CBE 40445

10/19/20

CONTINUED DISCUSSION OF "HEAT EFFECTS" IN CHEMICAL REACTORS

WE CONSIDER REACTIONS CAN HAVE SIGNIFICANT HEAT'S OF REACTION

- EXOTHERMIC
  - MAY NEED TO COOL FOR CONTROL & SAFETY
- ENDOTHERMIC
  - HEAT TO KEEP REACTION GOING HAS TO COME FROM SOMEWHERE

ANALYSIS WILL INVOLVE ONE OR MORE COMPONENT MASS BALANCES, WITH TEMPERATURE EFFECT ON KINETICS INCLUDED

BATCH

$$r = k C_A$$

$$= A \exp\left(-\frac{E_a}{RT}\right) C_A$$

$$\frac{dC_A}{dt} = A \exp\left(\frac{-E_a}{RT}\right) C_A$$

MASS

$$\frac{df_A}{dt} = k\,(1 - f_A)$$

ENERGY

HEAT EMMITED BY REACTION

$$U A_H (T^* - T) = \Delta H_r \dot{m}_A \frac{df_A}{dt} + \left(\dot{m}_A (1 - f_A) C_{pA} + \dot{m}_A f_A C_{pM}\right) \frac{dT}{dt}$$

HEAT REMOVED

" $\dot{Q}$ "

HEAT ABSORBED BY FLUIDS

SOLVE SIMULTANEOUSLY

$$\frac{df_A}{dt} = A \exp\left(\frac{-E_a}{RT}\right)(1-f_A)$$

$$\frac{dT}{dt} = \frac{UA_H(T^* - T) - \Delta H_r n_A^\circ A \exp\left(\frac{-E_a}{RT}\right)(1-f_A)}{n_A^\circ(1-f_A)C_{pA} + n_A^\circ f_A C_{pM}}$$

COULD ASK ONE OF THREE QUESTIONS

1) WHAT ARE CONCENTRATION AND TEMPERATURE AS A FUNCTION OF TIME IF ADIABATIC?

REACTION IN WATER AS SOLVENT: $\frac{1 \text{ MOLE}}{\text{kg}} \times \frac{50 \text{ kJ}}{\text{MOLE}} \times \frac{\text{kg K}}{4.184 \text{ kJ}} = 12 \text{ K}$

REACTION AT 1 BAR $\frac{1 \text{ MOLE}}{24 \ell} \times \frac{50 \text{ kJ}}{\text{MOLE}} \times \frac{900 \ell}{\text{kg}} \times \frac{\text{MOLE K}}{29 \text{ J}} \times \frac{29 \text{ g}}{\text{MOLE}}$

$= 1875 \text{ K}$

SOLVENT USED AS A HEAT DILUENT

GAS REACTIONS NEED SUBSTANTIAL COOLING

2. FOR "FIXED" COOLING, WHAT ARE $c(t)$ + $T(t)$

$$U_A = 1000 \frac{KW}{K\,m^2}$$

$$A_A = N\ m^2$$

$$T^* = \text{CONST}$$

3. WHAT COOLING IS NECESSARY TO KEEP REACTION ISOTHERMAL

SOLVE $$\frac{df_A}{dt} = A \exp\left(\frac{-E_a}{RT}\right)(1 - f_A)$$

USE $f_A(t)$ IN

$$\frac{UA_H (T^* - T) - \Delta H_r n_A^\circ \frac{df_A}{dt}}{n_A^\circ (1 - f_A) C_{pA} + n_A^\circ f_A C_{pM}}$$

$$T^*(t) = \frac{\Delta H_r n_A^\circ \frac{d f_A(t)}{dt}}{U A_H}$$

EX: 9.3.3

$A + B \rightarrow C$

BATCH REACTOR

REACTOR WALL IS AT CONST. T.

WE WILL NEED TO SOLVE ENERGY + MASS BALANCES SIMULTANEOUSLY...

