CBE 40445

10/21/20

WE DID: BATCH REACTORS

TUBULAR REACTORS

NOW:

EFFECTS OF HEAT OF REACTION AND HEATING/COOLING ON CSTR'S

— STABILITY + MULTIPLE STEADY STATES

TEMPERATURE EFFECTS IN A CSTR

HEAT REMOVAL = HEAT GENERATED − HEAT TAKEN UP BY COMPONENTS

$$\dot{Q} = \frac{\overset{(-)}{F_e^0 (\Delta H_r|_{T_0})}(f_e^f - f_e^0)}{\underset{(+)}{(-\nu_e)}} + \sum F_i^f \int_{T^0}^{T^f} c_p \, dT$$

FOR A → M CONST Cp

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

$$0 = F_A^0(1 - f_A) - k C_A^0 (1 - f_A) V$$

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

↑ INERTS

FOR CSTR, USUALLY
f_A IS SPECIFIED

IF SO, YOU CAN SOLVE
ENERGY BALANCE FOR T.

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

F_N ↑ INERTS

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

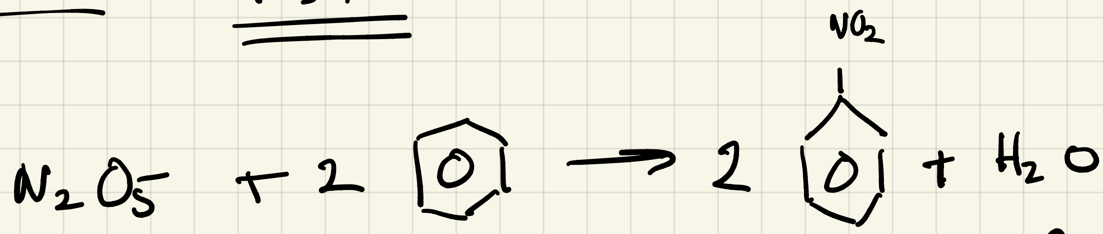
THEN USE THIS T IN:

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

FOR F_A^0 FIXED SOLVE FOR V

("τ")

EXAMPLE 9.5.1



A B C D

ADIABATIC CSTR, 35% CONVERSION

$$r = k C_A C_B^2$$

$\Delta H_r = -370.1$ kJ/MOLE

$Cp_A = 84.5 \dfrac{J}{MOL\text{-}K}$

$Cp_B = 137 \dfrac{J}{MOL\text{-}K}$

$Cp_C = 170 \dfrac{J}{MOL\,K}$

$Cp_D = 75 \dfrac{J}{MOL\,K}$

$T^0 = 303$ K

$F_A^0 = 10$ MOL/MIN

$F_B^0 = 30$ MOL/MIN

$q = 1000$ L/MIN

$C_A^0 = .01$ MOL/L

$$k = .090 \exp\left[\frac{40\ \text{kJ/MOL}}{R}\left(\frac{1}{303} - \frac{1}{T}\right)\right] (L/MOL)^2/MIN$$

$$\dot{Q} = \frac{F_\ell^0 (\Delta H_r|_{T^0})(f_\ell^f - f_\ell^0)}{(-v_\ell)} + \sum \left(F_i^f \int_{T^0}^{T^f} C_{p_i} dT \right)$$

FOR $A \to M$:

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

INERTS

SO FOR $A + 2B \to 2C + D$, $\dot{Q} = 0$

$$0 = \Delta H_r F_A^0 f_A + F_A^0 (1 - f_A) C_{p_A} (T - T^0) +$$
$$F_A^0 (3 - 2f_A) C_{p_B} (T - T^0) +$$
$$2 F_A^0 f_A C_{p_C} (T - T^0) +$$
$$F_A^0 f_A C_{p_D} (T - T^0)$$

