

last Minute comments on Design Problem

- ① $2 < d_p < 5 \text{ mm}$ for fixed Bed Walas, S.M. "Chemical Process Equipment" Selection & Design
- ② $P \leq 0.10 P_T$

~~_____~~

ρ_c - catalyst density $\text{g cat/cm}^3 \text{ pellet}$
 ρ_b - bulk density of catalyst $\text{g cat/cm}^3 \text{ Reactor}$

$\rho_b = \rho_c (1 - \phi)$ given on page 156 chapter 4 Fogler

$\frac{\rho_{\text{cat}}}{\text{cm}^3 \text{ R}} = \frac{\rho_{\text{cat}}}{\text{cm}^3 \text{ P}} \frac{\text{cm}^3 \text{ P}}{\text{cm}^3 \text{ R}}$

Example
 CHEMICAL ENG SCI (1985) Skrzypek et al 40 pp 611 (need p 620)

$d_p = 6 \text{ mm}$
 $\rho_b = 980 \text{ kg cat/m}^3 \text{ reactor}$
 surface area $1 \text{ m}^2/\text{g}$ ← this is low
 Activated carbon $500 \text{ m}^2/\text{g} - 1500 \text{ m}^2/\text{g}$
 Silica-Alumina Cracking catalysts surface area of $300 \text{ m}^2/\text{g}$
 for spheres from Perry's 5th ed. $\phi = 0.45$ (fig 5-70 p 5-53)

$\rho_c = \left(\frac{980 \text{ kg cat}}{\text{m}^3 \text{ reactor}} \right) \left(\frac{\text{m}^3 \text{ reactor}}{0.4 \text{ m}^3 \text{ P}} \right) = 1,780 \frac{\text{kg cat}}{\text{m}^3 \text{ Pellet}}$

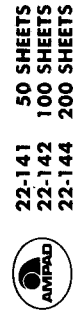
What is it made off?
 V_2O_5 7.5 mol%
 T_iO_2 promoter 0.2 mol% } 10 wt%
 support carborundum } 90 wt%

(Safety)

Feed mixtures: General keep below flammability limits
 (Inflammability or LEL UEL) CRC 57th ed. pD-106 IN AIR 1 atm 200C

NH_3 : 15.50 - 27.0	Methanol 6.72 - 36.5 mol%	Methane 5 - 15
	ethylacetate 2.18 - 11.4 mol%	o-xylene 1 - 6
		Benzene 1.4 - 7.0%

V_2O_5
 Calderbank 1977
 $\rho_c = 2,280 \text{ kg/m}^3$
 $d_p = 2.54 \text{ cm}$
 $\phi = 0.56$
 surface area = $4.18 \text{ cm}^2/\text{g}$



Chapter 10 - Catalysis

$\frac{1}{3}$ GNP involves a catalyst somewhere
from raw materials \rightarrow products

Projected sales of catalyst: 1989 5.1 billion \$ \leftarrow U.S. 35%

Catalyst cost \sim 0.1% of final product \circ

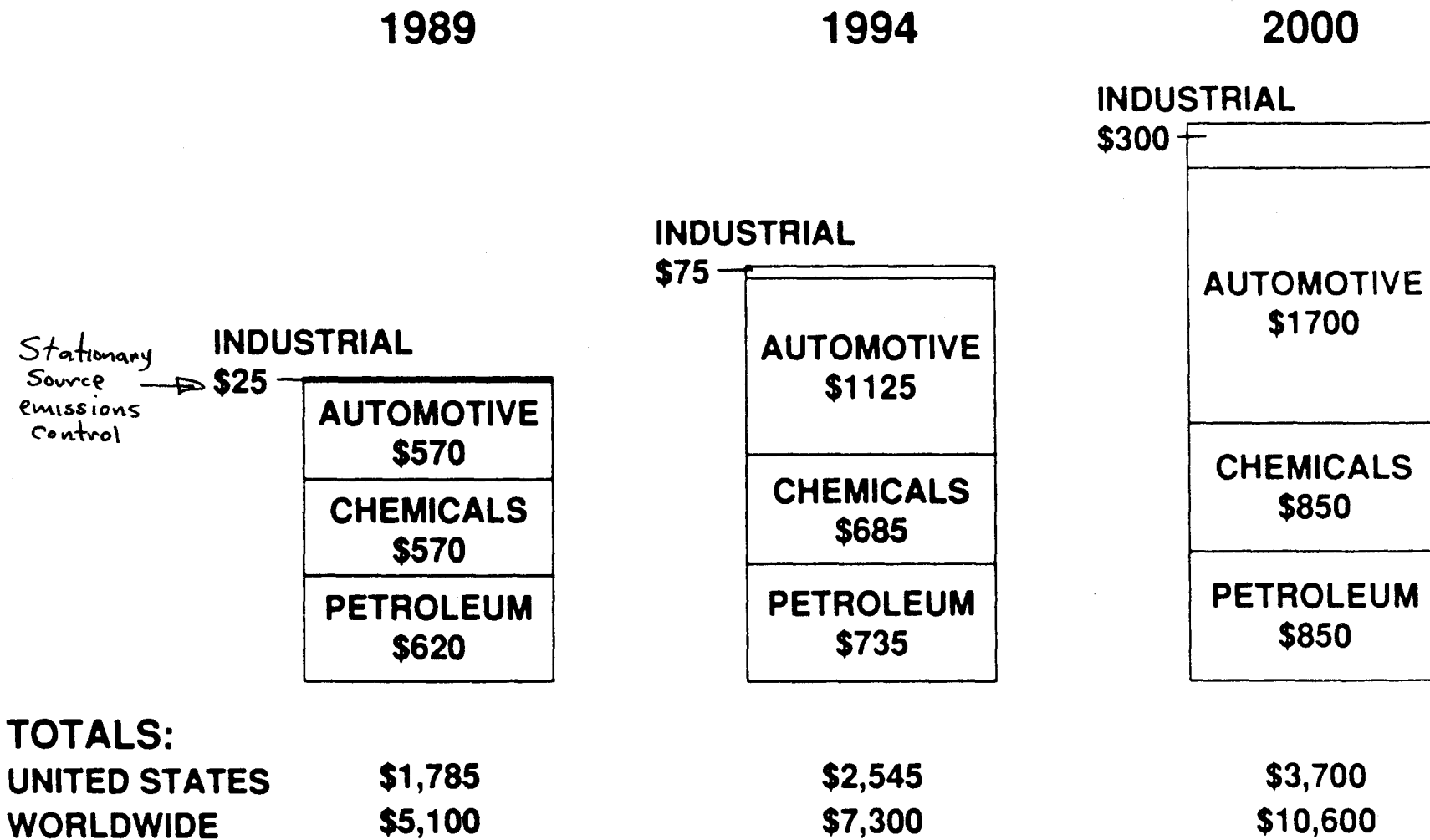
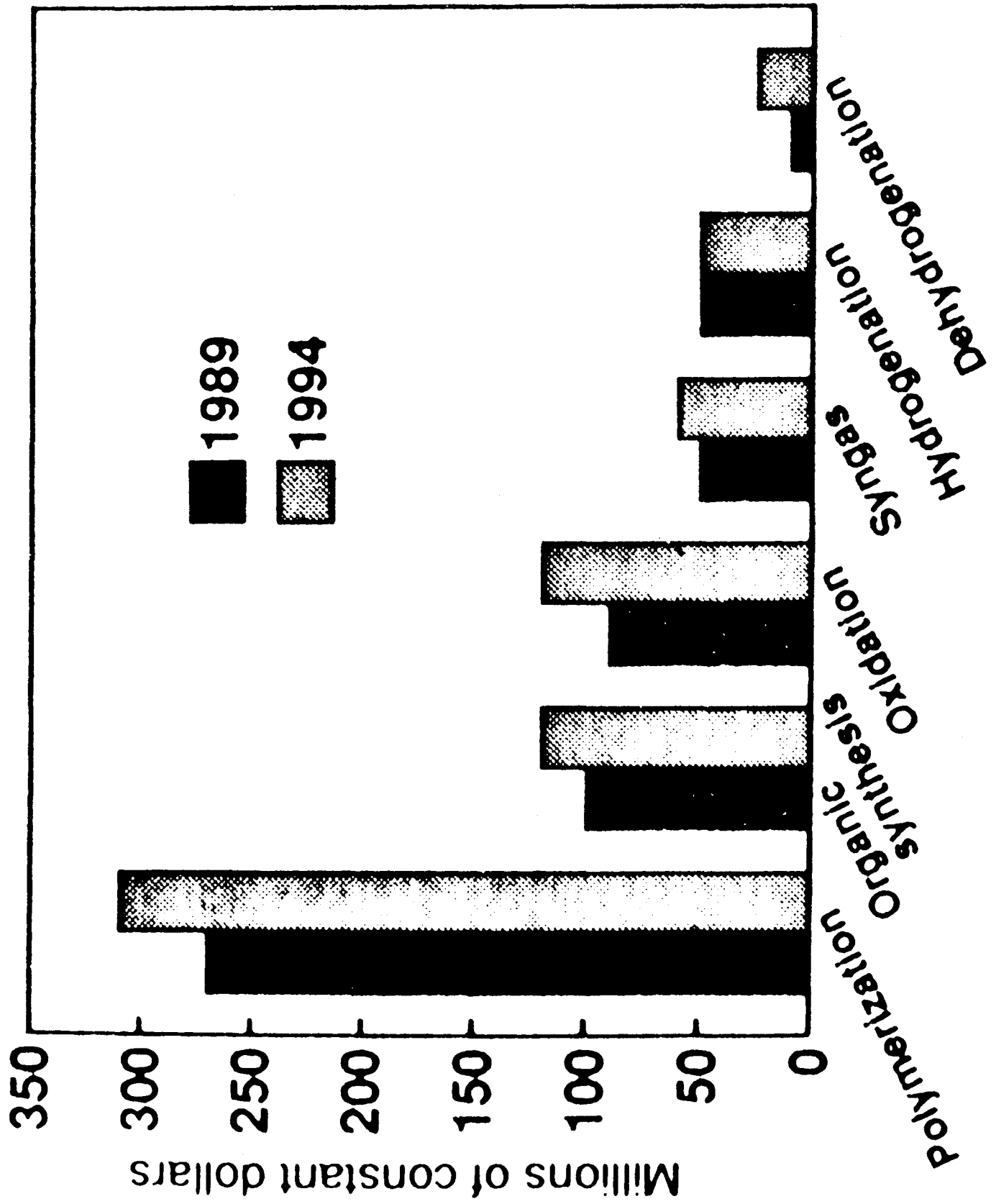
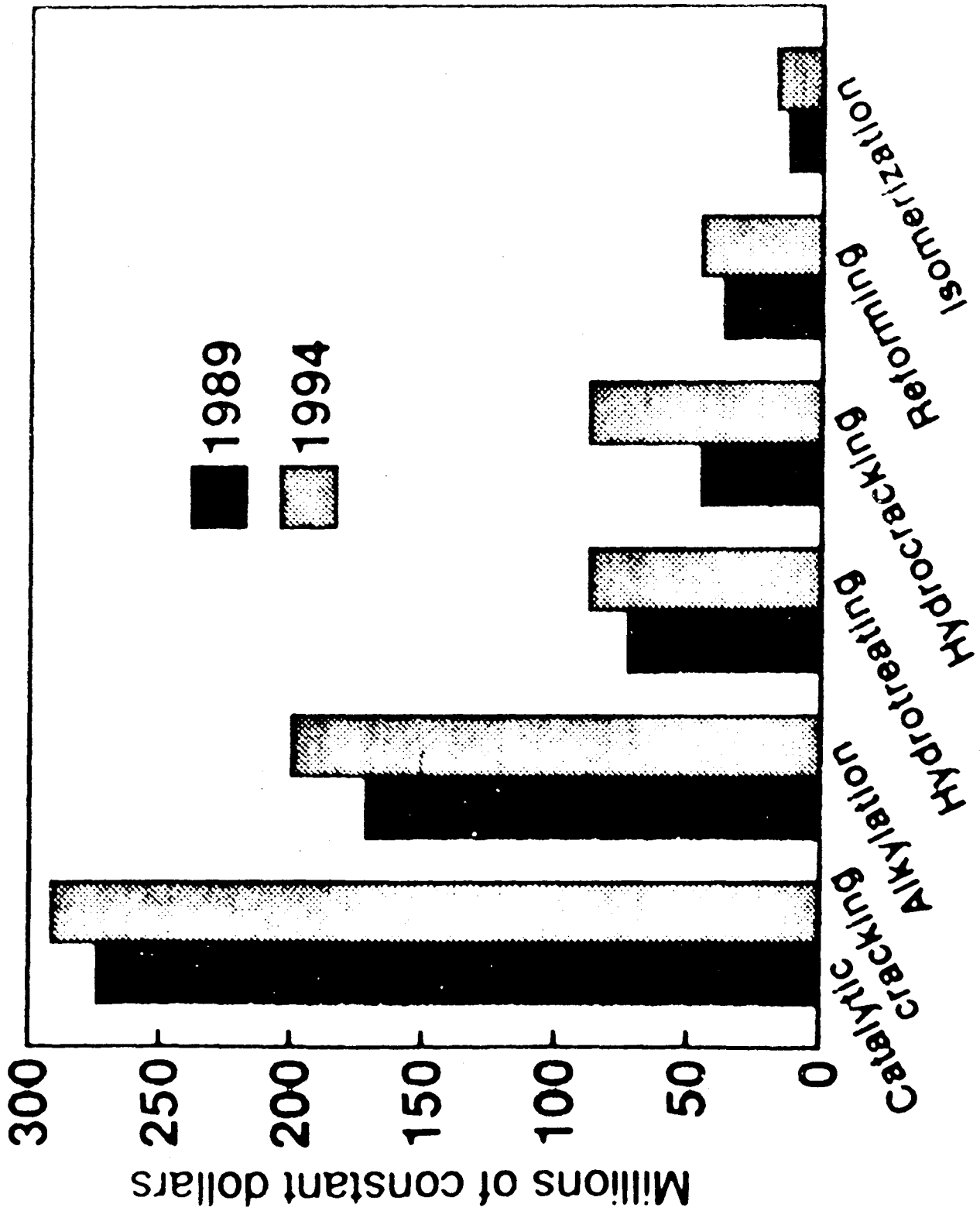


Fig. 1. Projected catalyst sales in the United States (in millions of constant dollars).





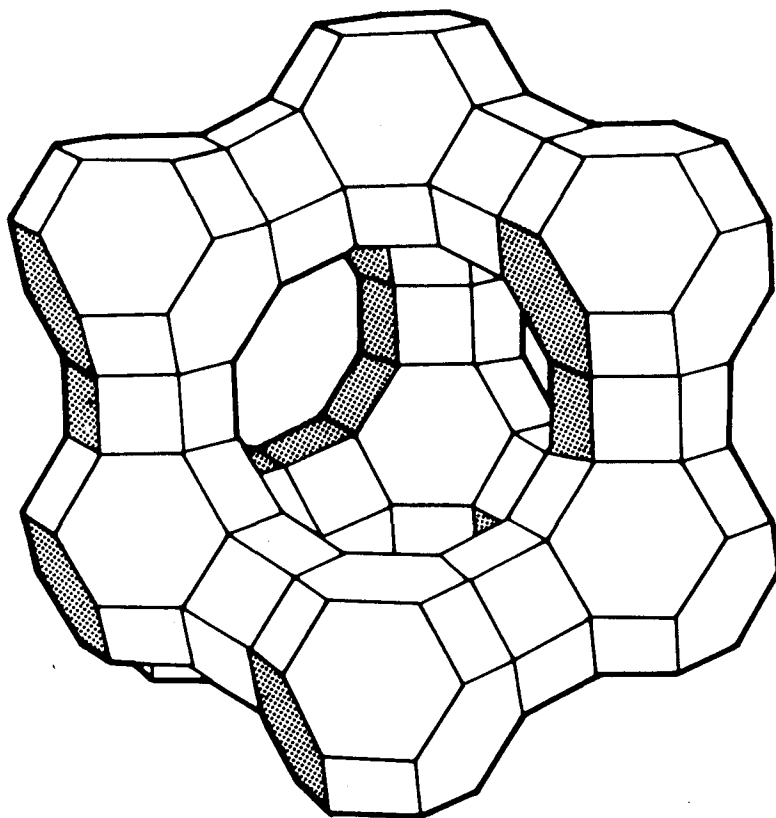
Mobil
5/1

Figure 3.7 Arrangement of cubo-octahedra in the framework structure of faujasite

Table 3.1 (From Breck *et al.*¹⁵)

Zeolite	Chemical analysis	Unit cell composition	Ref.
A	Na_2O , Al_2O_3 , 2SiO_2 , $4.5\text{H}_2\text{O}$	$\text{Na}_{96}[(\text{AlO}_2)_{96}(\text{SiO}_2)_{96}]216\text{H}_2\text{O}$	16, 17
X	Na_2O , Al_2O_3 , 2.5SiO_2 , $6\text{H}_2\text{O}$	$\text{Na}_{86}[(\text{AlO}_2)_{86}(\text{SiO}_2)_{106}]264\text{H}_2\text{O}$	18
Y	Na_2O , Al_2O_3 , 5SiO_2 , $8\text{H}_2\text{O}$	$\text{Na}_{56}[(\text{AlO}_2)_{56}(\text{SiO}_2)_{136}]250\text{H}_2\text{O}$	19



Satterfield

Figure 4.12 Topsøe ammonia-synthesis catalyst KMI. The three sizes are about 1.5 to 3 mm, 6 to 10 mm, and 12 to 21 mm. (Courtesy of Haldor Topsøe, A/S, Copenhagen, Denmark)



Figure 4.4 Extrudates of different sizes with a trilobal cross section, termed Trilobes®. Note the shadows. (Courtesy of American Cyanamid Company)

Hydrotreating (HDS etc.)