$C_A^0 = .5$ MOL/L

$C_B^0 = .6$ MOL/L

$C_{P_A} = C_{P_B} = 65$ J/MOLE-K

$C_{P_C} = 150$ J/MOL-K

$N_A^0 = 100$ MOL

$\Delta H_R = -15$ KJ/MOL

$UA_H = 50$ J/S-K

$$k = 5 \times 10^3 \exp\left[\frac{20000 \text{ J/MOL}}{R_G}\left(\frac{1}{300} - \frac{1}{T}\right)\right] \frac{L}{\text{MOL-S}}$$

$$r = k C_A C_B$$

MASS BALANCE

$$\frac{df_A}{dt} = k C_A^{\circ} (1 - f_A)(1.2 - f_A)$$

ENERGY BALANCE

$$UA_H (T^* - T) = \Delta H_r m_A^{\circ} \frac{df_A}{dt} +$$

$$\left[m_A^{\circ}(1 - f_A) C_{pA} + m_A^{\circ}(1.2 - f_A) C_{pB} + m_A^{\circ} f_A C_{pC} \right] \frac{dT}{dt}$$

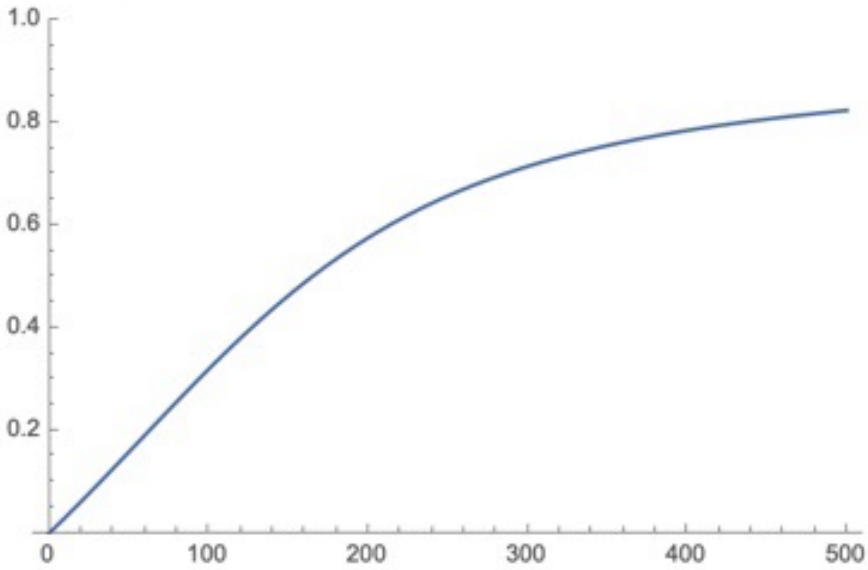
WE CAN ARRANGE:

$$\frac{df_A}{dt} = k(T) C_A^{\circ} (1 - f_A)(1.2 - f_A)$$

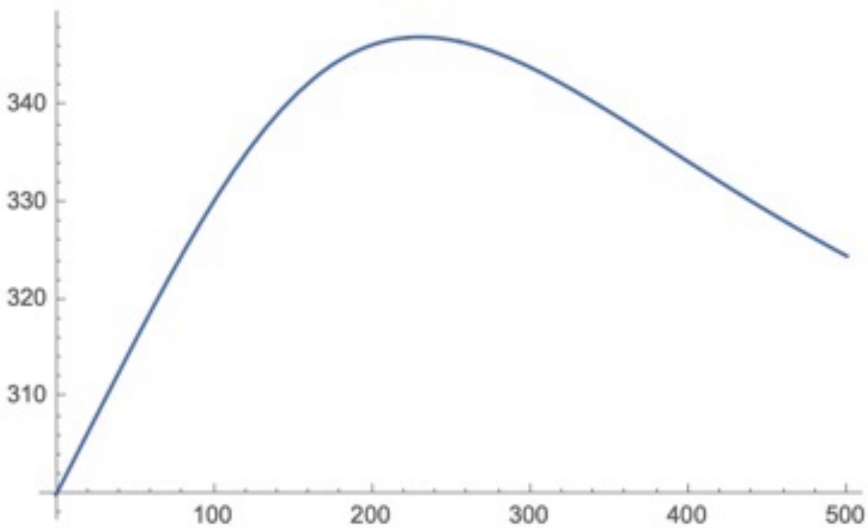
$$\frac{dT}{dt} = \frac{UA_H (300 - T) - \Delta H_r m_A^{\circ} k(T) C_A^{\circ} (1 - f_A)(1.2 - f_A)}{m_A^{\circ}(1 - f_A) C_{pA} + m_A^{\circ}(1.2 - f_A) C_{pB} + m_A f_{A_0} C_{pC}}$$