3 MOLES B FOR 1 OF A IN FEED

MASS BALANCE

COMPONENT A

$$0 = q C_A^0 - q C_A - k C_A C_B^2 V$$

$$0 = F_A^0 - F_A^0 (1 - f_A) - k C_A^0 (1 - f_A) C_A^{0\,2} (3 - 2f_A)^2 V$$

$$V = \frac{F_A^0 f_A}{k C_A^{0\,3} (1 - f_A)(3 - 2f_A)^2}$$

NOW SOLVE ENERGY BALANCE

$$0 = \left(-370.1\ \frac{kJ}{MOLE}\right)\left(10\ \frac{MOL}{MIN}\right)(.35) +$$

$$10\ \frac{MOL}{MIN}\Big[(1-.35)\,84.5\ \frac{J}{MOL\text{-}K}(T-303)+(2.3)(137)(T-303)$$

$$+(2)(.35)\,170(T-303)+.35(75)(T-303)$$

$$T = 554\ K$$

NOW SOLVE MASS BALANCE FOR VOLUME, V

$$k = 119.8\ \frac{L^2}{MOL^2}\ \frac{1}{MIN}$$

$$V = \frac{(10\ MOL/MIN)(.35)}{120(.01)^3(1-.35)(3-.7)}$$

$$V = 8500\ L$$

$$\tau = \frac{V}{q} = 8.5\ MIN$$

CONSIDER SAME REACTION WITH COOLING.

$$UA_H = 9000 \frac{J}{MIN \cdot K}$$

$$T_c^0 = 323 \quad (\text{CONSTANT})$$

NEW VALUES
$$\begin{cases} q = 100\ L/MIN \\ C_A^0 = .1\ MOL/L \end{cases}$$

$$F_A^0 = q C_A^0 = 10 \frac{MOL}{MIN} \quad (\text{SAME})$$

ENERGY BALANCE

$$9000 \frac{J}{MIN \cdot K}(323 - T) =$$

$$\left(370.1 \frac{kJ}{MOLE}\right)\left(10 \frac{MOL}{MIN}\right)(.35) +$$

$$10 \frac{MOL}{MIN}\left[(1-.35) 84.5 \frac{J}{MOL \cdot K}(T-303) + (2.3)(137)(T-303)\right.$$