Figure 4.1 High-temperature water-gas shift catalyst, iron oxide promoted with chromia; 5 × 5-mm pellets. (Courtesy of United Catalysts Inc., Louisville, Ky.)

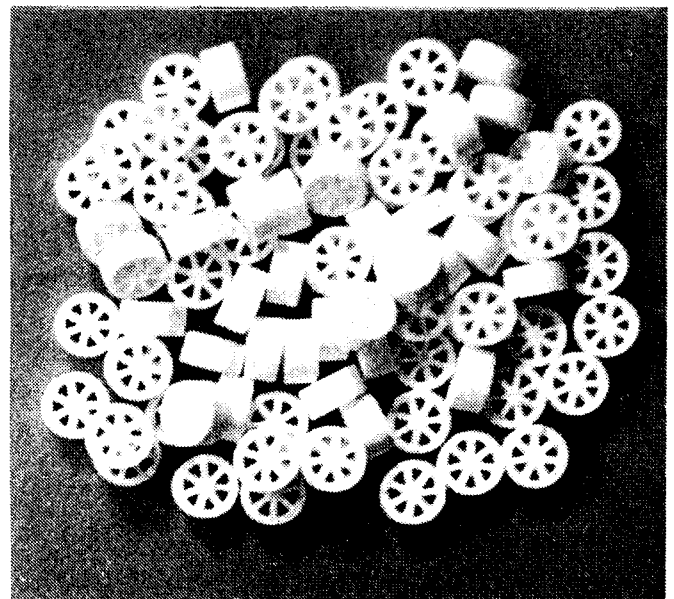
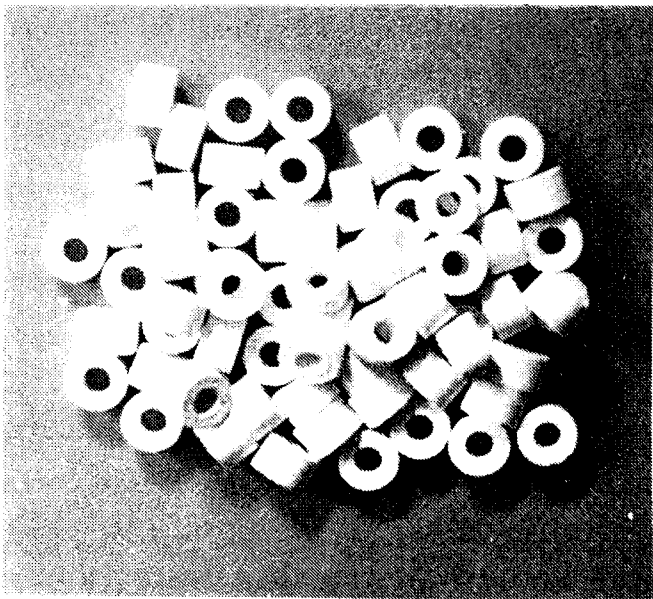
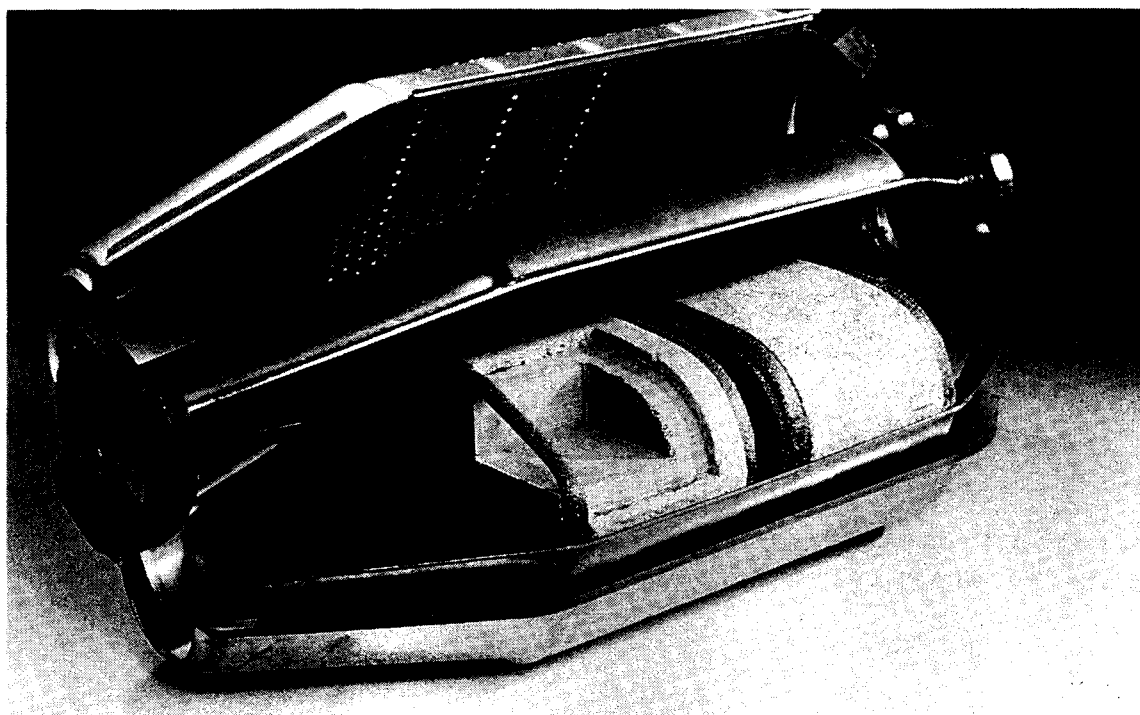


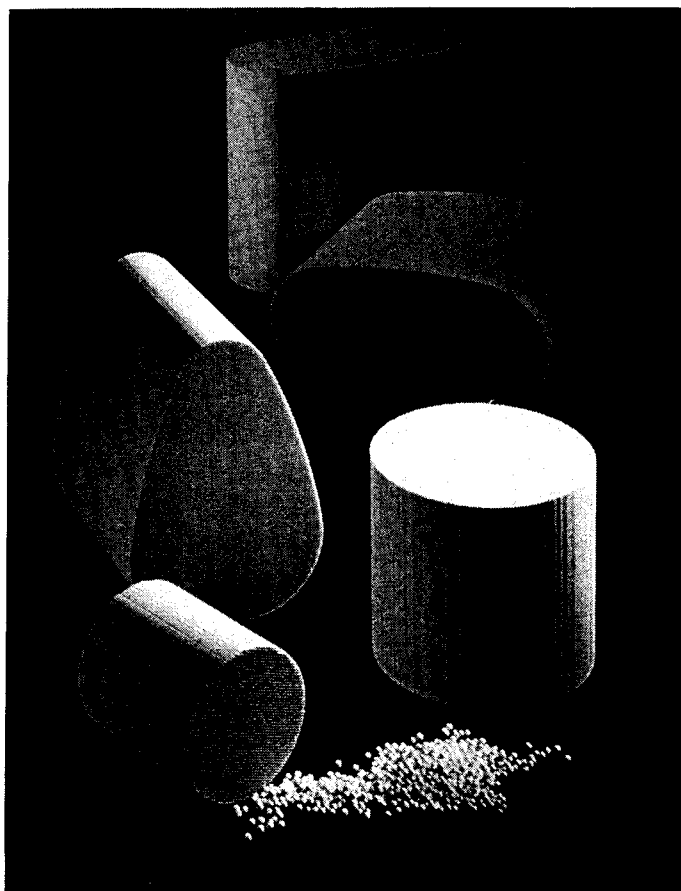
Figure 4.2 Two forms of steam-reforming catalysts. Outside diameter = 16 mm, thickness ~ 10 mm. (Courtesy of United Catalysts Inc., Louisville, Ky.)

Satterfield



Top: Cutaway view of an automotive catalytic converter. The catalyst monolith, with a segment removed, is shown cushioned by fiber blanket insulation inside the metal canister.

Bottom: A variety of ceramic honeycomb monoliths displayed with conventional catalyst pellets in the foreground. Monolith flow channels, about 1 mm square, are coated with a high surface area layer of porous alumina as illustrated in the magnified photographs of Figure 7-2. Tiny platinum particles on the surface of the alumina (see page 74) promote reactions between traces of carbon monoxide and hydrocarbons with oxygen in the exhaust gases.



(Allied-Signal Automotive Catalysts Company, by permission.)

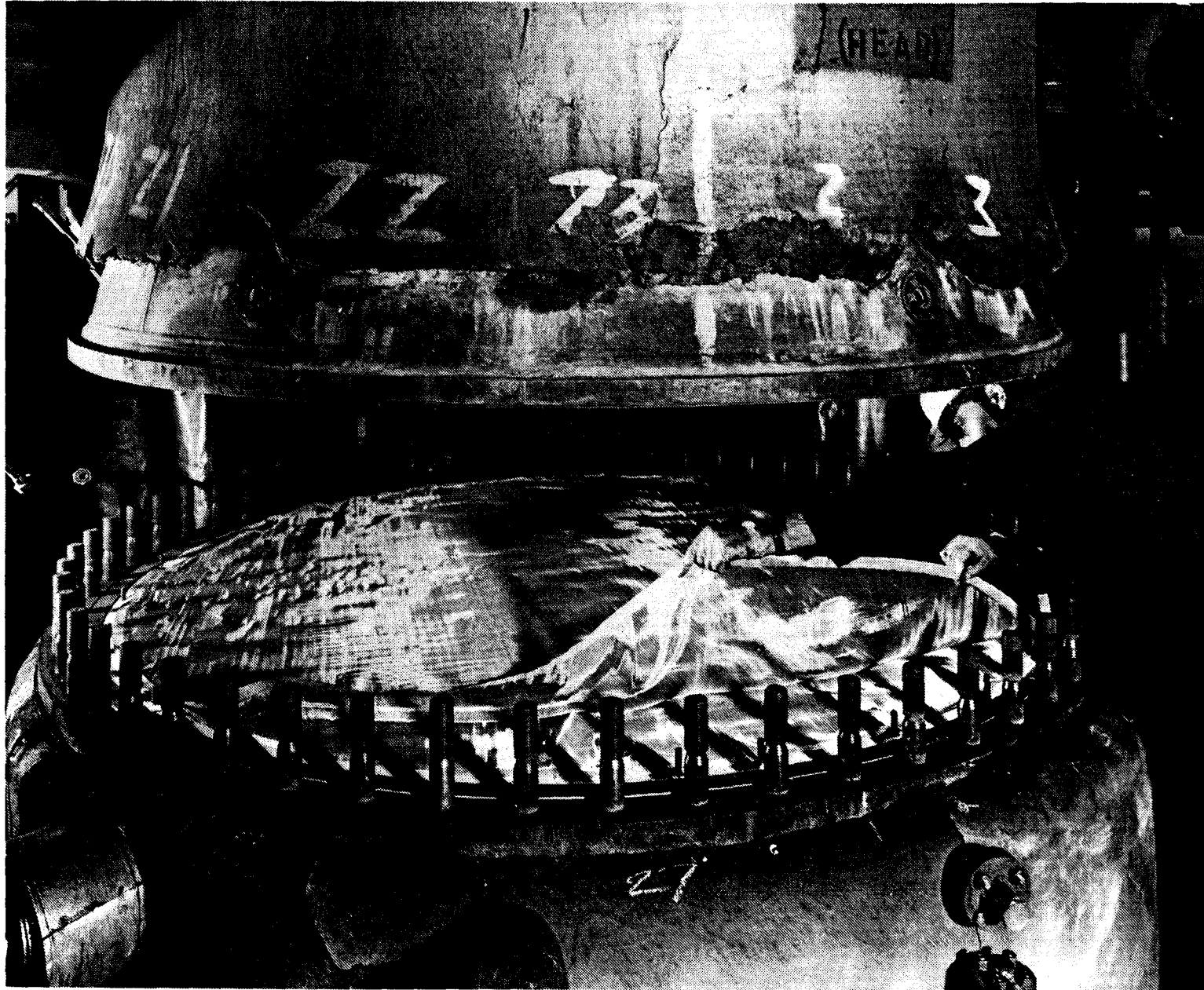
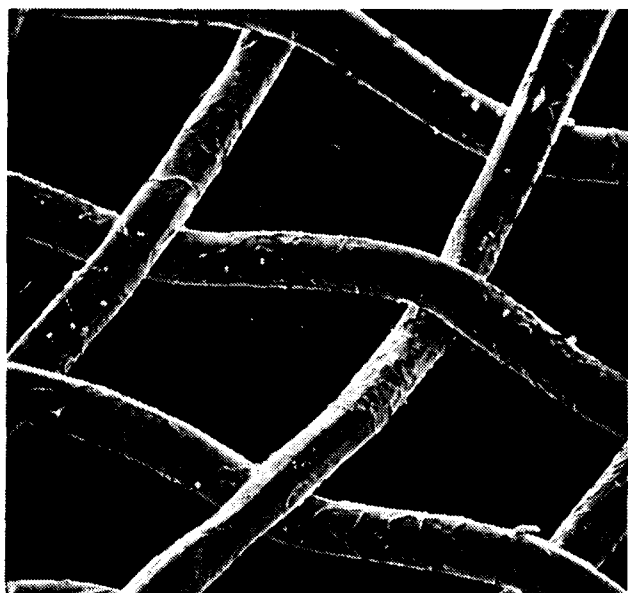


Figure 8.10 Installation of new catalyst gauzes in an ammonia oxidation plant. (Courtesy of Johnson Matthey & Co., Ltd. and Thames Nitrogen Co., Ltd.)

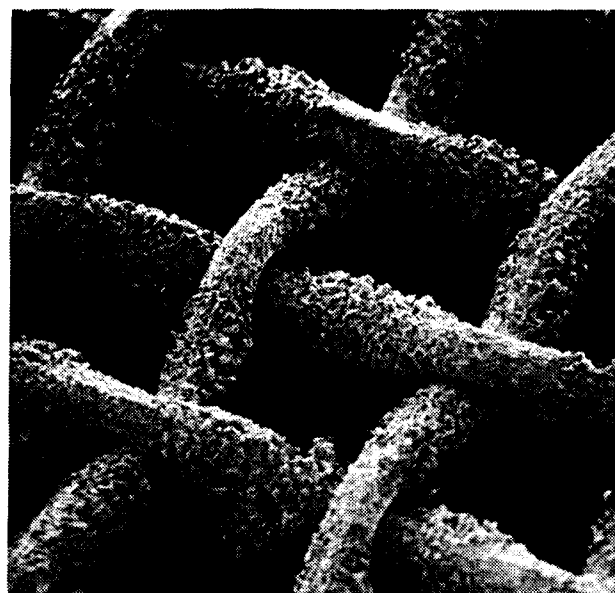
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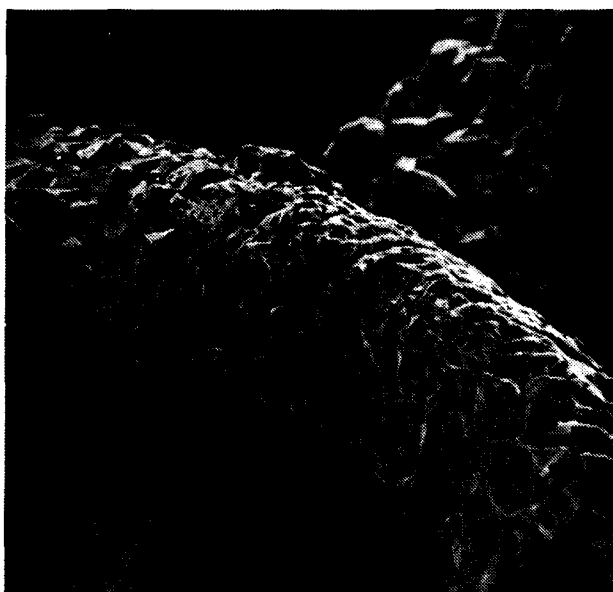
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(a)



(b)



(c)

Figure 8.11 Scanning electron micrographs of 10% Rh-90% Pt gauze wire 0.075 mm (0.003 in) in diameter. (a) Original gauze, as drawn, showing uniform grain structure and absence of nodules on the wires. (b) The gauze in part (a) after one-half the normal gauze life installed in a nitric acid plant, showing the nodular pattern typical of an active gauze. (c) An enlarged view of the crossover point of two gauze wires in part (b) showing the characteristic octagonal crystal structure and the nodules, which are concentrated on the wire surfaces between crossover points. [Courtesy of *Platinum Metals Review*, vol. 15, p. 52 (1971)]

in which gauzes of pure palladium or a 20% gold-80% palladium alloy are placed directly below the platinum-alloy catalyst pad. The palla-