$\Rightarrow$ SOLVE

```
Plot[fa[t] /. %[[1]], {t, 0, 500}, PlotRange → {0, 1}]
```




```
Plot[T[t] /. %167[[1]], {t, 0, 500}]
```



SAME CONSIDERATIONS FOR TUBULAR REACTOR

CHAPTER 9 Nonisothermal Reactors

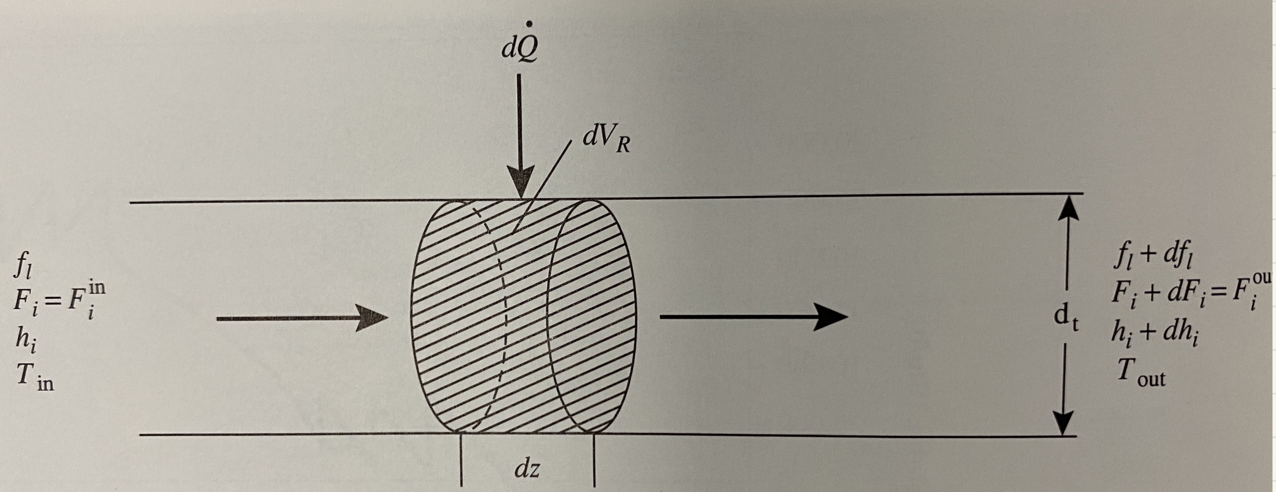


Figure 9.4.1 |
Schematic of differential fluid volume in a nonisothermal PFR.

MASS

$A \Rightarrow M$

$$\frac{dF_i}{dV_R} = \nu_i r \,, \qquad \frac{df_A}{d\tau} = -k(1-f_A)$$

$$u\frac{df_A}{dz} = -k(1-f_A)$$

ENERGY BALANCE :

