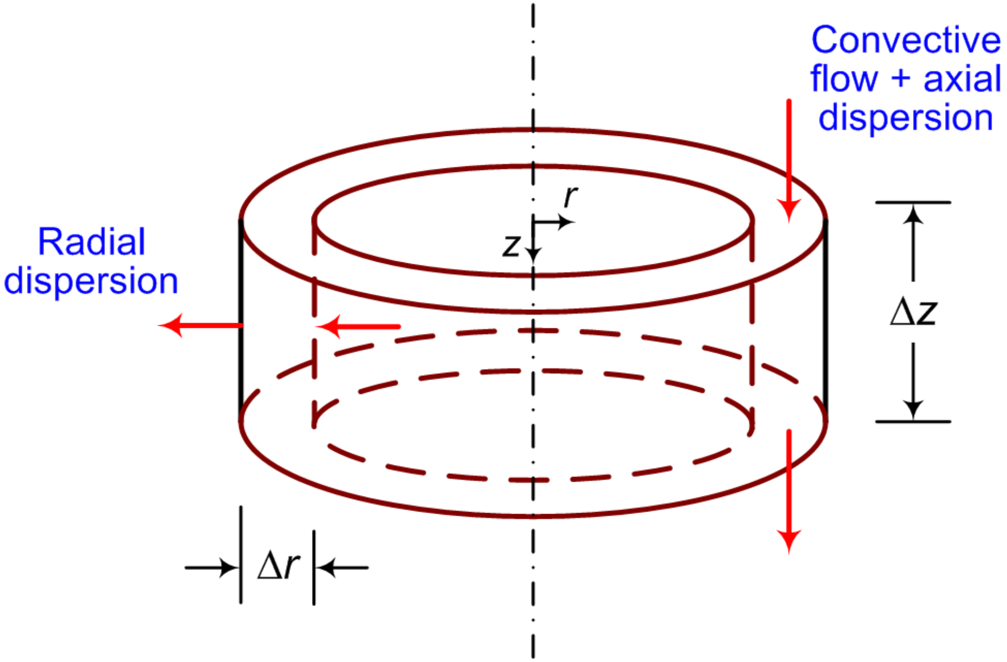
CHE 611
Advanced Chemical Reaction Engineering



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Course contents (1.5 + 1.5 credit hours)

- Homogeneous and heterogeneous reaction rate expressions
- Characterization of solid catalysts
- General characteristics of heterogeneous reactors. Simultaneous mass and heat transports with chemical reaction in porous catalysts
- Analysis and design of gas-liquid reactors: Mechanically agitated vessels, bubble columns, and packed columns
- Non-catalytic reactors
- Analysis and design of three phase reactors: Slurry reactors, trickle bed reactors, and fluidized bed reactors

Relevant books

- ✓ Froment, G.F.; Bischoff, K.B.; De Wilde, J. 2011. Chemical reactor analysis and design. 3rd ed. John Wiley & Sons, Inc.
- ✓ Fogler, H.S. 2006. Elements of chemical reaction engineering. 4th ed. Prentice-Hall.
- ✓ Levenspiel, O. 1999. Chemical reaction engineering. 3rd ed. Wiley & Sons, Inc., Singapore.
- ✓ Missen, R.W.; Mims, C.A.; Saville, B.A. 1999. Introduction to chemical reaction engineering and kinetics. John Wiley & Sons, Inc., New York.
- ✓ Carberry, J.J. Chemical and catalytic reaction engineering. Dover Publications, Inc. New York
- ✓ Smith, J.M. 1981. Chemical engineering kinetics. 3rd ed. McGraw-Hill Int. Book Co., Singapore.
- ✓ Hill, Jr., C.G.; Root, T.W. 2014. Introduction to chemical engineering kinetics and reactor design. 2nd ed. Wiley.

Course objectives (1.5 credit hours)

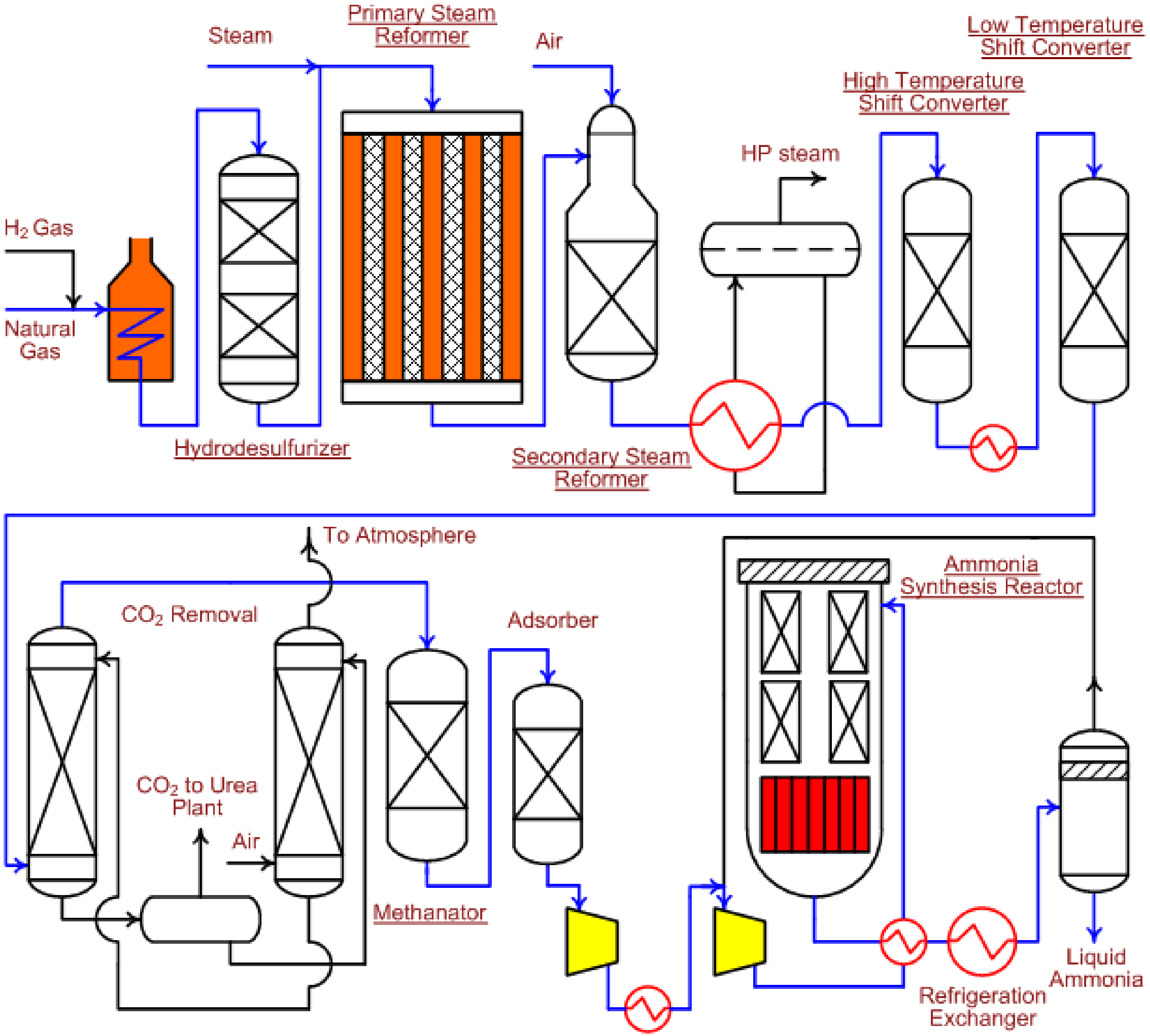
The objective of the part of my course is to develop the understanding of heterogeneous catalytic (gas-solid) reactions.

