CBE 40445

10/16/20

NON ISOTHERMAL REACTORS

The generalized, time-dependent energy balance is written as

$$\frac{d}{dt}\left\{M\left(\hat{U}+\frac{v^2}{2}+gh\right)\right\}=\boxed{\sum_{j=1}^{j=J}\left\{\dot{m}_{j,\text{in}}\left(\hat{H}_j\right.\right.}\left.\left.+\frac{v_j^2}{2}+gh_j\right)\right\}$$
$$-\boxed{\sum_{k=1}^{k=K}\left\{\dot{m}_{k,\text{out}}\left(\hat{H}_k\right.\right.}\left.\left.+\frac{v_k^2}{2}+gh_k\right)\right\}+\dot{W}_S+\dot{W}_{EC}\boxed{+\dot{Q}} \quad (3.34)$$

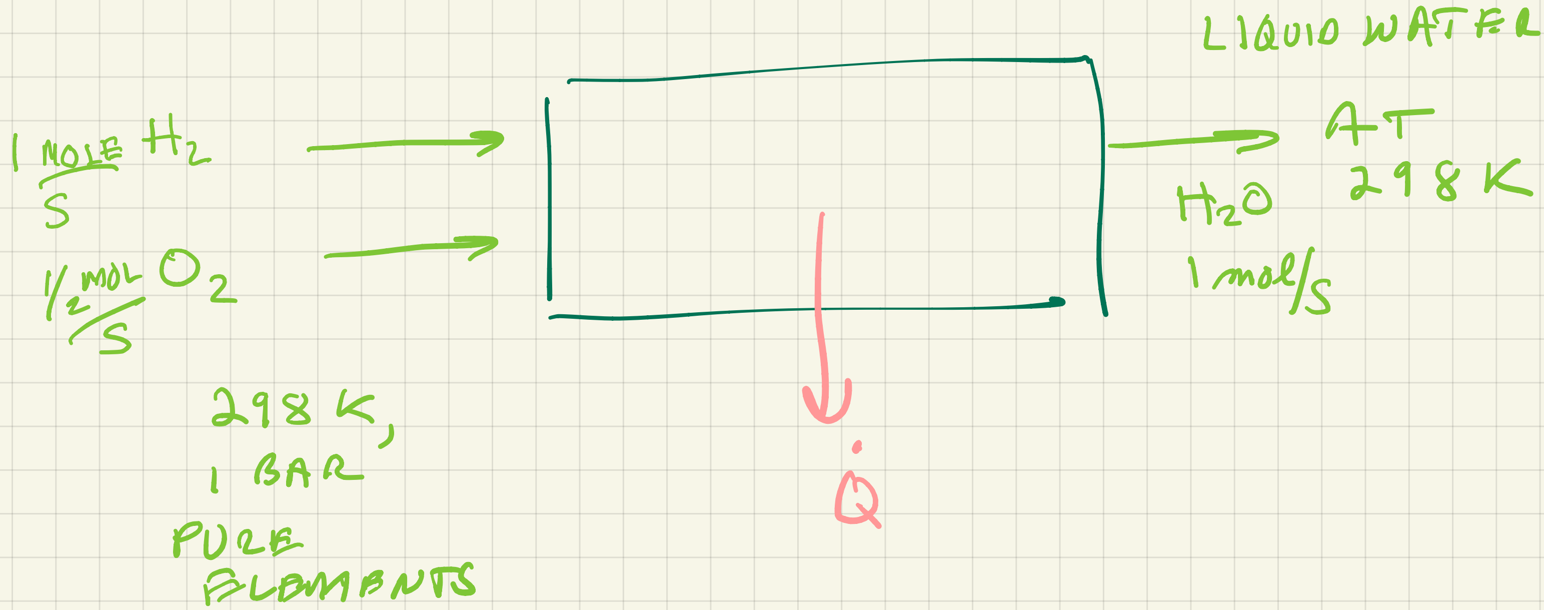
IF NOT STEADY STATE

where

- t is time.
- M is the total mass of the system.
- $\hat{U}$ is the specific internal energy of the system.
- v is the velocity of the system.
- h is the height of the system.
- g is the acceleration due to gravity, equal to 9.81 m/s² on Earth.
- $\dot{m}_{j,\text{in}}$ and $\dot{m}_{k,\text{out}}$ are the mass flow rates of individual streams entering and leaving the system, respectively, and the summations are carried out over all such streams.
- $\hat{H}_j$ and $\hat{H}_k$ are the specific enthalpies of streams entering and leaving the system.
- v_j and v_k are the velocities of streams entering and leaving the system.
- h_j and h_k are the heights at which streams enter and leave the system.
- $\dot{W}_{EC}$ is the rate at which work is added to the system through expansion or contraction of the system.
- $\dot{W}_S$ is the rate at which shaft work is added to the system.
- $\dot{Q}$ is the rate at which heat is added to the system.

