CBE 40445
10/26/20

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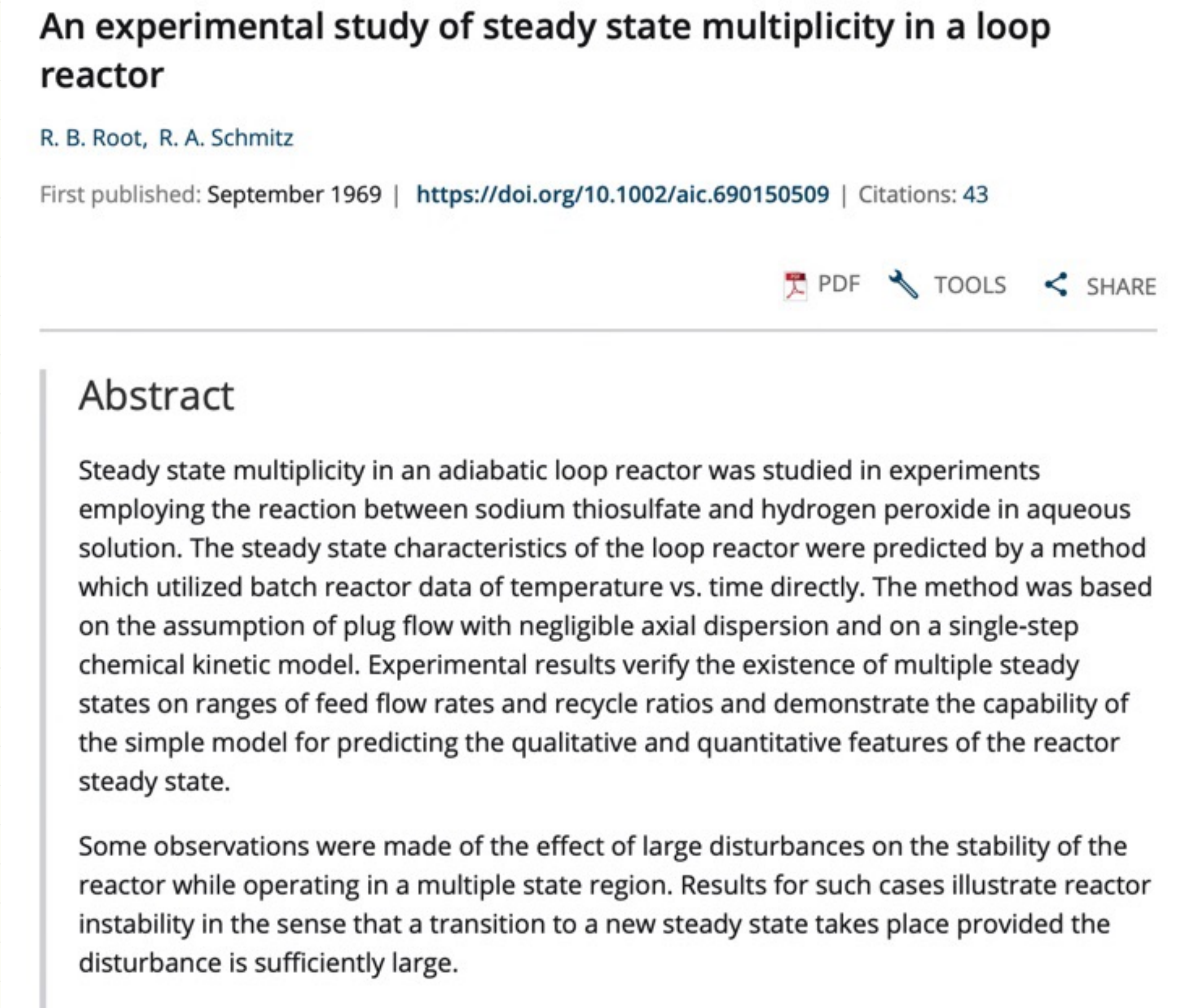
1) MULITIPLE STEADY STATES

MORE OR LESS JUST A CURIOSITY!!

2) MORE DETAILS ABOUT REACTOR INTERNALS



An experimental study of steady state multiplicity in a loop reactor

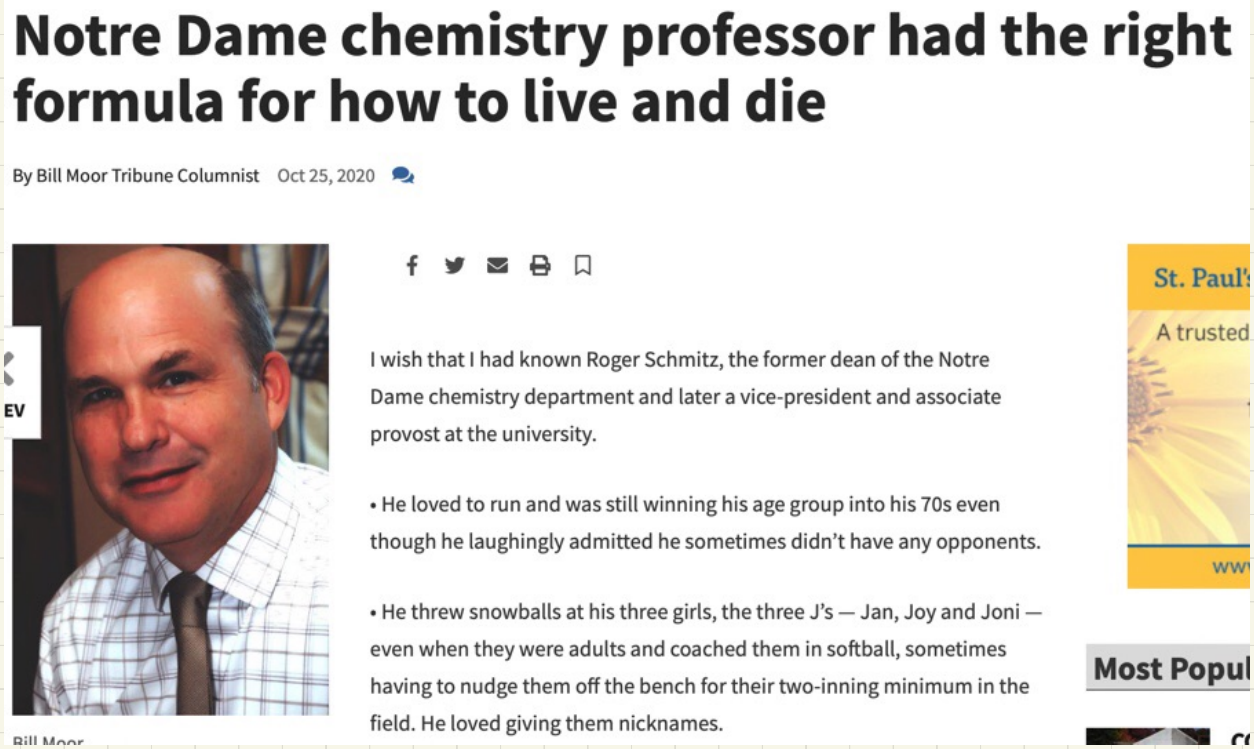
R. B. Root, R. A. Schmitz

First published: September 1969 | https://doi.org/10.1002/aic.690150509 | Citations: 43

Abstract

Steady state multiplicity in an adiabatic loop reactor was studied in experiments employing the reaction between sodium thiosulfate and hydrogen peroxide in aqueous solution. The steady state characteristics of the loop reactor were predicted by a method which utilized batch reactor data of temperature vs. time directly. The method was based on the assumption of plug flow with negligible axial dispersion and on a single-step chemical kinetic model. Experimental results verify the existence of multiple steady states on ranges of feed flow rates and recycle ratios and demonstrate the capability of the simple model for predicting the qualitative and quantitative features of the reactor steady state.

Some observations were made of the effect of large disturbances on the stability of the reactor while operating in a multiple state region. Results for such cases illustrate reactor instability in the sense that a transition to a new steady state takes place provided the disturbance is sufficiently large.