$$+ (2)(.35)\ 170(T-303) + .35(75)(T-303)$$

SOLVE $\longrightarrow$ $T = 407\ K$ ✓

NEW $k = 5.20 \frac{L^2}{MOL^2 MIN}$, $C_A^\circ = .1 \frac{MOL}{L}$

$$V = 196\ L \quad \left(\approx 200\ L \right.$$

$$\left. \tau = 1.96\ M \quad \approx 2\ MIN \right)$$

STABILITY AND SENSITIVITY OF REACTORS FOR EXOTHERMIC REACTIONS

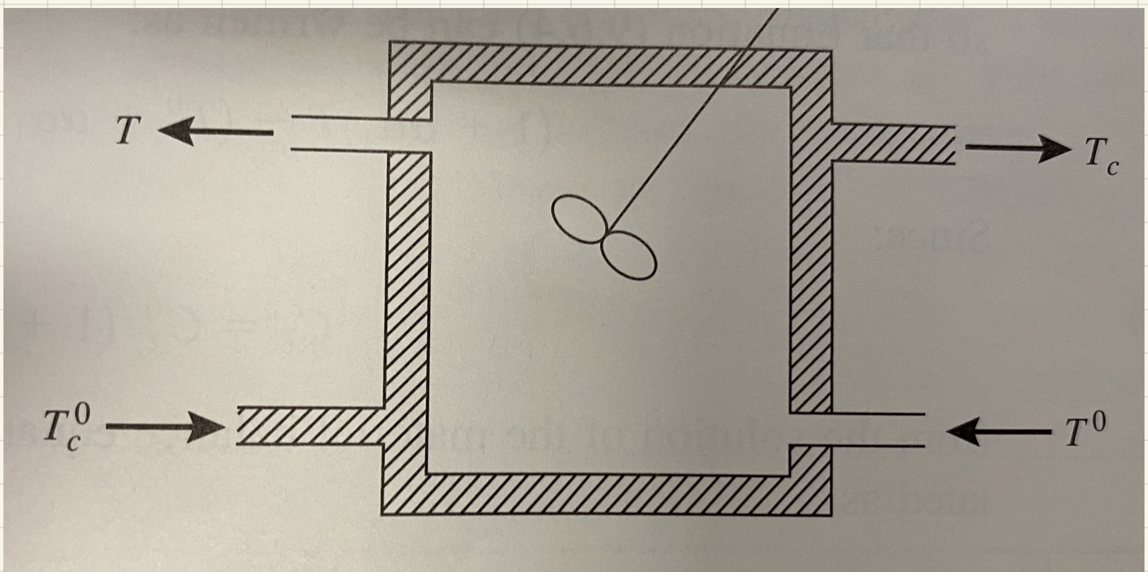


Figure 9.6.1 |
Schematic illustration of a CSTR that is maintained at temperature T by transferring heat to a coolant fluid ($T_c > T_c^0$).