FROM DAHM + VISCO

HEAT OF REACTION/ COMBUSTION



$$0 = \dot{m}_{H_2}\hat{H}_{H_2} + \dot{m}_{O_2}\hat{H}_{O_2} - \dot{m}_{H_2O}\hat{H}_{H_2O} + \dot{Q}$$

$$0 = (1)(0) + (1/2)(0) - (1\ mol/s)(285.8)\frac{KJ}{MOLE} + \dot{Q}$$

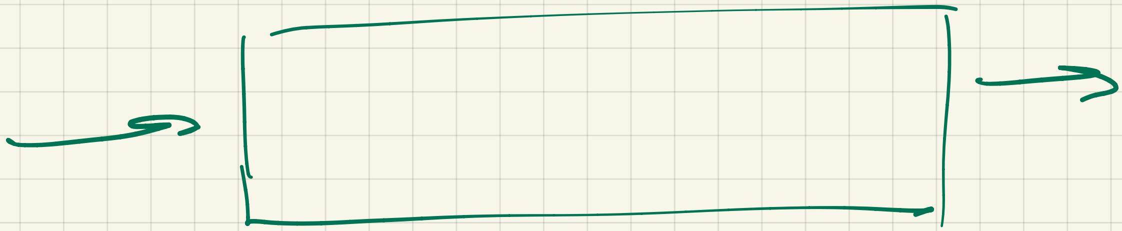
ENTHALPY OF FORMATION

$$\dot{Q} = -285.8\ \frac{KJ}{S}$$

THUS IF $CH_4 + 3O_2 \rightarrow CO_2 + 2H_2O$

$(-74.9) + 0$ $\quad 393.5\ \frac{KJ}{MOLE} + 2(285\ KJ/MOLE)$

$$\dot{Q} = -888.6\ KJ/MOLE$$



REACTION OUTCOME WILL BE A FUNCTION OF T

$$\frac{dF_i}{dV_R} = \nu_i\, r(F_i, T)$$

added to the system and negative signs if energy is removed from the system.

The complete energy balance is as follows:

$$\boxed{\frac{d}{dt}\left\{M\left(\hat{U}\right.\right.}\left.\left.+\cancel{\frac{v^2}{2}}^{\,0}+\cancel{gh}^{\,0}\right)\right\} = \sum_{j=1}^{j=J}\left\{\dot{m}_{j,\mathrm{in}}\left(\underbrace{\boxed{\hat{U}_j+P_j\hat{V}_j}}_{\hat{H}}+\cancel{\frac{v_j^2}{2}}^{\,0}+\cancel{gh_j}^{\,0}\right)\right\} \qquad (3.33)$$

$$-\sum_{k=1}^{k=K}\left\{\dot{m}_{k,\mathrm{out}}\left(\underbrace{\boxed{\hat{U}_k+P_k\hat{V}_k}}_{\hat{H}}+\cancel{\frac{v_k^2}{2}}^{\,0}+\cancel{gh_k}^{\,0}\right)\right\}+\dot{W}_S+\cancel{\dot{W}_{EC}}+\dot{Q}$$

CONST V

BATCH OR UNSTEADY STATE FLOW REACTOR

USUALLY 0

= HEAT IN OR OUT

USUAL EQ FOR ENERGY!

S.S:

$$\dot{Q} = \dot{m}_{OUT}\, h_{OUT} - \dot{m}_{IN}\, h_{IN}$$

$$h_i \equiv \hat{H}_i \qquad \frac{\text{ENTHALPY}}{\text{MASS}}$$

NON ISOTHERMAL BATCH REACTOR

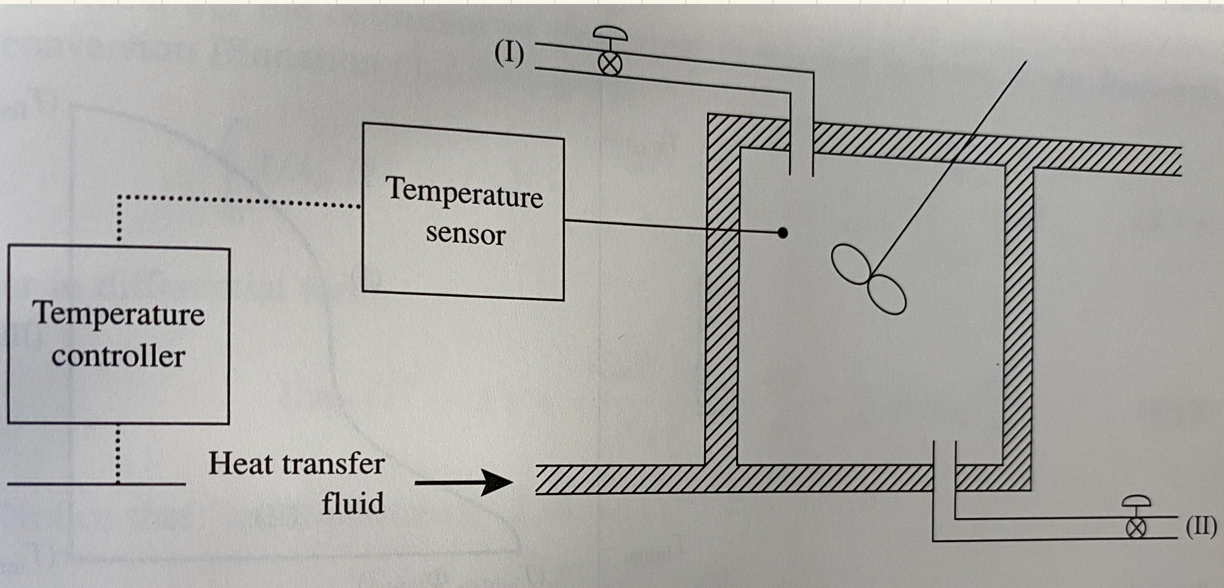


Figure 9.3.1 |
Schematic of a batch reactor.

LOAD REACTOR

SOME HEATING + COOLING INVOLVED

$$\frac{1}{V}\frac{dn_i}{dt} = \nu_i r(n_i, T)$$

LIQUID PHASE WOULD APPROXIMATE THIS...

PICK CONST P, NONISOTHERMAL CASE....

THE VOLUME MUST BE:

$$V = V_0 \left(1 + \varepsilon f_i\right) \frac{T}{T_0}$$

INITIAL VOLUME

INITIAL T

TO FOLLOW D + D WITH CHANGING VOLUME, WORK WILL BE DONE ON REACTOR THUS

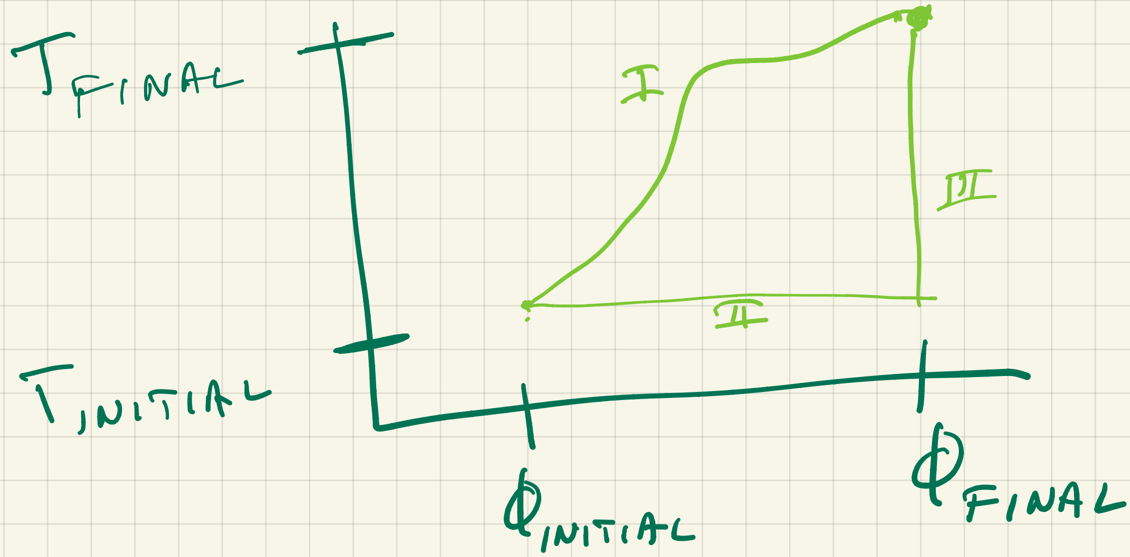
$$Q = \Delta H$$

EXTENT OF REACTION

$$Q = \int_{T_{INITIAL},\, \phi_{INITIAL}}^{T_{FINAL},\, \phi_{FINAL}} \left(\overline{MS}\, \overline{C}_p\, dT + \Delta H_r\, d\phi \right)$$

HEAT CAPACITY

TOTAL MASS



WE CAN FIND SENSIBLE HEAT EFFECTS...

$$\int_{T_{INITIAL}}^{T_{FINAL}} \overline{MS}\ \overline{C_p}\, dT = \int_{T_{INITIAL}}^{T_{FINAL}} \sum_i M_i C_{p_i}\, dT$$

HEAT TRANSFER TO OUTSIDE IS

$$Q = \int \dot{Q}\, dt = \int U A_H (T^* - T)\, dt$$

SO WE CAN WRITE!