Notre Dame chemistry professor had the right formula for how to live and die

By Bill Moor Tribune Columnist Oct 25, 2020

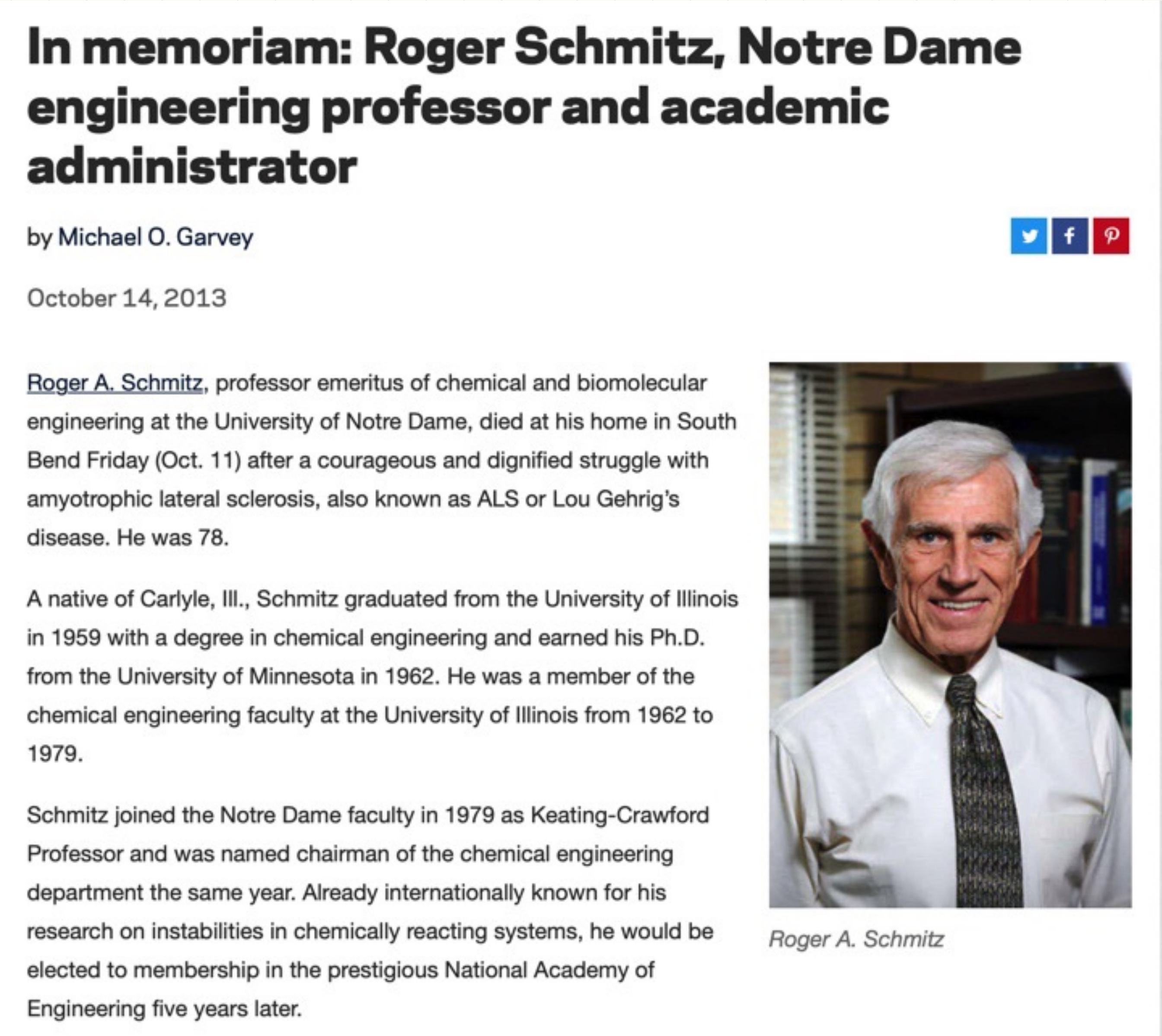
Bill Moor

I wish that I had known Roger Schmitz, the former dean of the Notre Dame chemistry department and later a vice-president and associate provost at the university.

- He loved to run and was still winning his age group into his 70s even though he laughingly admitted he sometimes didn't have any opponents.

- He threw snowballs at his three girls, the three J's — Jan, Joy and Joni — even when they were adults and coached them in softball, sometimes having to nudge them off the bench for their two-inning minimum in the field. He loved giving them nicknames.

St. Paul'
A trusted
ww



In memoriam: Roger Schmitz, Notre Dame engineering professor and academic administrator

by Michael O. Garvey

October 14, 2013

Roger A. Schmitz, professor emeritus of chemical and biomolecular engineering at the University of Notre Dame, died at his home in South Bend Friday (Oct. 11) after a courageous and dignified struggle with amyotrophic lateral sclerosis, also known as ALS or Lou Gehrig's disease. He was 78.

A native of Carlyle, Ill., Schmitz graduated from the University of Illinois in 1959 with a degree in chemical engineering and earned his Ph.D. from the University of Minnesota in 1962. He was a member of the chemical engineering faculty at the University of Illinois from 1962 to 1979.

Schmitz joined the Notre Dame faculty in 1979 as Keating-Crawford Professor and was named chairman of the chemical engineering department the same year. Already internationally known for his research on instabilities in chemically reacting systems, he would be elected to membership in the prestigious National Academy of Engineering five years later.

Roger A. Schmitz

FOR A CSTR THAT HAS AN EXOTHERMIC REACTION TO BE AT STEADY STATE

HEAT PRODUCED BY REACTION = HEAT REMOVED BY COOLING

SO IF $k = A\exp\left(-\frac{E_A}{RT}\right)$

TEMP WILL INCREASE UNTIL SOMETHING HAPPENS!

$$= \dot{m} c_p (T^* - T^*_{out})$$

JACKET

$$\underline{\underline{\dot{Q}}} = UA\,(T^* - T_R)$$

BALANCES

$(\Delta H_r\, r)$

REACTOR

WHERE DOES BALANCE OCCUR?

YOU COULD CONTROL THIS BY ADJUSTING EITHER F_A, OR $\dot{m}$

MIGHT EXPECT THAT COULD PICK WHAT YOU WANT.

IT TURNS OUT THAT FOR FIXED $\dot{m}$, IT IS POSSIBLE THAT THE BALANCE COULD BE AT A LOW (T^*-T_R) OR A HIGH (T^*-T_R) IF SO!

3 STEADY STATES

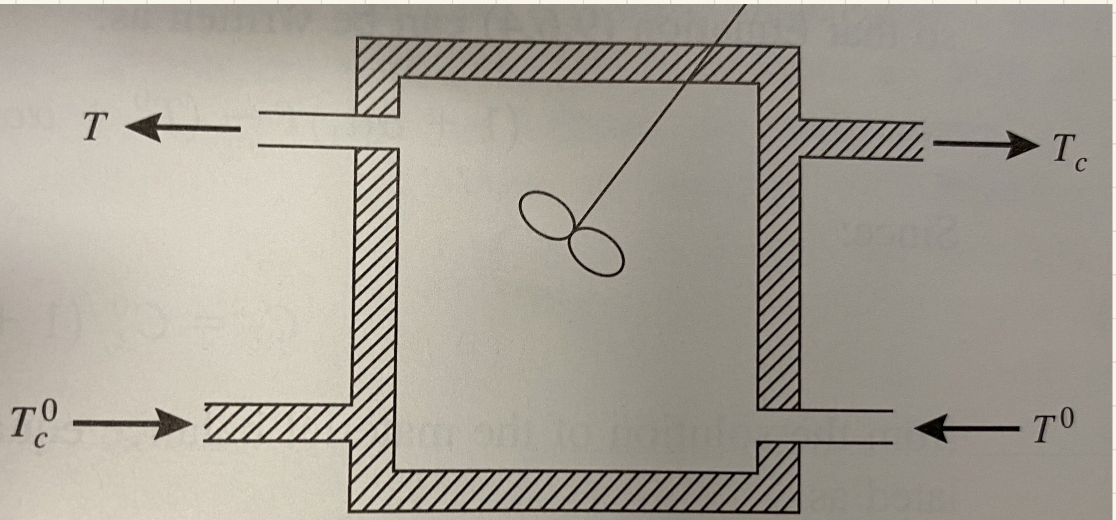


Figure 9.6.1 |
Schematic illustration of a CSTR that is maintained at temperature T by transferring heat to a coolant fluid ($T_c > T_c^0$).

LOOK AT JUST THE COOLING JACKET

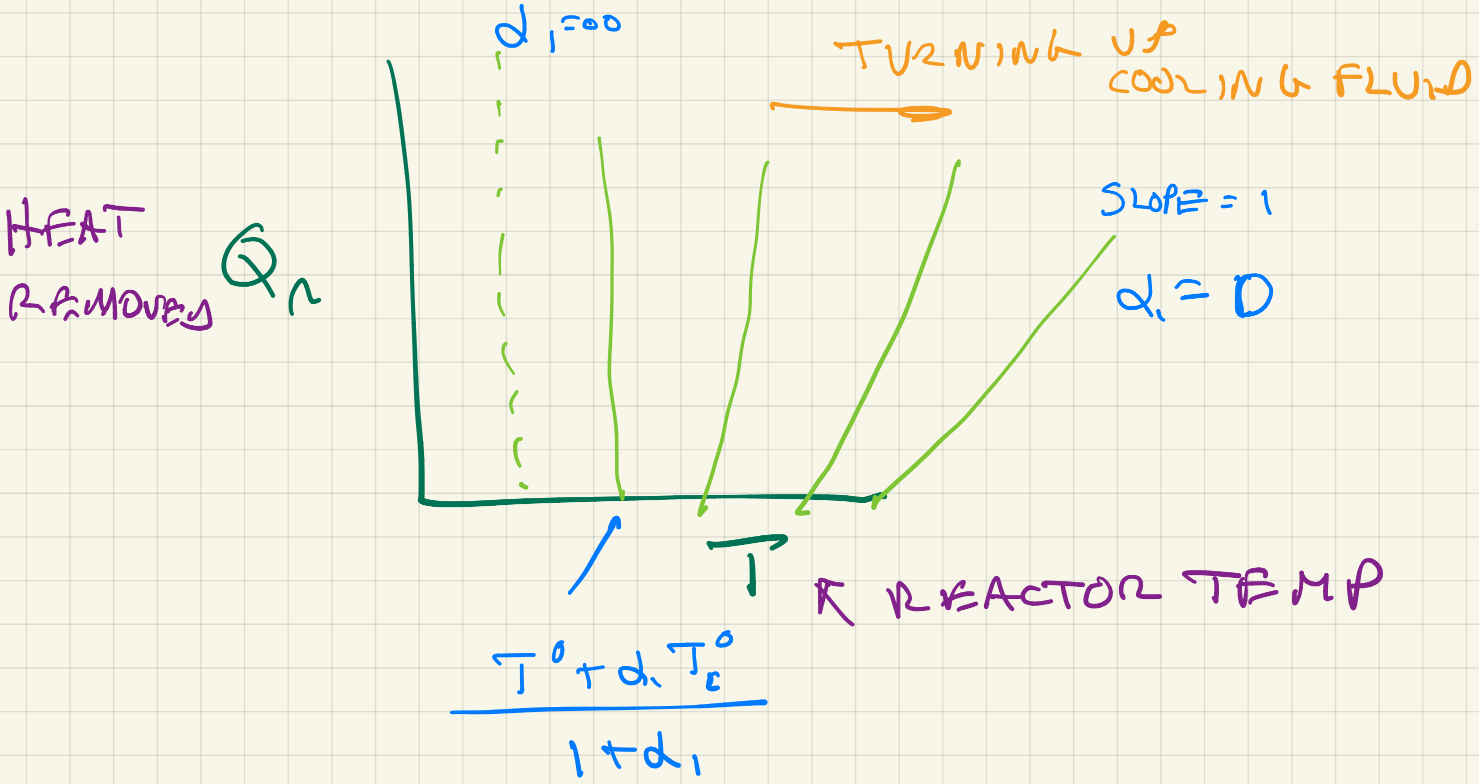
$$\dot{Q} = UA_H(T - T_c) = q_c C_{p_c}(T_c - T_c^0)$$