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 $\rightarrow$

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

PLUG BACK IN

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

$$= \lambda_\lambda (T - T_c^0)$$

NOW BACK TO E-BALANCE FOR CSTR

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

MASS BALANCE

$$0 = q (C_A^0 - C_A) - k C_A V$$

$$0 = F_A^0 (1 - f_A) - k C_A V$$

WE GET

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

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

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

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

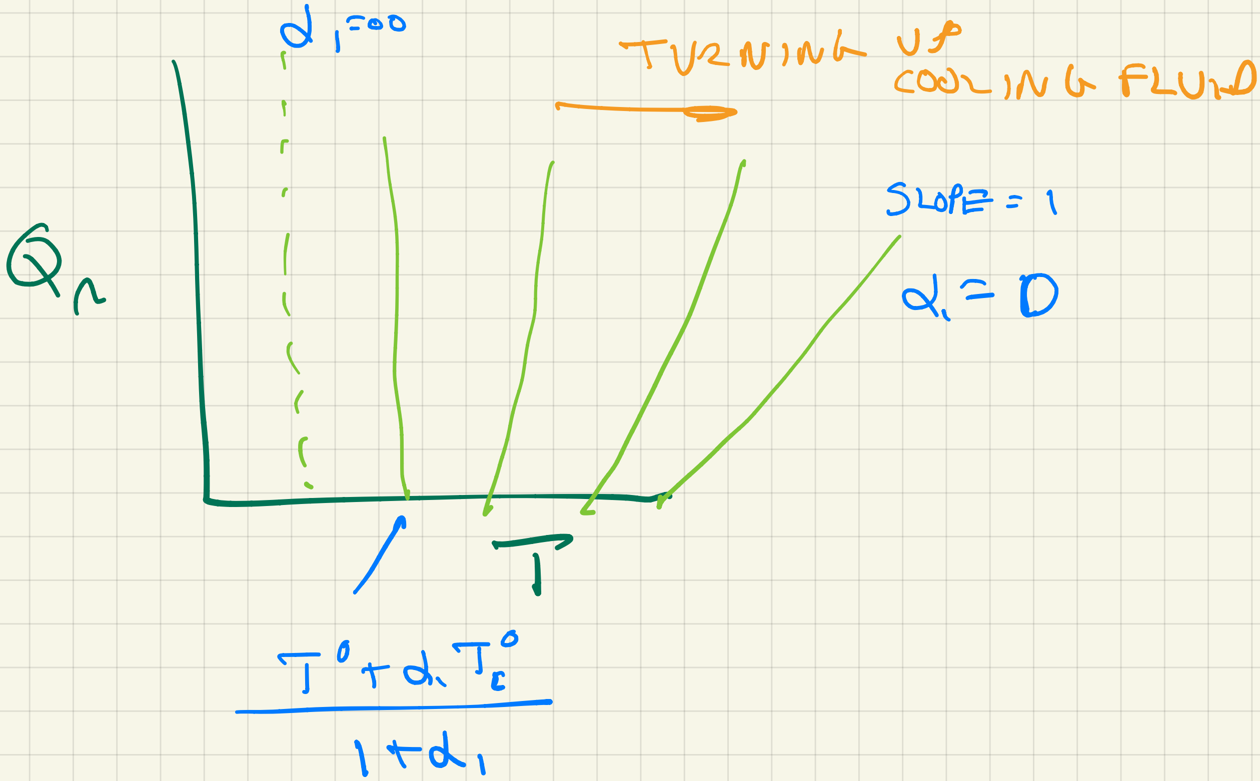
$$C_A = \frac{C_A^0}{1+k\tau}$$

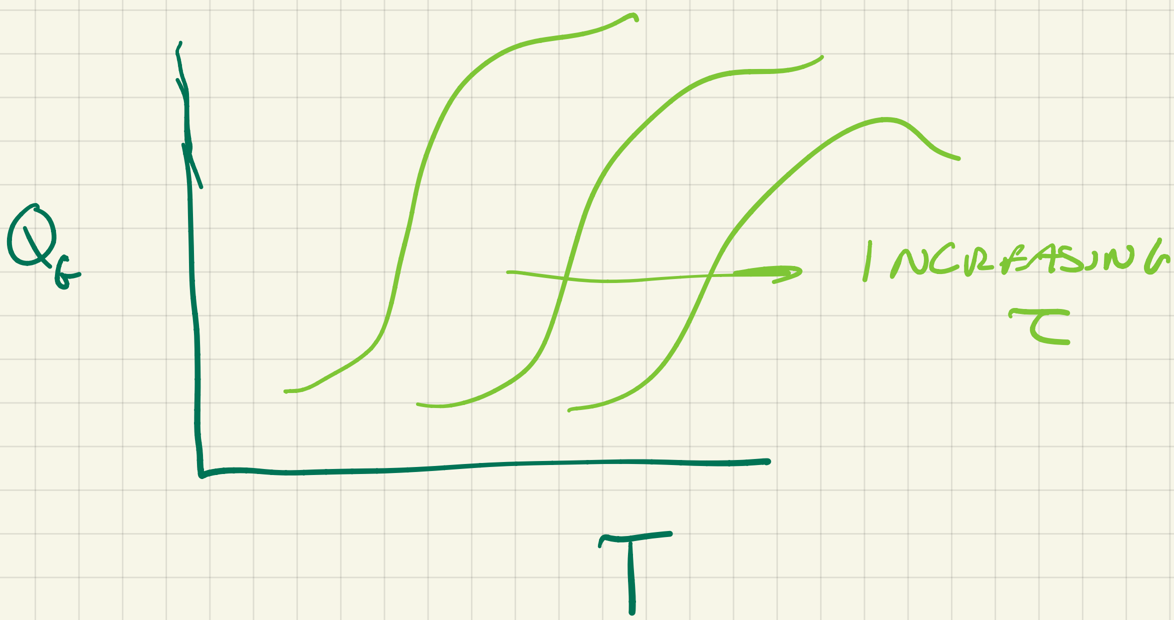
WHICH GIVES

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

Q_r (HEAT REMOVED) $= Q_G$ HEAT GENERATED

NOW LOOK AT EACH MECHANISM SEPARATELY





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

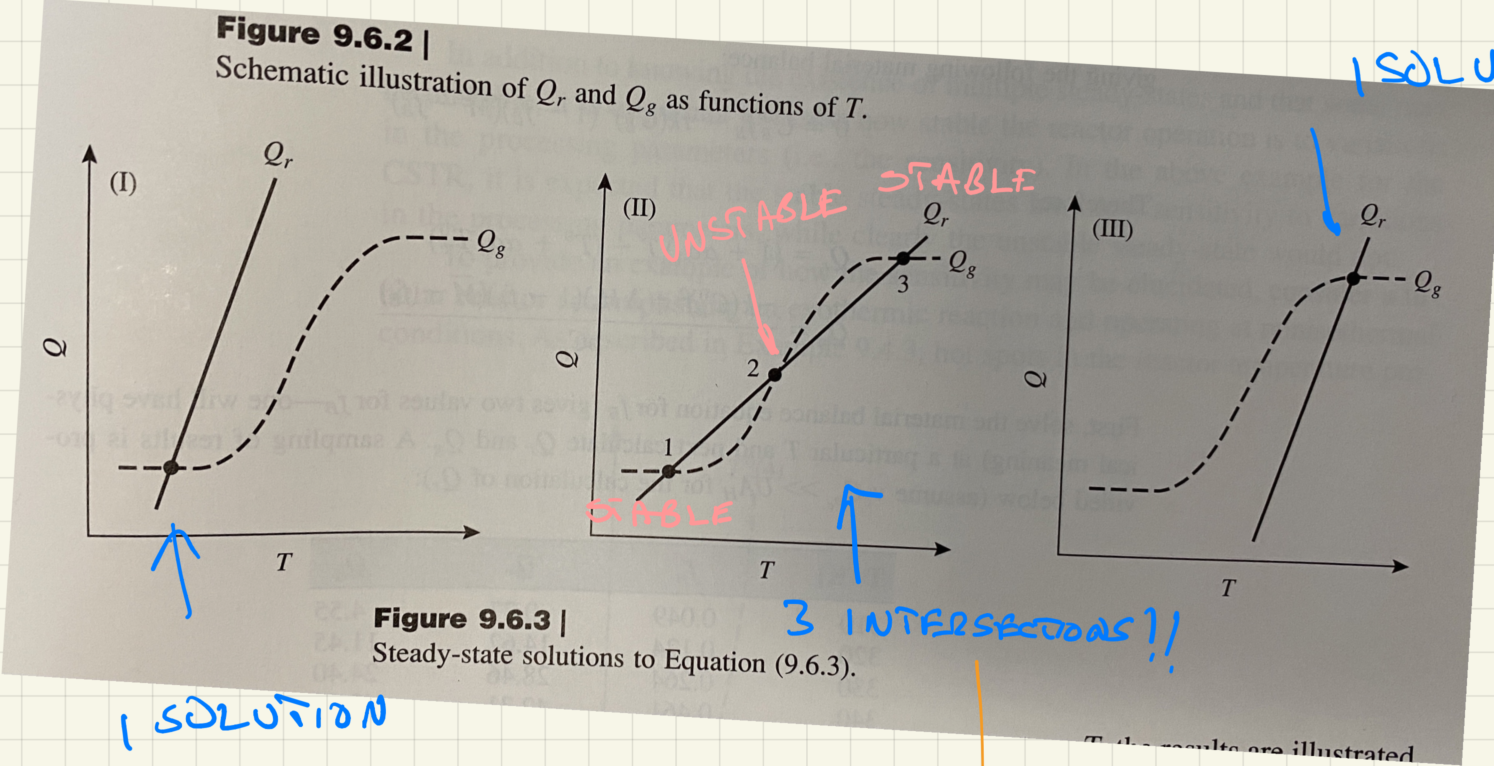


Figure 9.6.2 |
Schematic illustration of Q_r and Q_g as functions of T.

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

1 SOLUTION

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.