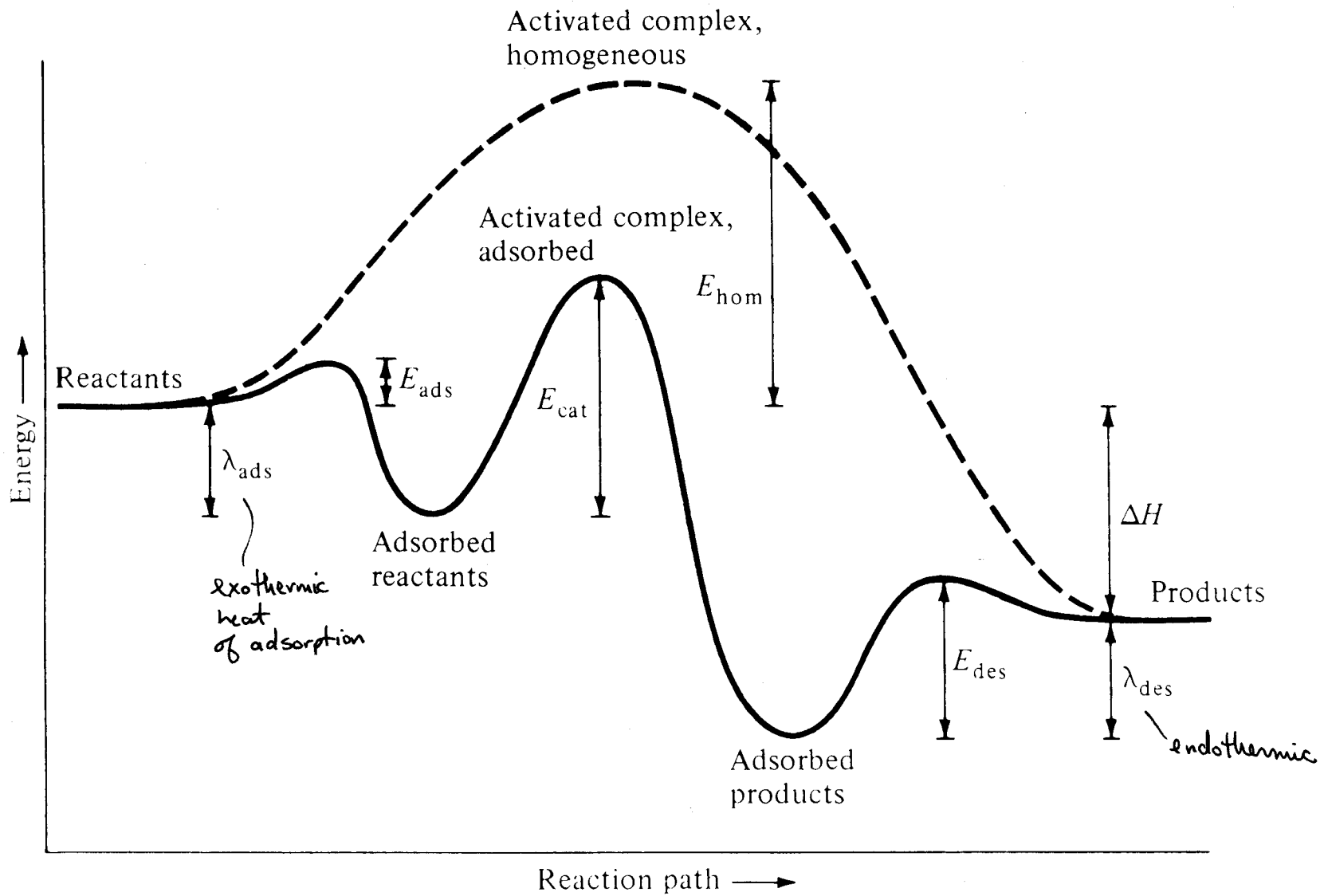


Figure 1.1 Energy changes associated with individual steps of a reaction.

Definitions:

Fogler, "A man inciting a mob to riot and then ducking out before the tanks roll in can be regarded as a catalyst"

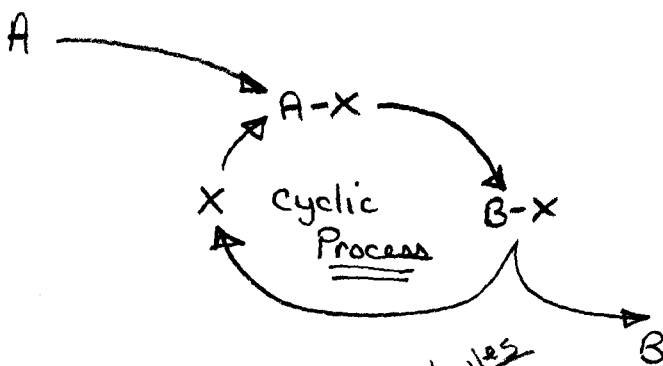
No universal agreement on the definition of a catalyst

** A catalyst changes the rate of reaction; it does not affect the equilibrium. **

not irradiation thermal energy excitation $K_p = \exp\left(-\frac{\Delta G_{im}^0}{RT}\right)$

Satterfield, "A catalyst is a substance that increases the rate of reaction toward equilibrium without being appreciably consumed in the process"

Depends only on reactants & products
accelerates forward & reverse



Catalyst

activity: $\frac{\text{moles}}{\text{site s}}$

$\frac{\text{molecules}}{\text{s site}}$

known as a turnover frequency number

selectivity: A → Desired / undesired

Yield: A → Desired

For a review:

See Parshall, G.W. Homogeneous Catalysis Wiley New York (1980)

heterogeneous: 2 phase { your design problems }

homogeneous: ^{Same} 1 phase (or more) Catalyst the same phase as fluids

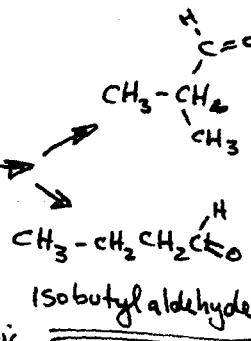
Industrially Important Reactions

① Oxo process: $\text{CH}_3-\text{CH}=\text{CH}_2 + \text{O}_2 + \text{H}_2 \xrightarrow{\text{Co}}$

Catalyst and reactants are in the same phase

② Carbonylation $\text{CH}_3\text{OH} + \text{CO} \xrightarrow[1-4 \text{ MPa}]{175^\circ\text{C}} \text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{OH}$
dissolved organo-metallic complex

③ addition of HCN



Problems

- 1) Corrosion
- 2) Separation of catalyst from reactants

Reaction Pathways

$A \rightleftharpoons B$ gas phase

Catalyst — "Reduces E_a "

Figure 1.1

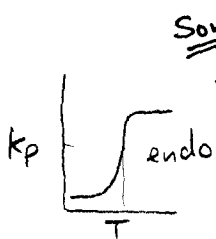


Catalyst provides a pathway whereby the activation energy for the formation of the intermediate surface complex is much less than for the homogeneous reaction.

$$E_{a \text{ homo}} \gg E_{a \text{ adsorbed complex}}$$

the other factor is surface Area or more precisely # of active sites.

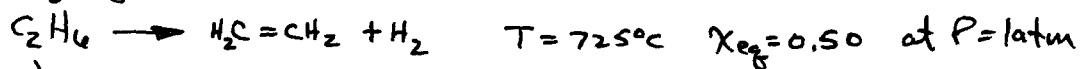
Note: ΔH_{rxn} is the same for both pathways.



Some

Endothermic Reactions: \rightarrow Require high temperatures for a substantial amount of product at equilibrium
— If the T is too high a catalyst will have no effect.

Dehydrogenation



Industrially — process is homogeneous thermal rxn

this is not the case with butane \rightarrow butene or higher molecular weight species.

Catalyst Structure & Properties

Heterogeneous catalysis: need a fluid-solid interface

1) Porous catalyst

2) molecular sieves - zeolites see figure 6-1 { high selectivity due to physical properties }

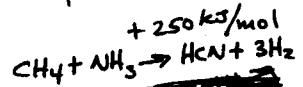
3) monolithic → ceramic

→ wire gauze

→ HCN synthesis



↑
Required for nitric acid manufacture



Porous catalyst typically properties Hill 1977

Cumene cracking on Silica Alumina

Cornigan et al Chem Eng Prog 49 603 1953

$$d_p = 0.43 \text{ cm}$$

$$\rho_c = 1.114 \text{ g/cm}^3$$

$$S_a = 342 \text{ m}^2/\text{g}$$

$$\text{Porosity } \epsilon = 0.51$$

$$\phi = 0.447 \text{ cm}^3/\text{g}$$

↳ void per gram of catalyst

16 THEORETICAL AND CONCEPTUAL BACKGROUND

Summary of Data on Commercial Catalysts

The empirical nature of the practice of catalysis necessarily requires heavy dependence on the lore associated with individual practical catalysts. Of particular interest are the activity and selectivity characteristics of the catalyst and the type of reactor used. Tables 2.2 through 2.6 present a summary of some of this lore. These tables should serve as a useful reference in early planning and problem solving. Manufacturers of catalysts through their sales and technical service representatives supply invaluable details and assistance to both customers and potential customers. Licensors of proprietary processes offer similar services along with detailed assistance in planning, design, and troubleshooting.

Table 2.2 Characteristics of Typical Gas-Phase Industrial Solid-Catalytic Processes in Fixed Beds

<i>Reaction</i>	<i>Operating Conditions^a</i>	<i>Catalyst</i>	<i>Typical Life (Years)</i>	<i>Process Affecting Life of Catalyst Charge</i>	<i>Catalyst Property Affected</i>
Ammonia synthesis $N_2 + 3 H_2 \rightleftharpoons 2 NH_3$	450–550°C 200–500 atm SA	Fe with promoters (K ₂ O) & stabilizer (Al ₂ O ₃)	5–10	Slow sintering	Activity
Methanation (ammonia & hydrogen plants) $CO/CO_2 + H_2 \rightleftharpoons CH_4 + H_2O$	250–350°C 30 atm A	Supported nickel	5–10	Slow poisoning (e.g., S & As from plant upsets)	Activity
Acetylene hydrogenation (“front end”) $C_2H_2 + H_2 \rightarrow C_2H_4$	30–100°C 50 atm A	Supported palladium	5–10	Slow sintering, increased bed temperature	Activity/selectivity
Sulfuric acid $2 SO_2 + O_2 \rightarrow 2 SO_3$	420–600°C 1 atm SA	Vanadium & potassium sulfates on silica	5–10	Slow physical deterioration (formation of dust)	Pressure drop & mass transfer
Methanol synthesis (low temperature) $CO + 2 H_2 \rightleftharpoons CH_3OH$	200–300°C 50–100 atm SA or NA	Copper on zinc & aluminum oxides	2–8	Slow sintering	Activity
Low-temperature carbon monoxide shift $CO + H_2O \rightleftharpoons CO_2 + H_2$	200–250°C 30 atm A	Copper on zinc & aluminum oxides	2–6	Slow poisoning, & accelerated sintering by poisons	Activity
Hydrocarbon hydrodesulfurization (including natural gas) $R_2S + 2 H_2 \rightarrow 2 RH + H_2S$	300–400°C 30 atm A	Cobalt & molybdenum sulfides on aluminum oxide	2–8	Slow coking, metal deposits in some cases (feed-stock important)	Mass transfer, pressure drop
High-temperature carbon monoxide shift $CO + H_2O \rightleftharpoons H_2 + CO_2$	350–500°C 30 atm A	Fe ₃ O ₄ on chromia	2–4	Slow sintering, pellet breakage due to water condensation	Activity & pressure drop

Steam reforming natural gas $\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{CO} + 3\text{H}_2$	500–850°C 30 atm DFNA	Nickel on calcium aluminate or alumina	2–4	Sintering, occasionally carbon formation & pellet breakage due to plant upsets	Activity pressure drop
Ethylene partial oxidation $2\text{C}_2\text{H}_4 + \text{O}_2 \rightarrow 2\text{C}_2\text{H}_4\text{O}$	200–270°C 10–20 atm NA	Silver on α -alumina with promoters	1–4	Slow sintering increasing bed temperature	Activity & selectivity
Benzene oxidation to maleic anhydride $\text{C}_6\text{H}_6 + \text{O}_2 \rightarrow \text{C}_4\text{H}_2\text{O}_3$	350°C 1 atm NA	Vanadium & molybdenum oxides with promoters on α -alumina	1–2	Irreversible formation of inactive vanadium phase	Activity & selectivity
Reduction of aldehydes to alcohols $\text{RCHO} + \text{H}_2 \rightarrow \text{RCH}_2\text{OH}$	220–270°C 100–300 atm A	Copper on zinc oxide	0.5–1	Slow sintering, pellet breakage (depends on feed-stock)	Activity or pressure drop
Partial oxidation of methanol to formaldehyde $\text{CH}_3\text{OH} \rightarrow \text{CH}_2\text{O} + \text{H}_2$ $\text{CH}_3\text{OH} + \frac{1}{2}\text{O}_2 \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O}$	600–700°C 1 atm NA	Silver granules	0.3–1	Poisoning, e.g., iron, some coking (due to poisons)	Selectivity
Acetylene hydrogenation ("tail end") $\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$	30–100°C 50 atm A	Supported palladium	0.1–0.5	Coke & oil formation (regeneration possible)	Mass transfer
Catalytic hydrocarbon reforming	460–525°C 8–502 atm SA	Platinum alloys on treated alumina	0.01–0.5	Coking (depends on hydrogen pressure), frequent regeneration	Mass transfer
Catalytic cracking of oils	500–560°C 2–3 atm (fluidized bed)	Synthetic zeolites	0.000002	Very rapid coking (continuous regeneration)	Mass transfer

0.68 yr = 1 month

4 dys = 6 mon

$(2 \times 10^{-4} \text{ yr}) \left(\frac{365 \text{ dy}}{\text{yr}} \right) \left(\frac{24 \text{ hr}}{\text{dy}} \right) \left(\frac{1 \text{ day}}{\text{regeneration}} \right) = 63 \text{ s}$

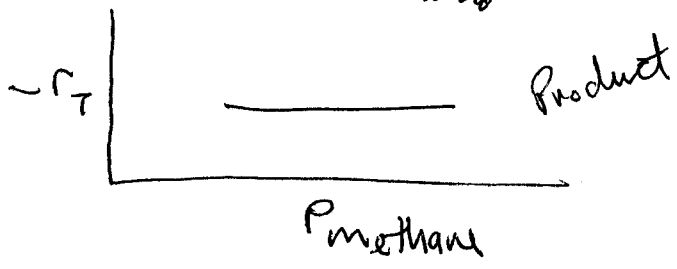
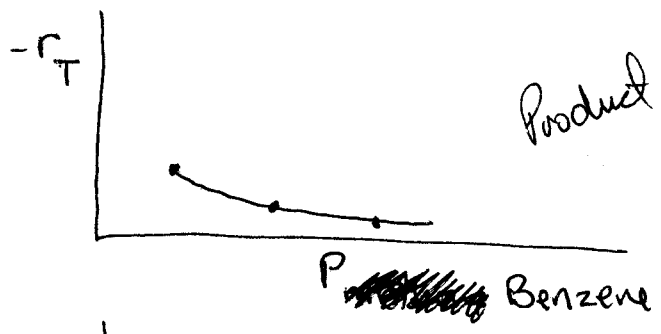
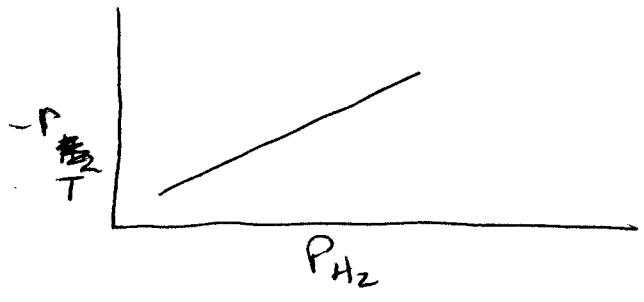
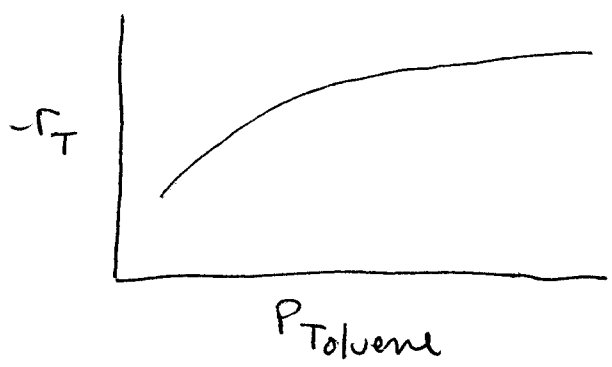
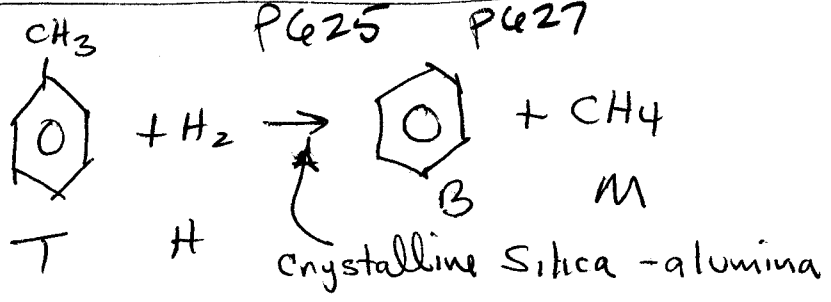
*A = adiabatic fixed bed; NA = nonadiabatic fixed bed (multitubular); SA = staged adiabatic with intermediate heating or cooling; DFNA = direct-fired nonadiabatic tubular reactor.

Reproduced by permission: Denny, P.J. and Twigg, M.V. in "Catalyst Deactivation," Intl. Symp. Antwerp, Oct., 1980, ed. Delmon, B. and Froment, G.F., Elsevier, Science Publishers, Physical Sciences & Engineering Div., New York and Amsterdam, 1980. Reactor designations added.