KEEP TRACK OF EACH COMPONENT TO THE EXTENT ITS T HAS CHANGED

$$d\dot{Q} = \underline{\sum_i F_i^{OUT} \int_{T_0}^{T_{OUT}} Cp_i \, dT} - \underline{\sum F_i^{IN} \int_{T^0}^{T_{IN}} Cp_i \, dT}$$

$$- \frac{\Delta H_r \big|_T}{\nu_e} F_e^0 \, df_e$$

↑ HEAT EMMITED BY REACTION

$A \rightarrow M \qquad Cp - \text{CONST}$

$$d\dot{Q} = F_{A_0} Cp_A \, dT + \Delta H_r F_A^0 \, df_A$$

$$U(T^a - T)\pi d_t \, dz = F_{A0} Cp_A \, dT + \Delta H_r F_A^0 \, df_A$$

$$u \frac{df_A}{dz} = k C_{A_0} (1 - f_A)$$

$$u \frac{df_A}{dt} = -k C_{A0}(1-f_A)$$

$$u \rho C_{pA} \frac{dT}{dz} = \Delta H_r \, k C_{A0}(1-f_A) - \frac{4U}{d_t}(T - T^*)$$

$$-u \frac{dC_A}{dz} = A \exp\left(-\frac{E}{RT}\right) C_A$$

$$u \rho C_p \frac{dT}{dz} = (-\Delta H_r) A \exp\left[-\frac{E}{RT}\right] C_A - \frac{4U}{d_t}(T - T^0)$$

LET'S NON DIMENSIONALIZE TO MAKE SIMPLER!

$$x = \frac{z}{L}, \quad y = \frac{C_A}{C_A^0}, \quad \theta = \frac{T}{T^0}$$

$$D_a \equiv \frac{Lk}{u}, \quad \beta_T \equiv \frac{C_A^0(-\Delta H_r)}{\rho u T^0}$$

$$\gamma \equiv \frac{E}{RT^0} \qquad H_w \equiv \frac{4U}{d_t}\left(\frac{L}{\rho C_p u}\right)$$

$$\frac{dy}{dx} = -D_a\, y \exp\left(\gamma\left(1-\frac{1}{\theta}\right)\right)$$

$$\frac{d\theta}{dx} = \beta_T (D_a)\, y \exp\left(\gamma\left(1-\frac{1}{\theta}\right)\right) - H_w(\theta-1)$$

IF ADIABATIC, $H_w = 0$

THEN

$$\frac{d}{dx}\left(\theta + \beta y\right) = 0 \qquad y = \theta = 1 \text{ @ } x=0$$

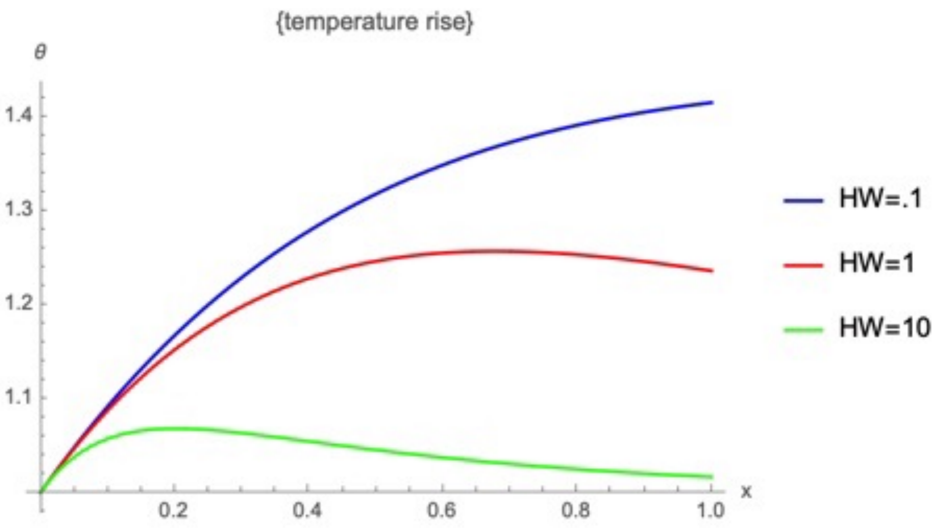
$$\Longrightarrow \quad \theta = 1 + \beta_T(1-y)$$

MASS $\Rightarrow$ $$\frac{dy}{dt} = -D_a\, y \exp\left[\frac{\gamma \beta_T (1-y)}{1+\beta_T(1-y)}\right]$$

$$y = 1 \text{ @ } x = 0$$

]:= Show[%50, %52, %54]