The course attendee will be encountered to the:

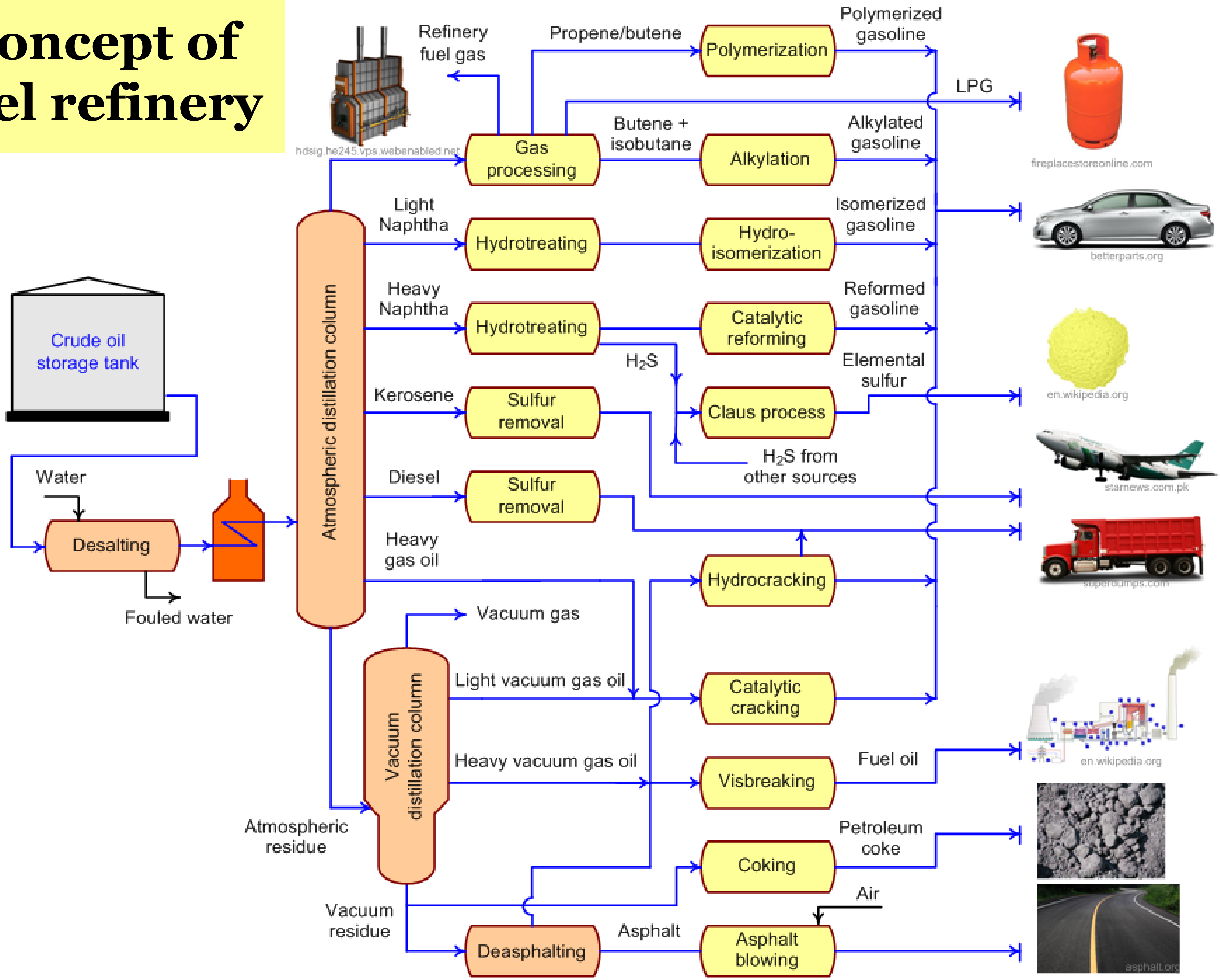
- ✓ Concepts of catalysts, catalytic kinetic rate expressions, pore diffusion, and effectiveness factor
- ✓ Use of rate expressions in the designing of a chemical reactor
- ✓ Concepts of one-dimensional and two-dimensional pseudohomogeneous models

Student will learn how can a chemical engineer develop a rate expression and design an industrial reactor

Ammonia synthesis



Concept of fuel refinery



hdsig.he245.vps.webenabled.net

fireplacestoreonline.com

betterparts.org

en.wikipedia.org

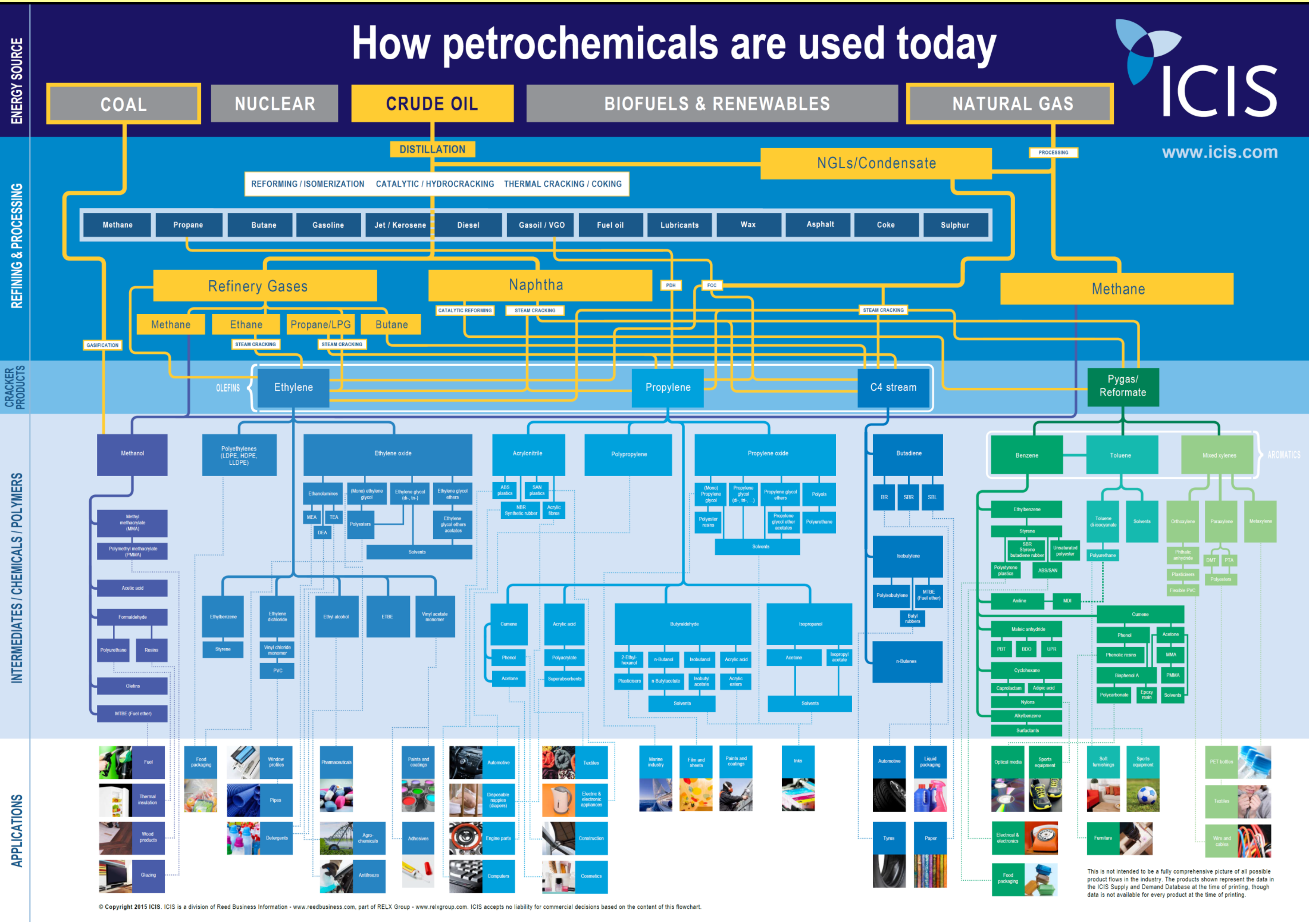
starnews.com.pk

superdumps.com

en.wikipedia.org

asphalt.org

Petrochemicals flowchart



How petrochemicals are used today

ICIS
www.icis.com

ENERGY SOURCE

COAL
NUCLEAR
CRUDE OIL
BIOFUELS & RENEWABLES
NATURAL GAS

REFINING & PROCESSING

DISTILLATION
NGLs/Condensate
PROCESSING
REFORMING / ISOMERIZATION
CATALYTIC / HYDROCRACKING
THERMAL CRACKING / COKING

Methane
Propane
Butane
Gasoline
Jet / Kerosene
Diesel
Gasoil / VGO
Fuel oil
Lubricants
Wax
Asphalt
Coke
Sulphur

Refinery Gases
Naphtha
PDH
FCC
Methane
CATALYTIC REFORMING
STEAM CRACKING
STEAM CRACKING
Methane
Ethane
Propane/LPG
Butane
GASIFICATION
STEAM CRACKING
STEAM CRACKING