EXTENT OF REACTION

$$\int_0^t UA_H\left(T^* - T\right)dt = \frac{-\Delta H_r|_{T_0}}{V_\ell}\, m_\ell^0 f_\ell + \sum_i \left(m_i \int_{T_{INITIAL}}^{T_{FINAL}} C_{p_i}\, dT \right)$$

A MORE CONVENIENT FORM:

$$UA_H\left(T^* - T\right) = \Delta H_r\, r\, V + \sum m_i C_{p_i} \frac{dT}{dt}$$

HEAT REMOVED BY EXTERNAL SINK

HEAT GENERATION FROM REACTION

HEAT NEEDED TO INCREASE T

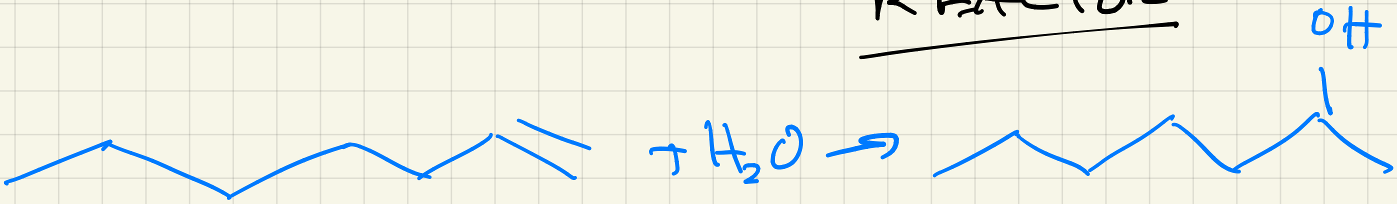
IF ADIABATIC!

$$0 = \frac{-\Delta H_r|_{T_0}}{V_\ell}\, m_\ell^0 \frac{df_\ell}{dt} + \sum_i \left(m_i C_{p_i}\right) \frac{dT}{dt}$$

IF ISOTHERMAL!

$$UA_H\left(T^* - T^0\right) = -\frac{\Delta H_r|_{T_0}}{V_\ell}\, m_\ell^0 \frac{df_\ell}{dt}$$

EXAMPLE — ADIABATIC REACTOR



1000 kg 10 wt % H_2SO_4

200 kg 1-HEXENE @ 300 K

→ TIME TO 50% CONVERSION

	C_p (cal/(mol-K))	ΔH_f^0 (kcal/mol)
1-hexene	43.8	−10.0
H_2O	16.8	−68.0
2-hexanol	54.0	−82.0

$$k = 10^4 \exp\left(\frac{-10^4}{RT}\right) \;/s$$

MASS BALANCE

$$\frac{dC_A}{dt} = -k C_A$$

HERE IS A CASE WHERE "f" IS USEFUL

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

THE ENERGY BALANCE

$$0 = \frac{-\Delta H_r|_{T_0}}{\nu_\ell} m_\ell^\circ \frac{df_\ell}{dt} + \sum_i (m_i C_{p_i}) \frac{dT}{dt}$$

$$T = T_0 + \frac{\Delta H_r|_{T_0} \, m_\ell^\circ f_\ell}{\nu_\ell \sum_i m_i C_{p_i}}$$

$$\nu_\ell = -1$$

ΔH_r IS OBTAINED:

$$\Delta H_r = -82 + 68 + 10 = -4 \ \frac{\text{kCAL}}{\text{MOLE}}$$

FOR TEMPERATURE:

$$T = T_0 + \frac{4000 \, m_A^\circ f_A}{m_A^\circ (1-f_A) C_{p_A} + m_A^\circ (\bar{M} - f_A) C_{p_B} + m_A^\circ f_A C_{p_C}}$$

$$\bar{M} \equiv \frac{m_B^\circ}{m_A^\circ}$$

HEXENE: $n_A^o = (2\times10^5 g)(1\ mol/84\ g) = 2381\ mol$

WATER: $n_B^o = (9\times10^5 g)(1\ mol/18\ g) = 50000\ mol$

$$\frac{n_B^o}{n_A^o} = 21$$

THIS GIVES:

$$T = 300 + \frac{4000 f_A}{421.8 - 7.8 f_A}$$

FOR k:

$$k = 10^4 \exp\left[\frac{-10^4}{R_G\left(300 + \frac{4000 f_A}{421.8 - 7.8 f_A}\right)}\right]$$

$$\frac{df_A}{dt} = 10^4 \exp\left[\frac{-10^4}{R_G\left(300 + \frac{4000 f_A}{421.8 - 7.8 f_A}\right)}\right](1 - f_A)$$