Table 2.3 Generalized Methods for Preventing or Moderating Catalyst Deactivation

Problem	Cause	Method of Minimizing Problem
Poisoning		
Loss of catalytic surface sites	Adsorbed impurities	Purify feed Use additives that adsorb poison Select conditions that lower adsorption strength Select mass-transfer regimes that reduce activity loss

Example 10-2 \neq 10-3 later



MORE
later

$$-r_T = \frac{k P_{\text{H}_2} P_T}{1 + k_B P_B + k_T P_T}$$

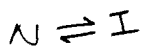
22-141 50 SHEETS
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 22-144 200 SHEETS
 ANIPAL

Langmuir-Hinshelwood (Tables) 2002

F & B
11/1/90

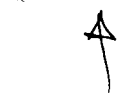
Problem 10-3
in class a) & b

PG-6



Adsorption controlling with inhibitor B

$$r_N = - \frac{(\text{kinetic } F)(\text{driving force})}{(\text{adsorption})}$$



① Adsorption

→ All K's are defined as
 $A + S \rightleftharpoons A \cdot S$
(whether desorption or adsorption)

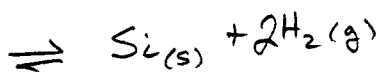
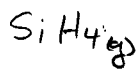
② K

Overall Reaction equilibrium constant

$$K = \frac{P_I}{P_N}$$

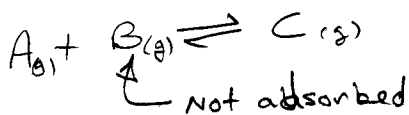
$$r_N = - \frac{k_{A1} (P_N - P_I/K)}{(1 + \frac{K_A P_N}{K} + K_B P_B)} \text{①}$$

Problem 6-2



can't do

Problem PG-7



- 1) Inhibitor I
- 2) B not adsorbed
- 3) A dissociative adsorption
- 4) Surface reaction controlling

$$r_A = - \frac{(k_{sr} K_A) (P_A P_B - \frac{P_C}{K})}{(1 + \sqrt{K_A P_A} + \cancel{K_B P_B} + K_I I)} \text{①}$$

\downarrow
 Δ
 0
 No K_B

$K_C P_C$

Chemical Reactor Analysis and Design

John Wiley & Sons
New York Chichester Brisbane Toronto

Gilbert F. Froment
Rijksuniversiteit Gent, Belgium

Kenneth B. Bischoff
University of Delaware

Kinetic equations for reactions catalyzed by solids based on the chemisorption mechanism may always be written as a combination of three groups:

a kinetic group: [e.g., in Eq. 2.2-18], $k'_A C_i = k_A$

a driving-force group: $(p_A - p_R p_S / K)$

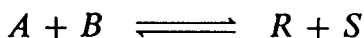
an adsorption group: $1 + \frac{K_A}{K} p_R p_S + K_R p_R + K_S p_S$

such that the overall rate is:

$$= \frac{(\text{kinetic factor})(\text{driving-force group})}{(\text{adsorption group})} \quad (2.2-21)$$

Summaries of these groups for various kinetic schemes are given in Table 2.2-1. (See Yang and Hougen [33].) The various kinetic terms k and kK all contain the

total number of active sites, C_i . Some of them also contain the number of adjacent active sites, s or $s/2$ or $s(s-1)$. Both C_i and s are usually not known and therefore they are not explicitly written in these groups. They are characteristic for a given catalytic system, however. An example of the use of the Yang-Hougen tables would be for the bimolecular reaction

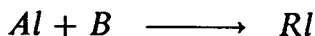


For surface-reaction controlling:

$$r_A = \frac{C_i k_{sr} K_A K_B (p_A p_B - p_R p_S / K)}{(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_I p_I)^2}$$

where I = any adsorbable inert.

Finally, schemes alternate to the L-H-H-W mechanisms are the Rideal-Eley mechanisms, where one adsorbed species reacts with another species in the gas phase:



These yield similar kinetic expressions, but they are somewhat different in detail.

Table 2.2-1 Groups in kinetic equations for reactions on solid catalysts

Driving-Force Groups

Reaction	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
Adsorption of <i>A</i> controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A - \frac{p_R}{K p_B}$	$p_A - \frac{p_R p_S}{K p_B}$
Adsorption of <i>B</i> controlling	0	0	$p_B - \frac{p_R}{K p_A}$	$p_B - \frac{p_R p_S}{K p_A}$
Desorption of <i>R</i> controlling	$p_A - \frac{p_R}{K}$	$\frac{p_A}{p_S} - \frac{p_R}{K}$	$p_A p_B - \frac{p_R}{K}$	$\frac{p_A p_B}{p_S} - \frac{p_R}{K}$
Surface reaction controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$
Impact of <i>A</i> controlling (<i>A</i> not adsorbed)	0	0	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$
Homogeneous reaction controlling	$p_A - \frac{p_R}{K}$	$p_A - \frac{p_R p_S}{K}$	$p_A p_B - \frac{p_R}{K}$	$p_A p_B - \frac{p_R p_S}{K}$

Replacements in the General Adsorption Groups
 $(1 + K_A p_A + K_B p_B + K_R p_R + K_S p_S + K_I p_I)^n$

Reaction	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
Where adsorption of <i>A</i> is rate controlling, replace $K_A p_A$ by	$\frac{K_A p_R}{K}$	$\frac{K_A p_R p_S}{K}$	$\frac{K_A p_R}{K p_B}$	$\frac{K_A p_R p_S}{K p_B}$
Where adsorption of <i>B</i> is rate controlling, replace $K_B p_B$ by	0	0	$\frac{K_B p_R}{K p_A}$	$\frac{K_B p_R p_S}{K p_A}$
Where desorption of <i>R</i> is rate controlling, replace $K_R p_R$ by	$K K_R p_A$	$K K_R \frac{p_A}{p_S}$	$K K_R p_S p_B$	$K K_R \frac{p_A p_B}{p_S}$
Where adsorption of <i>A</i> is rate controlling with dissociation of <i>A</i> , replace $K_A p_A$ by	$\sqrt{\frac{K_A p_R}{K}}$	$\sqrt{\frac{K_A p_R p_S}{K}}$	$\sqrt{\frac{K_A p_R}{K p_B}}$	$\sqrt{\frac{K_A p_R p_S}{K p_B}}$
Where equilibrium adsorption of <i>A</i> takes place with dissoci- ation of <i>A</i> , replace $K_A p_A$ by and similarly for other components adsorbed with dissociation	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$	$\sqrt{K_A p_A}$

Table 2.2-1 (Continued)

Where A is not adsorbed,
 replace $K_A p_A$ by
 and similarly for other
 components that are not
 adsorbed

0 0 0 0

Kinetic Groups

Adsorption of A controlling	k_A
Adsorption of B controlling	k_B
Desorption of R controlling	$k_R K$
Adsorption of A controlling with dissociation	k_A
Impact of A controlling	$k_A K_B$
Homogeneous reaction controlling	k

Surface Reaction Controlling

	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
Without dissociation	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A K_B$	$k_{sr} K_A K_B$
With dissociation of A	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A K_B$	$k_{sr} K_A K_B$
B not adsorbed	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$
B not adsorbed, A dissociated	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$	$k_{sr} K_A$

Exponents of Adsorption Groups

Adsorption of A controlling without dissociation	$n = 1$
Desorption of R controlling	$n = 1$
Adsorption of A controlling with dissociation	$n = 2$
Impact of A without dissociation $A + B \rightleftharpoons R$	$n = 1$
Impact of A without dissociation $A + B \rightleftharpoons R + S$	$n = 2$
Homogeneous reaction	$n = 0$

Surface Reaction Controlling

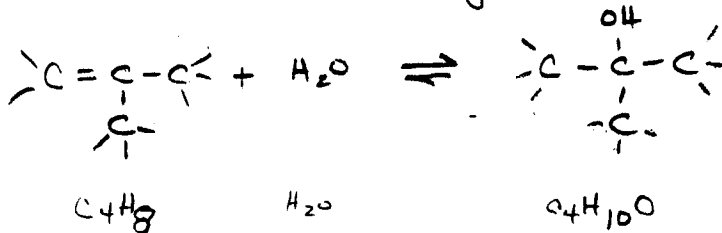
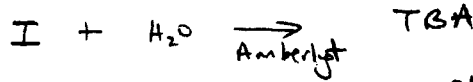
	$A \rightleftharpoons R$	$A \rightleftharpoons R + S$	$A + B \rightleftharpoons R$	$A + B \rightleftharpoons R + S$
No dissociation of A	1	2	2	2
Dissociation of A	2	2	3	3
Dissociation of A (B not adsorbed)	2	2	2	2
No dissociation of A (B not adsorbed)	1	2	1	2

From Yang and Hougen [33].

10-4
P 10-3

liquid phase hydration

t-Butyl Alcohol



Overall
RXN

$$1) I + S \rightleftharpoons I \cdot S \quad r_I = -k_I (C_I C_V - \frac{C_{I \cdot S}}{K_I}) \quad \left. \vphantom{r_I} \right\} K_I = \frac{C_{I \cdot S}}{C_I C_V} \Big|_{eq}$$

$$2) W + S \rightleftharpoons W \cdot S \quad r_W = -k_W (C_W C_V - \frac{C_{W \cdot S}}{K_W}) \quad \left. \vphantom{r_W} \right\} K_W = \frac{C_{W \cdot S}}{C_W C_V} \Big|_{eq}$$

$$3) W \cdot S + I \cdot S \rightleftharpoons \text{TBA} \cdot S + S \quad r_{SR} = -k_{SR} (C_{W \cdot S} C_{I \cdot S} - \frac{C_{\text{TBA} \cdot S} C_V}{K_{SR}})$$

$$4) \text{TBA} \cdot S \rightleftharpoons \text{TBA} + S \quad r_d = -k_d (C_{\text{TBA} \cdot S} - \frac{C_{\text{TBA}} C_V}{K_D})$$

Site Balance:

$$C_T = C_V + C_{I \cdot S} + C_{W \cdot S} + C_{\text{TBA} \cdot S}$$

$$K_D = \frac{C_{\text{TBA}} C_V}{C_{\text{TBA} \cdot S}} \Big|_{eq}$$

a) assume surface rxn limits rate:

$$r \approx r_{SR} = -k_{SR} (C_{W \cdot S} C_{I \cdot S} - \frac{C_{\text{TBA} \cdot S} C_V}{K_{SR}}) \quad \begin{array}{l} \neq \text{steps } 1, 2 \neq 4 \\ \text{are in equilibrium} \end{array}$$

$$\text{assume } \frac{r_{SR}}{k_{SR}} \ll \frac{r_1}{k_I}, \frac{r_2}{k_W}, \frac{r_4}{k_d}$$

since at steady-state
 $r_{SR} = r_1 = r_2 = r_4 = r$

eliminate all variables that can not be measured

$$C_{W.S}, C_{I.S}, C_{TBA.S}, C_V$$

$$C_{W.S} = k_W C_W C_V / e_g$$

$$C_{I.S} = k_I C_I C_V / e_g$$

$$C_{TBA.S} = \frac{C_{TBA} C_V}{K_D} / e_g$$

$$\begin{aligned} r \approx r_{SRXN} &= -k_{SR} \left[k_W C_V C_W k_I C_I C_V - \frac{C_{TBA} C_V C_V}{K_{SR} K_D} \right] \\ &= -k_{SR} C_V^2 \left(k_W k_I C_W C_I - \frac{C_{TBA}}{K_D K_{SR}} \right) \end{aligned}$$

from site balance

$$C_T = C_V + k_I C_I C_V + k_W C_W C_V + \frac{C_{TBA} C_V}{K_D}$$

$$C_V = \frac{C_T}{\left(1 + k_I C_I + k_W C_W + \frac{C_{TBA}}{K_D} \right)}$$

Substituting into r_{SR}

$$r \approx r_{SR} = - \frac{k_{SR} C_T^2 \left(k_W k_I C_W C_I - \frac{C_{TBA}}{K_D K_{SR}} \right)}{\left(1 + k_I C_I + k_W C_W + \frac{C_{TBA}}{K_D} \right)^2}$$

$$K = \frac{C_{TBA}}{C_W C_I} = \frac{C_{TBA.S} K_D / C_V}{\left(\frac{C_{W.S}}{k_W C_V} \right) \left(\frac{C_{I.S}}{k_I C_V} \right)} = \frac{K_D k_W k_I C_{TBA.S}}{C_{W.S} C_{I.S}}$$

$$\text{and } k_{SR} = \frac{C_{TBA.S}}{C_{W.S} C_{I.S}} \quad \therefore \quad K = K_D k_W k_I k_{SR}$$

P10-3 a)

$$r \approx r_{SR} = \frac{-k_{SR} C_T^2 K_I k_w \left[C_w C_I - \frac{C_{TBA}}{K_w K_I K_D k_{SR}} \right]}{\left(1 + K_I C_I + K_w C_w + \frac{C_{TBA}}{K_D} \right)^2}$$

$$r \approx \frac{-k_{SR} C_T^2 K_I k_w \left[C_w C_I - \frac{C_{TBA}}{K} \right]}{\left(1 + K_I C_I + K_w C_w + \frac{C_{TBA}}{K_D} \right)^2}$$

or defining all K 's as adsorption for adsorption
desorption steps

$$K_{TBA} = 1/K_D \quad \text{see page 606 in Fogler}$$

$$r \approx \frac{-k_{SR} C_T^2 K_I k_w \left[C_w C_I - \frac{C_{TBA}}{K} \right]}{\left(1 + K_I C_I + K_w C_w + K_{TBA} C_{TBA} \right)^2}$$

with $k = k_{SR} C_T^2 K_I k_w$

10-3 (b)

adsorption of I is limiting

remove using surface rxn (you can't use the adsorption equilibrium)

$$r \approx r_I = -k_I \left(C_I C_V - \frac{C_{I.S}}{K_I} \right)$$

$$r \approx -k_I \left(C_I C_V - \frac{C_{TBA.S} C_V}{C_{W.S} K_{SR} K_I} \right) \quad \text{from } \underline{r_{SR}} \quad C_{I.S} = \frac{C_{TBA.S} C_V}{K_{SR} C_{W.S}}$$

$$C_{TBA.S} = \frac{C_{TBA} C_V}{K_D} = K_{TBA} C_{TBA} C_V$$

$$C_{W.S} = C_W C_V K_W$$

$$C_{I.S} = \frac{C_{TBA.S} C_V}{K_{SR} C_{W.S}} = \frac{K_{TBA} C_{TBA} C_V C_V}{K_{SR} C_W C_V K_W} = \frac{K_{TBA}}{K_{SR} K_W} \left(\frac{C_{TBA}}{C_W} \right)$$

$$C_T = C_V + C_{I.S} + C_{W.S} + C_{TBA.S}$$

$$C_T = C_V + \left(\frac{K_{TBA} C_V C_{TBA}}{K_{SR} C_W C_W} \right) + C_W K_W C_V + K_{TBA} C_{TBA} C_V$$

$$C_V = \frac{C_T}{1 + \frac{K_{TBA} C_{TBA}}{K_{SR} C_W} + K_W C_W + K_{TBA} C_{TBA}}$$

$$r = \frac{-k_I C_T \left(C_I - \frac{K_{TBA} C_{TBA}}{K_{SR} K_W C_W} \right)}{\left(1 + \frac{K_{TBA} C_{TBA}}{K_{SR} C_W} + K_W C_W + K_{TBA} C_{TBA} \right)}$$

since $K = \frac{K_W K_I K_{SR}}{K_{TBA}}$

$$r = \frac{-k_I C_T \left(C_I - \frac{K}{K_I C_W} \right)}{\left(1 + \frac{K_{TBA} C_{TBA}}{K_{SR} K_W} + K_W C_W + K_{TBA} C_{TBA} \right)}$$

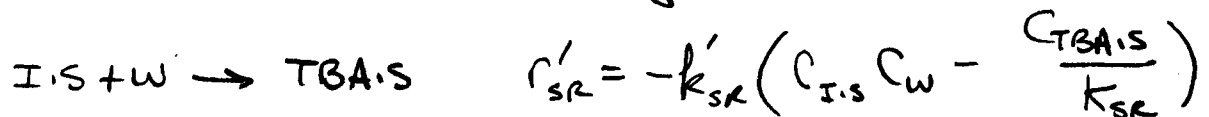
10-3b

$$r = \frac{-k_I C_T \left(C_I - \frac{C_{TBA}}{K C_W} \right)}{\left(1 + \frac{k_I}{K} \frac{C_{TBA}}{C_W} + k_W C_W + k_{TBA} C_{TBA} \right)}$$

$$\text{for } \frac{k_{TBA}}{k_{SR} k_W} = \frac{k_I}{K}$$

10-3(c)

Reaction is replaced by



$$r \approx -k'_{SR} \left(k_I C_I C_V C_W - \frac{k_{TBA} C_V C_{TBA}}{K_{SR}} \right)$$

Water not adsorbed

$$C_T = C_V + \cancel{k_W C_W C_V} + k_I C_I C_V + k_{TBA} C_V C_{TBA}$$

$$r = \frac{-k'_{SR} k_I C_T \left(C_I C_W - \frac{k_{TBA}}{k_{SR} k_I} C_{TBA} \right)}{\left(1 + k_I C_I + k_{TBA} C_{TBA} \right)}$$

$$\text{with } K' = \frac{k_W k_{SR}}{k_{TBA}}$$

10-3
(c)

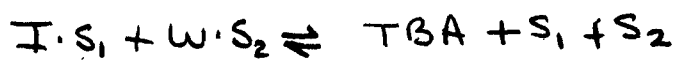
$$r = \frac{-k'_{SR} k_I C_T \left(C_I C_W - \frac{C_{TBA}}{K'} \right)}{\left(1 + k_I C_I + k_{TBA} C_{TBA} \right)}$$

10-3 (d)

Iso butene & water are adsorbed at different sites. TBA is not on surface. surface rxn controls.



