CBE 40455

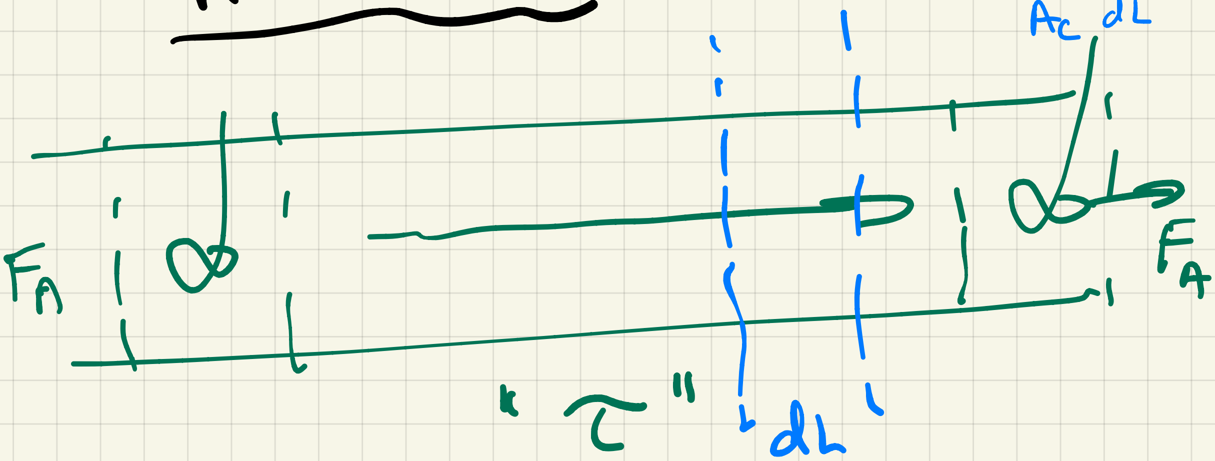
8/31/20

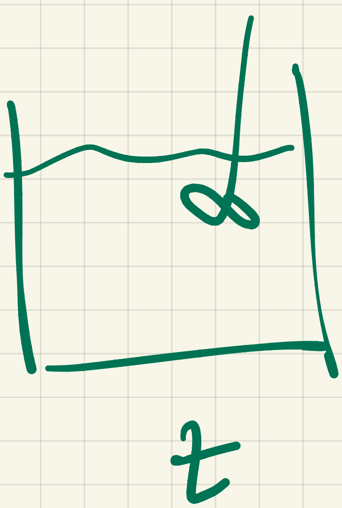
REVIEW

$$\frac{1}{A_c}\frac{dF_i}{dL} = \nu_i r$$

$$F_i = q\,C_i$$

$$\frac{q}{A_c}\frac{dC_i}{dL} = \boxed{\frac{dC_i}{d\tau} = \nu_i r}$$





$$\frac{dC_A}{dt} = \nu_A r$$

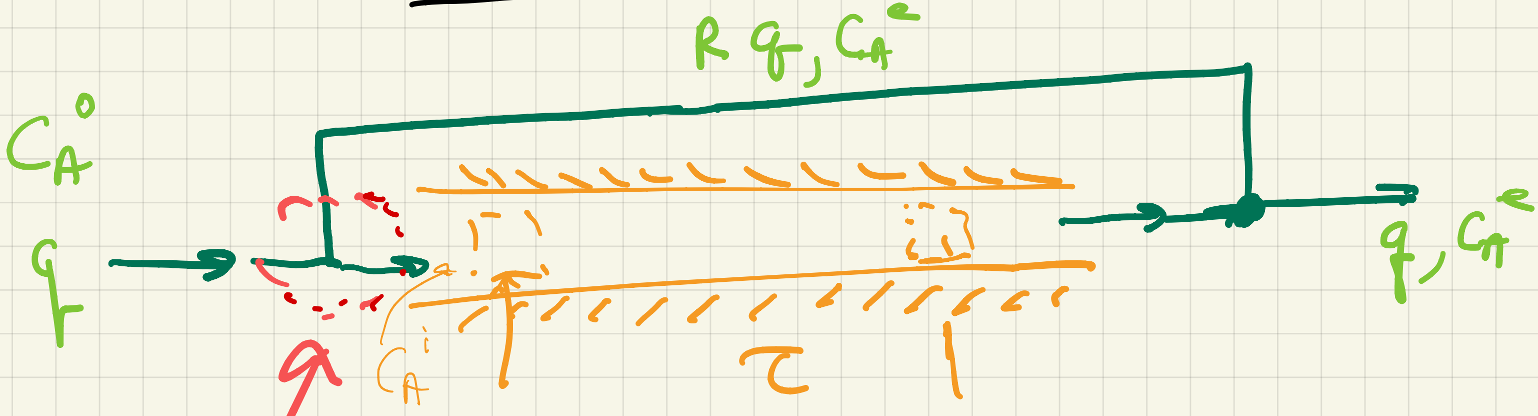
EXAMINATION OF RECYCLE ON A PLUG FLOW REACTOR

... 'TRUST' EQUATIONS ...