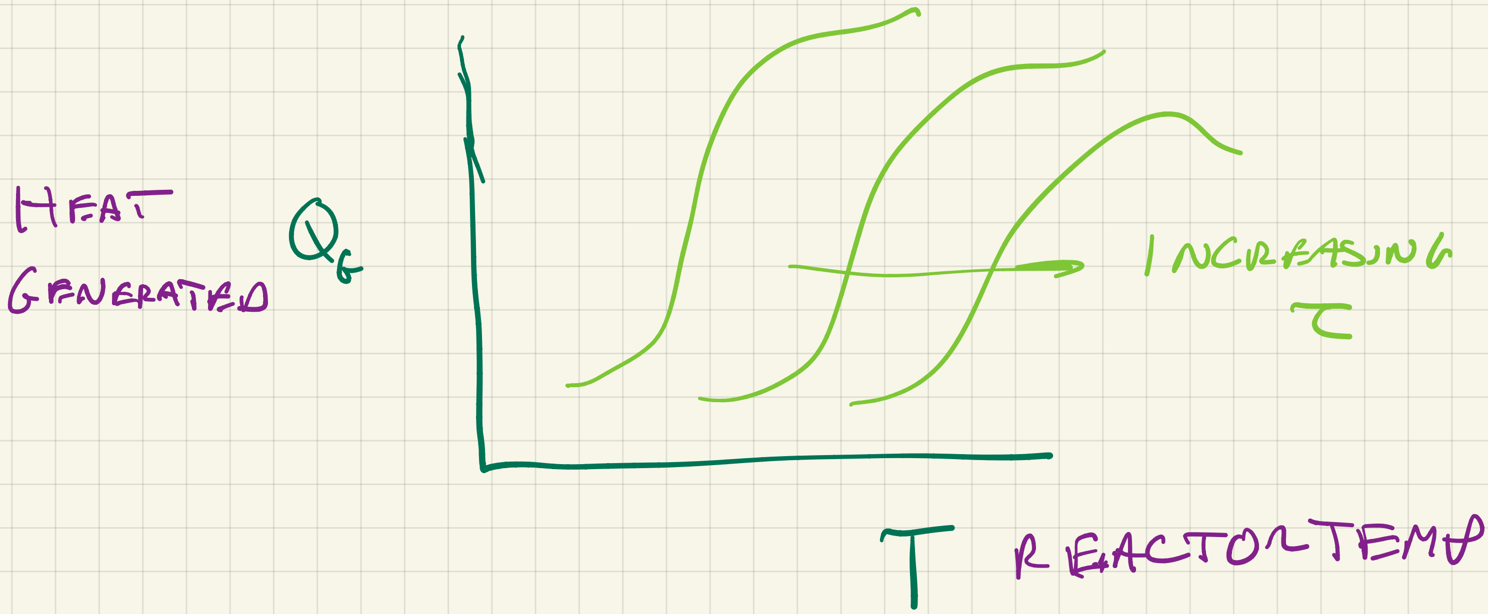
COOLANT T

SOLVE FOR Tc →

$$T_c = \frac{C_{pc}\, q_c\, T_{co} + UA_H T}{C_{pc}\, q_c + UA_H}$$

COOLING PROVIDES A FAMILY OF LINES

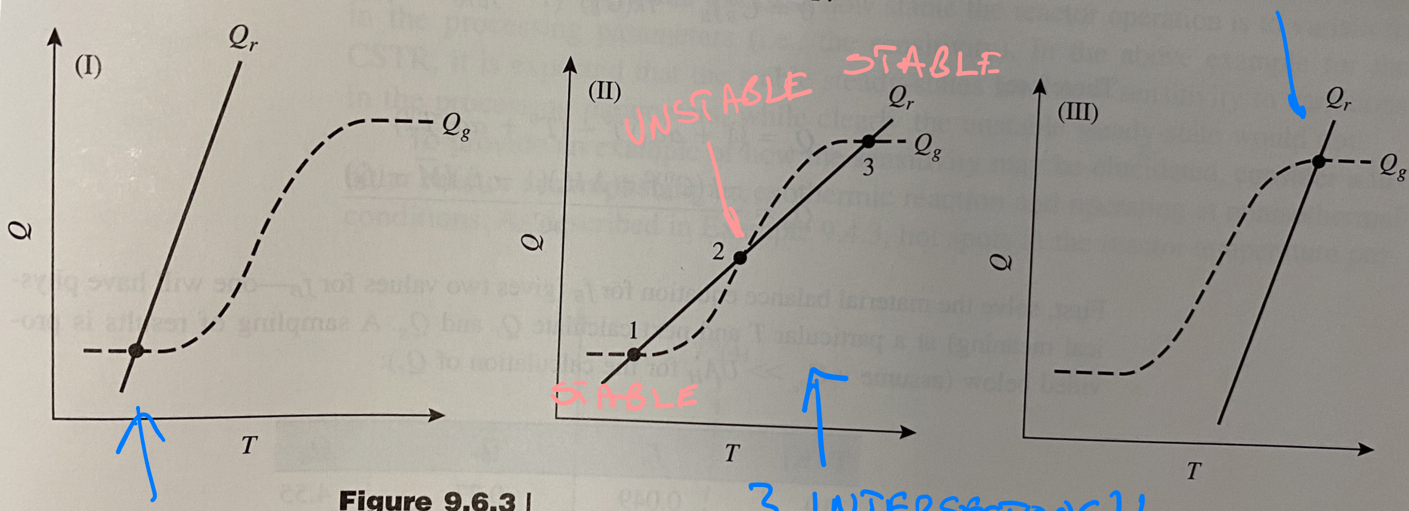




INTERSECTION OF Q_R + Q_G IS A SOLUTION TO T FOR REACTOR

Figure 9.6.2 |
Schematic illustration of Q_r and Q_g as functions of T.

1 SOLUTION



3 INTERSECTIONS !!

Figure 9.6.3 |
Steady-state solutions to Equation (9.6.3).