Reaction



$$r \approx -k_{SR}'' \left(C_{I \cdot S_1} C_{W \cdot S_2} - \frac{C_{TBA} C_{V1} C_{V2}}{K_{SR}''} \right)$$

$$K_{SR}'' = \frac{C_{TBA} C_{V1} C_{V2}}{C_{I \cdot S_1} C_{W \cdot S_2}}$$

Site balances

$$C_{T1} = C_{V1} + C_{I \cdot S_1} = C_{V1} + K_I C_I C_{V1}$$

$$C_{T2} = C_{V2} + C_{W \cdot S_2} = C_{V2} + K_W C_W C_{V2}$$

$$r \approx -k_{SR}'' \left(K_I C_I C_{V1} K_W C_W C_{V2} - \frac{C_{TBA} C_{V1} C_{V2}}{K_{SR}''} \right)$$

$$= -k_{SR}'' C_{V1} C_{V2} \left(K_I K_W C_I C_W - \frac{C_{TBA}}{K_{SR}''} \right)$$

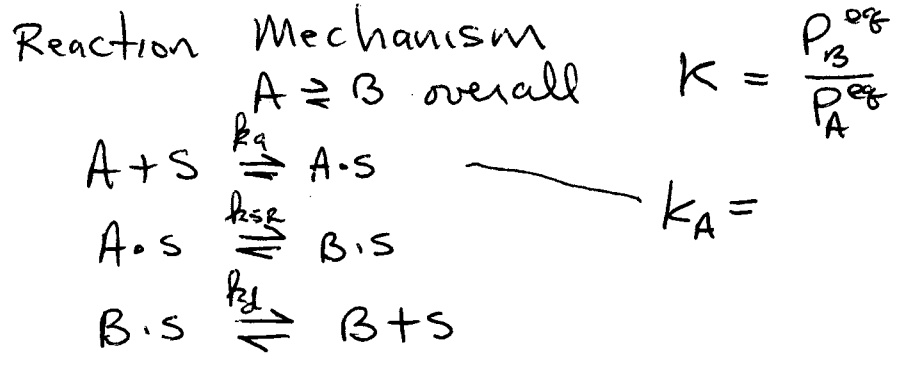
$$= -k_{SR}'' K_I K_W C_{T1} C_{T2} \left(C_I C_W - \frac{C_{TBA}}{K_I K_W K_{SR}''} \right)$$

$$\frac{r}{(1 + K_I C_I)(1 + K_W C_W)}$$

$$K = \frac{C_{TBA}}{C_I C_W} = \frac{K_{SR}'' C_{I \cdot S_1} C_{W \cdot S_2}}{C_{V1} C_{V2} \frac{C_{I \cdot S_1}}{K_I C_I} \frac{C_{W \cdot S_2}}{K_W C_W}} = K_{SR}'' K_I K_W$$

$$r = \frac{-k_{SR}'' K_I K_W C_{T1} C_{T2} \left(C_I C_W - \frac{C_{TBA}}{K} \right)}{(1 + K_I C_I)(1 + K_W C_W)}$$

Start of Lecture on Derivation of LHHW equation



① $r_a = -k_a (P_A C_v - \frac{C_{A \cdot S}}{K_A})$ at $r_a = 0$ $K_A = \frac{C_{A \cdot S}}{P_A C_v}$

② $r_{sr} = -k_{sr} (C_{A \cdot S} - \frac{C_{B \cdot S}}{K_s})$ at $r_{sr} = 0$ $K_{sr} = \frac{C_{B \cdot S}}{C_{A \cdot S}}$

③ $r_d = -k_d (C_{B \cdot S} - \frac{P_B C_v}{K_D})$ at $r_d = 0$ $K_D = \frac{P_B C_v}{C_{B \cdot S}}$

④ at steady-state $r_a = r_{sr} = r_d$

⑤ and total site balance $C_T = C_v + C_{A \cdot S} + C_{B \cdot S}$

General reaction rate:

Combine signs and definitions of k

$$r_A = \frac{-C_T (P_A - P_B/K)}{\left[\left(\frac{1}{K_A k_{sr}} + \frac{1}{k_a} + \frac{1}{k_d} \right) + \left(\frac{1}{K_{sr} K_A} + \frac{1 + K_{sr}}{K k_d} \right) K_A P_A + \left(\frac{1}{K_A k_s} + \frac{1 + K_s}{K_s k_a} \right) \frac{1}{K_D} P_B \right]}$$

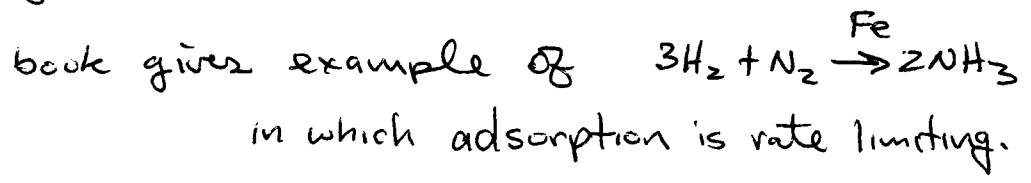
Rate limiting steps:

Book discusses this in terms of electric circuits



which step has the highest resistance?
or which step limits the rate?

In general most rxns are surface limited



Examine rate limiting by looking at k values
 k_a, k_{sr}, k_d

if k_{sr} is small compared to the others
 $k_{sr} \ll k_a \neq k_d$

since $r_a = r_{sr} = r_d = \text{a constant a.s.s.}$

$$\frac{r_{sr}}{k_{sr}} = - \left(C_{A,s} - \frac{C_{B,s}}{K_{rxn}} \right) \approx \underline{\underline{\text{large}}}$$

\uparrow $\frac{1}{\text{small}} = \text{large}$

$$K_{sr} \equiv \frac{C_{B,s}^{eq}}{C_{A,s}^{eq}}$$

$$\frac{r_a}{k_a} = \frac{\#}{\text{large}} = \text{small} = - \left(P_A C_V - \frac{C_{A,S}}{K_A} \right) \approx 0$$

this
is
considered
to be in equilibrium

$$\frac{r_d}{k_d} \approx \text{small} = - \left(C_{B,S} - \frac{P_B C_V}{K_D} \right) = 0$$

Procedure start : (write down presumed mechanism)

- 1) find or Assume rate limiting step, set overall rate ^(NET) equal to this step
- 2) let all other steps be in equilibrium
- 3) write site balance
- 4) eliminate unknown surface concentrations and vacant site concentrations

Surface Rxn limited

$$r_{SR} = r_{NETA} = -k_{SR} \left(C_{A,S} - \frac{C_{B,S}}{K_{SR}} \right)$$

The other two steps are in equilibrium

$$K_A = \frac{C_{A,S}}{P_A C_V} \quad K_D = \frac{P_B C_V}{C_{B,S}}$$

site balances $C_T = C_V + C_{A,S} + C_{B,S}$

$$C_T = C_V + K_A P_A C_V + \frac{P_B C_V}{K_D}$$

$$C_V = \frac{C_T}{1 + K_A P_A + P_B / K_D}$$

$$r_{NET} = -k_{SR} \left(K_A P_A C_V - \frac{P_B C_V}{K_D K_{SR}} \right)$$

$$r_{NET} = \frac{-k_{SR} C_T \left(K_A P_A - \frac{P_B}{K_D K_{SR}} \right)}{1 + K_A P_A + P_B / K_D}$$

We can make this above equation look nicer with the following steps

$$r_{NET} = \frac{-k_{SR} C_T K_A \left(P_A - \frac{P_B}{K_A K_D K_{SR}} \right)}{1 + K_A P_A + P_B / K_D}$$

$$K \equiv \frac{P_B^{eq}}{P_A^{eq}} = \frac{C_{B,S} K_D K_A}{C_V C_{A,S}} = K_{SR} K_D K_A$$

Since $K_{SR} = \frac{C_{B,S}}{C_{A,S}}$ →

$$r_{NET} = \frac{-k_{SR} C_T K_A (P_A - \frac{P_B}{K})}{(1 + K_A P_A + P_B/K_D)}$$

If you compare this with the Froment & Bischoff charts you will find that they define adsorption & desorption in one direction

$$K_A = \frac{\text{"surface"}}{\text{"free"}} \quad K'_D = \frac{\text{surface}}{\text{free}}$$

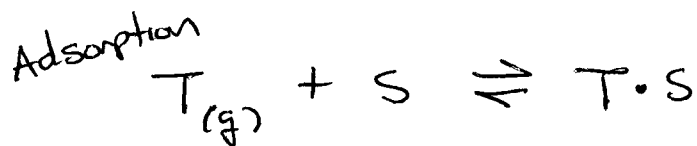
In our example

$$K_A = \frac{C_{A,S}}{C_V P_A} \quad K'_D = \frac{C_{B,S}}{C_V P_B}$$

$$r_{NET} \text{ Froment \& Bischoff} = \frac{-k_{SR} C_T K_A (P_A - P_B/K)}{(1 + K_A P_A + P_B K'_D)}$$

Proposed mechanism

Adsorption

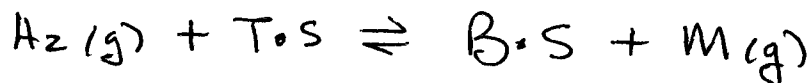


Section 10.5 continued

T - Toluene
B - Benzene
M - methane

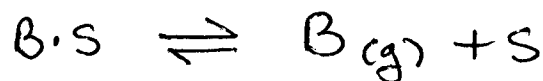
$$r_{AD} = k_A (C_V P_T - \frac{C_{T \cdot S}}{K_T})$$

surface rxn



$$r_S = k_{SR} (P_{H_2} C_{T \cdot S} - \frac{C_{B \cdot S} P_M}{K_S})$$

Desorption



$$r_D = k_D (C_{B \cdot S} - k_B P_B C_V)$$

assume surface rxn limits

$$-r_T = r_S \rightarrow \text{slow} = k_{SR} (P_{H_2} C_{T \cdot S} - \frac{C_{B \cdot S} P_M}{K_S})$$

$$\frac{r_{AD}}{k_A} \approx 0 = C_V P_T - \frac{C_{T \cdot S}}{K_T}$$

$$K_T = \frac{C_{T \cdot S}}{C_V P_T}$$

$$\frac{r_D}{k_D} \approx 0 = C_{B \cdot S} - k_B P_B C_V$$

$$(K_B = \frac{C_{B \cdot S}}{P_B C_V}) \text{ from Bischoff}$$

Site Balance

$$C_T = C_V + C_{T \cdot S} + C_{B \cdot S}$$

$$C_T = C_V + K_T C_V P_T + K_B P_B C_V / K_B$$

$$C_V = \frac{C_T}{1 + K_T P_T + K_B P_B / K_B}$$

$$-r_T = k_{SR} \left[P_{H_2} K_T C_V P_T - \frac{K_B P_B C_V P_M}{K_B K_S} \right] = k_{SR} C_V \left[P_{H_2} P_T K_T - \frac{P_B P_M}{K_B K_S} \right]$$

$$-r_T = \frac{k_{SR} C_T \left[P_{H_2} P_T k_T - P_B P_m \frac{k_B}{k_B k_S} \right]}{\left(1 + k_T P_T + k_B \frac{P_B}{k_B} \right)}$$

$$K_{eq} = \frac{P_B P_m}{P_T P_H}$$

$$k_{SR} = \frac{C_{B,S} P_m}{P_{H_2} C_{T,S}} \quad \text{or} \quad \frac{P_m}{P_{H_2}} = k_{SR} \frac{C_{T,S}}{C_{B,S}}$$

$$= \frac{\left(\frac{C_{B,S}}{k_B C_T} \right) P_m}{\left(\frac{C_{T,S}}{C_T k_T} \right) (P_H)} = \frac{\cancel{C_{B,S}} k_{SR} C_{T,S}}{\frac{C_{T,S}}{k_T} \cancel{C_{B,S}}} = \frac{k_{SR} k_T k_B}{k_B}$$

$$-r_T = \frac{k_{SR} C_T k_T \left[P_{H_2} P_T - \frac{P_B P_m k_B}{k_{SR} k_T} \right]}{\left(1 + k_T P_T + k_B P_B \right)}$$

$$= \frac{-(k_{SR} C_T k_T) \left[P_{H_2} P_T - \frac{P_B P_m}{K_{eq}} \right]}{\left(1 + k_T P_T + k_B P_B \right)}$$

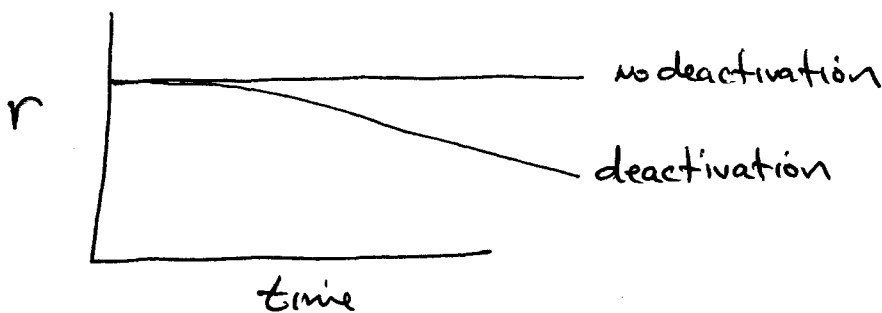
not
in
tables

Catalyst Deactivation 10.7

Objective: ① quantify the rate of catalyst deactivation from experimental data

② Design a reactor knowing that a catalyst will deactivate ~~again~~ ^{in a} repeatable manner.

1) Catalyst deactivate



2) look at lifetimes Rase (Handout LHHW from Froment & Bischoff)

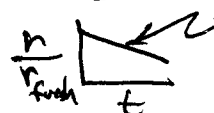
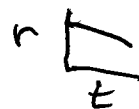
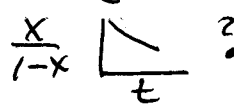
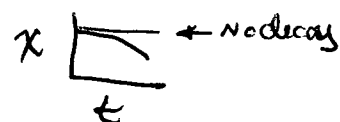
3) Look at 1991 Exam

How can we describe decay?

r_{fresh} ← typical measurement

r_{actual} ← in operation

look at data



straight line!



what other decay expressions are possible?

10.7.1

Sintering:
(Aging)

prolonged exposure - closing of catalyst pores
reduction in S_a

$$\text{Rate of decay} = k_d a^2 = - \frac{da}{dt}$$

$$\text{or } a = \frac{1}{1 + k_d t}$$

10.7.1 Coking or fouling

empirical: $a = \frac{1}{1 + 7.6 t}^{1/2}$ (gas oil cracking rxn)

Poison: - another chemical

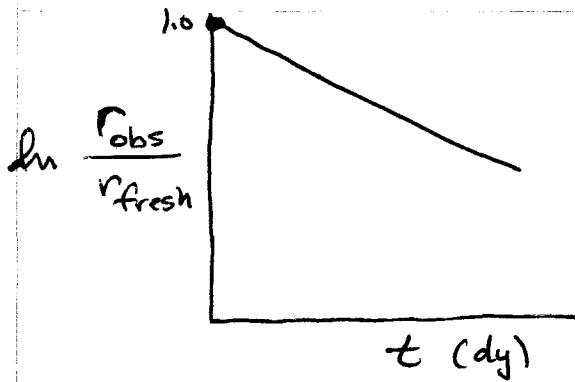
$$\frac{da}{dt} = - a(t) k_d C_{\text{poison}}$$

More examples of decay rates Table 10-6 p643

What happens if $r_{\text{obs}} \neq a r_{\text{fresh}}$

not covered in text

↑ ↑
you may not be able to separate these 2 terms



Fitting an equation

$$\ln\left(\frac{r_{obs}}{r_{fresh}}\right) = -k_d t \quad \text{or} \quad \frac{r_{obs}}{r_{fresh}} = \exp(-k_d t)$$

Now I can predict the reaction rate as a function of time in a reactor

$\left. \begin{array}{l} \text{Find } k_d? \\ \text{in class} \end{array} \right\}$
 $\text{slope} = \frac{\ln\left(\frac{r_{obs}}{r_f}\right)_1 - \ln\left(\frac{r_{obs}}{r_f}\right)_2}{t_1 - t_2}$
 $-k_d = \frac{\ln(1) - \ln(0.405)}{-30 \text{ day}} \Rightarrow k_d = -0.03 \text{ dy}^{-1}$

$$\boxed{V_e(1-\phi) = W}$$

Now plug into CSTR:

$$0 = F_{A0} - F_A + r_A W$$

$\left\{ \frac{dCAV}{dt} \right.$

d c

Remaining part of chapter

Packed Bed reactors - poison

Examples 10-5, 10-6, 10-7

10.7.2 Temperature - Time

Resist the effects of decay may
be done by increasing T

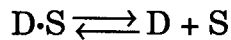
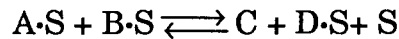
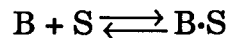
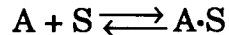
10.8 Micro electronics - Surface Rxns in
Micro electronic device Fabrication p 662

*In class
Examples*

EXAM 2
Chemical Reactor Design ChE 4063

21 November 1991

- (20%) 1. Derive a rate expression for A based on the following mechanism. The rate expression should contain only measurable properties. It is believed that the surface reaction rate is much slower than all the other steps.