- RECYCLING SOME OF PRODUCT STREAM WILL "DILUTE" REACTANT AND LOWER CONVERSION

- IN LIMIT OF HIGH RECYCLE, $R \gg 1$, PFR ⟶ CSTR

USE OF RECYCLE



MASS BALANCE AROUND MIXING POINT (ALL MASS)

$$0 = q + Rq - q^i$$

$$q^i = (R+1)q$$

$$\tau = \frac{V}{q(R+1)}$$

RECYCLE SHORTENS RESIDENCE TIME

(FOR C_A)

$$0 = C_A^0 q + C_A^e R q - (R+1) q C_A^i$$

$$C_A^i = \frac{C_A^0 + R C_A^e}{R+1}$$

WE WILL CONTINUE ON BUT

IF $R = 0$ $\quad C_A^i = C_A^0$

AS $R \to \infty$ $\quad C_A^i = C_A^e$??

CONSIDER 1ST ORDER KINETICS:

COMPONENT MASS BALANCE ON REACTOR

RATE CHANGE OF MOLES OF A WITH PROGRESS THROUGH REACTOR = RATE OF REACTION IN REACTOR

$$\frac{dF_A}{dV_R} = v_A r$$

$$F_A = (R+1) q C_A$$

$$V_R = A_c L$$

$$(1+R) q \frac{dC_A}{A_c dL} = -k C_A$$

$$d\tau = \frac{A_c dL}{(R+1) q}$$

$$\frac{dC_A}{d\tau} = -k C_A$$

$$\frac{dC_A}{C_A} = -k \, d\tau$$

$$\int_{C_A^i}^{C_A^e} \frac{dC_A}{C_A} = -k\, d\tau$$

$$\ln \frac{C_A^e}{C_{A_i}} = -k\,\tau$$

- WE WILL CHOOSE R.

- $$C_A^i = \frac{C_A^0 + R C_A^e}{R+1}$$

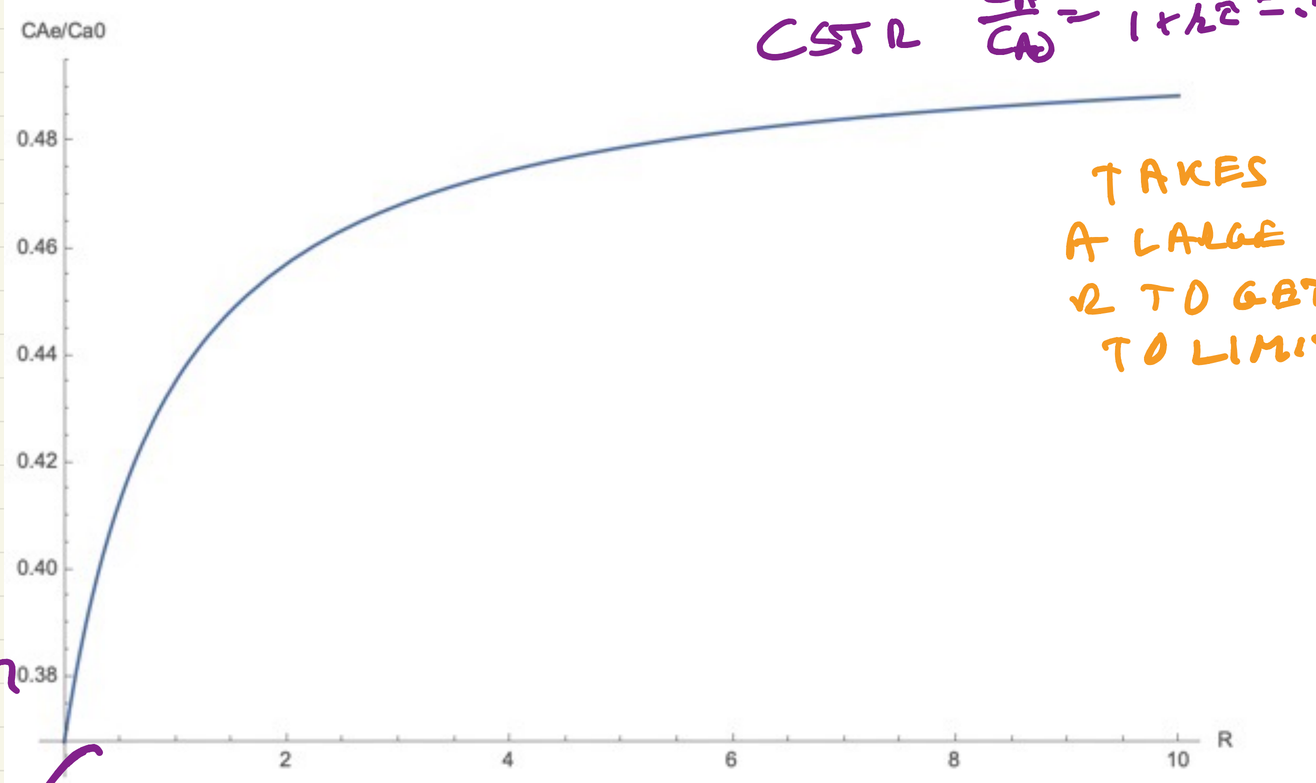
- $$\tau = \frac{V}{q(R+1)}$$

$$\ln \left(\frac{C_A^e}{\frac{C_A^0 + R C_A^e}{R+1}} \right) = -k \frac{V}{q(R+1)}$$

$$\frac{C_A^e}{C_{A0}} = \frac{1}{\exp\left(\frac{kV}{q(1+R)}\right)(1+R) - R}$$

WE CAN PLOT THIS AS A FUNCTION OF R

```
Plot[ans /. {ca0 → 1, k → 1, V → 1, q → 1}, {rr, 0, 10}, AxesLabel → {"R", "CAe/Ca0"},
 PlotRange → All]
```



