Example - Reversible Exothermic Reaction in PBR

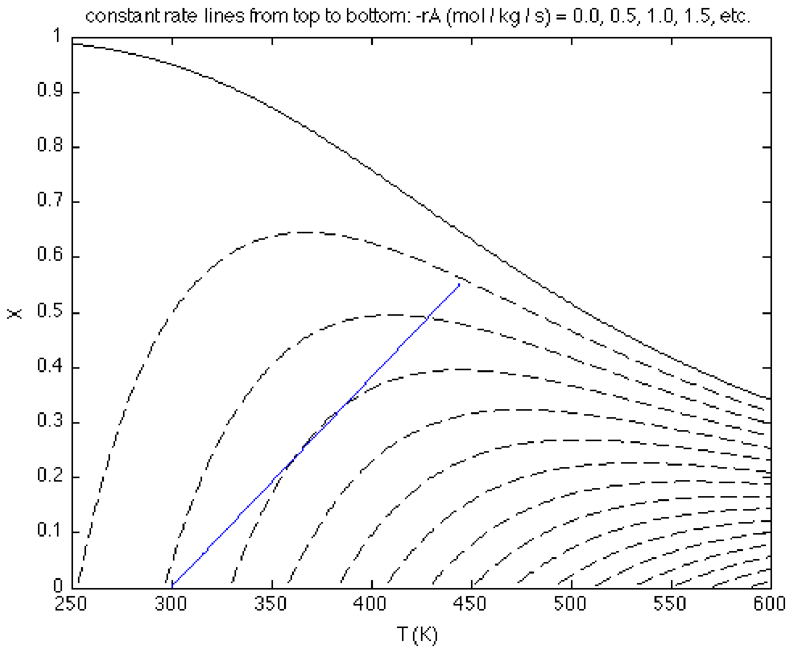
R. K. Herz <herz@ucsd.edu> 2011

Section 11.5 of H. Scott Fogler's "Essentials of Chemical Reaction Engineering" (2011) shows conversion vs. T plots for reversible exothermic reactions. However his plots do not show constant rates lines other than the zero-rate equilibrium line. A plot with constant rate lines is shown here.

Consider the reversible reaction A = B. The reaction is catalyzed by pellets of a porous solid catalyst, also called a heterogeneous catalyst. Here assume that the following parameters are constant.

$\Delta H = -18$ kJ/mol $C_p = 2$ kJ/kg/K $\rho = 1.2$ kg/liter

Below is a conversion vs. T plot for this reaction. The solid black and dashed black lines are lines of X_A at constant net forward rate vs. T. The net forward rate = $(-r_A) = k_f C_A - k_b C_B$ for example for the case where the reactions are first-order. The solid black line is a plot of the conversion at equilibrium vs. T where $(-r_A) = 0$, also called the equilibrium line.



The diagonal blue line is the "operating line" of an adiabatic PBR or PFR with an inlet temperature of 300 K, a total catalyst weight of 155 kg, and a final conversion of 0.55 for the following parameter values:

$v_0 = 10$ liter/s $C_{A0} = 35$ mol/liter $C_{B0} = 0$ mol/liter

Other types of reactors would have different operating lines, e.g., an isothermal reactor, shell-and-tube heat exchange reactor, and multi-stage adiabatic reactors.

The operating line for an adiabatic reactor can be obtained from the equation for the "adiabatic temperature rise" of a reaction. This equation can be obtained from the component and energy balances for an adiabatic PFR.

Here the equation is shown for constant parameter values:

$$T = T_0 + \left[\frac{(-\Delta H) C_{A0}}{\rho C_p}\right] X_A$$

where $T = T_0$ at $X_A = 0$. Rearranging to plot on the X vs. T plot,

$$X_A = (T - T_0)\left[\frac{\rho C_p}{(-\Delta H) C_{A0}}\right]$$

Let's say you have a problem where you have a plot like this, and know the slope of the operating line, the inlet temperature, and the final conversion. You do not know the weight of catalyst in the reactor.