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

```
Plot[generation /. {ca0 → 1, aa → 10^8, ea → 55000, rr → 8.314, τ → 10, ΔH → -100000,
   cp → 50, ρ → 10}, {T, 200, 400}, PlotLegends → {"τ->10"}]
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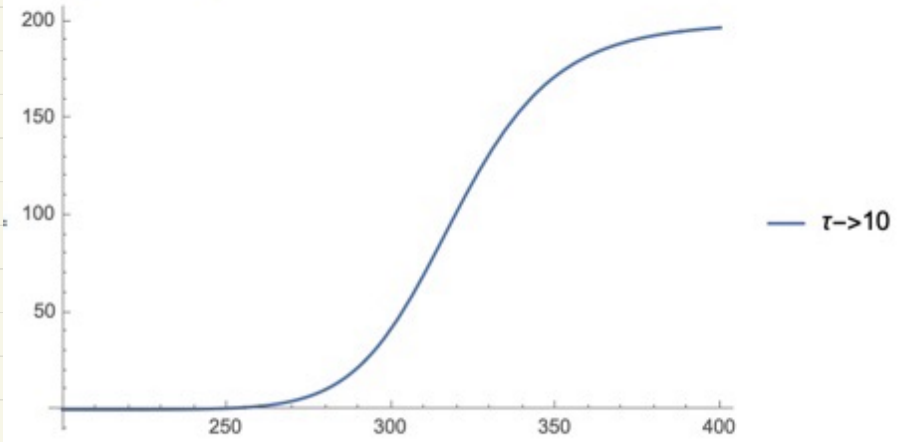

COOLING:

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

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Show[%157, %]
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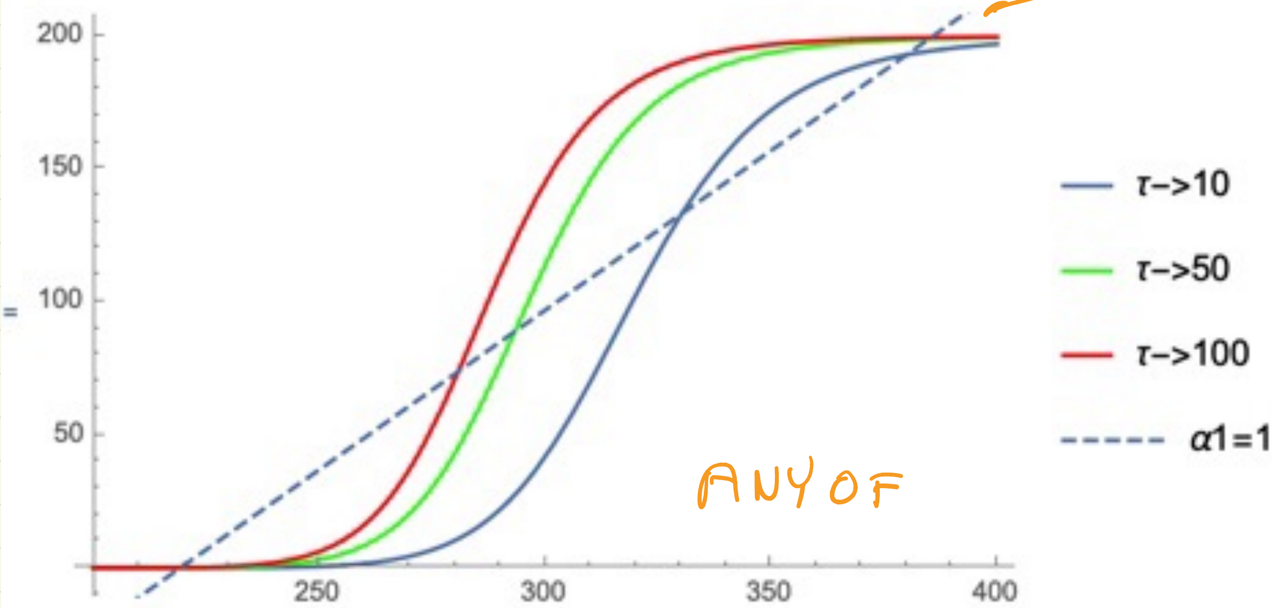

ANY OF THESE COULD HAVE MULTIPLE STEADY STATES

— HYSTERETIC BEHAVIOR

Autothermic Processes

Properties and Reactor Design

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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.