CSTR $\frac{C_A}{C_{A0}} = \frac{1}{1+k\tau} = .5$

TAKES A LARGE R TO GET TO LIMIT

~.367

PFR/BATCH IF NO RECYLE

$$\frac{C_A^o}{C_{A0}} = \exp(-k\tau)$$

$$= \exp(-1) = .367$$

$$\ln\left(\frac{C_A^e}{\frac{C_A^0 + R C_A^e}{R+1}}\right) = -k\frac{V}{q(R+1)}$$

$$\frac{C_A^e (R+1)}{C_A^0 + R C_A^e} \qquad -\frac{kV}{q}\frac{1}{(R+1)}$$

$R >> 1$

$$\frac{C_A^e\left(1+\frac{1}{R}\right)}{\frac{C_A^0}{R} + C_A^e} \qquad -\frac{kV}{qR}$$

$\varepsilon = \frac{1}{R}$

$$\ln\left(1 + \frac{C_{Ae} - C_A^0}{C_{Ae}}\varepsilon\right) \rightarrow \ln(1+x) \cong x$$

$$\cong \frac{C_A^e - C_A^0}{C_A^e}$$

$$\left(1 - \frac{C_A^0}{C_A^e}\right)\frac{1}{R} \cong -\frac{kV}{qR}$$

MATCHES CSTR

$$\left(1 - \frac{C_A^0}{C_A^e}\right)\frac{1}{R} \approx -\frac{kV}{qR}$$

$$\frac{C_A^0}{C_{Ac}} = 1 + \frac{kV}{q}$$

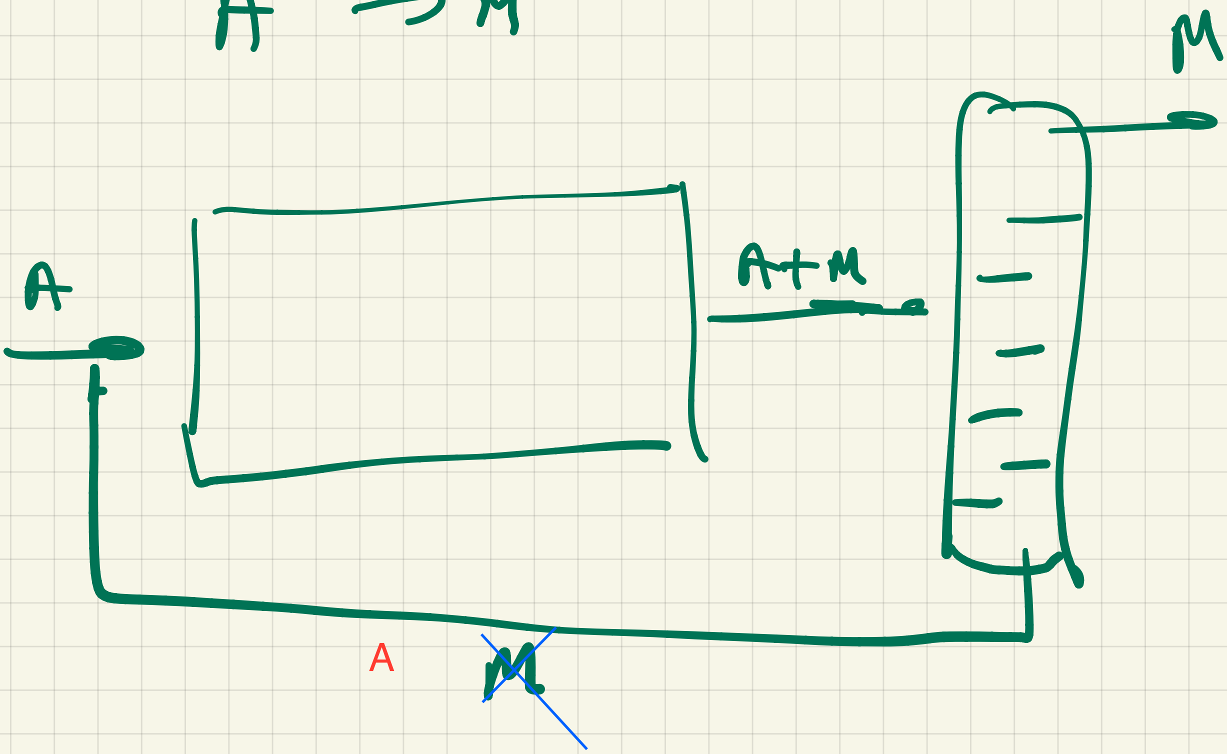
LOOKS LIKE CSTR

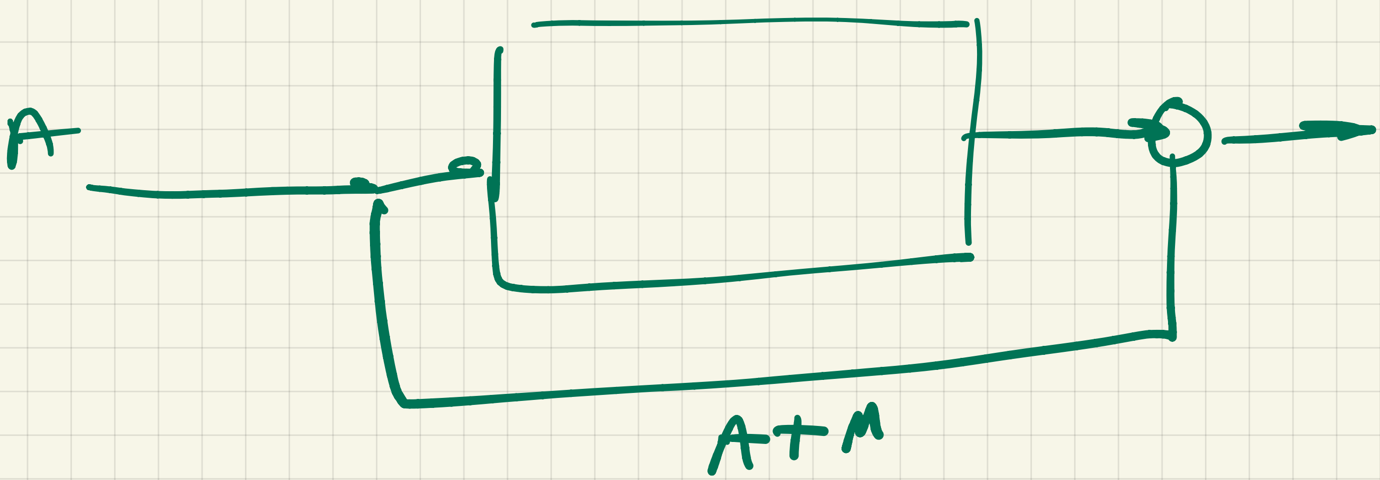
$$\frac{C_{Ac}}{C_A^0} = \frac{1}{1 + \frac{kV}{q}}$$

$$\frac{C_A^e}{C_{Ad}} = \frac{1}{1 + k\tau}$$

MORE COMMON USE OF RECYCLE:

A → M





M IS A DILUENT.