CRACKER PRODUCTS

OLEFINS
Ethylene
Propylene
C4 stream
Pygas/ Reformate

INTERMEDIATES / CHEMICALS / POLYMERS

Methanol
Methyl methacrylate (MMA)
Polymethyl methacrylate (PMMA)
Acetic acid
Formaldehyde
Polyurethane
Resins
Olefins
MTBE (Fuel ether)

Polyethylenes (LDPE, HDPE, LLDPE)

Ethylene oxide
Ethanolamines
MEA
TEA
DEA
(Mono) ethylene glycol
Polyesters
Ethylene glycol (di-, tri-)
Ethylene glycol ethers
Ethylene glycol ethers acetates
Solvents

Ethylbenzene
Styrene
Ethylene dichloride
Vinyl chloride monomer
PVC
Ethyl alcohol
ETBE
Vinyl acetate monomer

Acrylonitrile
ABS plastics
SAN plastics
NBR Synthetic rubber
Acrylic fibres

Polypropylene

Propylene oxide
(Mono) Propylene glycol
Polyester resins
Propylene glycol (di-, tri-, ...)
Propylene glycol ethers
Propylene glycol ether acetates
Polyols
Polyurethane
Solvents

Cumene
Phenol
Acetone
Acrylic acid
Polyacrylate
Superabsorbents

Butyraldehyde
2-Ethyl-hexanol
Plasticisers
n-Butanol
n-Butylacetate
Isobutanol
Isobutyl acetate
Acrylic acid
Acrylic esters
Solvents

Isopropanol
Acetone
Isopropyl acetate
Solvents

Butadiene
BR
SBR
SBL
Isobutylene
Polyisobutylene
MTBE (Fuel ether)
Butyl rubbers
n-Butenes

AROMATICS
Benzene
Toluene
Mixed xylenes

Ethylbenzene
Styrene
SBR Styrene butadiene rubber
Unsaturated polyester
Polystyrene plastics
ABS/SAN
Aniline
MDI
Cumene
Phenol
Acetone
Phenolic resins
MMA
Bisphenol A
PMMA
Polycarbonate
Epoxy resin
Solvents
Maleic anhydride
PBT
BDO
UPR
Cyclohexane
Caprolactam
Adipic acid
Nylons
Alkylbenzene
Surfactants

Toluene di-isocyanate
Polyurethane
Solvents

Orthoxylene
Phthalic anhydride
Plasticisers
Flexible PVC
Paraxylene
DMT
PTA
Polyesters
Metaxylene

APPLICATIONS

Fuel
Thermal insulation
Wood products
Glazing
Food packaging
Window profiles
Pipes
Detergents
Pharmaceuticals
Agro-chemicals
Antifreeze
Paints and coatings
Adhesives
Automotive
Disposable nappies (diapers)
Engine parts
Computers
Textiles
Electric & electronic appliances
Construction
Cosmetics
Marine industry
Film and sheets
Paints and coatings
Inks
Automotive
Liquid packaging
Tyres
Paper
Optical media
Sports equipment
Electrical & electronics
Food packaging
Soft furnishings
Sports equipment
Furniture
PET bottles
Textiles
Wire and cables

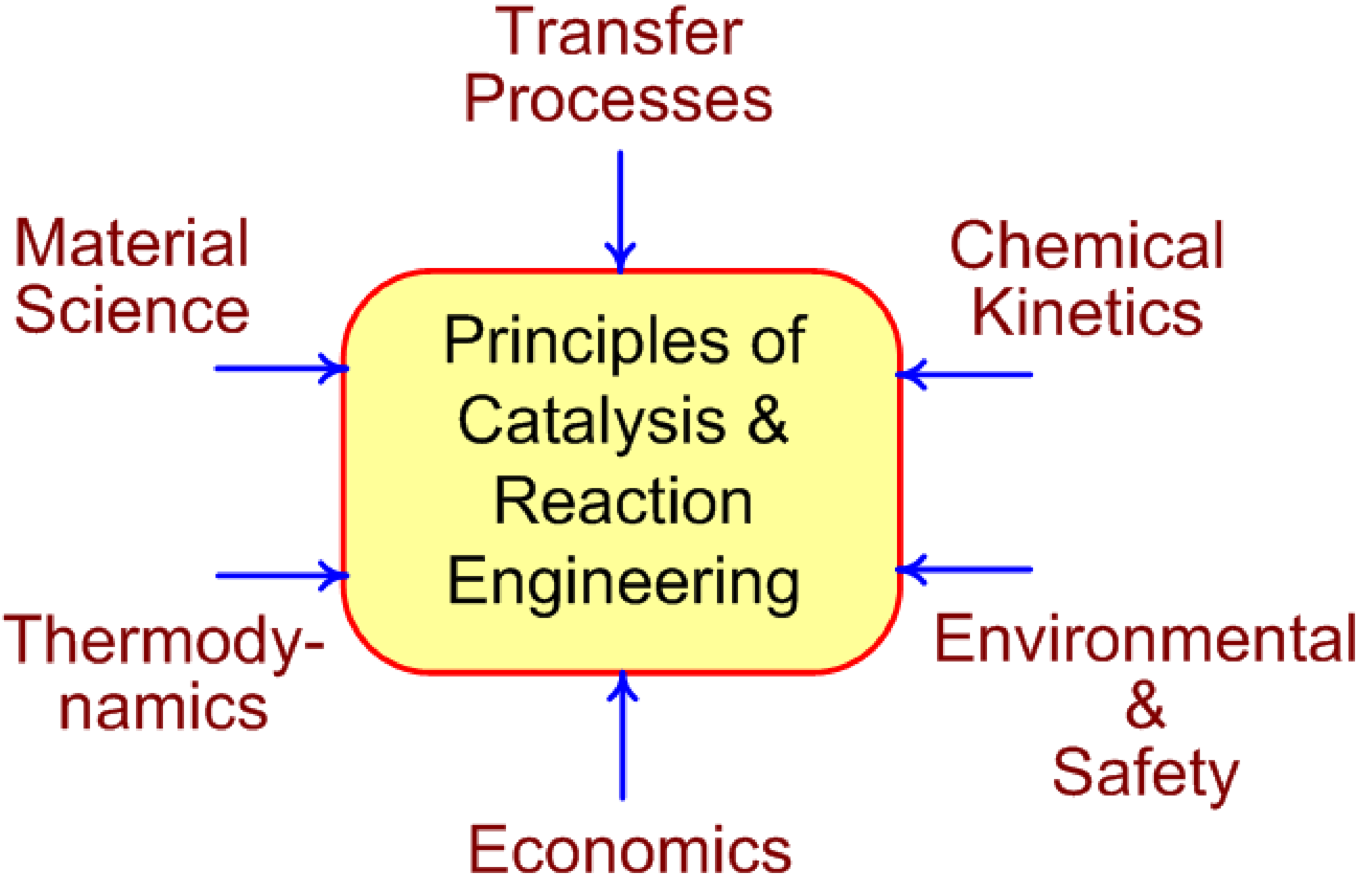
This is not intended to be a fully comprehensive picture of all possible product flows in the industry. The products shown represent the data in the ICIS Supply and Demand Database at the time of printing, though data is not available for every product at the time of printing.

Catalysis and reaction engineering

Catalysis and reaction engineering tries to answer to the following types of questions:

- ✓ What are the optimum operating conditions for a reaction system to carry out one ore more desired reactions?
- ✓ What is the optimum reactor design, i.e., size, type, energy considerations, and configuration of the reactor system?
- ✓ Is there a need of a catalyst? If yes, how to develop and design of an optimum industrial catalyst?
- ✓ What is the right reaction mechanism which will helpful for developing the basic science as well as in the design of a suitable catalyst?

Catalysis and reaction engineering



Transfer Processes

Material Science

Chemical Kinetics

Principles of Catalysis & Reaction Engineering

Thermodynamics

Environmental & Safety

Economics

Stoichiometric coefficient

For the reaction

ν

$$aA + bB \Leftrightarrow cC + dD$$

a, b, c and d are the stoichiometric coefficients.
If A_i is the ith component of a reaction, then one can write

$$0 = \sum \nu_i A_i$$

By convention:

- A stoichiometric coefficient for a reactant is *negative*
- A stoichiometric coefficient for a product is *positive*
- A stoichiometric coefficient for an inert, solvent, or catalyst is *zero*.