1 SOLUTION

T, the results are illustrated

LOW COOLING CAPACITY
JUST MATCHES
LOW REACTION TEMP

LOW COOLING
CAPACITY
BUT
REMOVE IF
T-REACTION
IS
HIGH
ENOUGH

HIGHER COOLING CAPACITY
CAN MATCH LOW T
OR HIGH T

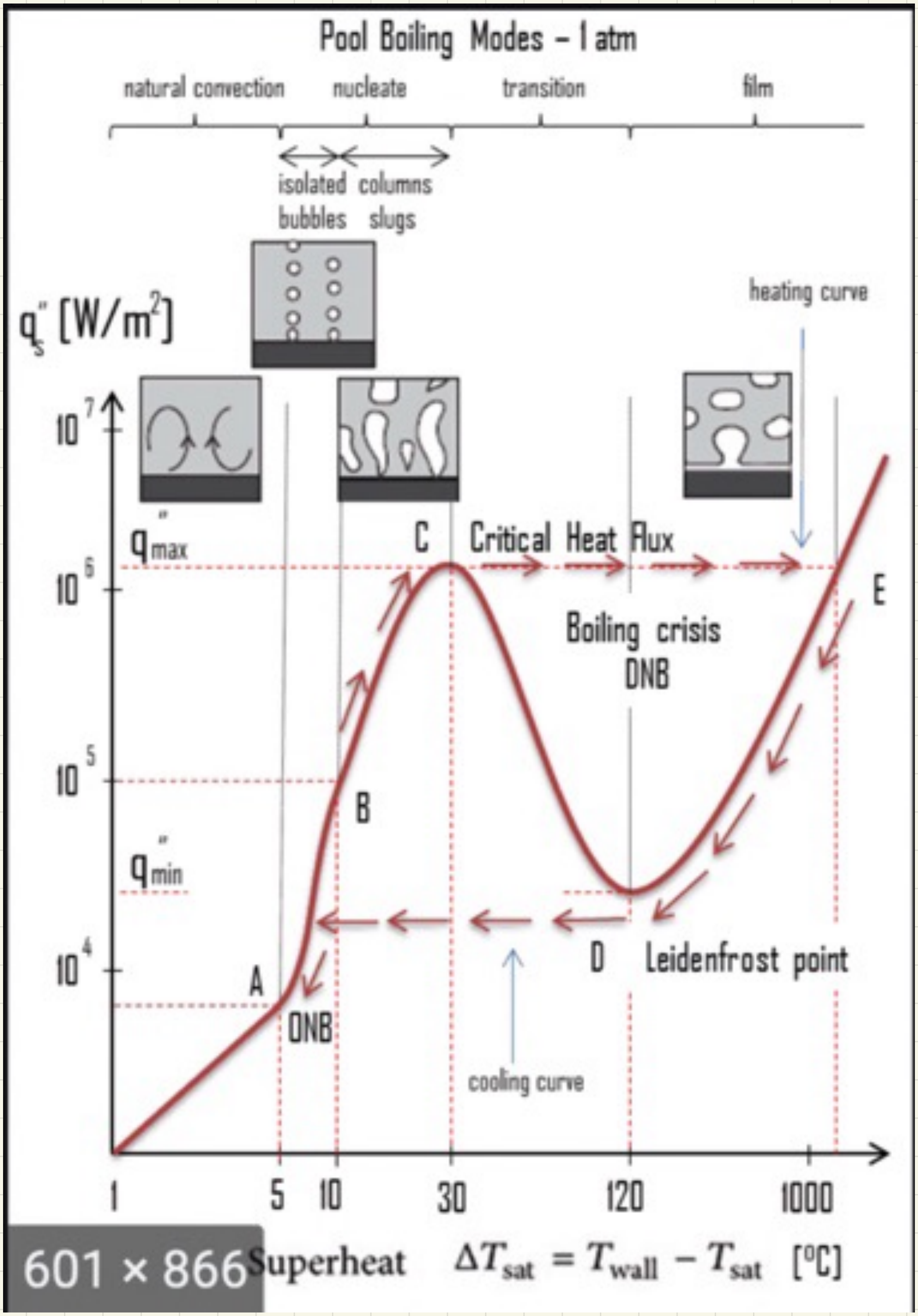
3 STEADY STATES

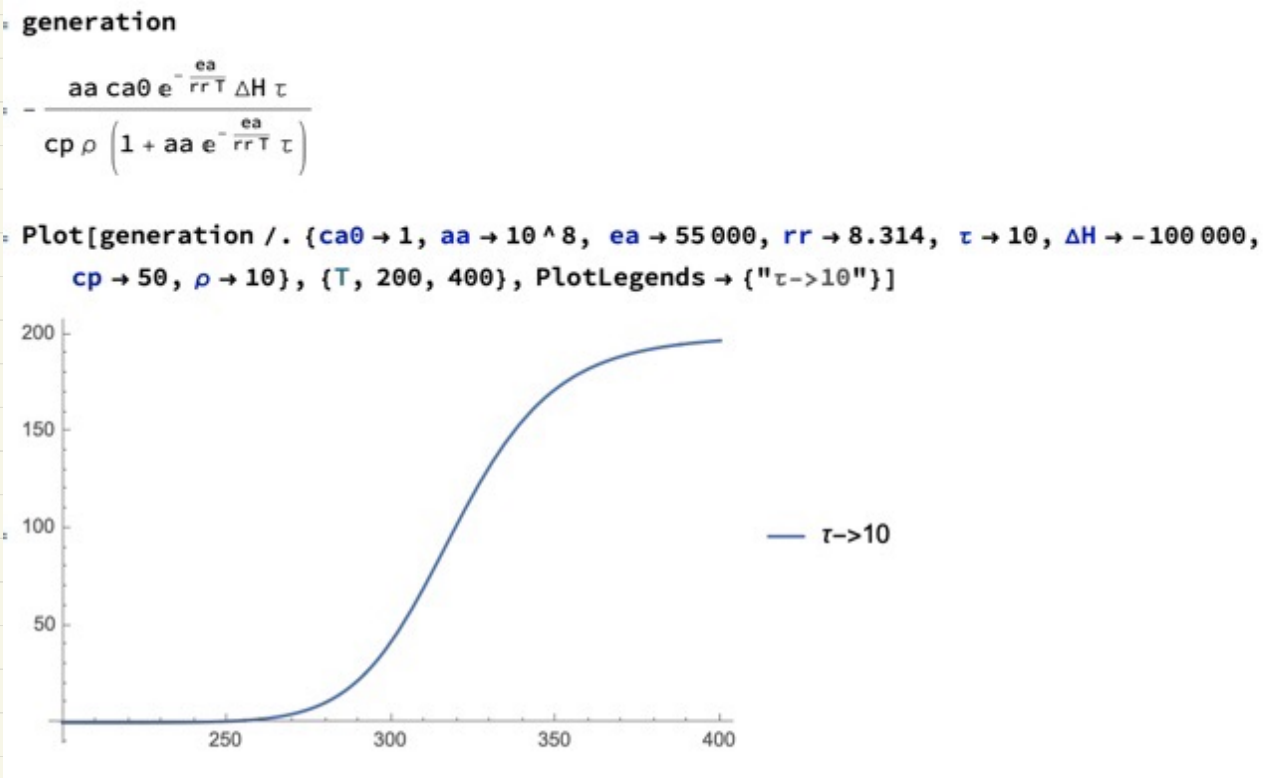
1 → SLIGHT INCREASE IN T $Q_r > Q_G$ SO IT GOES BACK

3 SAME

2 → SLIGHT INCREASE IN T, $Q_G > Q$ SO IT GETS HOTTER.