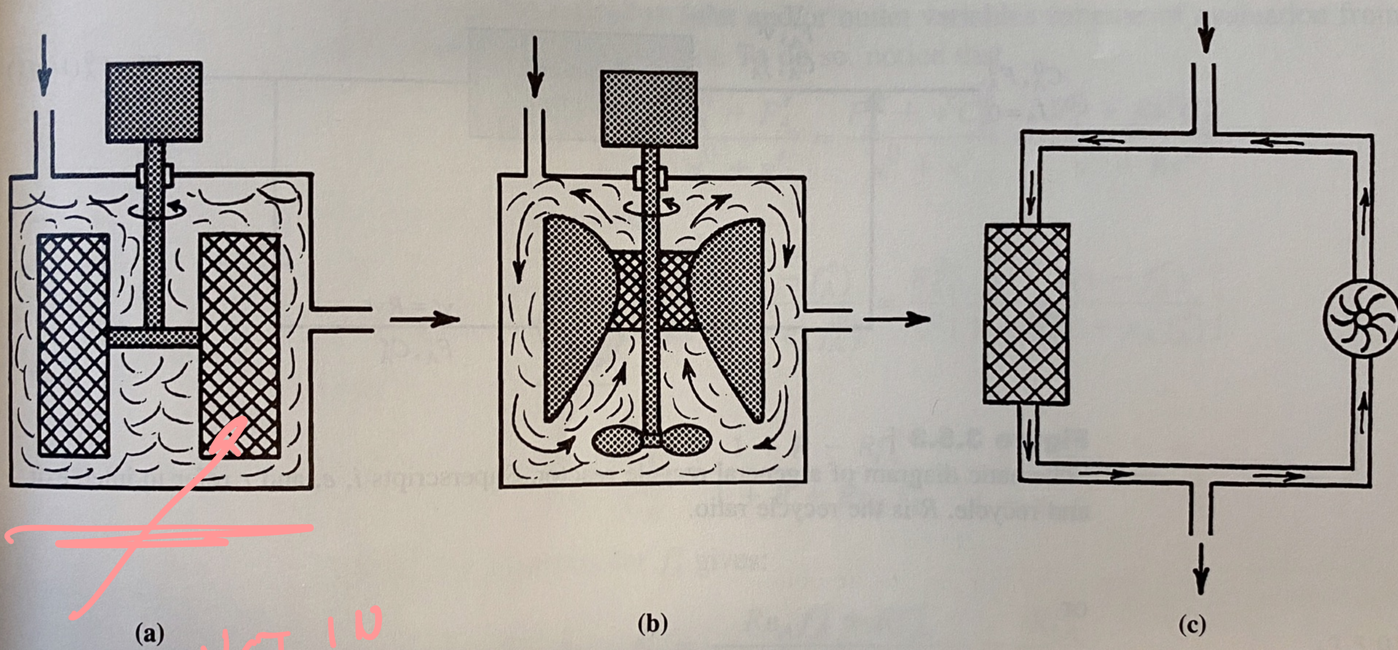


Figure 3.5.2 | Stirred contained solids reactors. [Reproduced from V. W. Weekman, Jr., *AIChE J.*, **20** (1974) p. 835, with permission of the American Institute of Chemical Engineers. Copyright © 1974 AIChE. All rights reserved.] **(a)** Carberry reactor, **(b)** Berty reactor (internal recycle reactor), **(c)** external recycle reactor.