Extent of a reaction

$$n_i = n_{i0} + \nu_i \cdot \xi$$

$$F_i = F_{i0} + \nu_i \cdot \xi'$$

$$\boxed{\xi = \frac{n_i - n_{i0}}{\nu_i} = \frac{\textit{changein moles of a species}}{\textit{stoichiometric coefficient}}}$$

$$\xi' = \frac{F_i - F_{i0}}{\nu_i} = \frac{\textit{changein molar flowrateof a species}}{\textit{stoichiometric coefficient}}$$

ξ extent of a reaction in terms of change in moles

ξ' extent of a reaction in terms of change in molar flowrate

ν_i stoichiometric coefficient of an *i*th species

Conversion or fractional conversion

Ratio of change in moles of a reactant (usually limiting reactant) to the moles of the reactant fed.

For a reactant *A*:

$$\boxed{X_A = \frac{n_{A0} - n_A}{n_{A0}} = \frac{F_{A0} - F_A}{F_{A0}}}$$

n_{A0} = initial moles of the reactant "*A*", mol; n_A = moles of "*A*" at any time *t* (s), mol; F_{A0} = initial molar flowrate, mol·s^{-1}, F_A = molar flowrate of *A* at any time *t* (s), mol·s^{-1}.

For an irreversible and single (no side reaction) reaction, an increase in the outlet conversion is an indication of higher rate of the reaction

Relationship between extent of a reaction and fractional conversion [1]

For reactant *A*:

$$\xi = \frac{n_A - n_{A0}}{\nu_A}$$

$$\xi = \frac{n_A - n_{A0}}{\nu_A} \times \frac{n_{A0}}{n_{A0}} \qquad \Rightarrow \xi = -\left(\frac{n_{A0} - n_A}{n_{A0}} \times \frac{n_{A0}}{\nu_A} \right)$$

$$X_A = \frac{n_{A0} - n_A}{n_{A0}}$$

$$\boxed{\xi = -\left(X_A \times \frac{n_{A0}}{\nu_A} \right) = -\frac{X_A n_{A0}}{\nu_A}}$$

Selectivity

It is the ratio of moles of the one (usually desired) product to the moles of another (usually undesired) product.

$$A \rightarrow B$$

$$A \rightarrow C$$

$$\boxed{\begin{aligned} Selectivity\ of\ B &= \frac{moles\ of\ B\ formed}{moles\ of\ C\ formed} \\ Selectivity\ of\ C &= \frac{moles\ of\ C\ formed}{moles\ of\ B\ formed} \end{aligned}}$$

The definition of selectivity may vary from source to source, so be careful while taking the value from a literature source

Yield

It is the ratio of moles of a certain product to the maximum possible moles of that product which can be formed.

Or

It is the ratio of moles of a certain product to the moles consumed of the limiting reactant.

Or

It is the ratio of moles of a certain product to the moles of the limiting reactant fed.

The definition of yield may vary from source to source. The definitions of yields defined above may be referred to as the definition of selectivity in some reference.

Limiting and excess reactant

- ✓ In a chemical reaction the reactant present in excess to that required stoichiometrically is the excess reactant the other is limiting reactant
- ✓ If the reactants are added in stoichiometric amounts, there is no point using the concept of limiting or excess reactant
- ✓ The limiting or excess reactant is indicated by dividing the number of moles of each reactant in the feed to the corresponding stoichiometric amount (from a balanced chemical equation) of the reactant. The reactant with the lowest ratio is the limiting reactant and will be the first to be fully consumed in the reaction, if the reaction goes to completion

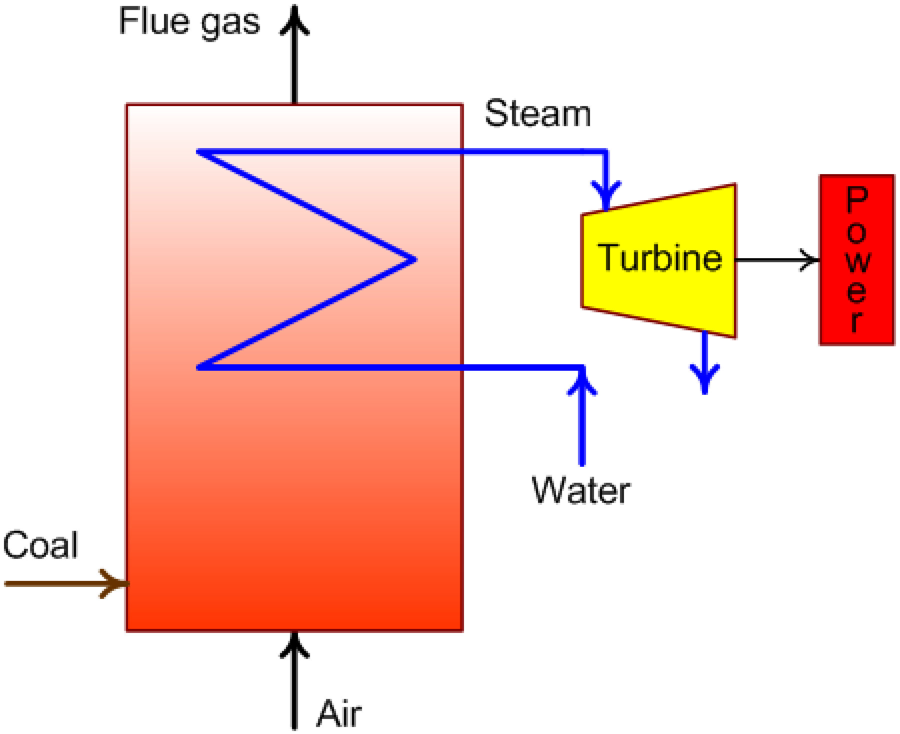
The choice of the limiting reactant is arbitrary and depends on the cost (profit) considerations

Limiting and excess reactant

Can you mention any example of an industrial process and indicate the limiting reactant?

What are the reasons for the choice of a particular limiting reactant in your example?

Combustion of a coal required excess air



Rate of a chemical reaction [2]

The rate of consumption of a reactant species is defined as the change in number of moles of the reactant species per unit volume of the reaction mixture per unit time.

Negative sign indicates that rate is decreasing with time and required as dn_A is negative for a reactant

$$\boxed{(-r_A) = -\frac{1}{V}\cdot\frac{dn_A}{dt}}$$

Perfectly general

Volume of reaction mixture

$$\boxed{(-r_A) = -\frac{dC_A}{dt}}$$

- ✓ Not general
- ✓ Applicable when volume of the reaction mixture does not change during the course of reaction
- ✓ It may be true for liquid phase reactions or for constant density gas phase reactions

The volume of a gas also changes due to changes in operating conditions (temperature and pressure) in addition to changes in number of moles

Rate of a chemical reaction

- ✓ The rate of a chemical reaction is usually based on the limiting reactant
- ✓ On the similar basis, a rate may be defined for the formation of a product species
- ✓ For the reaction:

$$aA + bB \rightarrow cC + dD$$

or

$$\boxed{\frac{(-r_A)}{a} = \frac{(-r_B)}{b} = \frac{r_C}{c} = \frac{r_D}{d}}$$

✓This minus sign is to show rate of consumption of a reactant
✓It has no mathematical importance, only a symbol

Various definitions of rate of a chemical reaction [3]

Based on unit volume of the reaction mixture

$$r_i = \frac{1}{V}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of fluid})\,(\text{time})}$$

Based on unit mass in fluid-solid system

$$r_i' = \frac{1}{W}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{mass of solid})\,(\text{time})}$$

Based on unit surface of solid in fluid-solid system or unit interfacial area in two fluid systems

$$r_i'' = \frac{1}{S}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{surface})\,(\text{time})}$$

Based on unit volume of solid in fluid-solid system

$$r_i''' = \frac{1}{V_s}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of solid})\,(\text{time})}$$

Based on unit volume of reactor when different from unit volume of the reaction mixture

$$r_i'''' = \frac{1}{V_r}\frac{dN_i}{dt} = \frac{\text{moles } i \text{ formed}}{(\text{volume of reactor})\,(\text{time})}$$

Various definitions of rate of a chemical reaction [3]

Rates defined on various basis are interchangeable and the following may be shown:

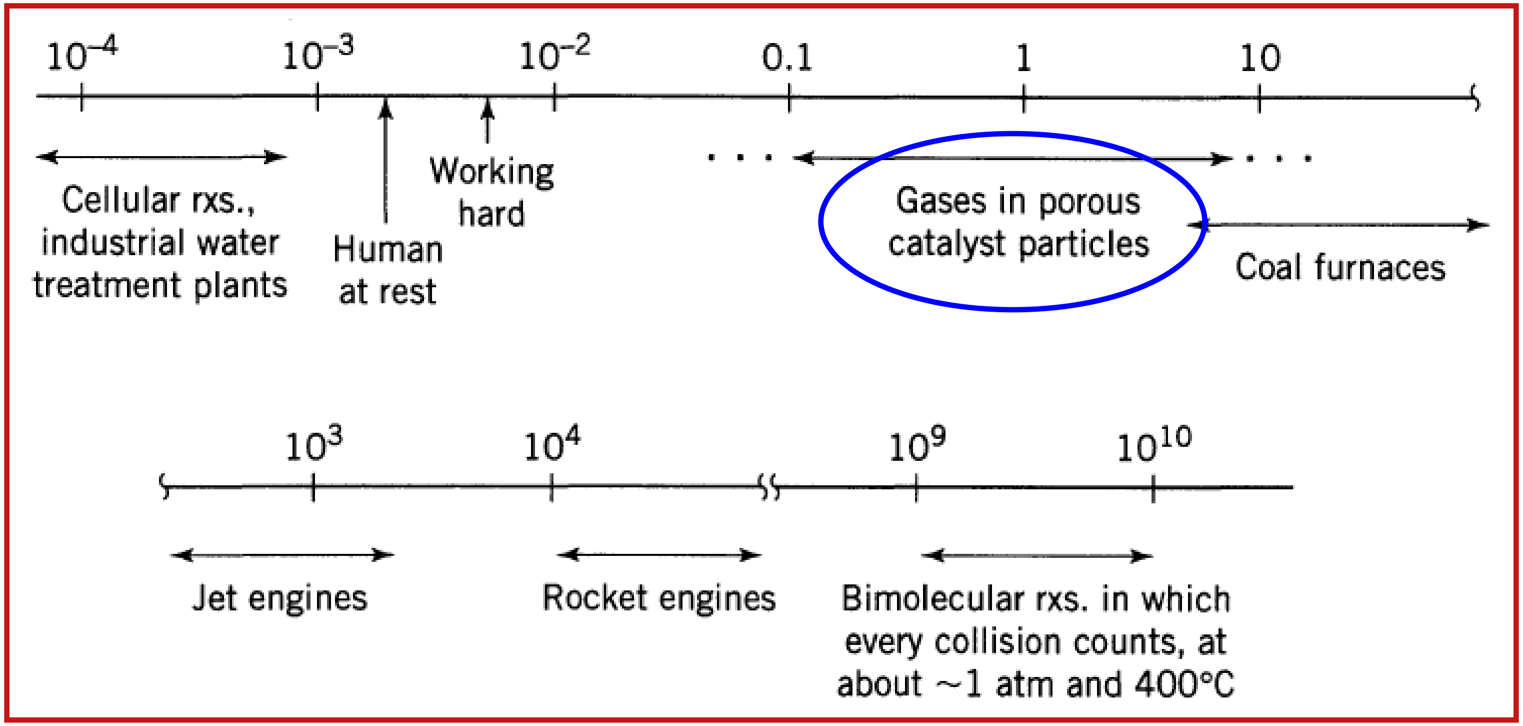
$$\begin{pmatrix}\text{volume}\\ \text{of fluid}\end{pmatrix} r_i = \begin{pmatrix}\text{mass of}\\ \text{solid}\end{pmatrix} r_i' = \begin{pmatrix}\text{surface}\\ \text{of solid}\end{pmatrix} r_i'' = \begin{pmatrix}\text{volume}\\ \text{of solid}\end{pmatrix} r_i''' = \begin{pmatrix}\text{volume}\\ \text{of reactor}\end{pmatrix} r_i''''$$

$$V r_i = W r_i' = S r_i'' = V_s r_i''' = V_r r_i''''$$

In our course we will use ($-r_A$) as the rate of consumption of a limiting reactant A having the SI unit of mol $A \cdot \text{s}^{-1} \cdot \text{g-kcat}^{-1}$

Relative values of rates of reactions [3]

Rates of reactions vary in a wide range. Some reaction are very fast and some reactions are extremely slow.



Why are we interested in rate?

- ✓A higher rate of reaction means less processing time in a batch reactor and smaller size of reactor vessel in a continuous flow reactor (CSTR and plug flow reactor)
- ✓As the residence time is dependent upon the rate, the knowledge of rate is required for the design of a reactor (remember basic design equations for batch and flow reactors)

The question is then how can we find rate?

We need an expression (rate equation) that describes the rate of a given reaction

Rate equation cannot be found reliably from the reaction stoichiometry or by any other theoretical means and therefore rate expressions are always to be empirical, i.e., to be discovered through experiments.

Types of reactions

Chemical reactions are either

- ✓Homogeneous (single phase) or
- ✓Heterogeneous (more than one phase is involved)

- ✓Catalytic or
- ✓Non-catalytic (or autocatalytic)

In a heterogeneous catalytic reaction, the catalyst should be present in a separate (distinct) phase. For a reaction when a component from the gas phase is absorbed in the liquid body and reacts in the presence of a catalyst that is mixed (dissolved) in the liquid, the term heterogeneous catalysis is not justified. This is a heterogeneous system with homogenous catalysis.

Nearly 90% of all industrial reactions involve heterogeneous catalysis, i.e., they are heterogeneous as well as catalytic

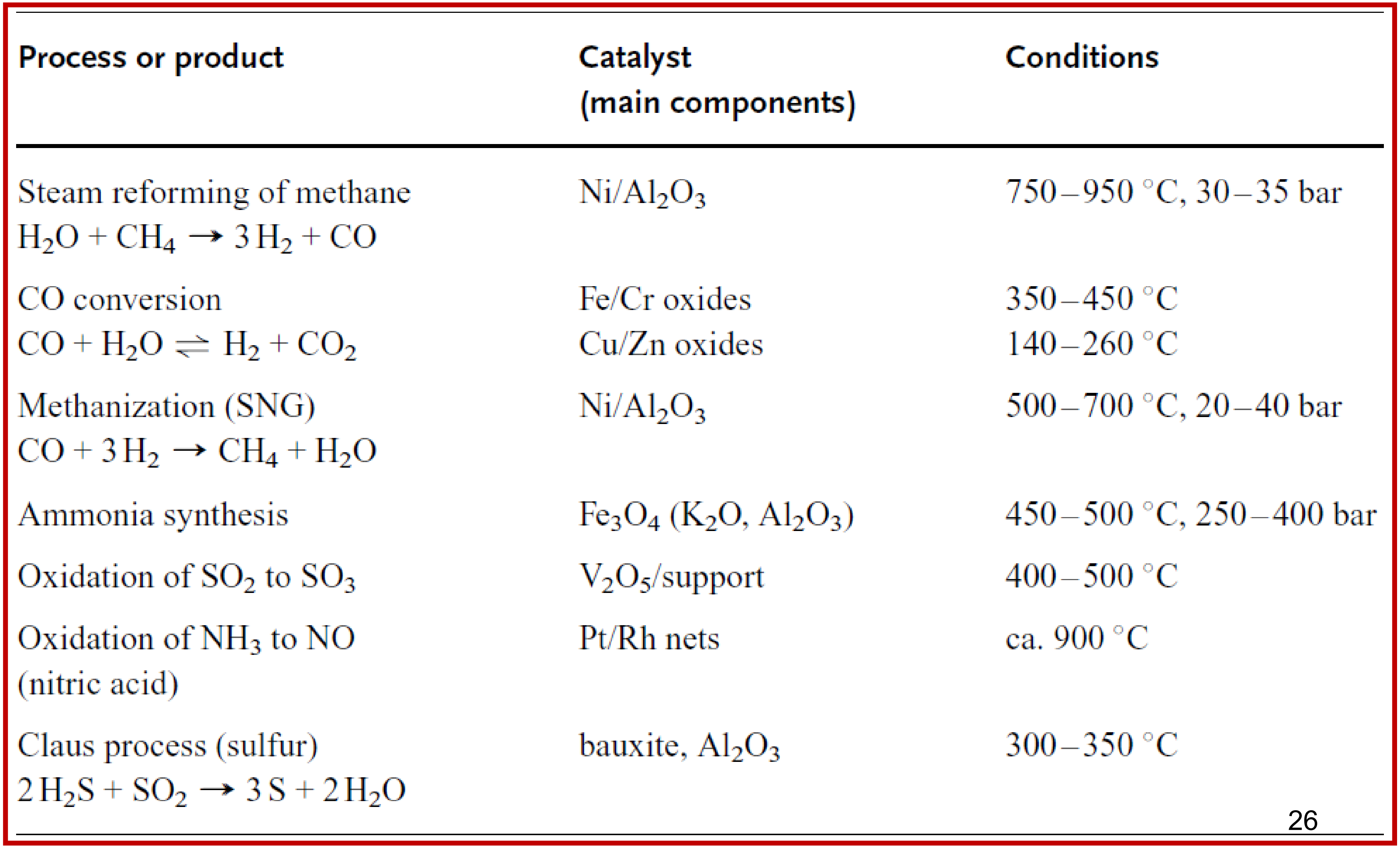
Types of reactions

Hydrogenation of vegetable oils in the presence of Ni (Raney nickel) catalyst is an example of heterogeneous catalysis and that the solid reactant is a distinct phase from the reacting components (liquid phase). Gas phase dehydrogenation of ethyl benzene is another example of heterogeneous catalysis.