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 d 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

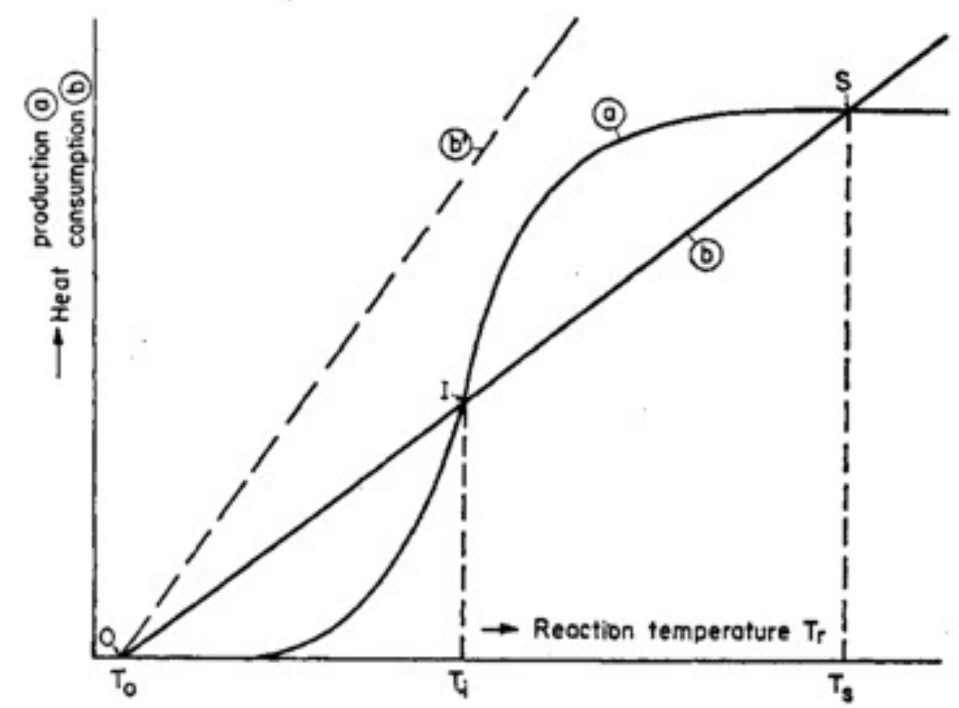


Figure 2. Schematic Diagram of Heat Production and Heat Consumption as Functions of Reaction Temperature

EX. 9.6.1

$$A + B \rightarrow 2C$$

$$V = L \; L, \quad k = 33 \times 10^{9} \exp\left[-\frac{20000}{RT}\right]$$

$$\Delta H = -20 \frac{kCAL}{MOL}$$

$$C_A^0 = 20 \; MOL/L$$

$$q = 100 \; cm^3/MIN$$

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

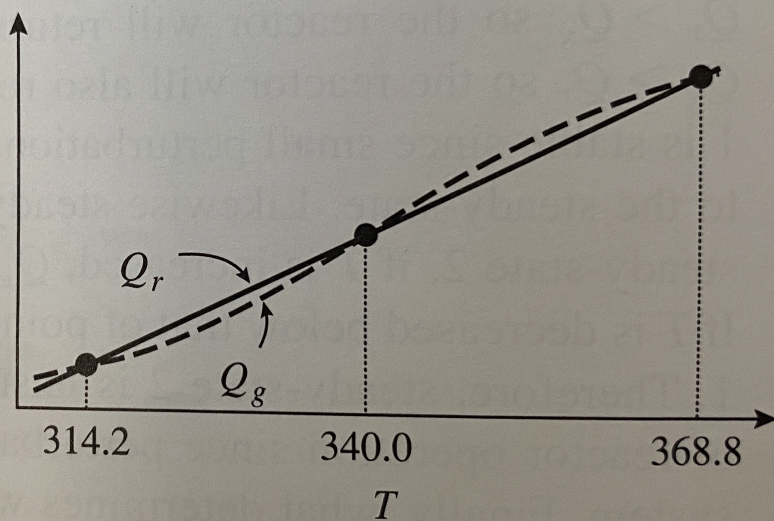
$$\rho C_p = 650 \frac{CAL}{L \; {}^oC}$$

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

$$A_H = 250 \; CM^2$$

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