6]=



$$A \rightarrow M$$

ADIABATIC PFR

$$C_{p_A} = C_{p_B} = \text{CONST} \qquad k = A\exp\left(\frac{-E_A}{RT}\right)$$

MASS : $$\frac{dF_A}{dV_r} = -k C_A$$

$$-F_A^0 \frac{df_A}{dV_r} = -\frac{F_A^0}{q}\frac{df_A}{d(V_r/q)} = -C_{A0}\frac{df_A}{d\tau}$$

ENERGY $$0 = (F_A + F_M)\int_{T^0}^{T} C_p \, dT - \frac{\Delta H}{(-1)} F_A^0 f_A$$

$$0 = F_A^0(1-f_A)C_p(T-T^0) + F_A^0(f_A)(T-T_0)$$

$$= F_A^0 C_p (T-T^0) + \Delta H_r F_A^0 f_A$$

$$(T-T^0) = -\frac{\Delta H_r}{C_p} f_A$$

SO WE SOLVE

$$\frac{df_A}{d\tau} = -k(1-f_A)$$

$$k = A\exp\left(-\frac{E_A}{RT}\right), \quad T = T_0 + \frac{-\Delta H_r}{C_p} f_A$$

$$\int_0^{\tau} d\tau = -\int_0^{f_A^{\circ}} \frac{df_A}{A\exp\left(\frac{-E_A}{R\left(T_0 - \frac{\Delta H}{C_p} f_A\right)}\right)(1-f_A)}$$

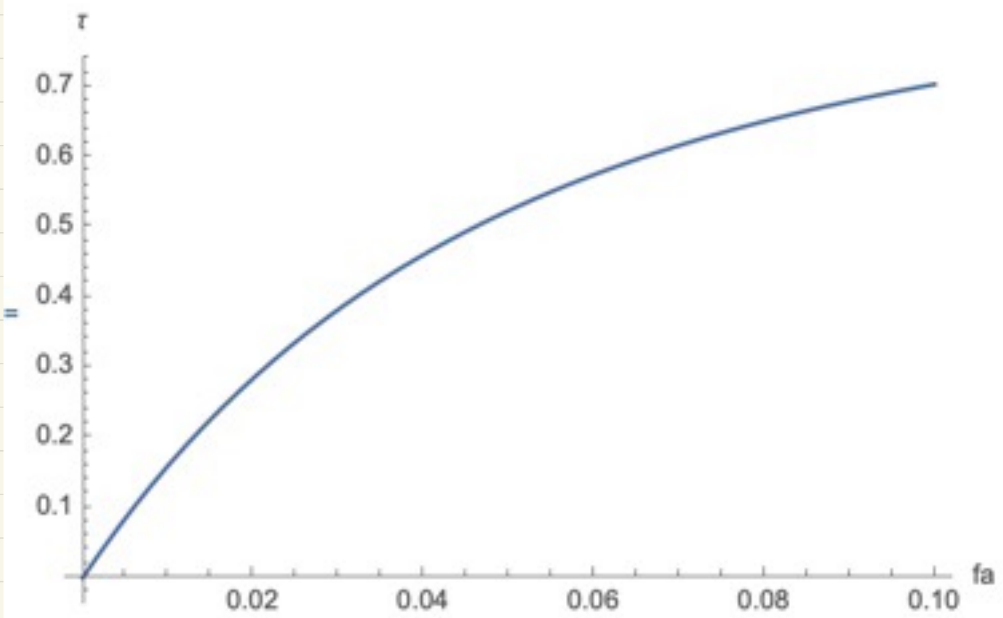
```
Integrate[1/ (A Exp[-Eₐ/R_g/(T₀ - ΔH/Cₚ/ fₐ)] (1 - fₐ)), fₐ]
```

$$= \frac{e^{\frac{e_a}{T_0 R_g}}\left(\mathrm{Ei}\left(\frac{\Delta H\, e_a}{R_g T_0 (C_p f_a T_0 - \Delta H)}\right) - e^{\frac{e_a \Delta H}{T_0 R_g (T_0 C_p - \Delta H)}}\,\mathrm{Ei}\left(-\frac{\Delta H\, C_p\, e_a (f_a - 1)}{R_g (\Delta H - C_p T_0)(\Delta H - C_p f_a T_0)}\right)\right)}{A}$$