Recall others! There are many.

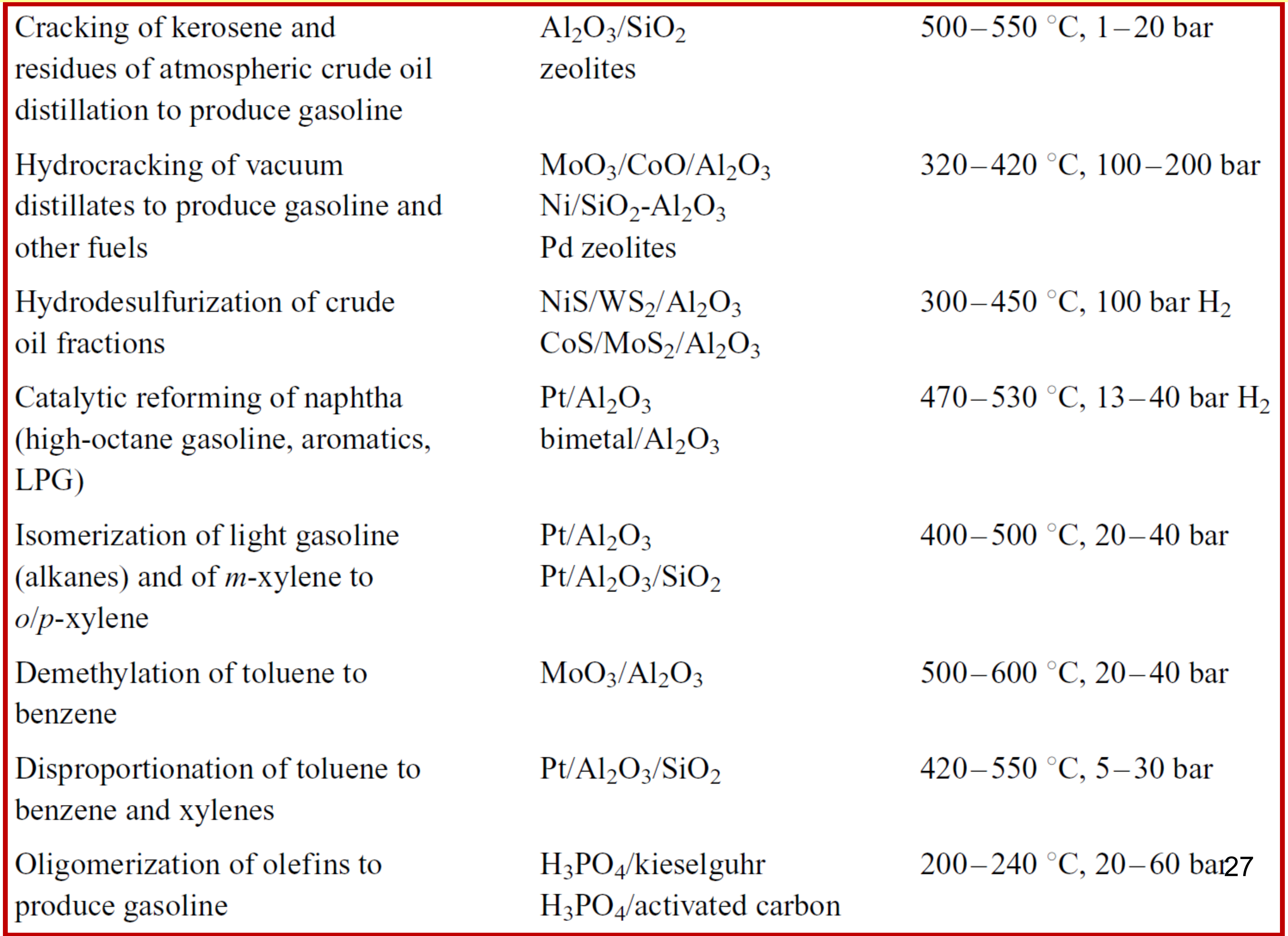
We will go through the reaction engineering principles and develop rate expressions based on gas-solid reactions mostly in a tubular reactor of fixed bed of catalysts. The principles would remain the same and may be employed for the other types of reactor systems.

Industrial examples of heterogeneous catalysis [5]



Process or product	Catalyst (main components)	Conditions
Steam reforming of methane $H_2O + CH_4 \rightarrow 3\,H_2 + CO$	Ni/Al_2O_3	750–950 °C, 30–35 bar
CO conversion $CO + H_2O \rightleftharpoons H_2 + CO_2$	Fe/Cr oxides Cu/Zn oxides	350–450 °C 140–260 °C
Methanization (SNG) $CO + 3\,H_2 \rightarrow CH_4 + H_2O$	Ni/Al_2O_3	500–700 °C, 20–40 bar
Ammonia synthesis	Fe_3O_4 (K_2O, Al_2O_3)	450–500 °C, 250–400 bar
Oxidation of SO_2 to SO_3	V_2O_5/support	400–500 °C
Oxidation of NH_3 to NO (nitric acid)	Pt/Rh nets	ca. 900 °C
Claus process (sulfur) $2\,H_2S + SO_2 \rightarrow 3\,S + 2\,H_2O$	bauxite, Al_2O_3	300–350 °C

Heterogeneous catalysis in refinery processing [5]



Cracking of kerosene and residues of atmospheric crude oil distillation to produce gasoline	Al_2O_3/SiO_2 zeolites	500–550 °C, 1–20 bar
Hydrocracking of vacuum distillates to produce gasoline and other fuels	$MoO_3/CoO/Al_2O_3$ Ni/SiO_2-Al_2O_3 Pd zeolites	320–420 °C, 100–200 bar
Hydrodesulfurization of crude oil fractions	$NiS/WS_2/Al_2O_3$ $CoS/MoS_2/Al_2O_3$	300–450 °C, 100 bar H_2
Catalytic reforming of naphtha (high-octane gasoline, aromatics, LPG)	Pt/Al_2O_3 bimetal/Al_2O_3	470–530 °C, 13–40 bar H_2
Isomerization of light gasoline (alkanes) and of *m*-xylene to *o*/*p*-xylene	Pt/Al_2O_3 $Pt/Al_2O_3/SiO_2$	400–500 °C, 20–40 bar
Demethylation of toluene to benzene	MoO_3/Al_2O_3	500–600 °C, 20–40 bar
Disproportionation of toluene to benzene and xylenes	$Pt/Al_2O_3/SiO_2$	420–550 °C, 5–30 bar
Oligomerization of olefins to produce gasoline	H_3PO_4/kieselguhr H_3PO_4/activated carbon	200–240 °C, 20–60 bar

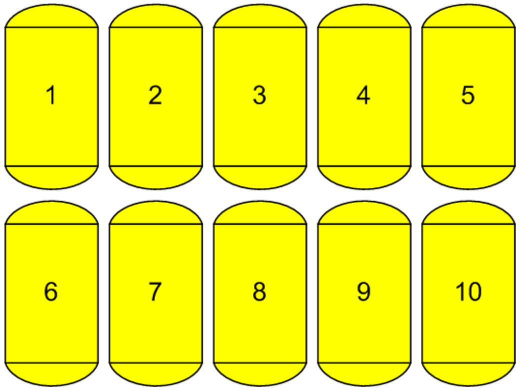
Space time and space velocity

Space time (τ): It is the time needed to process one reactor volume of feed measured at specified conditions

Space velocity (s): It is the number of reactor volumes of feed at specified conditions treated in unit time. A space velocity of 10 h^{-1} means that ten reactor volumes of the feed at specified conditions are processed in a reactor per hour.

$$\boxed{space\,time = \frac{1}{space\,veloicty}}$$

$$\tau = \frac{1}{s} = \frac{V}{v_0} = \frac{volume\,of\ reactor}{feed\,volumetric\,flowrate}$$



10 feed reactor volumes

Gas hourly space velocity (*GHSV*)

In chemical reaction engineering, space velocity is sometimes reported in terms of gas hourly space velocity, which is the ratio of volume per time in hours of the gaseous feed to the volume of the reactor.

$$\boxed{GHSV = \frac{volumetric\ flowrate\ of\ the\ gaseous\ feed\ in\ cubic\ meter\ per\ hour}{volume\ of\ reactor\ in\ cubic\ meter}}$$

It has unit of h^{-1}. It is usually reported for volumes measured at temperature of 25°C and pressure of 1.013 bar.