- (30%) 2. The catalytic reaction: $A \longrightarrow B$ has been studied in your laboratory. The reaction can be modeled using first order reaction kinetics: $r_A = -kC_A$. Your lab has determined these kinetics from experiments using compound A mixed with an inert. You have been asked to design an isothermal CSTR for a pilot plant using this data. You suspect that there may be a catalyst poison in the actual feed and ask the lab to run experiments using the feed for the pilot plant. They are astonished to find that the conversion of A in their lab CSTR decays over a period of days. They make six graphs for you (See following pages).

$$Q_0 = 1 \text{ L/s}$$

$$F_{A0} = 10 \text{ mol/h, } S$$

$$k = 0.1 \text{ L/(kg cat s)}$$

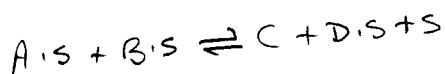
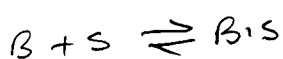
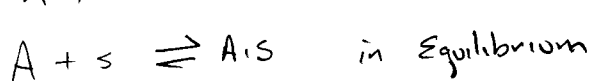
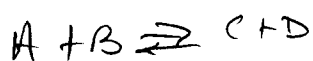
$$W = 50 \text{ kg}$$

- 15 a). Determine an expression for the activity of the catalyst. Assume that the concentration of poison is constant. (Mathematically describe the rate of deactivation of the catalyst.)
- 5 b). Determine the conversion of A after 50 days.
- 10 c). How would you improve this process to maximize the conversion of A?

Exam 2 solutions

10:22

1.



$$K_A = \frac{C_{A \cdot S}}{P_A C_V}$$

$$K_B = \frac{C_{B \cdot S}}{P_B C_V}$$

$$K_D = \frac{P_D C_V}{C_{D \cdot S}}$$

$$K_{SR} \equiv \frac{P_C C_{D \cdot S} C_V}{C_{A \cdot S} C_{B \cdot S}}$$

$$r_{rxn} = (k_{rev} P_C C_{D \cdot S} C_V - k_f C_{A \cdot S} C_{B \cdot S})$$

$$r_A = r_{rxn} = -k_f \left[C_{A \cdot S} C_{B \cdot S} - \frac{P_C C_{D \cdot S} C_V}{K_{SR}} \right] = -k_f \left[K_A P_A C_V K_B P_B C_V - \frac{P_C C_V P_D C_V}{K_{SR} K_D} \right]$$

$$C_t = C_V + C_{A \cdot S} + C_{B \cdot S} + C_{D \cdot S}$$

$$= C_V + K_A P_A C_V + K_B P_B C_V + \frac{P_D C_V}{K_D}$$

$$r_A = \frac{-k_f C_V^2 \left[P_A P_B K_A K_B - \frac{P_C P_D}{K_{SR} K_D} \right]}{\left(1 + K_A P_A + K_B P_B + P_D / K_D \right)^2}$$

$$K_{overall} = \frac{P_C P_D}{P_A P_B} = \frac{K_D C_{D \cdot S} K_A C_V K_B C_V P_D}{C_V C_{A \cdot S} C_{B \cdot S}}$$

$$K_{SR} = \frac{C_{D \cdot S} P_C C_V}{C_{A \cdot S} C_{B \cdot S}}$$

$$K_{overall} = K_D K_A K_B K_{SR}$$

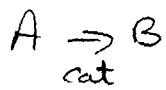
$$r_A = \frac{-k_f K_A K_B C_t^2 \left[P_A P_B - \frac{P_C P_D}{K_{overall}} \right]}{\left(1 + K_A P_A + K_B P_B + P_D / K_D \right)^2}$$

10:32

10min

Problem 2

10:35



$$r_A = -k C_A$$

$$W = 50 \text{ kg}$$

$$k = 0.1 \left(\frac{\text{L}}{\text{kg cat s}} \right)$$

$$Q_0 = 1 \text{ L/s}$$

$$F_{A0} = 10 \text{ mol/s}$$

$$\text{Catalyst activity} = \frac{r(C_A, T)}{r_{\text{fresh}}(C_A, T)} = a$$

from semi log plot we have a straight line

$$\ln \left(\frac{r_{\text{obs}}}{r_{\text{fresh}}} \right) = -k_d t$$

$$-k_d = \frac{\ln \left(\frac{r_{\text{obs}}}{r_f} \right)_2 - \ln \left(\frac{r_{\text{obs}}}{r_f} \right)_1}{t_2 - t_1} = \frac{\ln(1.0) - \ln(0.405)}{0 - 30} = -0.03 \text{ dy}^{-1}$$

$$r_{\text{obs}} = a r_{\text{fresh}} = a k C_A = e^{-k_d t} k C_A$$

Since the decay of the catalyst is much longer than the characteristic time of reaction or residence time than the CSTR can be approximated as steady-state.

$$0 = F_{A0} - F_A + r_A W \quad -F_{A0} X = -a k \frac{F_A W}{Q_0} = -\frac{a k}{Q_0} F_{A0} (1-X) W$$

$$\frac{F_{A0} X}{F_{A0} (1-X)} = \frac{a k W}{Q_0} \quad X = \frac{a k W}{Q_0} - \frac{a k W}{Q_0} X \quad X = \frac{a k W / Q_0}{a k W / Q_0 + 1}$$

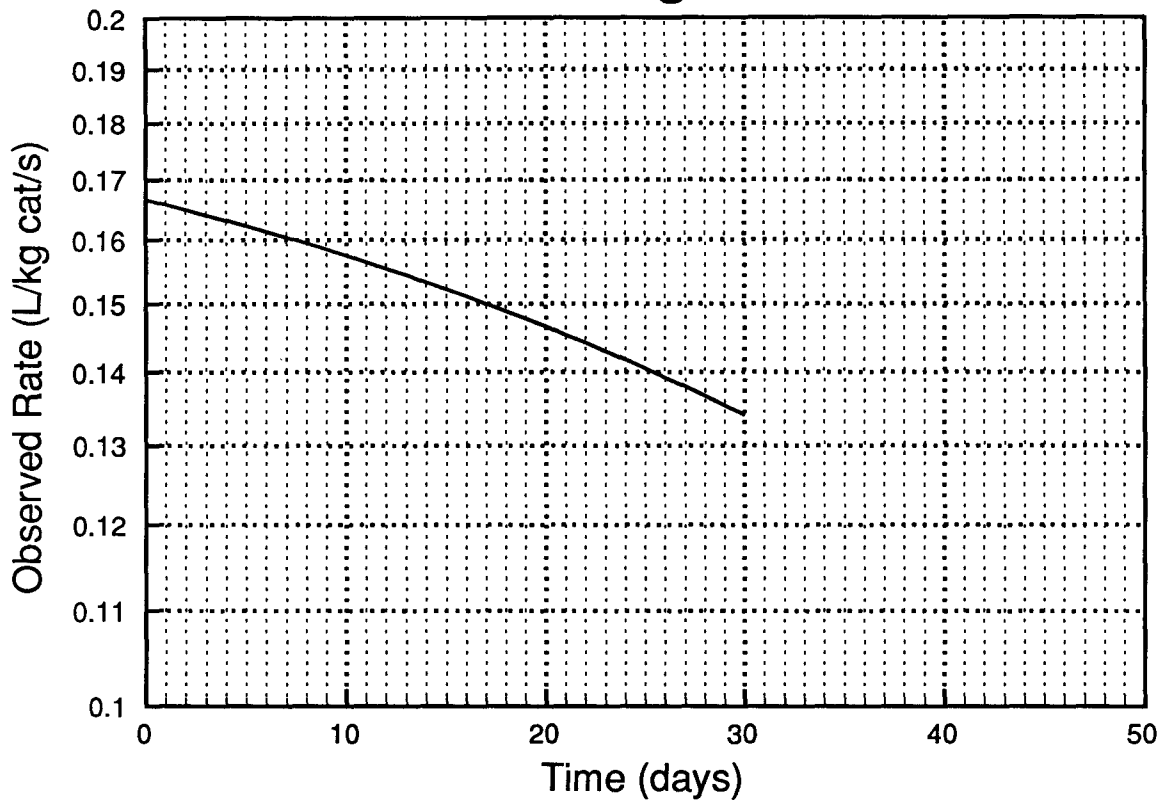
$$X = \frac{e^{-0.03(50)} (0.1 \text{ L/kg cat s}) (50 \text{ kg}) / 1 \text{ L/s}}{1 + e^{-0.03(50)} (0.1) (50) / 1 \text{ L/s}} = 0.53$$

10:47

10:53

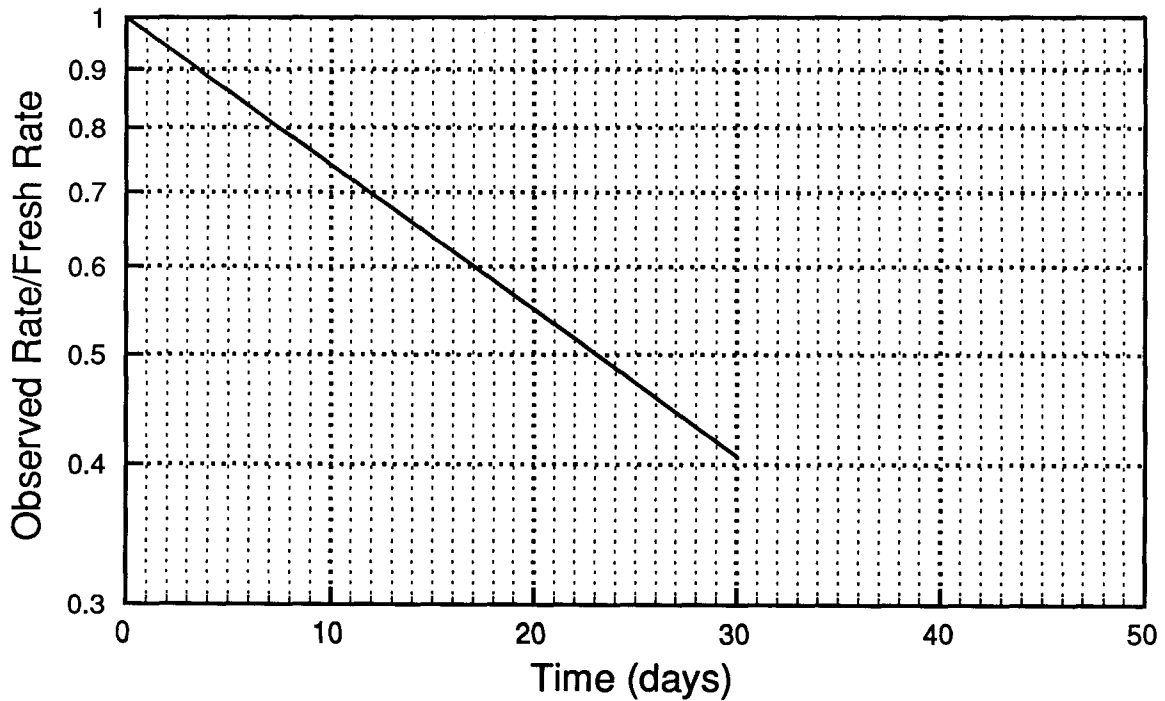
20 min

Observed Rate Using Actual Feed



Ratio of Observed Rate to Fresh Rate

Using Actual Feed. Fresh rate calculated at equivalent concentrations of A.



Rigorous Solution

$$\frac{dC_A}{dt} \left(\frac{W}{\rho_b} \right) = F_{A0} - F_A + (-r_A)W \exp(-0.03 t)$$

$$v_0 = (1 \text{ L/s}) \frac{86400 \text{ s}}{\text{day}}$$

$$F_{A0} = 10 \text{ mol/L}$$

$$k = \left(0.1 \frac{\text{L}}{\text{kg} \cdot \text{s}} \right) \left(\frac{3600 \text{ s}}{\text{day}} \right)^{24}$$

$$W = 50 \text{ kg}$$

or convert $\left(\frac{0.03}{\text{day}} \right) \left(\frac{\text{day}}{86400 \text{ s}} \right)$

$$\frac{0.03 \text{ min}}{\text{min}} \frac{60 \text{ min}}{\text{hr}} \frac{24 \text{ hr}}{\text{day}} = 86,400 \text{ s/day}$$

with fresh catalyst

$$0 = F_{A0} - F_A - k C_A W$$

$$F_A = \frac{C_A}{v_0} \text{ — no change}$$

$$0 = F_{A0} - F_A - k \frac{F_A W}{v}$$

$$F_{A0} = F_A \left(1 + \frac{k W}{v} \right)$$

$$F_A = F_{A0} (1 - X)$$

$$\frac{F_{A0}}{1 + \frac{k W}{v}} = F_{A0} (1 - X)$$

$$X = 1 - \frac{1}{1 + \frac{k W}{v}} = 0.833$$

$$F_A = F_{A0} (1 - X) = 10 \text{ mol/s} (1 - 0.833) = 1.67 \text{ mol/s}$$

$$C_{A0} = \frac{1.67 \text{ mol}}{\text{s}} / 1 \text{ L/s} = 1.67 \frac{\text{mol}}{\text{L}}$$

Catalyst Decay Exam 2 1991 question – Rigorous Solution

POLYMATH Results

Catalyst Decay Exam 2 1991 question 04-08-2002, Rev5.1.230

Calculated values of the DEQ variables

Variable	initial value	minimal value	maximal value	final value
t	0	0	50	50
CA	1.67	1.67	4.7266775	4.7266775
FA0	8.64E+05	8.64E+05	8.64E+05	8.64E+05
flow	8.64E+04	8.64E+04	8.64E+04	8.64E+04
FA	1.443E+05	1.443E+05	4.084E+05	4.084E+05
W	50	50	50	50
rA	-1.443E+04	-4.084E+04	-1.443E+04	-4.084E+04
a	1	0.2231351	1	0.2231351
XA	0.833	0.5273378	0.833	0.5273378

ODE Report (STIFF)

Differential equations as entered by the user

[1] $d(CA)/d(t) = FA0 - FA + rA * a * W$

Explicit equations as entered by the user

[1] $FA0 = 10 * 86400$

[2] $flow = 86400$

[3] $FA = CA * flow$

[4] $W = 50$

[5] $rA = -0.1 * 86400 * CA$

[6] $a = \exp(-0.03 * t)$

[7] $XA = (FA0 - FA) / FA0$

Comments

[2] $FA0 = 10 * 86400$

mol/dy

[3] $flow = 86400$

L/dy

Independent variable

variable name : t

initial value : 0

final value : 50

Precision

Independent variable accuracy.

eps = 0.00001

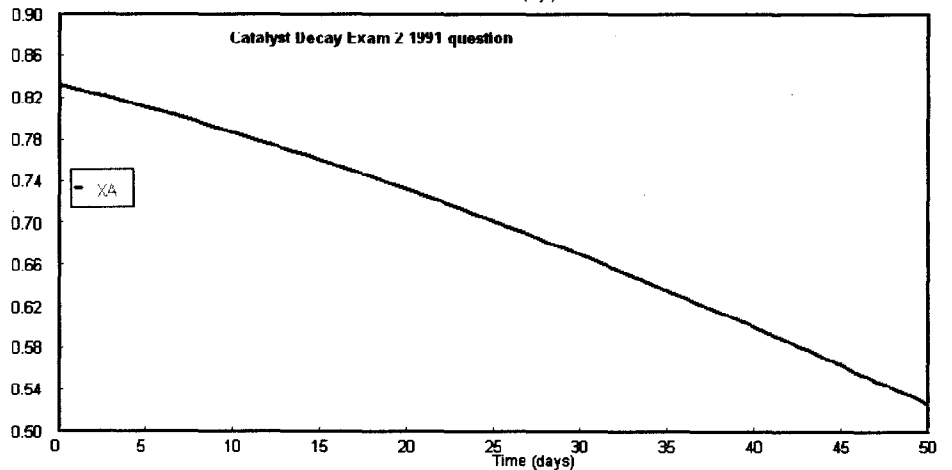
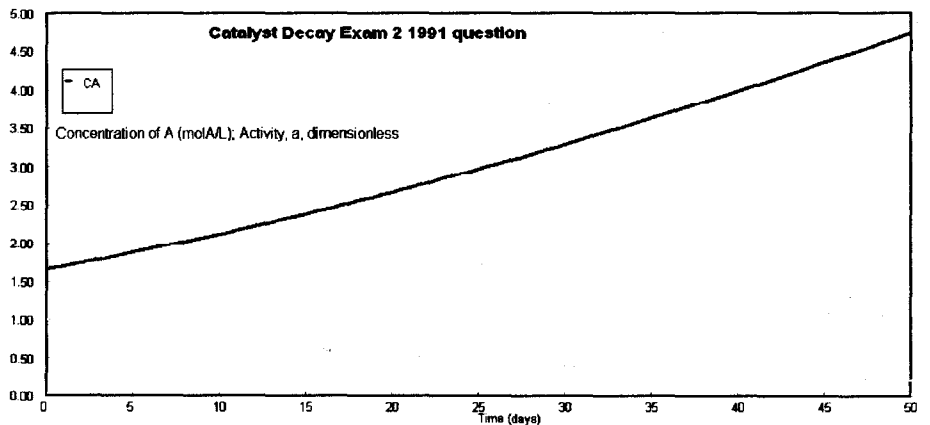
First stepsize guess. h1 = 0.0001