HYSTERESIS IN BOILING





```
generation
```

$$-\frac{aa\,ca0\,e^{-\frac{ea}{rr\,T}}\,\Delta H\,\tau}{cp\,\rho\left(1+aa\,e^{-\frac{ea}{rr\,T}}\,\tau\right)}$$

```
Plot[generation /. {ca0 → 1, aa → 10 ^ 8, ea → 55 000, rr → 8.314, τ → 10, ΔH → -100 000,
    cp → 50, ρ → 10}, {T, 200, 400}, PlotLegends → {"τ->10"}]
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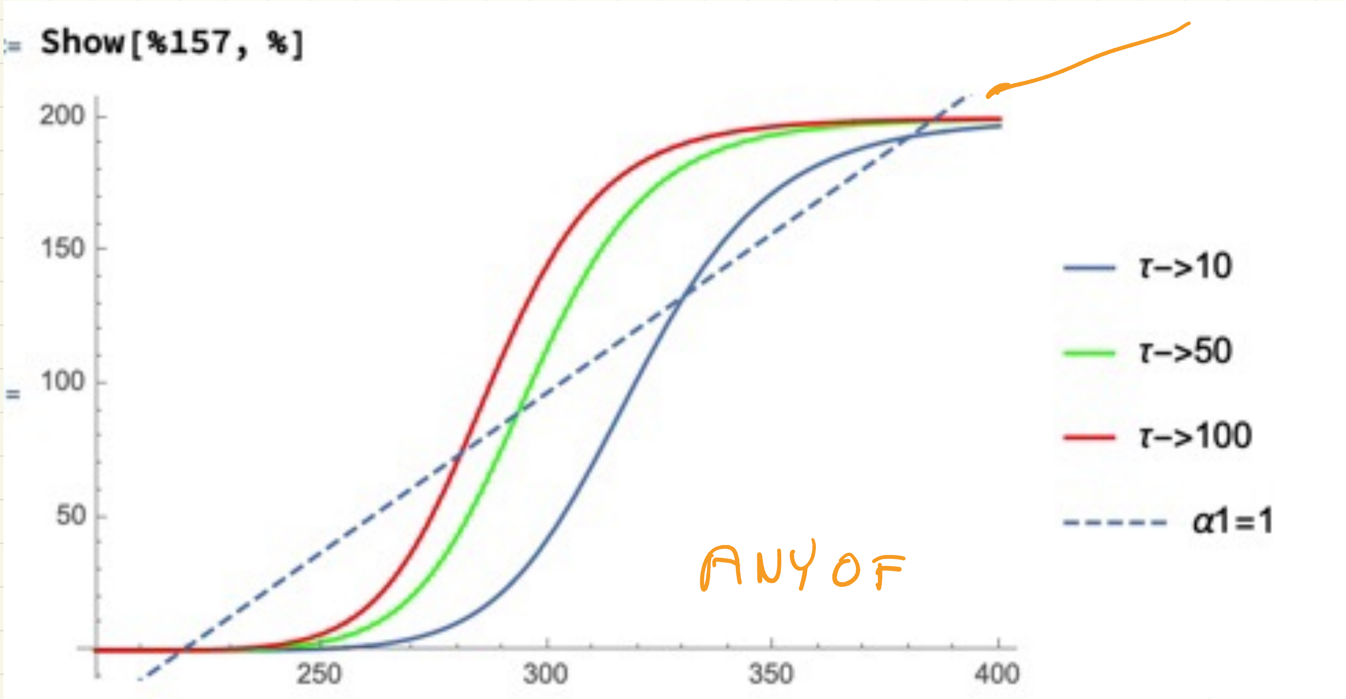
COOLING:

$(1+\alpha_1)T-(T_0-\alpha_1 T_c^0)$



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Show[%157, %]
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ANY OF THESE COULD HAVE MULTIPLE STEADY STATES

PLUG BACK IN

$$\dot{Q} = \frac{U A_H q_c C_{pc}}{U A_H + q_c C_{pc}} \left(T - T_c^0\right)$$

$$\boxed{= \lambda_\lambda \left(T - T_c^0\right)}$$

NOW BACK TO E-BALANCE FOR CSTR

$$\dot{Q} = -\Delta H_r \underline{F_A^0 (1 - f_A)} + F_A^0 C_p \left(T - T^0\right)$$

MASS BALANCE

$$0 = q\left(C_A^0 - C_A\right) - k C_A V$$

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

WE GET

$$\dot{Q} = \Delta H_r k C_A V + q \rho C_p \left(T - T^0\right)$$

$$\frac{\lambda_\lambda}{q \rho C_p}\left(T_c^0 - T\right) = \frac{k C_A \tau \Delta H_r}{\rho C_p}\left(T - T^0\right)$$

USING SLIGHTLY SIMPLER NOTATION

$$\alpha_1 \equiv \frac{\lambda_1}{q \rho C_p}$$

$$\alpha_2 \equiv \frac{-k \tau \Delta H_r}{\rho C_p}$$

WE GET

$$(1+\alpha_1)T - (T^0 - \alpha_1 T_c^0) = \alpha_2 C_A$$

$$C_A = \frac{C_A^0}{1+k\tau}$$

WHICH GIVES

$$(1+\alpha_1)T - (T^0 - \alpha_1 T_c) = \frac{\alpha_2 C_A^0}{1+k\tau}$$

Q_r (HEAT REMOVED) = Q_G HEAT GENERATED

ADDITIONAL DETAILS ABOUT THE "INSIDE" OF CHEMICAL REACTORS

→ PACKED BED FLOW + PRESSURE DROP

EFFECTIVENESS

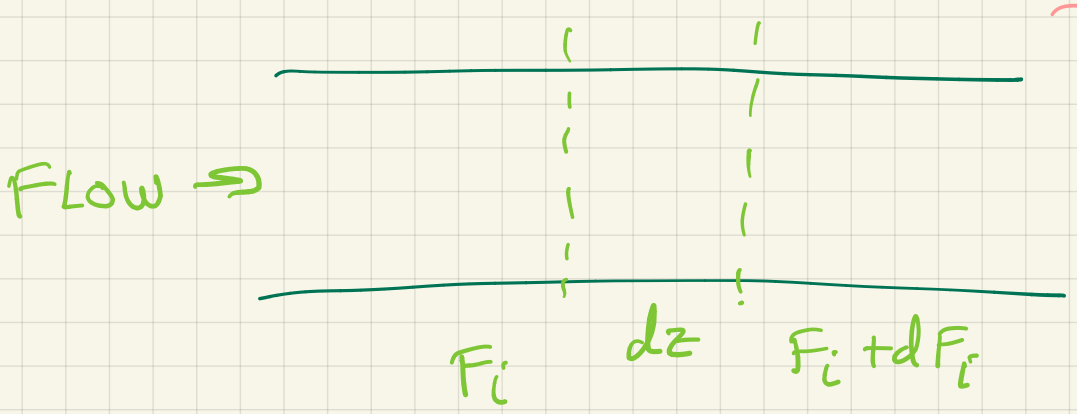
TRADE OFF WITH η_0

→ EFFECT OF CHANGE OF MOLES FOR GAS REACTIONS

→ RADIAL CONCENTRATION EFFECTS

— DIFFERENT CONFIGURATIONS FOR REACTORS

EFFECT OF CATALYST PARTICLE SIZE ON REACTOR PERFORMANCE

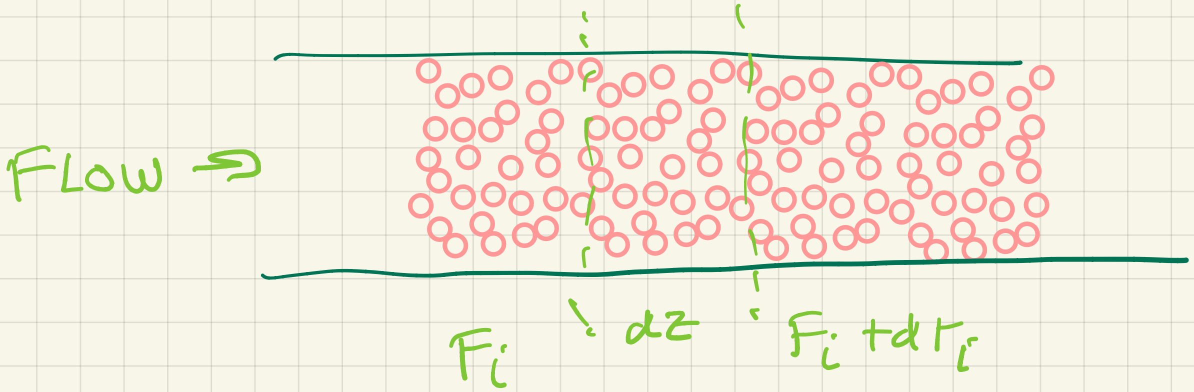


HOW WE HAVE BEEN TREATING ENTIRE REACTOR

$$F_i = F_i + dF_i + (-r_i)\,\rho\, dV$$

$$F = u_i A_c C_i \;, \quad V = A_c z$$

$$-u \frac{dC_i}{dz} = (-r_i)\,\rho$$



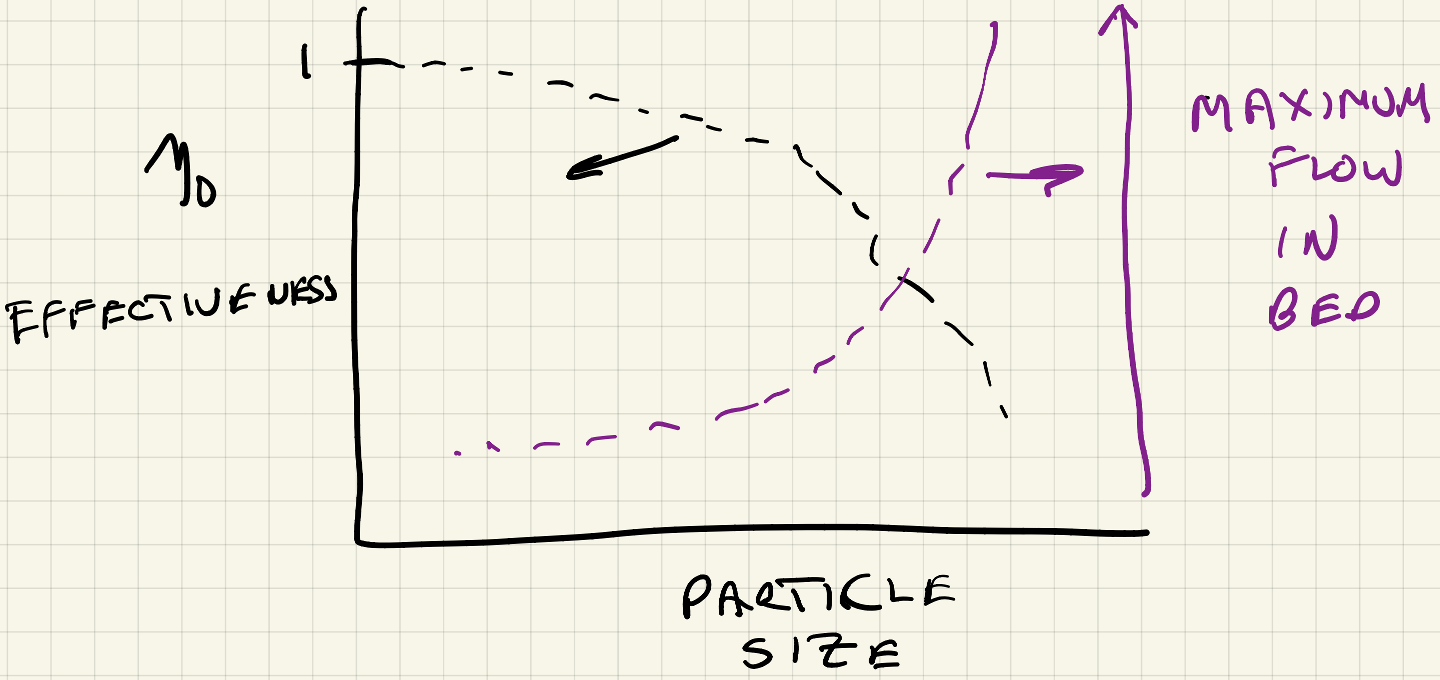
SO NOW, TO BE PRECISE FOR THE CASE WITH A CATALYST

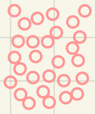
$$-u\frac{dC_i}{dz} = \eta_0 \, \rho_B \, (-r_i)\wedge$$

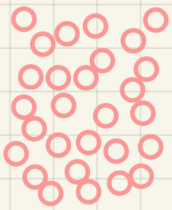
EFFECTIVENESS FACTOR

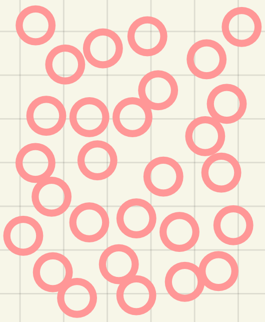
DENSITY OF CATALYST $\frac{\text{MASS}}{\text{VOLUM}}$

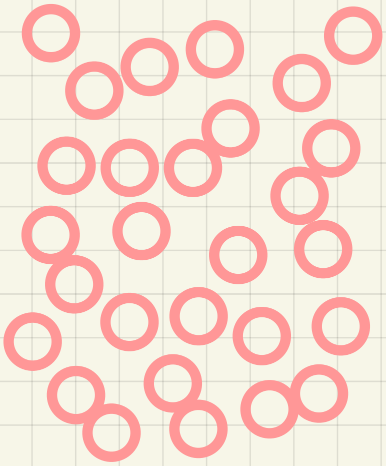
RATE: $\frac{\text{MOLES/TIME}}{\text{MASS CATALYST}}$

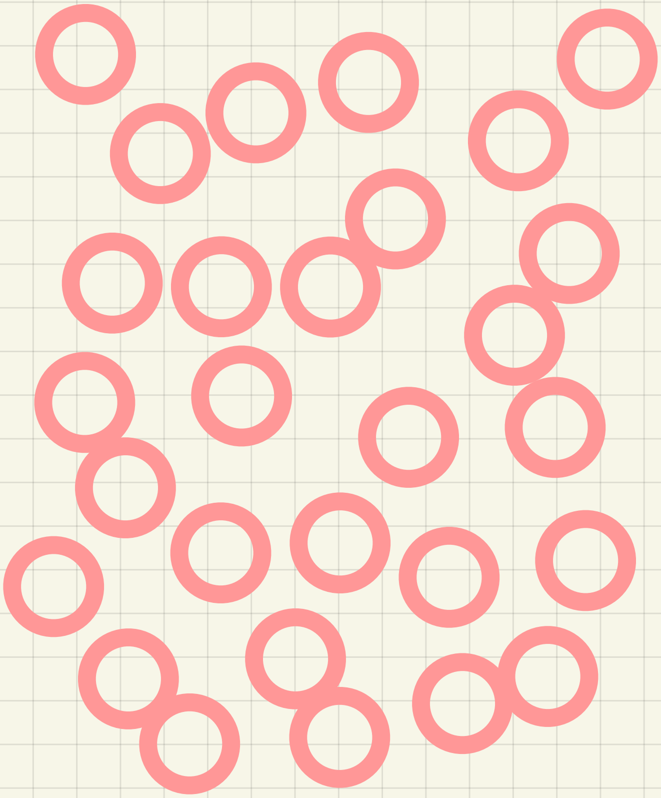












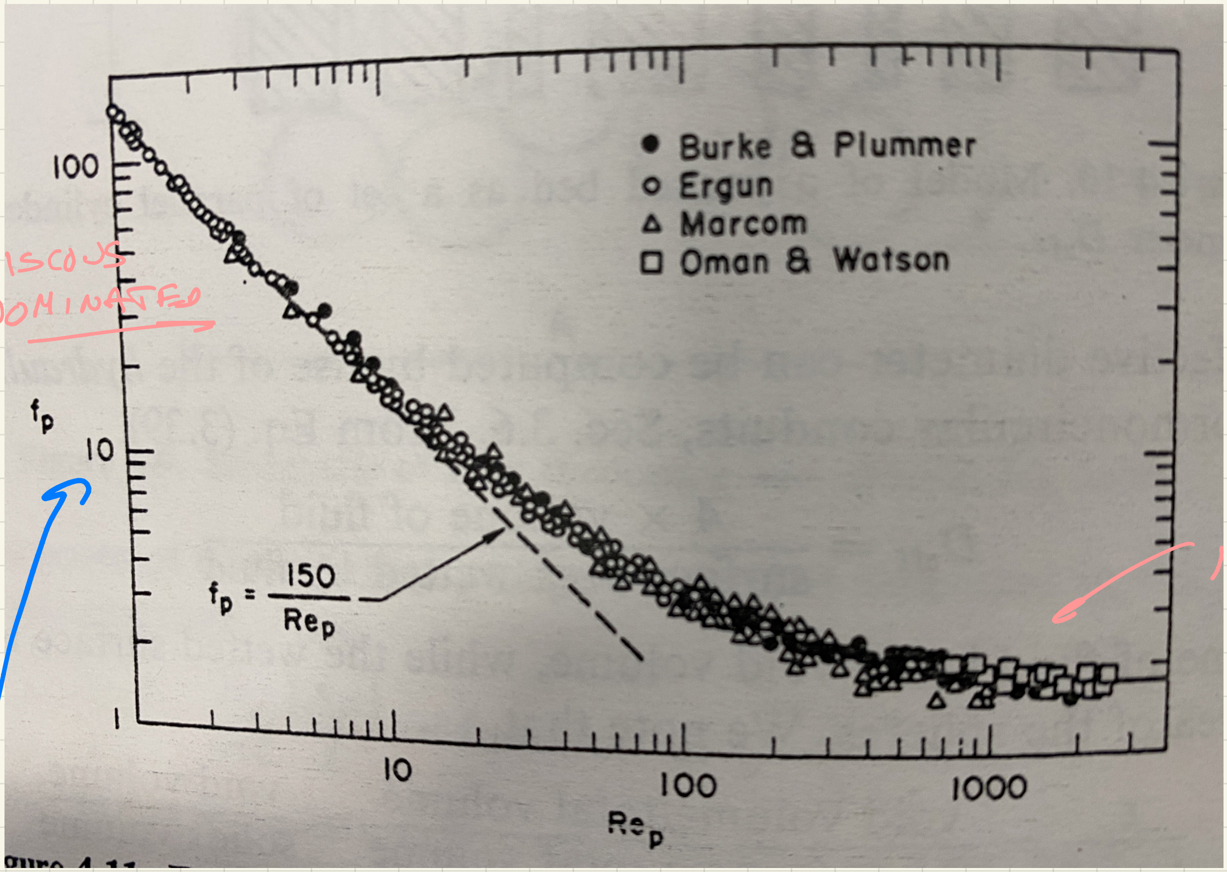
FOR SAME GEOMETRY OF PACKING, THE FRACTION OF VOLUME THAT IS CATALYST DOESN'T CHANGE

$\varepsilon \sim 0.37$ FOR RANDOM SPHERES

→ WITH A DISTRIBUTION OF SIZES ε WILL GO WAY DOWN

→ FOR FIGURES AS SHOWN η WILL GO DOWN AS $R \uparrow$

FLOW IN PACKED BEDS



FROM DENN: 'PROCESS FLUID MECHANICS"

VISCOUS DOMINATED

INERTIAL DOMINATED

"FORM DRAG"

$$f_p \equiv f_f\left(\frac{1-\bar{\varepsilon}_B}{\varepsilon_B^{3}}\right)$$

$$f_f \equiv \frac{d_p\,\Delta P}{\rho u^2 L}$$

$$f_f\left(\frac{1-\bar{\varepsilon}_B}{\bar{\varepsilon}_B^{2}}\right) = \left[1.75 + 150\,\frac{(1-\bar{\varepsilon}_B)}{Re}\right]$$

$$Re = \frac{d_p\,u\,\rho_f}{\mu_f}$$

MORE STANDARD DEFINITION FOR PACKED BED FLOW

$$Re_p \equiv \frac{d_p\,u\,\rho_f}{(1-\varepsilon)\mu_f}$$

FOR LOW Re

$$\frac{\Delta P}{L}\,\frac{d_p}{\rho u^2}\,\frac{\varepsilon^3}{(1-\varepsilon)} = \frac{150(1-\varepsilon)\mu}{\rho\, d_p\, u}$$

$$\frac{\Delta P}{L} = \frac{150\,(1-\varepsilon)^2\,\mu\, u}{d_p^2\,\varepsilon^3}$$

PRESSURE DROP IS LINEAR IN

$$U = \frac{q}{A_c}$$

ALSO CALLED "SUPERFICIAL VELOCITY"

BUT $\frac{\Delta P}{L}$ ↑ as $\frac{1}{d_p^2}$

COULD BE THAT $\eta_0 \sim \frac{1}{\phi_0}$

$$\phi_0 = d_p\sqrt{\frac{k}{D}}$$

THUS AS YOU REDUCE d_p, LINEAR GAIN IN EFFECTIVENESS BUT A QUADRATIC PENALTY IN $\frac{\Delta P}{L}$

"COMPLETE" EQUATIONS FOR PLUG FLOW REACTORS

$$-u \frac{dC_i}{dz} = \eta_o \rho_B (-\nu_i) r$$

MASS

ENERGY

$$u \rho C_p \frac{dT}{dz} = \left(-\Delta H_r\big|_{T_0}\right) \eta_o \rho_B (-\nu_i) r - \frac{4U}{d_t}\left(T - T^*\right)$$

$$-\frac{dP}{dz} = \frac{f_f \rho u^2}{g_c d_p}$$

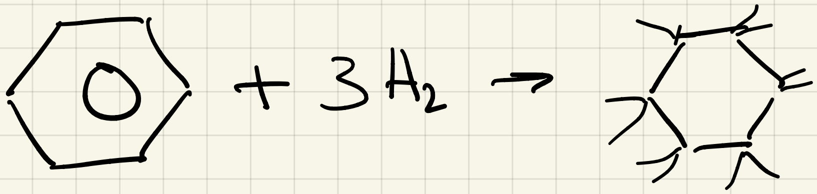
MOMENTUM

$$g_c \equiv 1 \frac{kg\ m}{N\ s^2}$$

$$g_c = 32.174 \frac{lb_m}{lb_f} \frac{ft}{s^2}$$

WE ARE FAMILAR WITH MASS+ENERGY WOULD NEED TO ALSO SOLVE MOMENTUM SIMULTANEOUSLY IF U CHANGED SIGNIFICANTLY.

EXAMPLE 10.2.1



$$r_B = P_{H_2} k_0 K_0 \exp\left[\frac{2700\ \text{CAL/MOL}}{R_G T}\right] C_B \quad \frac{\text{MOL}}{\text{g CAT s}}$$

1ST ORDER IN HYDROGEN

$$k_0 = 4.22\ \text{MOL}/\text{gCAT-s-TORR}$$

$$K_0 = 1.11 \times 10^{-3}\ \frac{\text{cm}^3}{\text{MOL}}$$

$$P_{H_2} \rightarrow \text{TORR}$$

REACTION

$$P_{H_2} = 685\ \text{TORR}$$

$$\rho_B = 1.2\ \text{gCAT}/\text{cm}^3$$

$$\frac{L}{u} = 0.0455\ \text{s}$$

$$T^0 = 150\ \text{C}$$

$$\overline{C_p} = 1.22 \times 10^5\ \frac{\text{J}}{\text{KMOL C}}$$

$$-\Delta H_r \big|_{T_0} = 2.09 \times 10^8\ \text{J/KMOL}$$

$$r_J = 0$$

MASS:
$$-u\frac{dC_B}{dz} = \rho_B r_B$$

$$u\rho\overline{C_p}\frac{dT}{dz} = (-\Delta H_r)\rho_B r_B$$

$$C_B = C_B^0, \quad T = T^0 \quad @\ z = 0$$

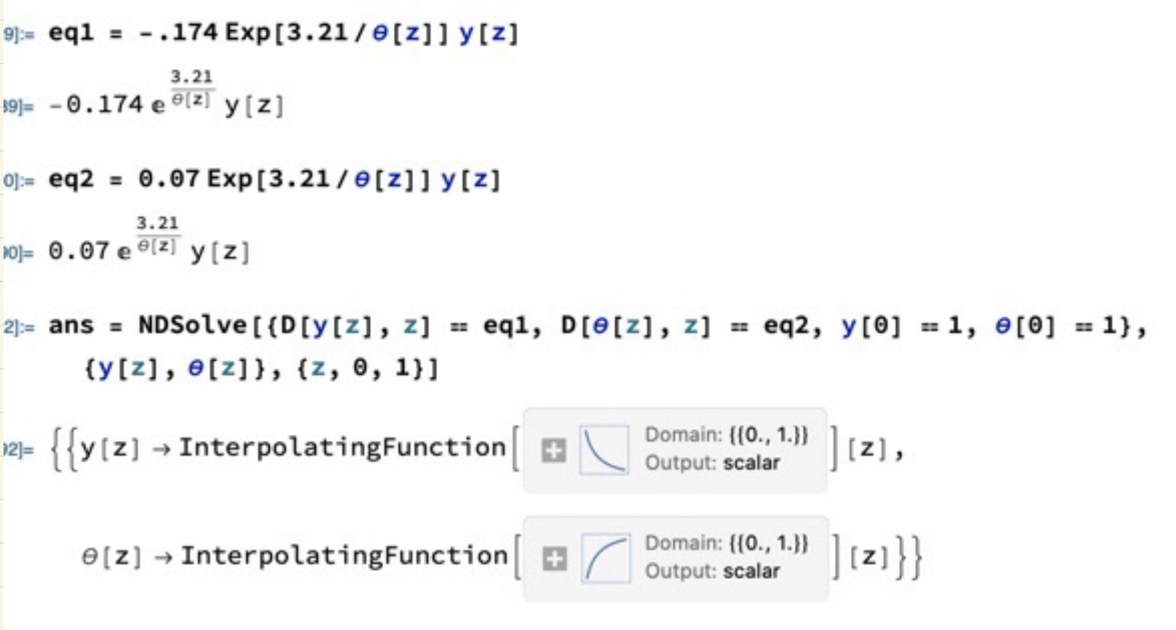
$$y = \frac{C_B}{C_B^0}, \quad \bar{\Theta} = \frac{T}{T_0} \quad Z = \frac{z}{L}$$

$$\frac{dy}{dZ} = \left(\eta\rho_B\frac{L}{u}\right)ky$$

$$\frac{d\Theta}{dZ} = \left(\frac{\rho_B - \Delta H_r\ L}{T\ \rho\overline{C_p}\ u}\right)k\ y$$

$$\frac{dy}{dZ} = -.174\exp\left(\frac{3.21}{\Theta}\right)y$$

$$\frac{d\bar{\Theta}}{dZ} = 0.07\exp\left(\frac{3.21}{\Theta}\right)y$$