IT IS CONVENIENT FOR THE CATALYST TO BE A SOLID

→ EASY SEPARATION FROM PRODUCTS

WOULD RATHER NOT CRUSH UP CATALYST IN EXPERIMENT OR PROCESS

{ CAN'T STIR LARGE PARTICLES

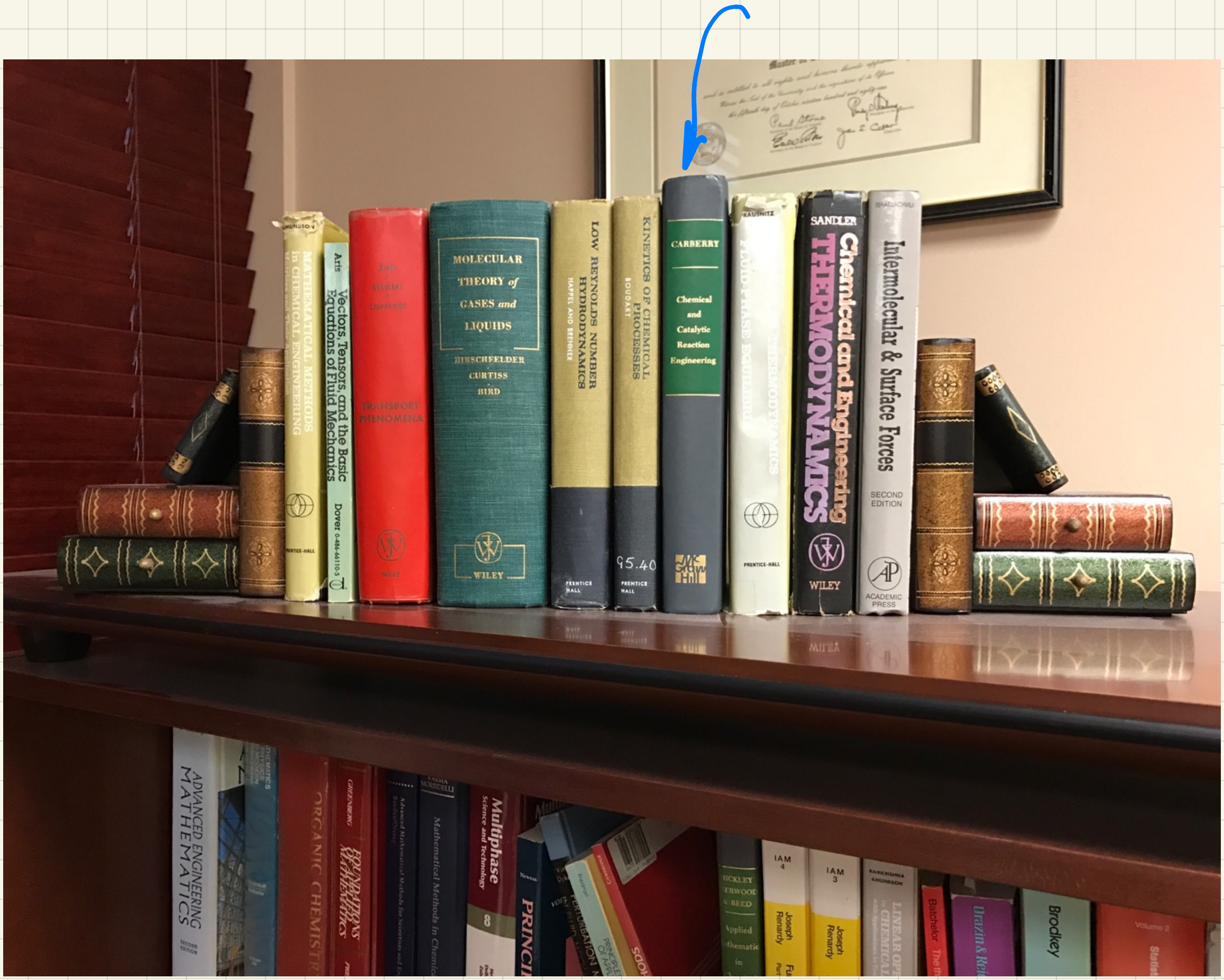
JAMES J. CARBERRY

PROFESSOR AT NOTRE DAME FROM 1963 — 2000

BESIDES PROFESSIONAL ACCOMPLISHMENTS

- FOA (FRIEND OF ARA PARSEGHIAN)
- OPERA AFICIONADO
- INTERHALL FOOTBALL COACH

  ... "GIPP" INCIDENT ...
- TAUGHT CHEG 445


MATHEMATICAL METHODS in CHEMICAL ENGINEERING
PRENTICE-HALL
Aris
Vectors, Tensors, and the Basic Equations of Fluid Mechanics
Dover
TRANSPORT PHENOMENA
WILEY
MOLECULAR THEORY of GASES and LIQUIDS
HIRSCHFELDER
CURTISS
BIRD
WILEY
LOW REYNOLDS NUMBER HYDRODYNAMICS
HAPPEL AND BRENNER
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KINETICS OF CHEMICAL PROCESSES
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ORGANIC CHEMISTRY
Multiphase
IAM 4
Joseph Renardy
IAM 3
Joseph Renardy
Batchelor
Brodkey

CBE 20255
Spring 2019
Test #2
3/20/19

1. Photo-isomerization of Resveratrol (50 points)

You have no doubt seen headlines such as:

Red wine and resveratrol: Good for your heart?

It is hard to know which of coffee, tea or (always) red wine is going to show up with health benefits in the weekly "science" press headline from one of the major news sources. These common beverages have many different molecular (if possibly trace) components so it is probably safe to expect more such headlines in the future (🙁 in contrast to eggs which just last week received a health downgrade!)

The reaction of trans to cis resveratrol has been studied by Benard, Britz-McKibbin and Gernigan (2007) in a photo-chemical reactor with UV illumination at 350 nm.

The reaction is:

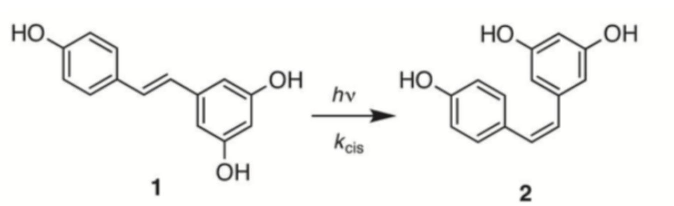


Figure 1. Photoisomerization of *trans*-resveratrol (**1**) into the sterically hindered *cis*-resveratrol (**2**) by UV irradiation in methanol-d_4.

The concentrations of trans and cis R were tracked using three different analysis techniques giving the data:

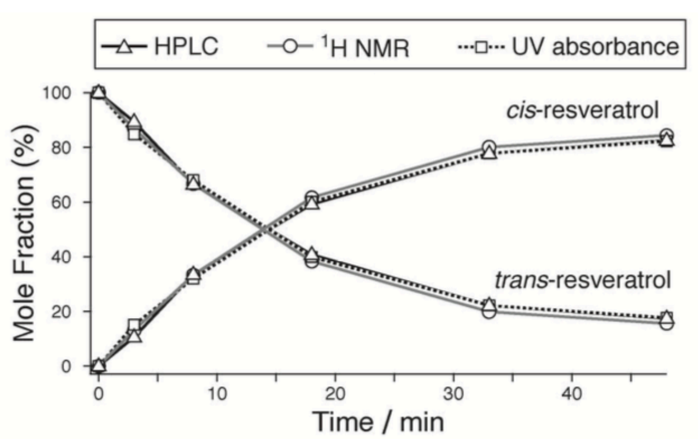


Figure 2. Assessment of the rate of photoisomerization of *trans*-resveratrol into *cis*-resveratrol by ^{1}H NMR, UV absorbance, and HPLC.