Minimum allowed stepsize. hmin =

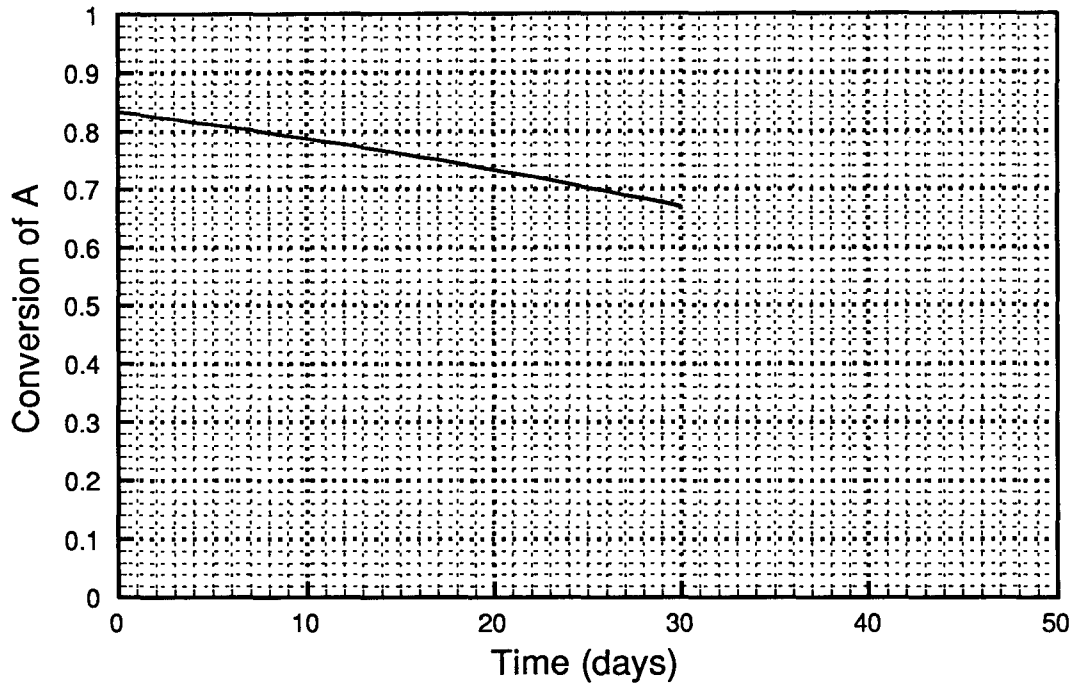
0.00000001

Good steps = 76

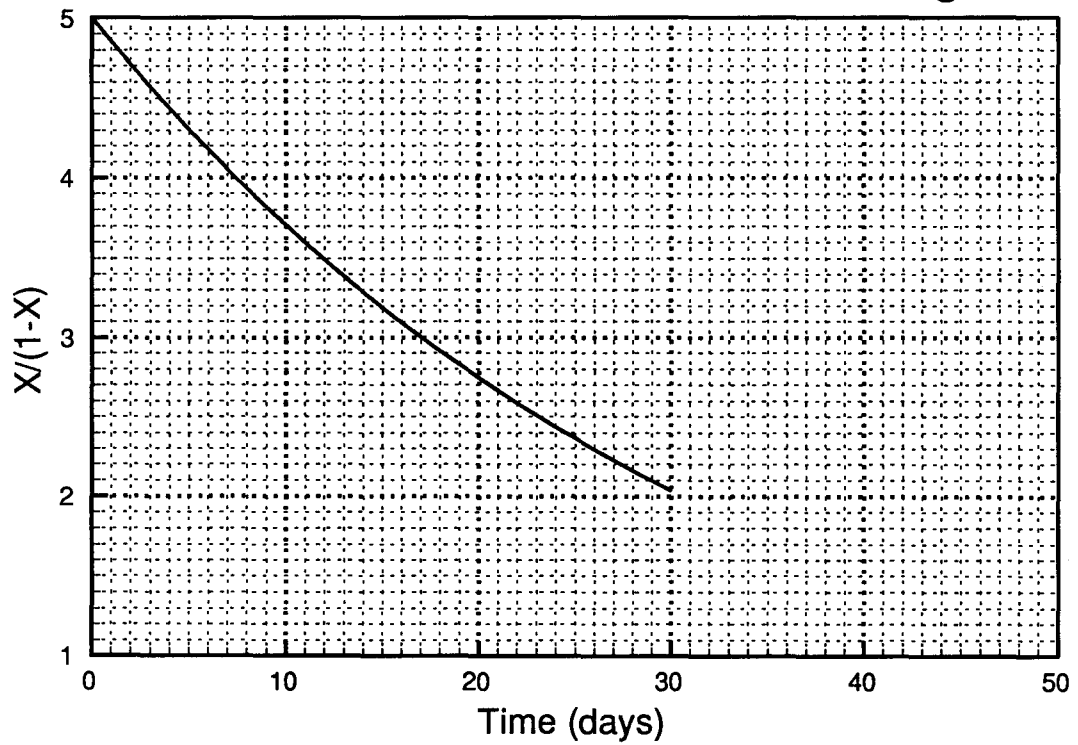
Bad steps = 1145



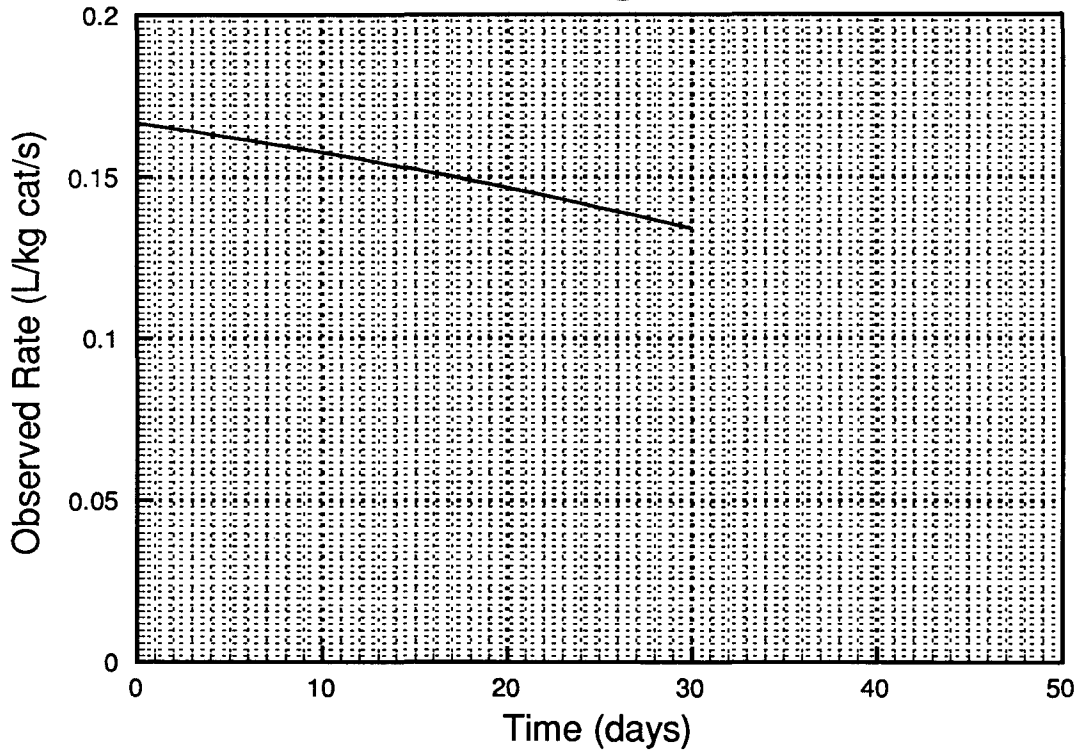
Conversion Using Actual Feed



Amount A Reacted/Amount of A Remaining

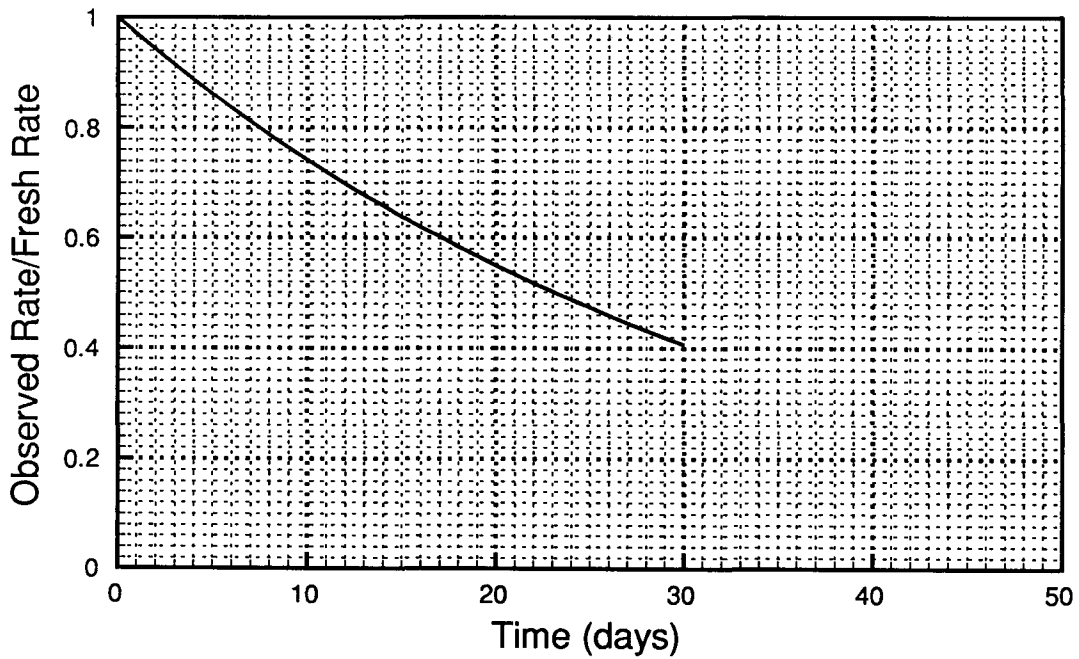


Observed Rate Using Actual Feed

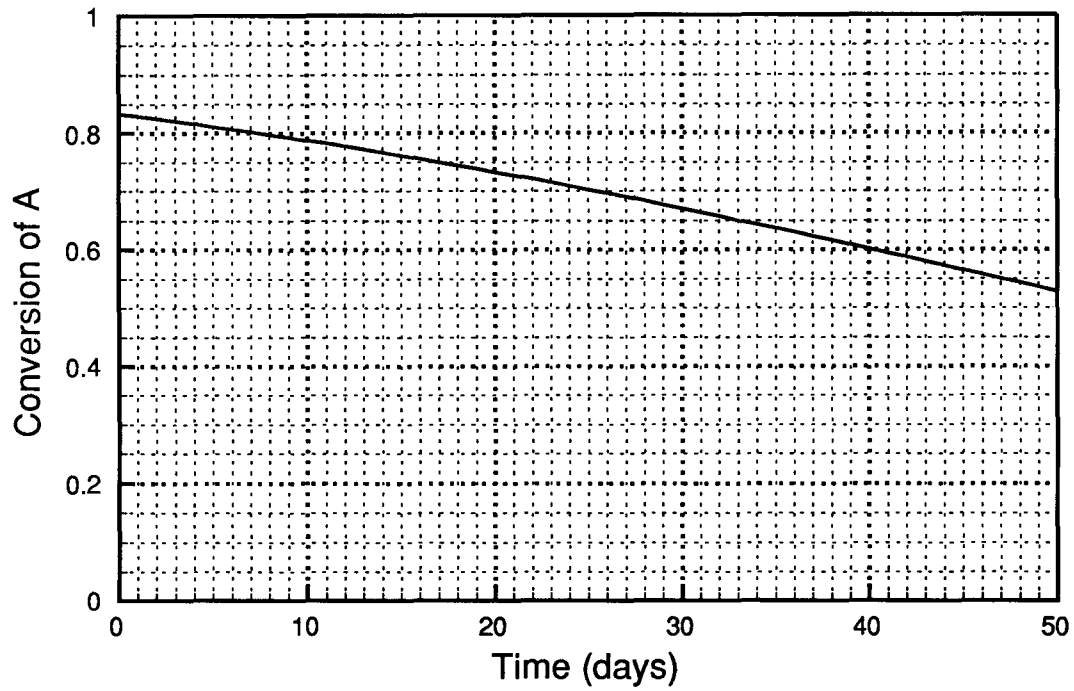


Ratio of Observed Rate to Fresh Rate

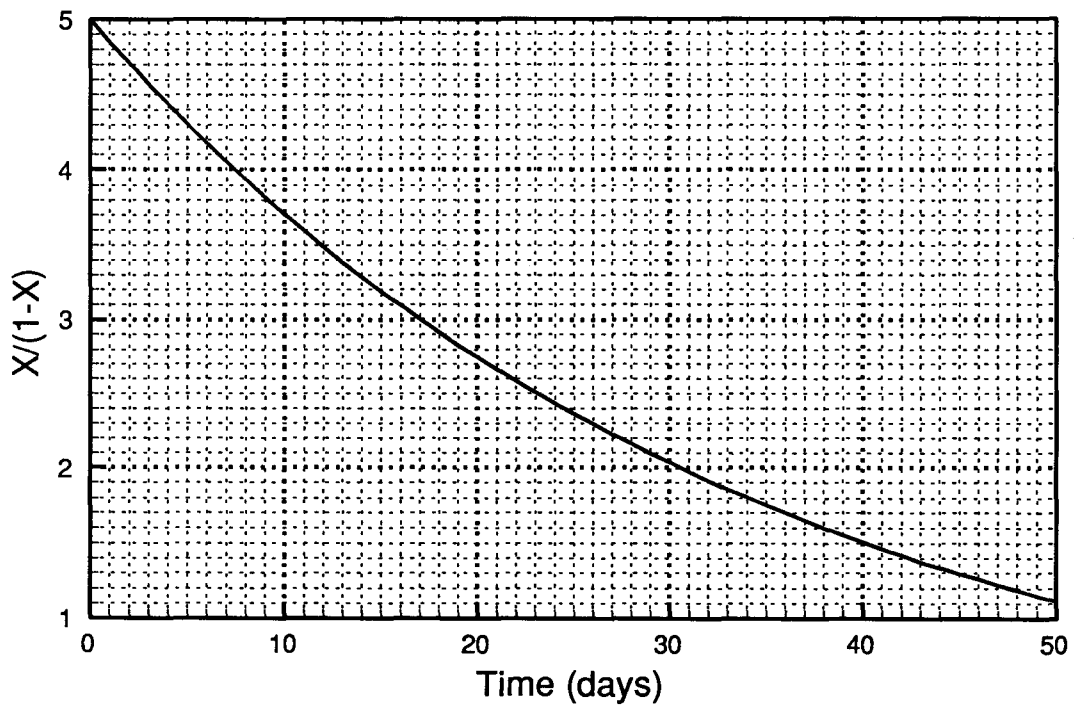
Using Actual Feed. Fresh rate calculated at equivalent concentrations of A.