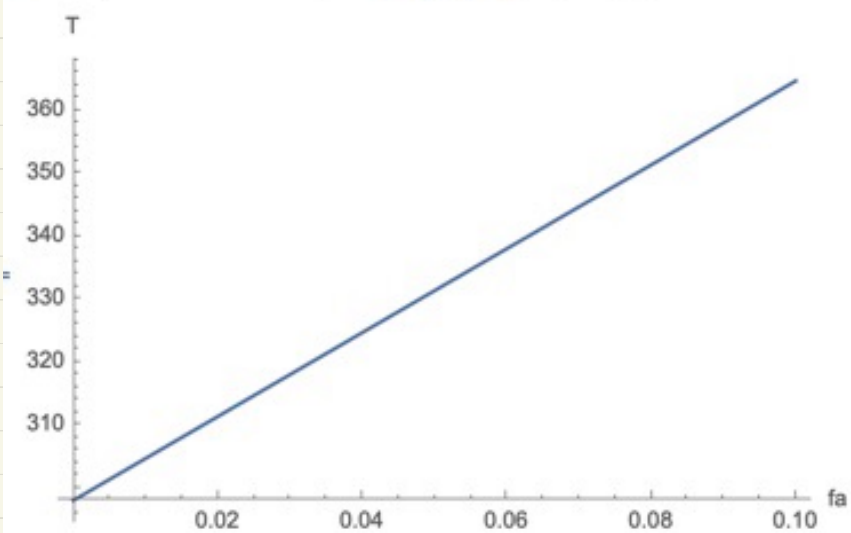
```
In:= %38 /. {aa → 10^4, ea → 30000, rr → 8.314, T0 → 298, δH → -20000, cp → 30, fa → 0}
Out= -0.885891

In:= %38 /. {aa → 10^4, ea → 30000, rr → 8.314, T0 → 298, δH → -20000, cp → 30, fa → 0}
Out= -0.885891

In:= %56 - %54
```

$$0.885891 + \frac{-42.1206\,\mathrm{ExpIntegralEi}\left[-\frac{74810.7\,(-1+fa)}{8940+20000\,fa}\right] + \mathrm{ExpIntegralEi}\left[\frac{900000}{74327.2+166280.\,fa}\right]}{10000}$$

```
Plot[%57, {fa, 0, .1}, AxesLabel → {"fa", "τ"}]
```

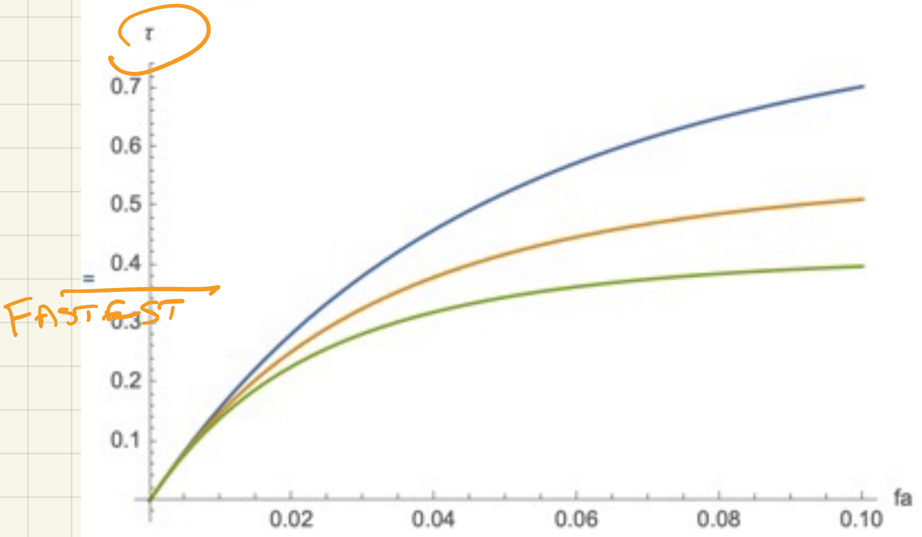



```
Plot[298 + 20000/30 fa, {fa, 0, .1}, AxesLabel → {"fa", "T"}]
```