These data, not surprisingly, suggest a plot of the form

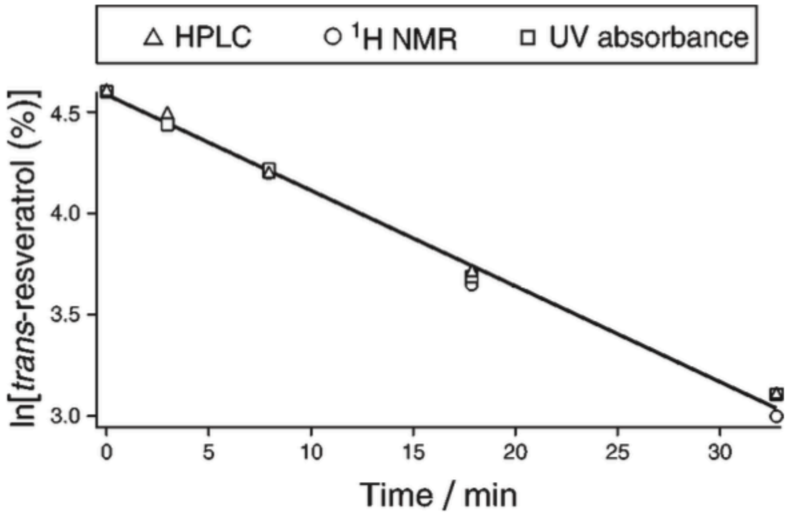
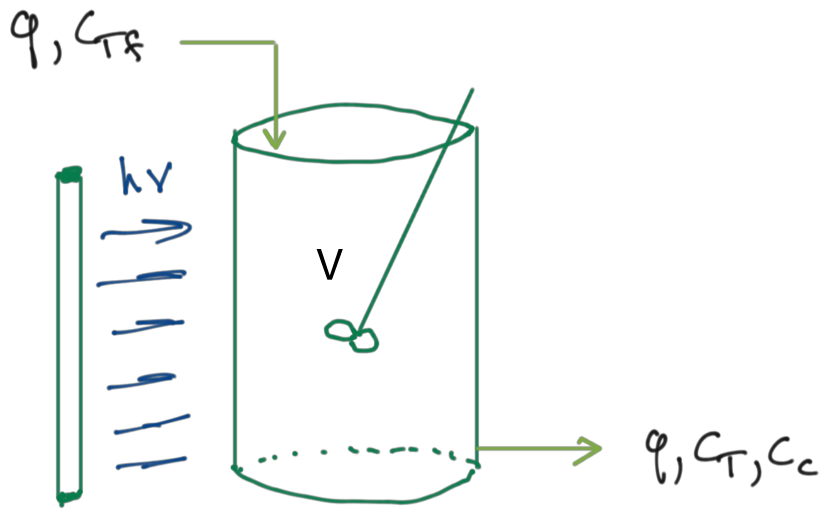


Figure 3. Determination of apparent rate constant (k_{cis}) and half-life ($t_{1/2}$) of *trans*-resveratrol photoisomerization based on pseudo-first-order kinetics by ¹H NMR, UV absorbance, and HPLC.

The trans-resveratrol had an initial concentration of 20 mM. (2.0 X10^{-2} mol/l) in methanol. We can assume that the liquid phase is well-mixed and uniformly illuminated.

A. What kinetic rate expression describes the concentration change trans to cis R?
B. What is the value of the rate constant associated with this kinetic expression?
C. Find an algebraic expression for the concentration of trans-R in the reactor at any time.
D. How long does it take for the initial contraction to be reduced to 1/2 of its initial value (a.k.a. "half-life")?
E. How long does it take for the initial concentration to be reduced to ~2% of its initial value?

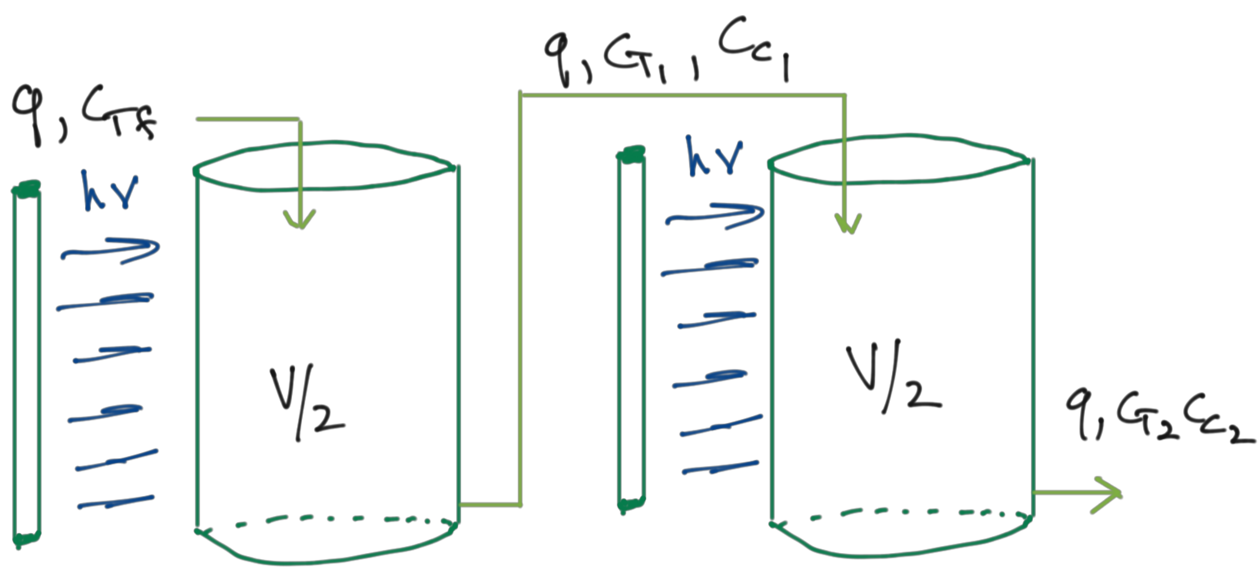
You have been asked to examine a business prospectus from a health - food startup company that intends to produce and market cis- R (hopefully without the methanol!). While they have a clever marketing plan and a well-known advertising agency is lined up, they are a little short on the technical details… such as how much cis-R they could produce in a 100 liter photo-reactor that is available to them and thus how many such reactors would be needed to produce 0.001 mol/s (which is about 16,000 lb/yr).