Weight hourly space velocity (*WHSV*)

The term is frequently used in heterogeneous reactor technology and it is defined as the ratio of mass of the feed per hour to the mass of the catalyst. Its unit is h^{-1}.

$$\boxed{WHSV = \frac{mass\ of\ the\ feed\ per\ hour}{mass\ of\ the\ catalyst}}$$

In the dehydrogenation of n-butane to 1-butene in an experimental gas phase fixed bed reactor, the catalyst weight in the reactor is 2.0 g, while the volumetric flowrate of the pure n-butane is 0.5 mL/min. The inlet conditions are 1.013 bar and 25 °C. Find out the *WHSV* for the given conditions.

Liquid hourly space velocity (*LHSV*)

It is defined as the ratio of the volume of the liquid feed per hour to the volume of the reactor or catalyst required. The volume of the liquid feed is usually taken at 60°F. 60°F is not worth mentioning as volume (density) of a liquid does not appreciably change with small changes in temperature. Again the unit is h^{-1}.

$$LHSV = \frac{Volume\, of\; the\, liquid\; feed\; per\; hour}{volume\, of\; the\, catalyst}$$

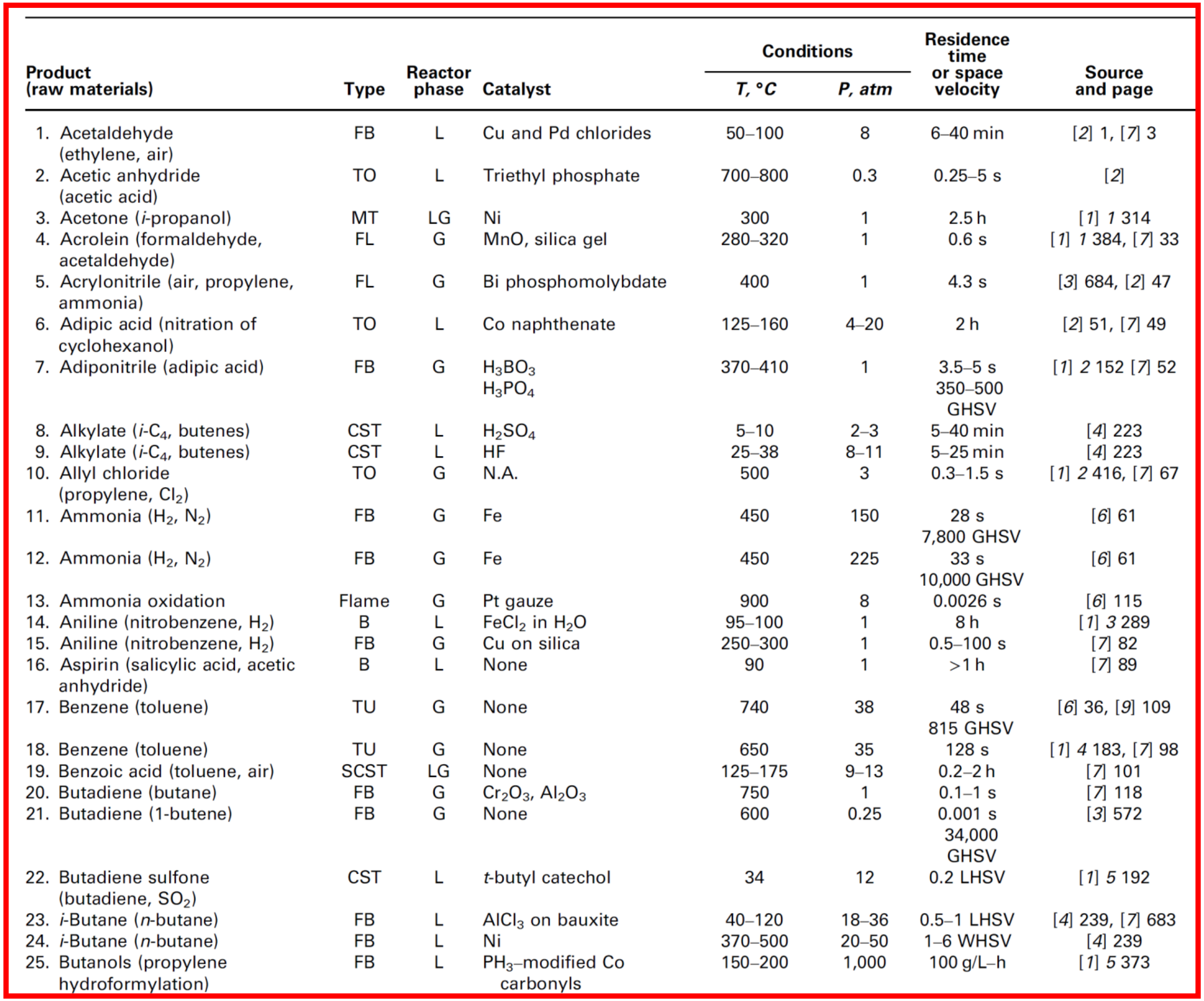
Space time and space velocity data

Residence times and space velocities of various industrial reactors are given in Chapter 17, p. 592 of Couper et al. [4] and in Section 19, p. 19-5 of Perry's Chemical Engineers' Handbook. 2008. 8th ed. McGraw-Hill.

These values are only guidelines and may not used in the actual reactor design calculations.

A part of the data from Couper et al. [4] is given in the next slide.

Space time and space velocity data [4]



Product (raw materials)	Type	Reactor phase	Catalyst	Conditions		Residence time or space velocity	Source and page
				T, °C	P, atm		
1. Acetaldehyde (ethylene, air)	FB	L	Cu and Pd chlorides	50–100	8	6–40 min	[2] 1, [7] 3
2. Acetic anhydride (acetic acid)	TO	L	Triethyl phosphate	700–800	0.3	0.25–5 s	[2]
3. Acetone (*i*-propanol)	MT	LG	Ni	300	1	2.5 h	[1] *1* 314
4. Acrolein (formaldehyde, acetaldehyde)	FL	G	MnO, silica gel	280–320	1	0.6 s	[1] *1* 384, [7] 33
5. Acrylonitrile (air, propylene, ammonia)	FL	G	Bi phosphomolybdate	400	1	4.3 s	[3] 684, [2] 47
6. Adipic acid (nitration of cyclohexanol)	TO	L	Co naphthenate	125–160	4–20	2 h	[2] 51, [7] 49
7. Adiponitrile (adipic acid)	FB	G	H_3BO_3 H_3PO_4	370–410	1	3.5–5 s 350–500 GHSV	[1] *2* 152 [7] 52
8. Alkylate (*i*-C_4, butenes)	CST	L	H_2SO_4	5–10	2–3	5–40 min	[4] 223
9. Alkylate (*i*-C_4, butenes)	CST	L	HF	25–38	8–11	5–25 min	[4] 223
10. Allyl chloride (propylene, Cl_2)	TO	G	N.A.	500	3	0.3–1.5 s	[1] *2* 416, [7] 67
11. Ammonia (H_2, N_2)	FB	G	Fe	450	150	28 s 7,800 GHSV	[6] 61
12. Ammonia (H_2, N_2)	FB	G	Fe	450	225	33 s 10,000 GHSV	[6] 61
13. Ammonia oxidation	Flame	G	Pt gauze	900	8	0.0026 s	[6] 115
14. Aniline (nitrobenzene, H_2)	B	L	$FeCl_2$ in H_2O	95–100	1	8 h	[1] *3* 289
15. Aniline (nitrobenzene, H_2)	FB	G	Cu on silica	250–300	1	0.5–100 s	[7] 82
16. Aspirin (salicylic acid, acetic anhydride)	B	L	None	90	1	>1 h	[7] 89
17. Benzene (toluene)	TU	G	None	740	38	48 s 815 GHSV	[6] 36, [9] 109
18. Benzene (toluene)	TU	G	None	650	35	128 s	[1] *4* 183, [7] 98
19. Benzoic acid (toluene, air)	SCST	LG	None	125–175	9–13	0.2–2 h	[7] 101
20. Butadiene (butane)	FB	G	Cr_2O_3, Al_2O_3	750	1	0.1–1 s	[7] 118
21. Butadiene (1-butene)	FB	G	None	600	0.25	0.001 s 34,000 GHSV	[3] 572
22. Butadiene sulfone (butadiene, SO_2)	CST	L	*t*-butyl catechol	34	12	0.2 LHSV	[1] *5* 192
23. *i*-Butane (*n*-butane)	FB	L	$AlCl_3$ on bauxite	40–120	18–36	0.5–1 LHSV	[4] 239, [7] 683
24. *i*-Butane (*n*-butane)	FB	L	Ni	370–500	20–50	1–6 WHSV	[4] 239
25. Butanols (propylene hydroformylation)	FB	L	PH_3–modified Co carbonyls	150–200	1,000	100 g/L–h	[1] *5* 373