```
9]:= eq1 = -.174 Exp[3.21/θ[z]] y[z]
```

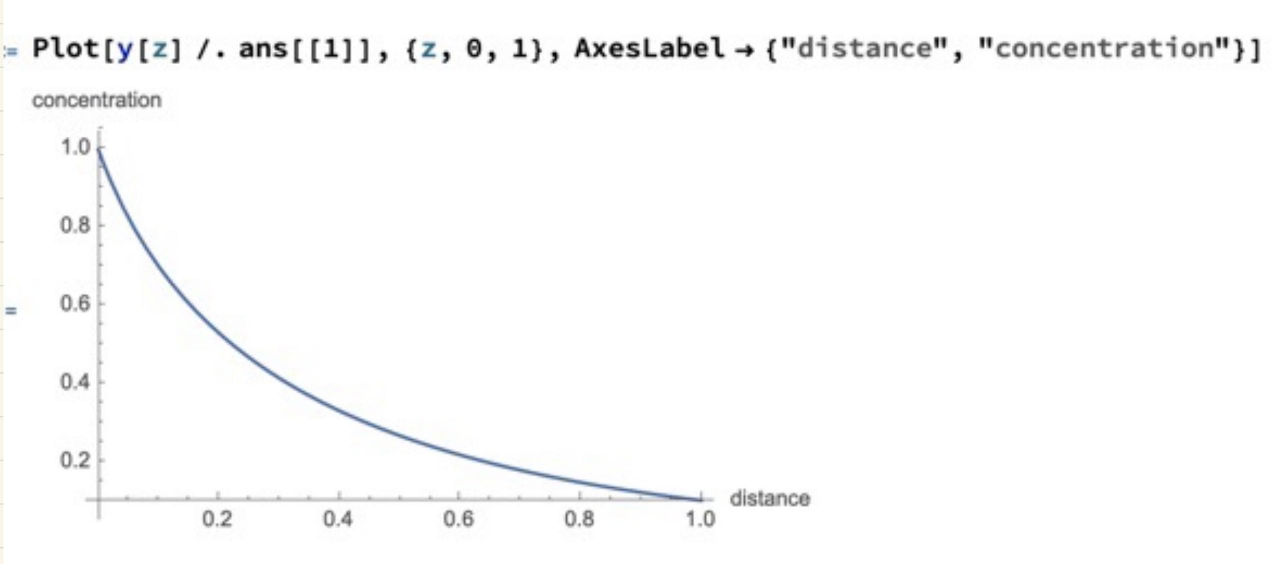
39]= $-0.174\, e^{\frac{3.21}{\theta[z]}}\, y[z]$