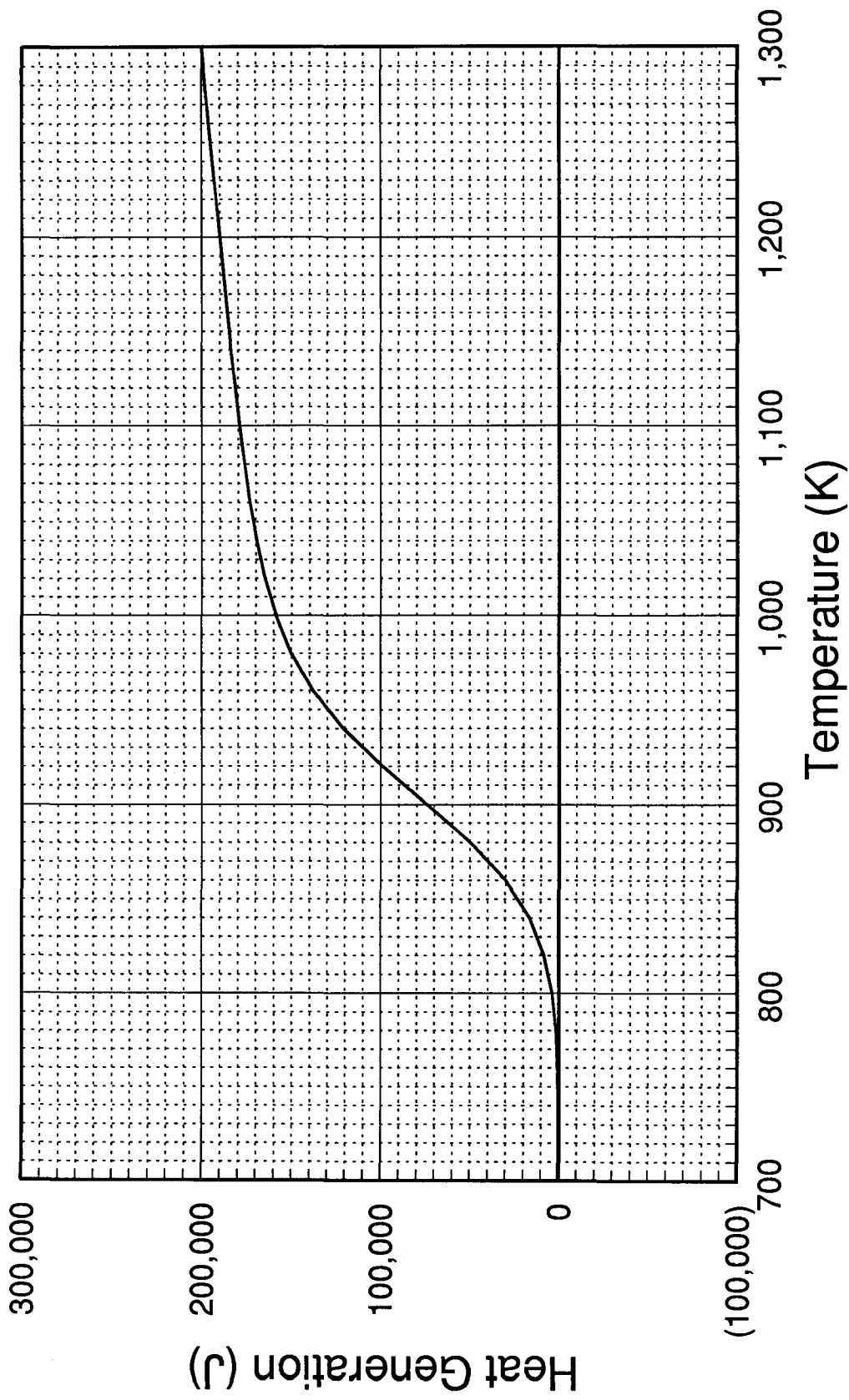
Conversion of A Solution



Amount A Reacted/Amount of A Remaining Solution



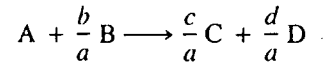
Heat Generation for Problem 3



Heat Generated _____

SUMMARY

For the reaction



(8-46)

$$\frac{dT}{dV} = \frac{U_a(T_a - T) + (-r_A)[- \Delta H_R(T)]}{F_{A0}(\sum \Theta_i C_{pi} + X \Delta C_p)}$$

2. The standard heat of reaction per mole of A at reference temperature T_R is given in terms of the heats of formation of each species:

$$\Delta H_R^\circ(T_R) = \frac{c}{a} H_C^\circ(T_R) + \frac{d}{a} H_D^\circ(T_R) - \frac{b}{a} H_B^\circ(T_R) - H_A^\circ(T_R) \quad (S8-2)$$

3. The mean heat capacity difference, $\Delta \hat{C}_p$, per mole of A is

$$\Delta \hat{C}_p = \frac{c}{a} \hat{C}_{pC} + \frac{d}{a} \hat{C}_{pD} - \frac{b}{a} \hat{C}_{pB} - \hat{C}_{pA} \quad (S8-3)$$

where \hat{C}_{pi} is the mean heat capacity of species i between temperatures T_R and T , not to be confused with \bar{C}_{pi} , which is the mean heat capacity of species i between temperatures T_0 and T .

4. When there are no phase changes, the heat of reaction at temperature T is related to the standard reference heat of reaction by

$$\Delta H_R(T) = \Delta H_R^\circ(T_R) + \Delta \hat{C}_p(T - T_R) \quad (S8-4)$$

5. Neglecting changes in potential energy, kinetic energy, and viscous dissipation, the steady-state energy balance is

$$\frac{\dot{Q}}{F_{A0}} - \frac{\dot{W}_s}{F_{A0}} - X[\Delta H_R^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] = \sum_{i=1}^n \Theta_i \bar{C}_{pi} \Delta T_i \quad (S8-5)$$

where n is the number of species entering the reactor,

$$\Theta_i = \frac{F_{i0}}{F_{A0}} \text{ and } \Delta T_i = T - T_{i0}$$

6. If all species enter at the same temperature, $T_0 = T_{i0}$, and no work is done on the system, the energy balance reduces to

$$\frac{\dot{Q}}{F_{A0}} - X[\Delta H_R^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] = \left(\sum_{i=1}^n \Theta_i \bar{C}_{pi} \right) (T - T_0) \quad (S8-6)$$

Energy balance on PFR with heat transfer

W. W. W. W. W.

ON EXAM

$$\dot{Q} - \dot{W}_s - F_{A0} \sum_{i=1}^n \int_{T_{i0}}^T \Theta_i C_{pi} dT - \left[\Delta H_R^\circ(T_R) + \int_{T_R}^T \Delta C_p dT \right] F_{A0} X = 0$$

(8-38)

These are the forms of the steady-state balance we will use

Rearranging yields the steady-state balance for the case of *constant or mean heat capacities* in the form

$$\dot{Q} - \dot{W}_s - [\Delta H_R^\circ(T_R) + \Delta \hat{C}_p(T - T_R)] F_{A0} X = F_{A0} \sum_{i=1}^n \Theta_i \bar{C}_{pi} (T - T_{i0})$$

(8-39)

8.2.8 Heat Added to the Reactor, \dot{Q}

The heat flow to the reactor, \dot{Q} , is given in many instances in terms of the overall heat-transfer coefficient, U , the heat-exchange area, A , and the difference between the ambient temperature, T_a , and the reaction temperature, T .

For a CSTR in which both fluid temperatures inside and outside the exchanger are essentially constant (e.g., condensing steam),

$$\dot{Q} = UA(T_a - T) \quad (8-34)$$

(20%) 4. You have been asked to help design a semibatch reactor process. The liquid phase reaction, $A + B \longrightarrow C$, is first order in B: $r_B = -k C_B$. The feed to the reactor has a flowrate of Q_0 and contains a concentration of B of C_{B0} . The reactor initially contains a concentration of A of C_{Ai} and has a liquid volume of V_i .

Give the differential equation describing this process as well as the initial condition. The differential equation must be in the form of:

$$\frac{dC_B}{dt} = \text{a function of constants, } C_B \text{ and } t.$$

10 points EXTRA CREDIT: integrate the above expression.

Problem 3

Mole Balance:

$$0 = F_{A0} - F_A + r_A V$$

$$= F_{A0} - F_A - k C_A V$$

for liquids with $\rho = \rho_0$

$$X = \frac{C_{A0} - C_A}{C_{A0}}$$

$$F_{A0} = \phi C_{A0}$$

$$-X C_{A0} = -k C_{A0} \frac{V}{\phi} (1-X)$$

$$L = \frac{V}{\phi}$$

Solving for X

$$X = \frac{k L}{1 + k L}$$

Rearranging heat balance: equations 8-39 and 8-34

$$UA(T_a - T) - \left[\Delta H_{rxn} + \Delta C_p (T - T_R) \right] F_{A0} X = F_{A0} C_{pA} (T - T_0)$$

$T_{ref} = 25^\circ C$ only A enters

Heat Generation

$$- \left[\Delta H_{rxn} + \Delta C_p (T - 25^\circ C) \right] F_{A0} X = F_{A0} C_{pA} (T - T_A) + UA(T - T_a)$$

$T_{ref} = 25^\circ C$

This part given in graph. Heat loss graph this part

$$\text{Heat loss} = \left(10 \frac{\text{mol}}{\text{s}} \right) \left(40 \frac{\text{J}}{\text{mol K}} \right) (T - 700\text{K}) + 2,000 \frac{\text{J}}{\text{K s}} (T - 313)$$

$$\dot{Q}_{\text{Removed}} = 2,400 T - 906,000$$

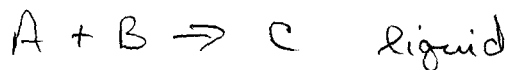
T = 919	$\dot{Q}_R = 1,299,600 \text{ J/s}$	} 10/10
T = 800	$\dot{Q}_R = 1,014,000 \text{ J/s}$	
T = 1,300	$\dot{Q}_R = 2,214,000 \text{ J/s}$	

No reaction is possible at this cooling rate!

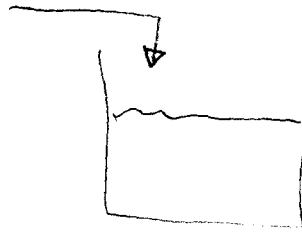
- a) $X_A = 0$ b) Nothing c) Reduce the cooling rate - $UA \ll 2000!$

Solution to #4

start 6:06



$$r_B = -k_B C_B$$



$$Q_0 = 2 \text{ L/s}$$

$$C_{B_0} = 10 \text{ mol/L}$$

$$C_{A_i} = 100 \text{ mol/L}$$

$$V_0 = 10 \text{ L}$$

mole balance on B

$$\frac{d(C_B V)}{dt} = Q_0 C_{B_0} - 0 + r_B V = Q_0 C_{B_0} - k C_B V \quad 5 \text{ pts}$$

$$V \frac{dC_B}{dt} + C_B \frac{dV}{dt} = Q_0 C_{B_0} - k C_B V$$

mass balance - assuming constant density

$$V = V_0 + Q_0 t \quad 5 \text{ pt}$$

$$\frac{dV}{dt} = Q_0$$

5 pts

Volume change
total points 10

$$V \frac{dC_B}{dt} + Q_0 C_B = Q_0 C_{B_0} - k C_B (V_0 + Q_0 t)$$

$$\frac{dC_B}{dt} + C_B \left(\frac{Q_0}{V_0 + Q_0 t} + k \right) = \frac{Q_0 C_{B_0}}{V_0 + Q_0 t} \quad \underline{\underline{5 \text{ pts}}}$$

integrating factor μ

$$\frac{L/s}{L + L/s} \cdot \frac{1}{s}$$

$$\frac{d(\mu C_B)}{dt} = \mu \frac{dC_B}{dt} + \mu C_B \left(\frac{Q_0}{V_0 + Q_0 t} + k \right) = \frac{Q_0 C_{B_0}}{V_0 + Q_0 t} \mu$$

$$\cancel{\mu} \frac{dc_B}{dt} + \cancel{\rho_B} \frac{d\mu}{dt} = \cancel{\mu} \frac{dc_B}{dt} + \mu \cancel{\rho_B} \left(\frac{\phi_0}{V_0 + \phi_0 t} + k \right)$$

$$\frac{d\mu}{\mu} = \int \left[\frac{\phi_0}{V_0 + \phi_0 t} + k \right] dt$$

$$\ln \mu = \ln [V_0 + \phi_0 t] + kt$$

$$\ln \left[\frac{\mu}{V_0 + \phi_0 t} \right] = kt$$

$$\mu = (V_0 + \phi_0 t) \exp(kt)$$

$$(V_0 + \phi_0 t) \exp(kt) c_B = \int \frac{\phi_0 c_{B_0}}{V_0 + \phi_0 t} (V_0 + \phi_0 t) \exp(kt) dt + k$$

$$(V_0 + \phi_0 t) \exp(kt) c_B = \frac{\phi_0 c_{B_0} \exp(kt)}{k} + k$$

$$c_B = \frac{c_{B_0} \phi_0}{k(V_0 + \phi_0 t)} + \frac{k}{V_0 + \phi_0 t} \exp(-kt)$$

$$t=0 \quad c_B = c_{B_i}$$

$$c_{B_i} = \frac{c_{B_0} \phi_0}{k V_0} + \frac{k}{V_0} \quad (1) \quad k = c_{B_i} V_0 - \frac{c_{B_0} \phi_0}{k}$$

$$c_B = \frac{c_{B_0} \phi_0}{k(V_0 + \phi_0 t)} + \left[\frac{c_{B_i} V_0}{V_0 + \phi_0 t} - \frac{c_{B_0} \phi_0}{k(V_0 + \phi_0 t)} \right] \exp(-kt)$$

$$c_B = \frac{c_{B_0} \phi_0}{k(V_0 + \phi_0 t)} \left[1 - \exp(-kt) \right] + \frac{c_{B_i} V_0}{V_0 + \phi_0 t} \exp(-kt)$$

SRI -

new Reactor for
exothermic reactions

Sulfonations

Nitrations

hydrogenations

Polymerizations

Also Refer to SO_2 example on page 436

Figures 8-15 & 8-16

ture within about 25°C of the exit temperature. For technical purposes the approach to equilibrium is sometimes expressed by a phrase such as "the exit temperature is within $x^\circ\text{C}$ of the equilibrium temperature." For generation of gas for ammonia synthesis, CH_4 content is typically in the range of 10 percent (dry basis) (Sec. 10.5). Reactor temperatures are some 100 to 200°C lower for naphtha conversion than for methane conversion. Even when the product will be utilized at essentially atmospheric pressure, operation at elevated reactor pressure is usually economically advantageous. High pressure reduces the reactor volume necessary, and pressure drop through the bed is less for a specified mass flow rate, thus reducing compression costs. Natural gas and refinery gases are also generally available under pressure.

For ammonia synthesis, reduction of the methane content in the product gases from the primary reformer to a very low level is desirable in order to minimize the purge of methane in the subsequent ammonia synthesis step. To do this and to introduce nitrogen, the exit gas from the primary reformer, which contains up to about 10% methane (dry basis) is mixed with air and fed to a secondary, adiabatic reformer. Here the exothermic reaction of methane and air supplies heat to raise the temperature another 150 to 200°C, i.e., to the neighborhood of 1000°C or higher. Such temperatures would be difficult to achieve with externally fired metal-alloy tubes. The amount of air introduced is adjusted to form the ultimate 1:3 $\text{N}_2\text{-H}_2$ ratio required for ammonia-synthesis gas. The primary and secondary reformer operations clearly must be closely coupled to provide the necessary overall mass and thermal balance. Typically, the secondary reactor is refractory-lined, and the catalyst is nickel supported on a form of alumina that is thermally and mechanically resistant at these very high temperatures. Sometimes a nickel supported on chromia-alumina, which has high thermal resistance, is placed in the top portion of the bed in the secondary reformer.

Product gas is then cooled, additional steam is added, and additional H_2 is produced by passing the mixture through a water-gas shift reactor (Sec. 10.3). CO_2 is then removed by absorption, as by use of an amine-promoted aqueous K_2CO_3 solution. Remaining traces of CO and CO_2 are removed by applying the methanation reaction (Sec. 10.6). For making feed gas for synthesis of CH_3OH or for the Oxo process (CO-H_2 ratios of 1:2 or 1, respectively), the shift reaction is not used. CO_2 is added or H_2 removed for the overall mass balance.

Figure 10.3 is a photograph of the reforming operations of a large ammonia-synthesis plant. The primary reformer is in the center and consists of two furnace chambers with eight rows of burners on the side walls. Gases enter through inlet hairpins apparent at the top. The

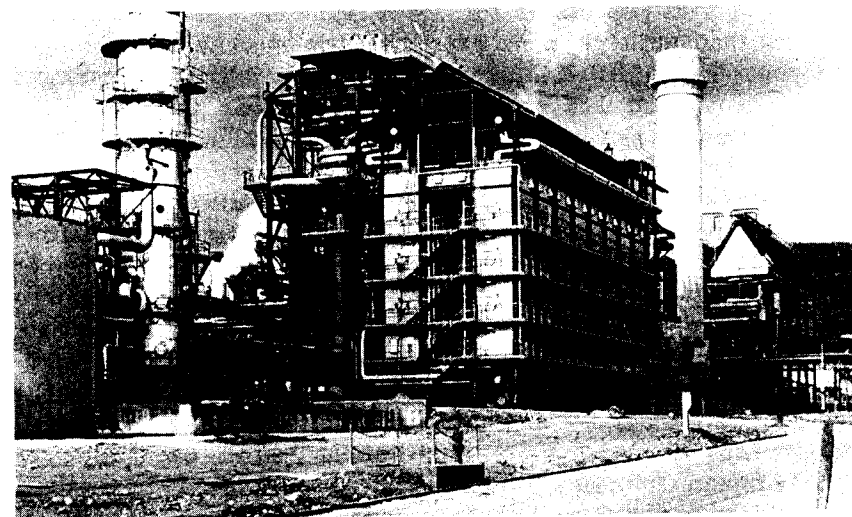


Figure 10.3 Reforming operations of a 1250 metric ton/day ammonia plant. Anic, Manfredonia. (Courtesy of J. R. Rostrup-Nielsen)

vertical cylindrical vessel to the immediate left is the waste-heat boiler to which the exit gases from the secondary reformer are passed (the secondary reformer is hidden behind the waste-heat boiler). The high- and low-temperature shift reactors are contained together in the large vertical vessel to the far left. To the immediate right of the primary reformer is the stack for reformer flue gas and to its right is the compressor house.

10.1.3 Reforming catalysts

The high temperature of the steam-reforming reaction and the presence of steam set stringent requirements on the formulation of the supported nickel catalyst. Silica, unless suitably combined, may be slowly volatilized by steam at these temperatures, leading to catalyst degradation and deposition of silica downstream, an effect which is accelerated at higher pressures. Transition aluminas such as γ and η are not stable. The support is therefore a low-area, refractory-type material. In early processes operating at pressures up to about 0.3 MPa, the most common support was a calcium aluminate silicate, which was inexpensive and gradually became stronger with use. This catalyst support was unsatisfactory at higher pressures (up to about 3 MPa) because of migration of silica at the higher steam partial pressures.

In the early 1960s this support was replaced with a low-silica calcium aluminate; it, however, had a lower crush strength, gradually lost strength on use, and lost activity by gradual formation of nickel