The feed concentration, C_{Tf} = 0.1 mol/l. You can assume that the temperature and illumination intensity are the same as for the batch reactor. Also, it is possible to recover the CIS-R by crystallization from the MeOH solutions.

F. As a first cut, you choose an exit concentration of CIS-R, C_C = 0.09 mol/l. What residence time, $\theta = V/q$, (V = reactor volume and q is volumetric flow rate) is necessary to achieve this concentration?
G. What feed flow rate is needed and how much total reactor volume is necessary to produce the requisite 0.001 mol/s of CIS-R?
H. For the same reactor volume and feed concentration, if you increase the flow rate to the reactor, does the production rate increase? Give an algebraic expression that shows this.
I. You determine that the current reactor requires 1 *W* of power per liter of reactor volume. How much electrical work is needed for each mol of cisR produced?

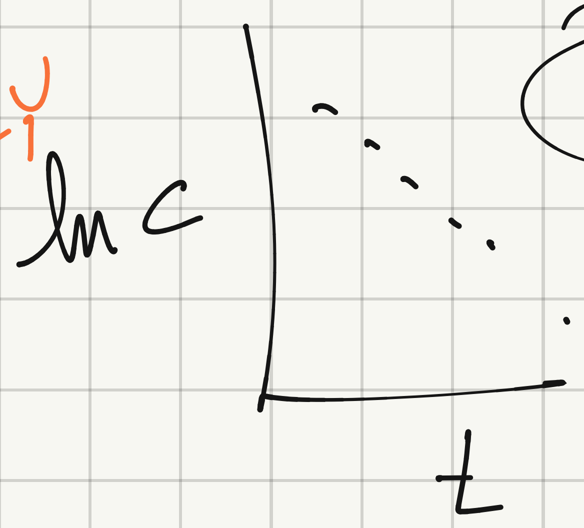
Extra Credit:
J. Since it is obvious that more than one reactor will be needed, you suggest configuring them as pairs of 2 that are in series. That is, the feed goes to the first reactor and the exit from the first reactor goes to the second reactor. Show that this is a "good" idea and give an explanation that will put you in good standing with your boss who is not a chemical engineer.



#1

TRANS-R $\longrightarrow$ CIS-R

ACTUALLY 55+ F.C.



(A) $r = -kC$ (5)

$\ln C - \ln C_0 = -kt$

(B) $-k = \dfrac{4.6 - 3.3}{33} = .04/\text{MIN}$ (5)

$= .00066/s$

(C) $C = C_0 \exp(-kt)$ (5)

(D) $\dfrac{\ln 1/2}{.04} = 17 \text{ MIN}$ (5)

(E) $\dfrac{\ln(.02)}{.04} = 98 \text{ MIN}$ (5) $\ln(.4) \sim 100 \text{ MIN}$

F

5 FOR EQ'S

$0 = qC_{Tf} - qC_T - kC_T V$

$0 = C_{TF} - C_T - kC_T \tau$

$\tau = \dfrac{V}{q}$

$\tau = \dfrac{C_{TF} - C_T}{C_T k}$, IF $C_c = .09$

$C_T = .01$

$$\tau = \frac{C_{TF} - C_T}{C_T k}, \quad \text{IF } C_c = .09, \quad C_T = .01$$

(5) FOR ANSWER

(F) $$\tau = \frac{.1 - .01}{(.01)(.04)} = 225 \text{ MIN} = 13500 \text{ S}$$

(G) $$P = .001 \frac{\text{MOL}}{\text{S}} \qquad C_c = .09 \text{ MOL}/l$$

$$= q C_c$$

(5)

$$q = \frac{.001 \text{ MOL/S}}{.09 \text{ MOL}/l} = .011 \, l/\text{S}$$

(5)

$$V = q\tau = .011 \, l/\text{s} \times 13500 \text{ s} = 150 \, l$$

(H)

$$P = q C_c \qquad 0 = q C_{Tf} - q C_T - k C_T V$$

$$0 = -q C_c + k C_T V$$

$$C_c = \frac{kV/q}{1 + kV/q}$$

$$p = \frac{C_{TF}\, k\, V/q}{1 + kV/q}\, q$$

q	p
.011	.001
.02	.0017
.03	.0023
.04	.0029

5 FOR EXPRESSION
5 TO EXPLAIN

(10)

(H)

i. $\left(\frac{1\,W}{l}\right) 150\,l = 150\,W$

$$= \frac{150\,J/s}{.001\,mol/s} = \frac{150000\,J}{MOL}$$

(5)

j.

$$0 = C_{TF} - C_{T_1} - k\tau C_{T_1}$$

$$0 = C_{T_1} - C_{T_2} - k\tau C_{T_2}$$

5

$$0 = C_{TF} - C_{T_1} - k\tau_2 C_{T_1}$$

$$0 = C_{T_1} - C_{T_2} - k\tau_2 C_{T_2}$$

$$C_{T_1} = \frac{C_{TF}}{1 + k\tau_2}$$

$$\tau_2 = V/2q$$

$$C_{T_2} = \frac{C_{TF}}{(1 + k\tau_2)^2}$$

$$\tau_2 = 6750$$

$$C_{T_2} = .003$$

5