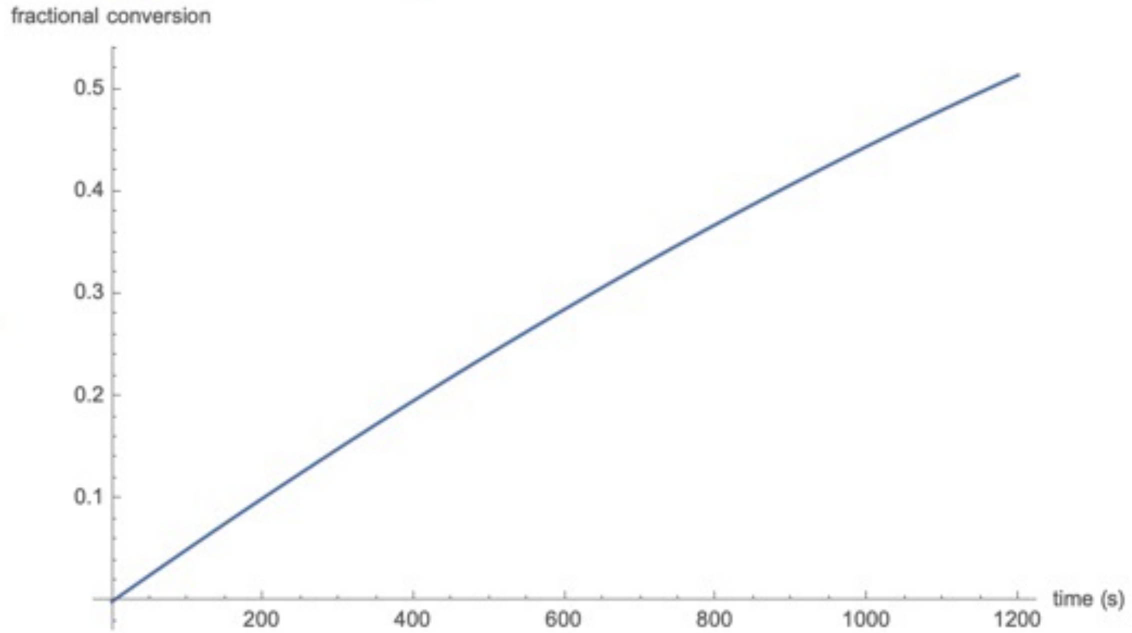
$f_A = .5$, t 1111 s, $T = 304.8$ K

($t \approx 1158$)

```
NDSolve[
  {D[fa[t], t] == 10^4 Exp[-10^4/1.987/(300 + 4000 fa[t]/(421.8 - 7.8 fa[t]))]
     (1 - fa[t]), fa[0] == 0}, fa[t], {t, 0, 1200}]
```

```
{{fa[t] → InterpolatingFunction[ Domain: {{0., 1.20×10^3}} Output: scalar ][t]}}
```

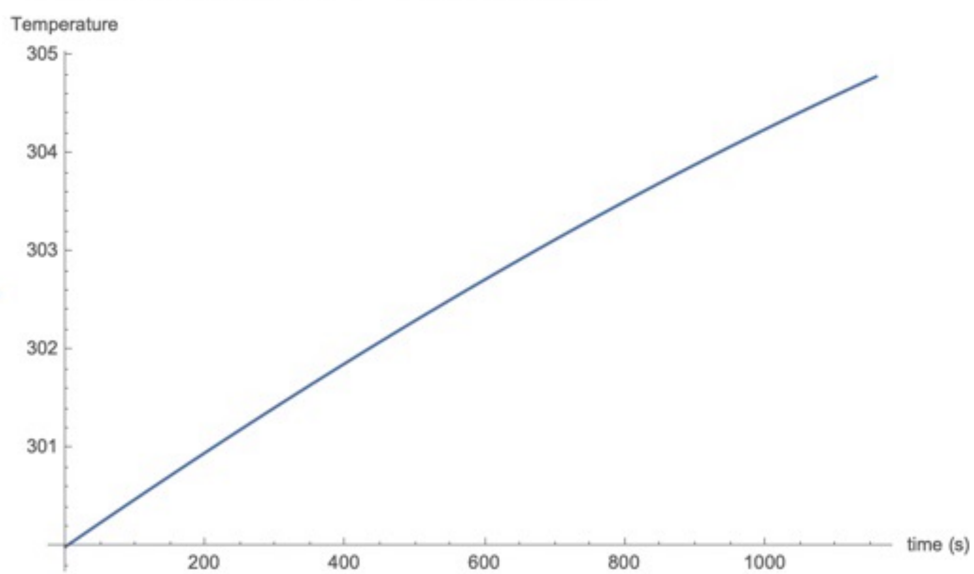
```
Plot[fa[t] /. %12[[1]], {t, 0, 1200}, AxesLabel → {"time (s)", "fractional conversion"}]
```




```
(fa[t] /. %12[[1]]) /. t → 1158
```

```
0.499921
```

```
Plot[((300 + 4000 fa[t]/(421.8 - 7.8 fa[t])) /. %12[[1]], {t, 0, 1158},
 AxesLabel → {"time (s)", "Temperature"}]
```




```
(((300 + 4000 fa[t]/(421.8 - 7.8 fa[t]))) /. %12[[1]]) /. t → 1158
```

```
304.785
```