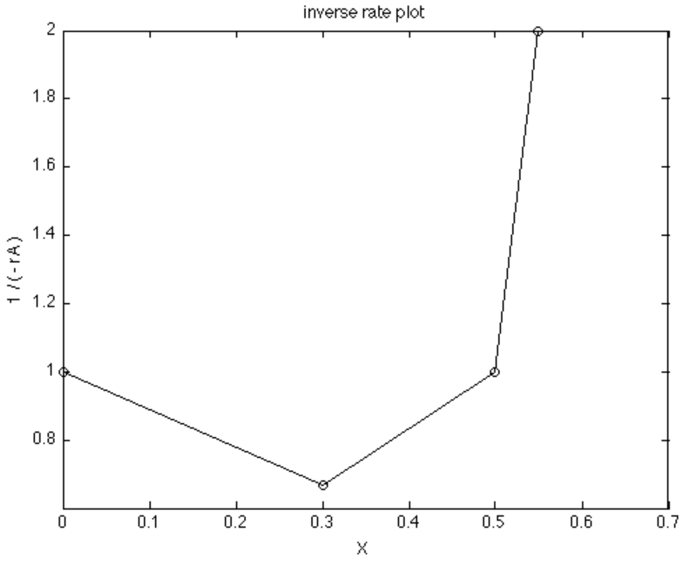
You can estimate the weight of catalyst by using an inverse rate plot, also known as a Levenspiel plot.

$$\frac{dF_A}{dW} = r_A \quad ; \quad \frac{dX_A}{dW} = \frac{-r_A}{F_{A0}} \quad ; \quad \frac{dX_A}{-r_A} = \frac{dW}{F_{A0}}$$

For the blue line above, estimate the following points:
(X=0, $-r_A$=1.0), (0.3, 1.5), (0.5, 1.0), (0.55, 0.5)

Then make an inverse rate plot using these points by plotting $1/(-r_A)$ vs. X.

Using the trapezoid method, the total area under the curve = W/F_{A0} = 0.492 (kg-s/mol). F_{A0} = 350. This gives W = 172 kg vs. the actual 155 kg.



MATLAB LISTING for X vs. T plot

```
% reversible reaction
% lines of constant net forward rate
% and adiabatic reactor operating line
clear all
fprintf('-------------------------------- \n') % run separator
```

```
CA0 = 35; % mol/liter
kf300 = 0.0300; % liter/kg/s
kb300 = 0.00157; % liter/kg/s
Ef = 10; % kJ/mol
Eb = 28; % kJ/mol
R = 8.314472e-3; % (kJ/mol/K), ideal gas constant
T = 250:600; % K
kf = kf300*exp((-Ef/R)*(1./T - 1/300));
kb = kb300*exp((-Eb/R)*(1./T - 1/300));
K = kf./kb;
% plot equilibrium line
xeq = K./(1+K);
plot(T,xeq,'k')
axis([min(T) max(T) 0 1])
hold on
% add constant rate lines
rnet = 0.5:0.5:12;
[r c] = size(rnet);
for i = 1:c
    x = xeq .* (1 - (rnet(i)./(kf*CA0)));
    plot(T,x,'k--')
end
title('constant rate lines, top to bottom: -rA (mol/kg/s) = 0.0, 0.5, 1.0, 1.5, etc.')
ylabel('X')
xlabel('T (K)')
% now add integration section
% to plot adiabatic reactor operating line & get catalyst weight
% CLEAR ARRAYS ABOVE
clear i x w T kf kb
delH = Ef - Eb; % kJ/mol
Cp = 2; % kJ/kg/K
rho = 1.2; % kg/liter
% CA0 must be same as value above for x vs. T plot
v0 = 10; % liter/s
T0 = 300; % K
i = 1;
% initial x, w, T for current catalyst bed
% you can start at values from the end of preceding catalyst beds
x(i) = 0.0;
w(i) = 0;
T(i) = T0;
dw = 0.1;
xfinal = 0.55;
% Here use simple Euler's method of numerical integration
% to get catalyst weight and draw operating line.
% By hand, draw operating line and estimate weight with inverse rate plot
% (Levenspiel plot).
while x(i) < xfinal % *** WARNING - MAY HANG IF HITS EQUIL LINE ***
    T(i) = T0 + (x(i)-x(1)) * (-delH)*CA0/rho/Cp;
    kf = kf300*exp((-Ef/R)*(1./T(i) - 1/300));
    kb = kb300*exp((-Eb/R)*(1./T(i) - 1/300));
    dxdw = (1/v0)*(kf*(1-x(i)) - kb*x(i));
    if (dxdw < 1e-3*kf/v0)
        fprintf('WARNING: TRYING TO INTEGRATE TO/PAST EQUIL LINE! \n')
        break
    end
    x(i+1) = x(i) + dxdw * dw;
    T(i+1) = T0 + (x(i)-x(1)) * (-delH)*CA0/rho/Cp;
    w(i+1) = w(i) + dw;
    i = i+1;
end
Tin = T(1)
Xin = x(1)
Wend = w(end)
Xend = max(x)
Tend = T(end)
% add reactor operating line to plot
plot(T,x)
hold off
```