta n} \right) \]

Now use the information for the mole numbers in the reaction rate for each component to close the system. To know the volume for the above equation, and you should be able to see the effect. So let's solve for \( \Delta A/N = \text{const.} \) and add the two equations – which results in the reaction term canceling and add the two equations – which results in the reaction term canceling.

\[ \frac{dL}{dN} \left( \frac{\Delta H}{\Delta n} \right) = \Delta A/N - \left( \frac{\Delta H}{\Delta n} \right) \]

Finally, we get a formula relating the fuel mole fraction to the total fuel.

\[ \frac{dL}{dN} \left( \frac{\Delta H}{\Delta n} \right) = \Delta A/N - \left( \frac{\Delta H}{\Delta n} \right) \]

Integrate this to get

\[ \frac{dP}{dN} = \frac{dL}{dN} \left( \frac{\Delta H}{\Delta n} \right) \]

For every mole of fuel, there's a mole of CO on the product side, so the net consumption in O is 0. For 2 moles, you might think from the reactants alone (3 moles of O), but this is not the case.

\[ \text{Apply to the initial conditions (or condition of the problem) and integrate where subscript zero denotes the initial state.} \]

Now, write Eq. (10) for N = N_0.

\[ \int_0^N \frac{d\tau}{\tau} = 0^{\text{co}}N = (1)^N \]

Integrate this to get

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Themassis

\[ m = \frac{m_1 V_{RT}}{P_1} \]

\[ T_1 + \frac{3}{2} = \frac{(MW_R)}{P_1 V_{RT}} \]

The total number of moles initially in the system is

\[ N = \frac{m}{MW} \]

and the initial mole numbers (from the reactant composition) are

\[ N_F;_0 = N_{1+3} \times 4.76; N_{2+0} = 3 \times N_{1+3} \times 4.76 \]

MatLab Solution

Equation (21) requires numerical integration to solve. Some sophisticated numerical methods are required to perform this integration, because the equation is mathematically stiff. Stiffness, for our purposes, basically means that the value of the derivative (i.e., the rate of temperature change) can change by a large amount over a very small time interval. Physically, this is what we expect out of a thermal explosion. Physically meaningful methods are required to perform this integration.

I used a black-box numerical integrator in MatLab to solve this equation. To use this, you need to write a few lines of code (in an m-file). I used the following code as a MatLab function. Basically, the code performs the calculations needed to evaluate Eq. (21) for a given initial \( T_1 \) and \( P_1 \), and a specified current temperature \( T \) (in the code).

\[
\text{function } dydt = \text{stir}(t, y, tempinit, pinit) \\
\text{lhv} = 50.e3; cv = 0.8; mass = pinit * 101.32 * 0.01 * 28.1 / (8.314 * tempinit); nmoles0 = mass / 28.1; nf0 = nmoles0 / (1 + 3 * 4.76); noxmoles0 = 3 * nf0; m = -0.3; n = 1.3; a = 1.3e8 * (1000)^(1-m-n); ta = 24358.; temp = y(1); \\
fmoles = nmoles0 - mass * cv * (temp - tempinit) / lhv; if nf <= 0 \\
dydt = [0.]; \\
else \\
noxmoles = noxmoles0 - 2 * (fmoles - nf0); dydt = [a * lhv * exp(-ta / temp) * fmoles^m * noxmoles^n / mass / cv]; end; \\
end; \\
\]

I then call the integrator in the MatLab command window:

```
[t, y] = ode23tb(@stir, [0, 1.5], [1000], [], 1000, 1); 
plot(t, y(:, 1))
```

Shown in Fig. 1 is a plot of \( T \) vs. time for conditions of \( T_1 = 1000 \) K, \( P_1 = 1 \) atm. Notice how the rate of temperature increase changes significantly over the timespan of 1.5 seconds. The point of a `thermal explosion' is obvious from the plot. The final temperature of the system, at the moment that the derivative of \( T \) becomes infinite, is what we would predict from a constant \( c_v \) analysis and likely overestimate the actual temperature. The analysis, however, does give us a method of estimating the time it takes the reaction to be complete (a given initial \( T_1 \), and \( P_1 \), and a specified current temperature \( T \)).