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

$C_{pA} = C_{pB} = 65$ J/MOLE-K

$C_{pC} = 150$ 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

$$UA_H(T^* - T) = \Delta H_r m_A^\circ \frac{df_A}{dt} + \left[m_A^\circ (1-f_A) C_{p_A} + m_A^\circ (1.2-f_A) C_{p_B} + m_A^\circ f_A C_{p_C} \right] \frac{dT}{dt}$$

WE CAN ARRANGE:

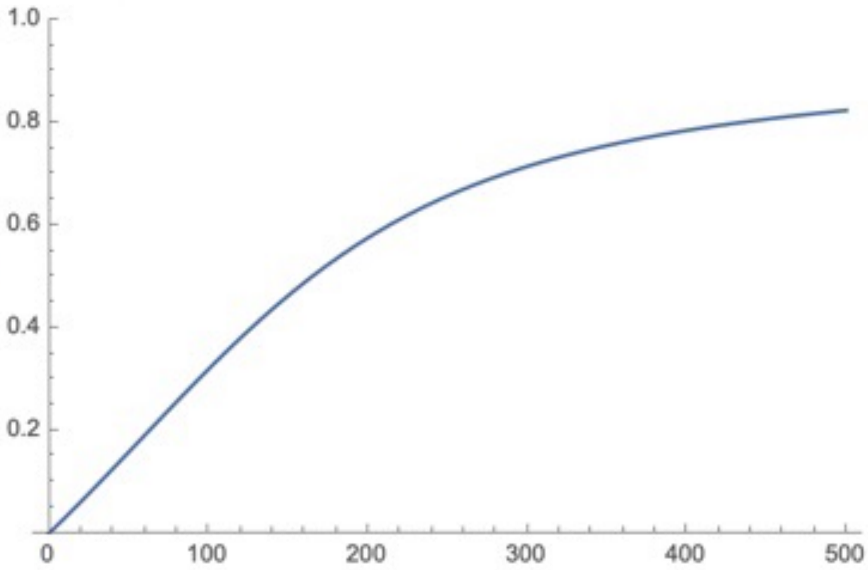
$$\frac{df_A}{dt} = k(T) C_A^\circ (1-f_A)(1.2-f_A)$$

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

$\Longrightarrow$ SOLVE

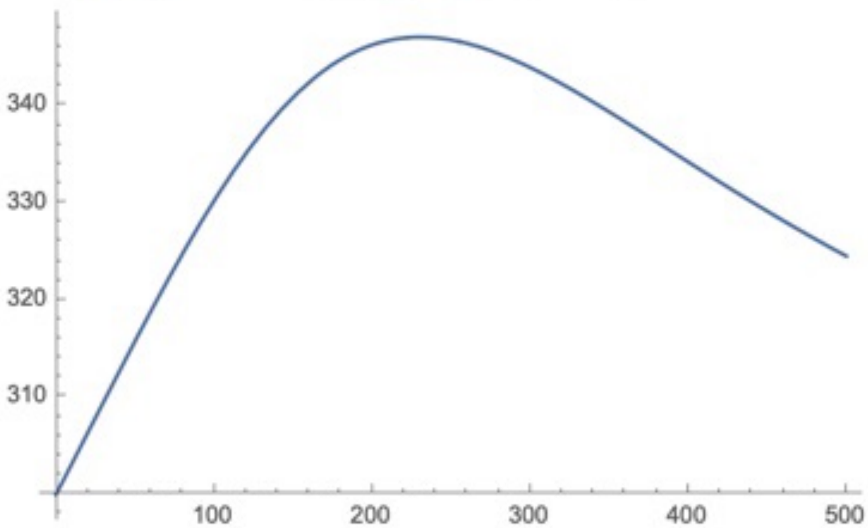
```
3]:= Plot[fa[t] /. %[[1]], {t, 0, 500}, PlotRange → {0, 1}]
```