```
0]:= eq2 = 0.07 Exp[3.21/θ[z]] y[z]
```

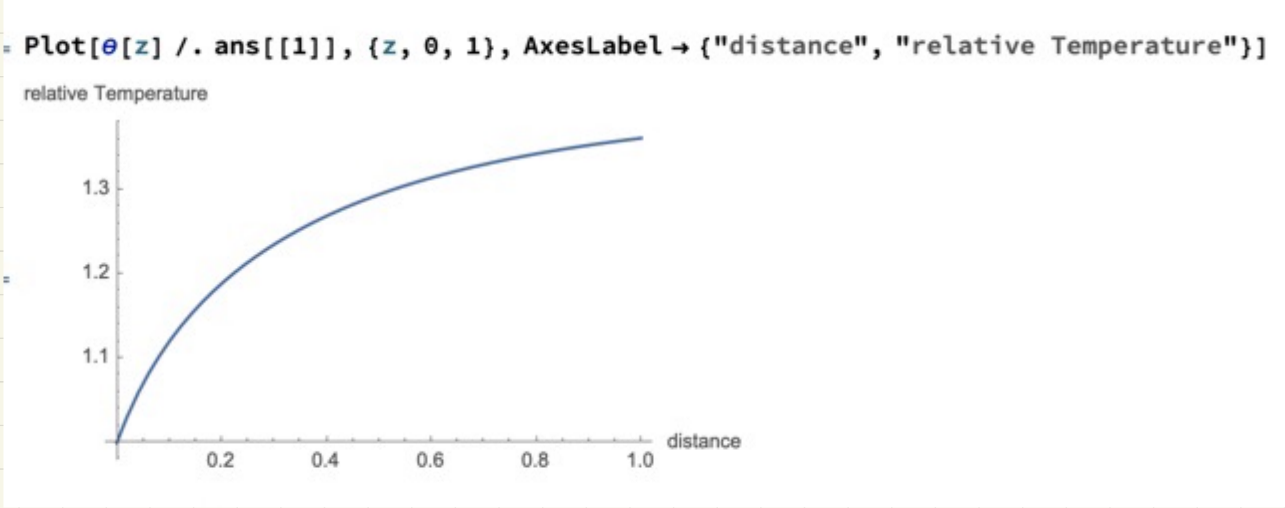
0]= $0.07\, e^{\frac{3.21}{\theta[z]}}\, y[z]$

```
2]:= ans = NDSolve[{D[y[z], z] == eq1, D[θ[z], z] == eq2, y[0] == 1, θ[0] == 1},
       {y[z], θ[z]}, {z, 0, 1}]
```

```
2]= {{y[z] → InterpolatingFunction[ Domain: {{0., 1.}} Output: scalar ][z],
    θ[z] → InterpolatingFunction[ Domain: {{0., 1.}} Output: scalar ][z]}}
```



```
:= Plot[y[z] /. ans[[1]], {z, 0, 1}, AxesLabel → {"distance", "concentration"}]
```