The Well-Stirred, Open Reactor

contains in the reactor. An open reactor, on the other hand, is not considered a reactor with perfect mixing. Overall mass conservation then

\[ \sum_{i \in \text{inlet}} m_i = \sum_{i \in \text{outlet}} m_i \]

enters a well-stirred reactor, assumption that the reactor is perfectly mixed, and some simplification, allows the overall mass conservation equation to be written as:

\[ m_1 V_{RT} = \frac{m_1 V_{RT}}{P_1} \]

The initial mole numbers (from the reactant composition) are

\[ N_F;_0 = N_{1+3} \times 4.76; N_{2+0} = 3 \times N_{1+3} \times 4.76 \]

The mass is

\[ \frac{M_W}{A_d} \frac{dN}{dA_d} \]

\[ \frac{M_W}{A_d} \frac{dN}{dA_d} = \frac{M_W}{A_d} = \frac{M_W}{A_d} \]

\[ \frac{A_d}{M_W} = \frac{A_d}{M_W} \]

\[ \frac{A_d}{M_W} \frac{dA_d}{dM_W} = \frac{A_d}{M_W} = \frac{A_d}{M_W} \]
Figure 1: Constant-volume reactor predictions

The local flame temperature for mass fraction to be consistent with
counter-current within the reactor – and it is not obvious how we would
be written for all of the species taking place in the reactor.

\[ \frac{\partial \rho}{\partial t} = \nabla \cdot (\rho \mathbf{v}) \]
The reaction appears when we consider the

\[ \frac{\partial \rho}{\partial t} = \nabla \cdot (\rho \mathbf{v}) \]

Notice then the outlet reaction – which is ending place inside the

\[ \frac{\partial \Psi}{\partial t} = \nabla \cdot (\rho \mathbf{v}) \]

When negligible KE and no work transfer, the first law for the open

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NOTE: I am now using Turn's notation for mass fraction – to be consistent with

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You can now see that, in order to introduce the counter-current, we may

\[ \frac{\partial \rho}{\partial t} = \nabla \cdot (\rho \mathbf{v}) \]

The reaction: $\frac{\partial \rho}{\partial t} = \nabla \cdot (\rho \mathbf{v})$ can

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When negligible KE and no work transfer, the first law for the open

\[ \frac{\partial \Psi}{\partial t} = \nabla \cdot (\rho \mathbf{v}) \]
The inlet conditions: temperature and mass fractions at the inlet.

Now write Eq. (24) for fuel and for \( O_2 \) in the reactor.

\[
\left( \frac{\mu_2}{\mu_1} \right) \mu = \Lambda_{2,1} \Omega_2 S_{2,1}
\]

Now assume that the reactor is adiabatic, and put the above relations into the first law and solve for \( L \).
The `dependent' variable of this problem is typically the reactor fuel mass fraction $Y_F$, and a typical problem would be, for a given set of conditions 1-3 in the above list, to solve the equations for $Y_F$ as a function of $m$. This is a difficult numerical problem, due to the nonlinearity of the equations.

The trend we would expect to see is that as $m$ increases, so does $Y_F$ (simply because as we force more mass through the reactor, the reaction has less time to consume all the fuel and some unburnt fuel will appear at the exit. For $m$ greater than a certain critical value, the equations would admit no solution for $Y_F$, which physically would correspond to the reaction blowing out.

A more realistic way to approach the problem is to make $m$ the dependent variable, and solve for it as a function of $Y_F$. Note that we can do this explicitly: $m$ only appears in the first equation in the above set, and it appears linearly. We know the possible range for $Y_F$: $0 < Y_F < 1$. Suppose $Y_F$ were a function of $m$. Note that we can do this挥发的满出点, and solve for $Y_F$ as a function of $m$. For each value of $m$, two possible values of $Y_F$ appear. Only the values of $Y_F$ that lie below the dotted line are physically realiable. For each $Y_F$, the mass flow rate at this mass fraction is a function of $m$. The blowout condition occurs at the maximum value of $m$ at this mass fraction. The blowout condition occurs at the maximum value of $m$, and this mass fraction is a function of $m$. Only the values of $Y_F$ that lie below the dotted line are physically realiable. For each $Y_F$, the mass flow rate at this mass fraction is a function of $m$. The blowout condition occurs at the maximum value of $m$ at this mass fraction.

Figure 2: Open system predictions

As an example, for a propane/air system, with $\phi = 2$, $V = 0.1$ m$^3$, and $P = 1$ atm, was examined. From Table 2, the global parameters

\begin{align*}
\phi &= 1.5 \\
\frac{1}{2} &= \frac{d}{2}
\end{align*}

were used. Other properties are

\begin{align*}
s &= \frac{1}{2} (u_1 + u_2) (1 + \frac{1}{2} a_2^2) \\
T &= a_2^2 (1 + \frac{1}{2} a_2^2) \\
\psi &= \frac{\sqrt{a}}{2} \\
\psi &= \frac{\sqrt{a}}{2}
\end{align*}

are