8]=




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

0]=



NONISOTHERMAL PLUG FLOW REACTOR

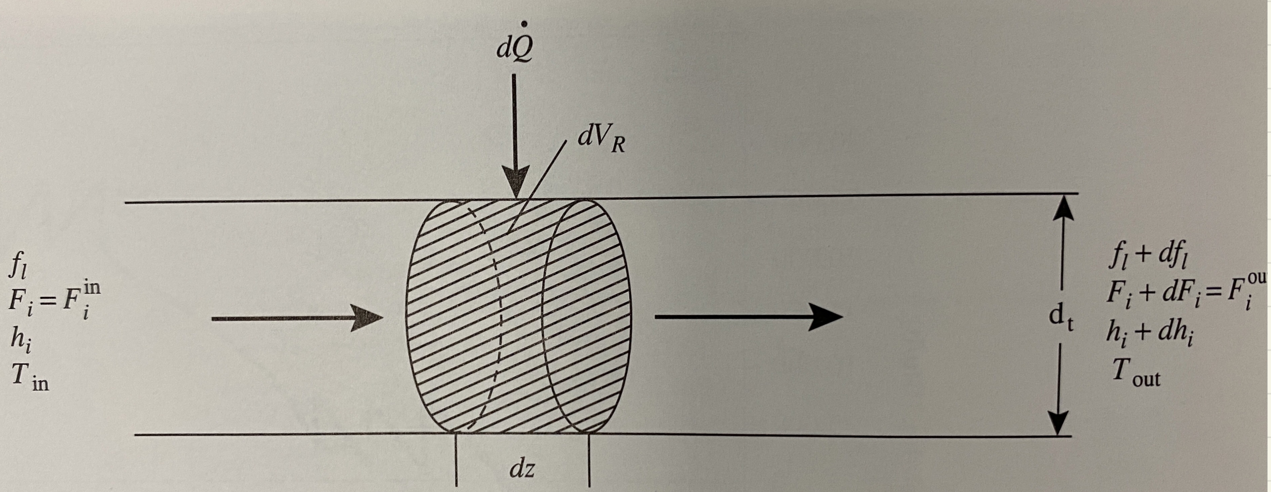


Figure 9.4.1 |
Schematic of differential fluid volume in a nonisothermal PFR.

RECALL MASS BALANCE:

$$\frac{dF_i}{dV_R} = \nu_i r$$

ENERGY BALANCE:

$$d\dot{Q} = \sum_i F_i^{OUT} \int_{T_0}^{T_{OUT}} C_{p_i} dT - \sum F_i^{IN} \int_{T_0}^{T_{IN}} C_{p_i} dT$$

$$- \frac{\Delta H_r|_T}{\nu_\ell} F_\ell^{0} df_\ell$$

$$A \rightarrow M$$

ADIABATIC PFR

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

MASS :
$$\frac{dF_A}{dV_r} = -kC_A$$

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

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

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

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

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

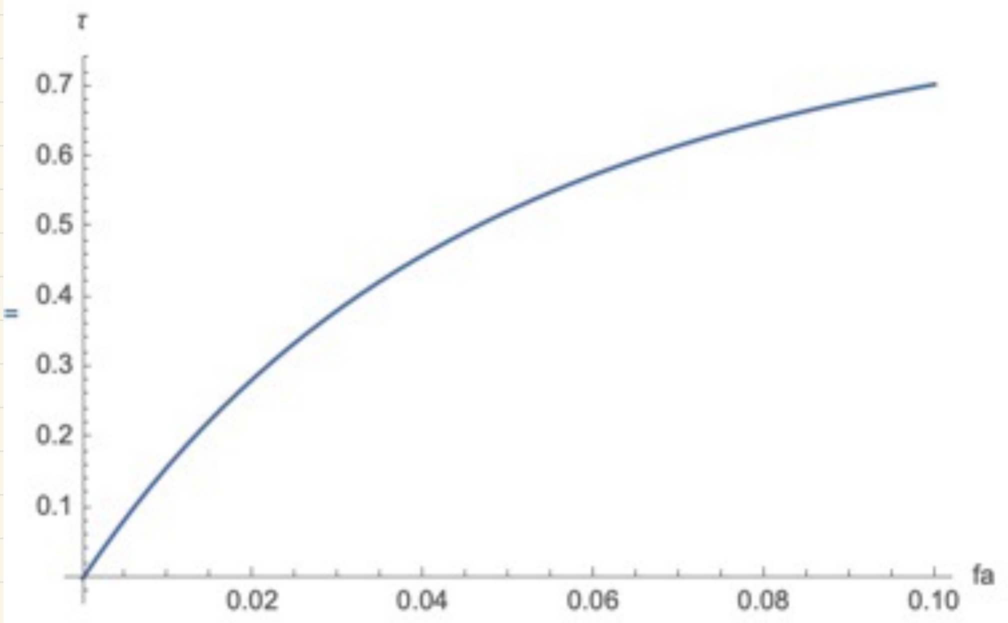
```
Integrate[1/ (A Exp[-Ea/Rg/(T0 - ΔH/Cp/ fa)] (1 - fa)), fa]
```