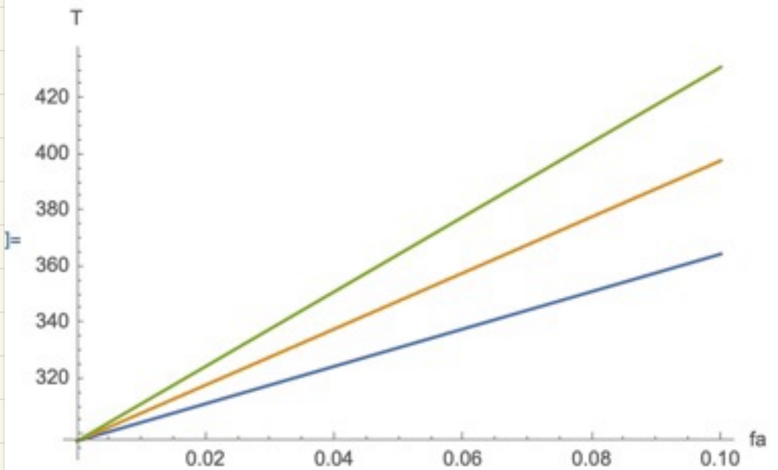


LET'S TRY DIFFERENT HEATS OF REACTION!

```
Plot[{plotexp20k, plotexp30k, plotexp40k}, {fa, 0, .1}, AxesLabel → {"fa", "τ"},
  PlotLegends → "Expressions"]
```




```
Plot[ {298 + 20 000 / 30 fa, 298 + 30 000 / 30 fa, 298 + 40 000 / 30 fa}, {fa, 0, .1},
  AxesLabel → {"fa", "T"}, PlotLegends → {"ΔH = 20000", "ΔH = 30000", "ΔH = 40000",}]
```



TEMPERATURE EFFECTS IN A CSTR

HEAT REMOVAL = HEAT GENERATED − HEAT TAKEN UP BY COMPONENTS

$$\dot{Q} = \frac{F_\ell^{\circ}\left(\Delta H_r|_{T_0}\right)\left(f_\ell^{f} - f_\ell^{\circ}\right)}{(-\nu_\ell)} - \sum F_i^{f} \int_{T^0}^{T^f} C_p \, dT$$

FOR $A \rightarrow M$ CONST C_p

$\boxed{f_A^{\circ} = 0}$

$$0 = F_A^{\circ}(1 - f_A) - k C_A^{\circ}(1 - f_A) V$$

$$\dot{Q} = -F_A^{\circ} \, \Delta H_r \, f_A - F_A^{\circ} C_p (T - T^0) - F_N C_p (T - T_0)$$

INERTS

FOR CSTR, USUALLY
f_A IS SPECIFIED

IF SO, YOU CAN SOLVE
ENERGY BALANCE FOR T.

$$\dot{Q} = -F_A^0 \Delta H_r f_A - F_A^0 c_p (T - T^0) - F_N^0 c_{p_N} (T - T_0)$$

INERTS

$$(T - T^0) = \frac{\dot{Q} - F_A^0 \Delta H_r f_A}{F_A^0 c_{p_A} + F_N^0 c_{p_N}}$$

THEN USE THIS T IN:

$$0 = F_A^0 (1 - f_A) - A \exp\left(-\frac{E}{RT}\right) C_A^0 (1 - f_A) V$$

FOR F_A^0 FIXED SOLVE FOR V

("τ")