```
= Plot[θ[z] /. ans[[1]], {z, 0, 1}, AxesLabel → {"distance", "relative Temperature"}]
```

HYSTERETIC

BEHAVIOR

Autothermic Processes

Properties and Reactor Design

C. VAN HEERDEN
STAATSMIJNEN IN LIMBURG, GELEEN, THE NETHERLANDS

In autothermic processes the temperature level at which the reaction proceeds is maintained by the heat of reaction alone. It is shown in this paper that these processes are characterized by a simple diagram consisting of two curves which give the production and the consumption of heat as functions of some reference temperature. From this diagram the typical properties of autothermic reactions—the need of an ignition by external heating being the most peculiar one—can easily be understood. This type of diagram is indispensable for the calculation of industrial converters in which autothermic processes are carried out. As an illustration of the principles involved, the temperature and the concentration distributions in an ammonia synthesis converter are calculated.

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WHEN the temperature level at which an exothermic chemical reaction proceeds is above room temperature, this level is often maintained by the heat of reaction alone. The combustion of fuels belongs to this group of autothermic processes. Besides, it is common practice in chemical industry to make a conversion proceed autothermically if possible, in order to avoid expensive heating by external means. Well-known examples are the Haber-Bosch ammonia synthesis and the shift-reaction of carbon monoxide with steam.

In these processes a steady state must be established at which the heat consumption is balanced by the heat production. As the rate of reaction generally varies very rapidly with temperature, the fractional conversion will change from near zero to near unity within a relatively small temperature region. However, the heat consumed—which mainly consists of the sensible heat of the reaction products leaving the system and of the heat losses to the surroundings—will change approximately linearly with temperature. From the general behavior of heat consumption and heat production, the peculiar properties of autothermic properties can be easily understood. The most characteristic feature is the necessity of an ignition by external heating before a steady state at which the reaction processes can be established.

The principles discussed in this paper are generally applicable to all autothermic processes and are applied to a practical example, the ammonia synthesis column.

GENERAL DIAGRAM OF AUTOTHERMIC PROCESSES

The simplest diagram of an autothermic process is shown in Figure 1. It is assumed that the reaction proceeds isothermally at a temperature, T_r, that the reaction products leave the reactor at the same temperature, T_r, and that the reactants enter at a temperature, T_0, normally room temperature. For the moment, it is assumed that the reaction also proceeds adiabatically, so that the heat consumed consists solely of the sensible heat of the reaction product. To simplify the discussion, all heat quantities will be expressed per gram mole of a suitably chosen reaction component.

At a given residence time of the reactants in the reactor, the heat, Q_r, produced by the reaction will depend on the reaction temperature in a way schematically represented by curve *a* in Figure 2.

Starting at low temperatures the reaction will at first be so slow that Q_r is practically zero. At a certain temperature level the reaction rate starts rising rapidly with temperature; as a result, the heat produced will arrive at a constant maximum value within a relatively small temperature interval. When the value of Q_r remains constant the conversion is complete.

The heat consumption is given by the relation

$$Q_c = c(T_r - T_0)$$

where *c* is the heat capacity of the reaction products per gram mole of one of the reaction components. If it is assumed that *c* is independent of temperature and of the degree of conversion, Q_c is represented by a straight line, *b*, which intersects the temperature axis at T_i.

At points of intersection *O*, *I*, and *S* of curves *a* and *b* the production and consumption of heat are equal. At point *I* this equilibrium is unstable. With a small rise in temperature the heat production increases more rapidly than the heat consumption and the temperature will continue to rise until a stable equilibrium at *S* is reached. In the opposite case of a small temperature drop at *I* the temperature will continue to fall until it reaches the value T_0 at *O*. Point *I* corresponds to a state of ignition and T_i is the ignition temperature. The equilibrium at *O* correspond with the stable nonreacting state before ignition, while at the temperature T_s the stationary reacting state is established after ignition by external heating to temperature T_i.

Of course it is possible for curves *a* and *b* to have no points of

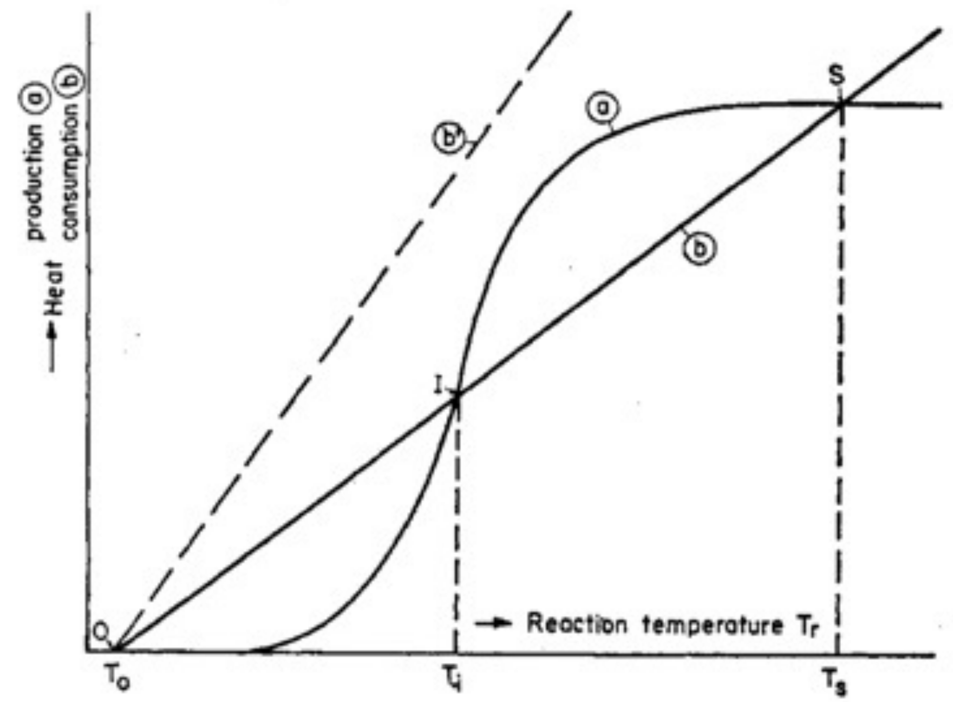


Figure 2. Schematic Diagram of Heat Production and Heat Consumption as Functions of Reaction Temperature

EX. 9.6.1

$$A + B \rightarrow 2C$$

$V = L$ L, $k = 33\times10^{9} \exp\left[-\frac{20000}{RT}\right]$

$$\Delta H = -20 \, \frac{\text{KCAL}}{\text{MOL}}$$

$C_A^0 = 20$ MOL/L

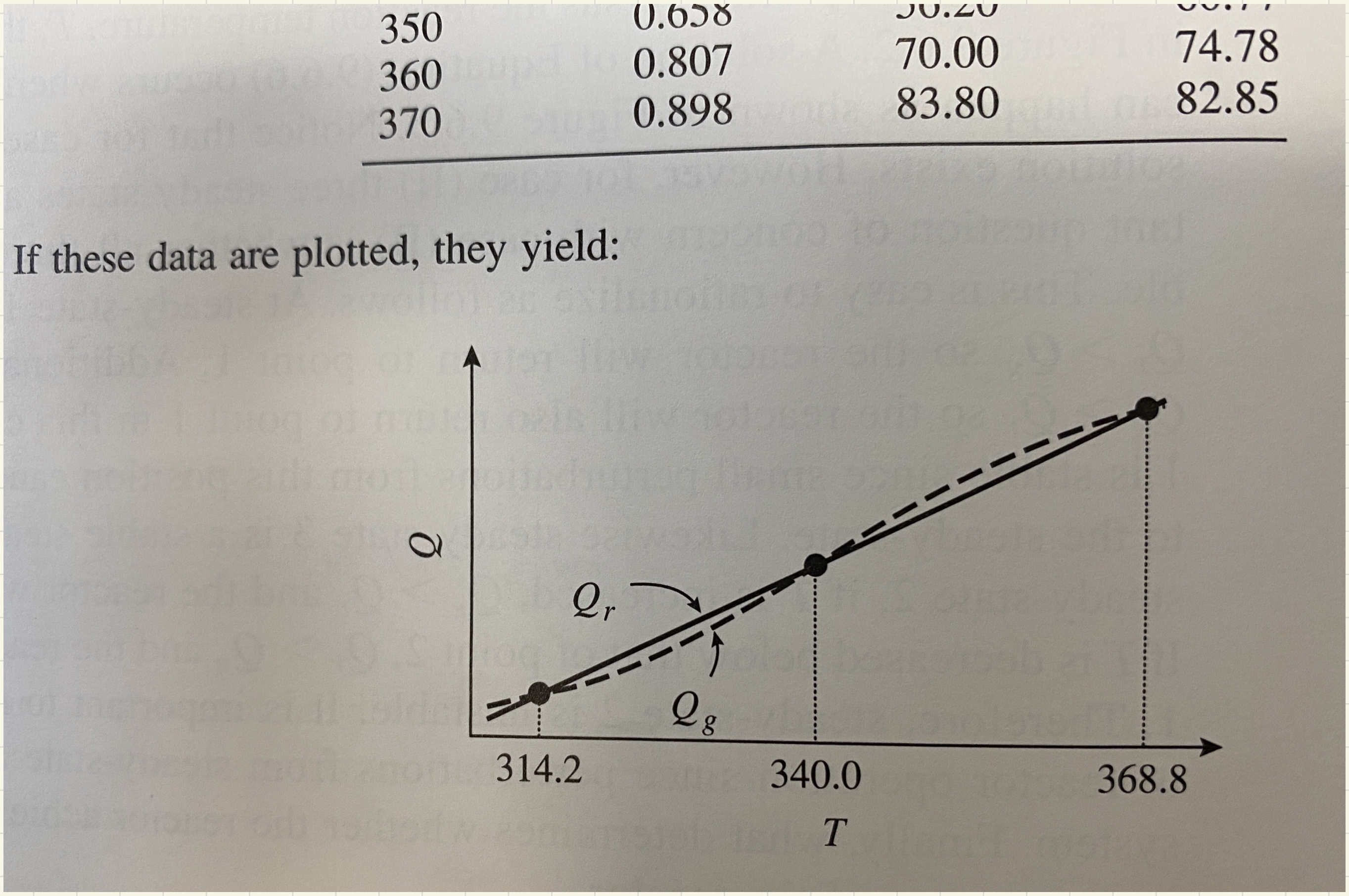
$q_f = 100 \ \text{cm}^3/\text{MIN}$

$T^0 = 17C$, $T_c^0 = 87C$

$$\rho C_p = 650 \, \frac{\text{CAL}}{\text{L}\ {}^{\circ}\text{C}}$$

$$U = .1 \, \frac{\text{CAL}}{\text{cm}^2 \, \text{MIN K}}$$

$$A_H = 250 \ \text{CM}^2$$



350	0.658	[illegible]	[illegible]
360	0.807	70.00	74.78
370	0.898	83.80	82.85

If these data are plotted, they yield:

SUCH PHENOMENA
CAN BE FOUND IN
LABORATORIES