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

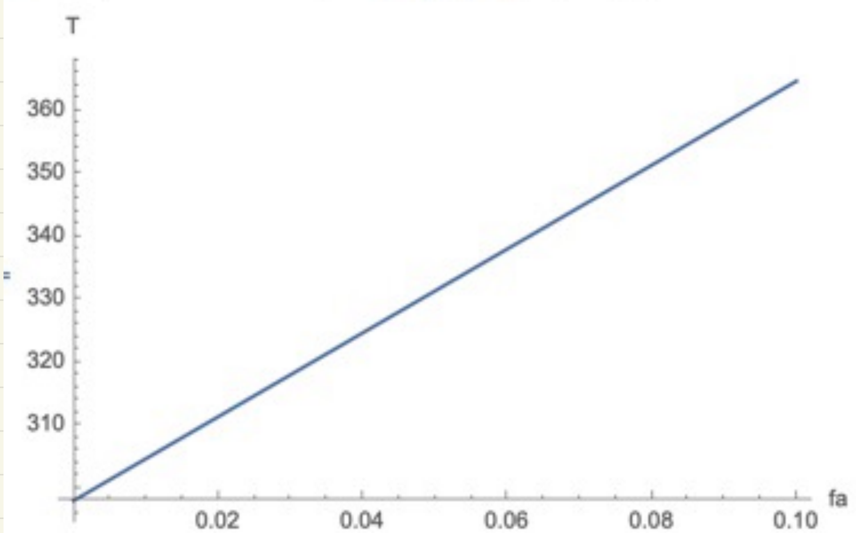
```
In[]:= %38 /. {aa → 10^4, ea → 30000, rr → 8.314, T0 → 298, δH → -20000, cp → 30, fa → 0}
Out[]= -0.885891
In[]:= %38 /. {aa → 10^4, ea → 30000, rr → 8.314, T0 → 298, δH → -20000, cp → 30, fa → 0}
Out[]= -0.885891
In[]:= %56 - %54
```

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

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

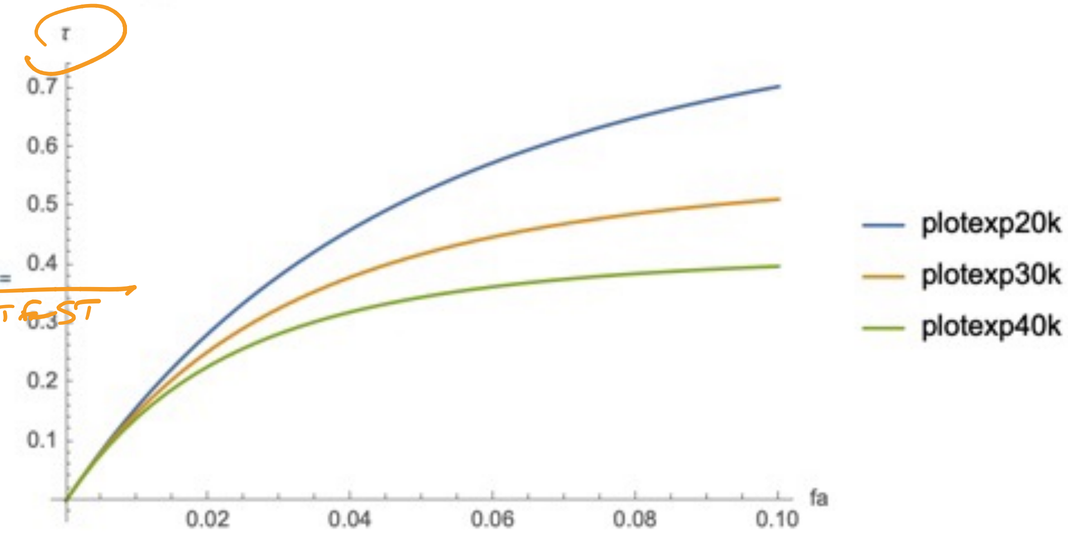



```
Plot[298 + 20000/30 fa, {fa, 0, .1}, AxesLabel → {"fa", "T"}]
```



LET'S TRY DIFFERENT HEATS OF REACTION!

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



FASTEST

```
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",}]
```