Possibility of a reaction

For a thermodynamically possible reaction means that a catalyst works only for those reactions for which Gibbs free energy of reaction ΔG_{rxn} is less than zero, i.e., the reactants have higher free energy than the products.

A useful criterion (although not exact) for knowing the possibility of reaction occurrence is to know the standard state Gibbs free energy of reaction, $\Delta G_{rxn}{}^{o}$. A reaction, however, may not be feasible at the standard conditions but may occur at the other conditions.

What is the reason for using $\Delta G_{rxn}{}^{o}$ and not ΔG_{rxn}?

Possibility of a reaction [6]

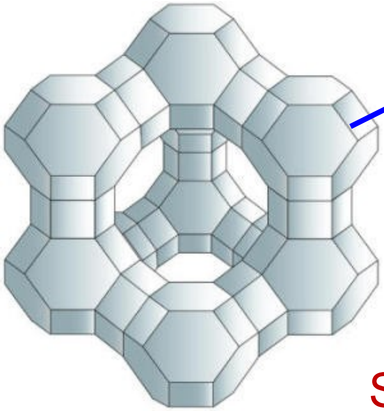
Value of ΔG_{rxn}^{o}	**Possibility of reaction occurrence**
< –10 kcal/mol (–41.8 kJ/mol)	Reaction is possible with very high equilibrium conversions
0 to –10 kcal/mol (–41.8 kJ/mol)	Reaction is possible with moderately high equilibrium conversions
0 to 10 kcal/mol (41.8 kJ/mol)	Reaction is possible at the other process operating conditions but usually with low equilibrium conversions
> 10 kcal/mol (41.8 kJ/mol)	Reaction may be possible at the other process operating conditions and if possible occurs with generally very low equilibrium conversions

Catalyst

- ✓ A catalyst is a substance that modifies (accelerates or decelerates) the rate of a chemical reaction without itself being used up. However, the term catalyst is usually employed when the objective is to increase the rate of the desired reaction.
- ✓ The term inhibitor is used when the rate of the desired reaction is required to decrease.
- ✓ A catalyst can only alter the rate of a chemical reaction and cannot affect the thermodynamics associated with the reaction. It is, therefore, cannot affect equilibrium compositions and energy changes per mole of the reaction.
- ✓ For a thermodynamically possible reaction, a catalyst modifies the path of the reaction and lowers the activation energy. This results in increasing the rate of the corresponding reaction.

Examples of catalysts

Sulfuric acid, hydrofluoric acid, vanadium pentaoxide, metal over alumina, and zeolites with and without loading of metals are common examples of catalysts.



explainthatstuff.com

Structure of zeolite Y

mecsglobal.com

ssplprints.com

SO$_2$ conversion catalysts

Zeolite ZSM-5

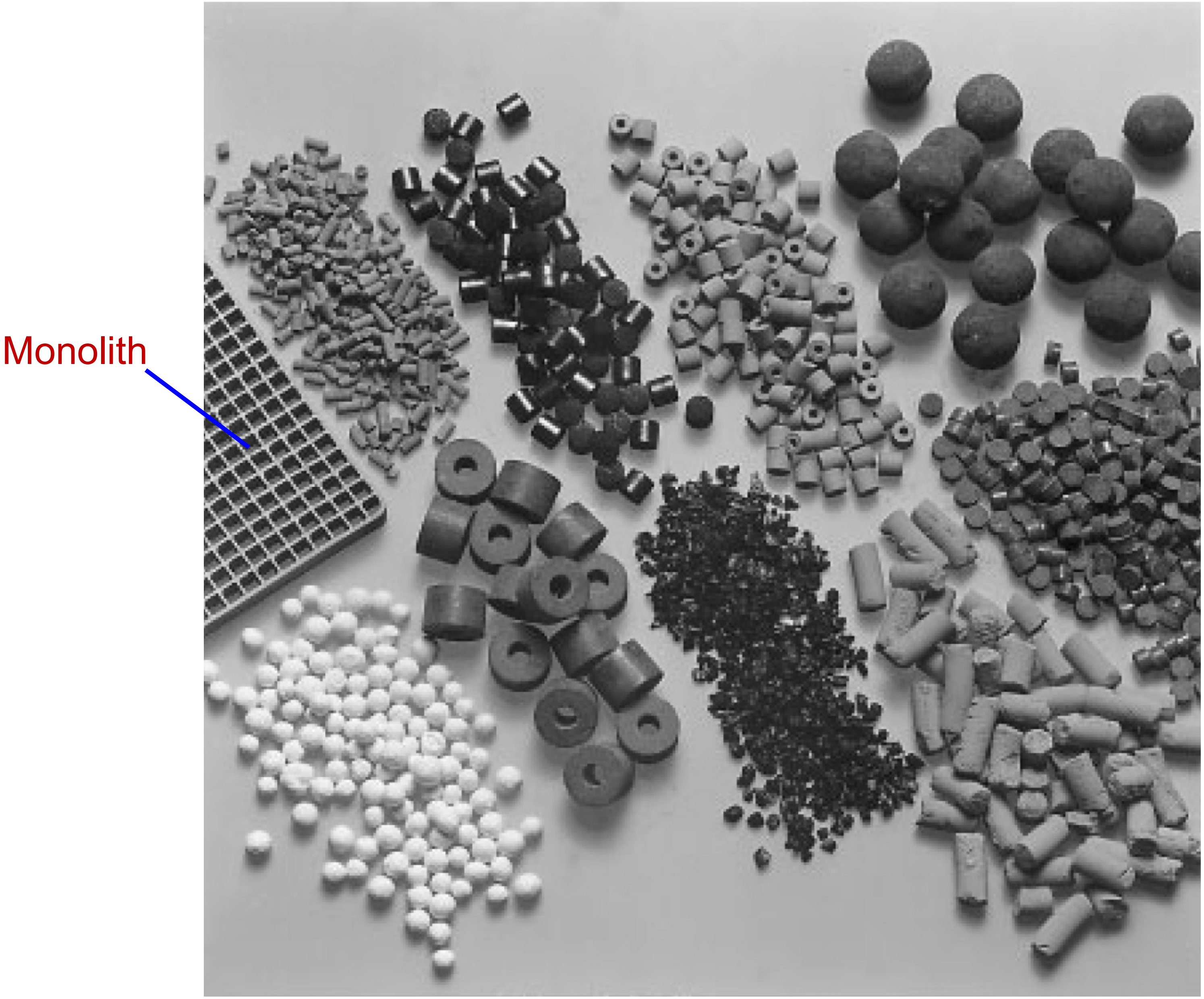
acsmaterial.com

mecsglobal.com

diytrade.com

Hydrotreating catalyst

Variety of commercial catalysts [5]



Variety of commercial catalysts

http://www.sud-chemie-india.com/prod.htm

Ammonia synthesis

✓The reaction of ammonia synthesis from N_2 and H_2 is favorable thermodynamically

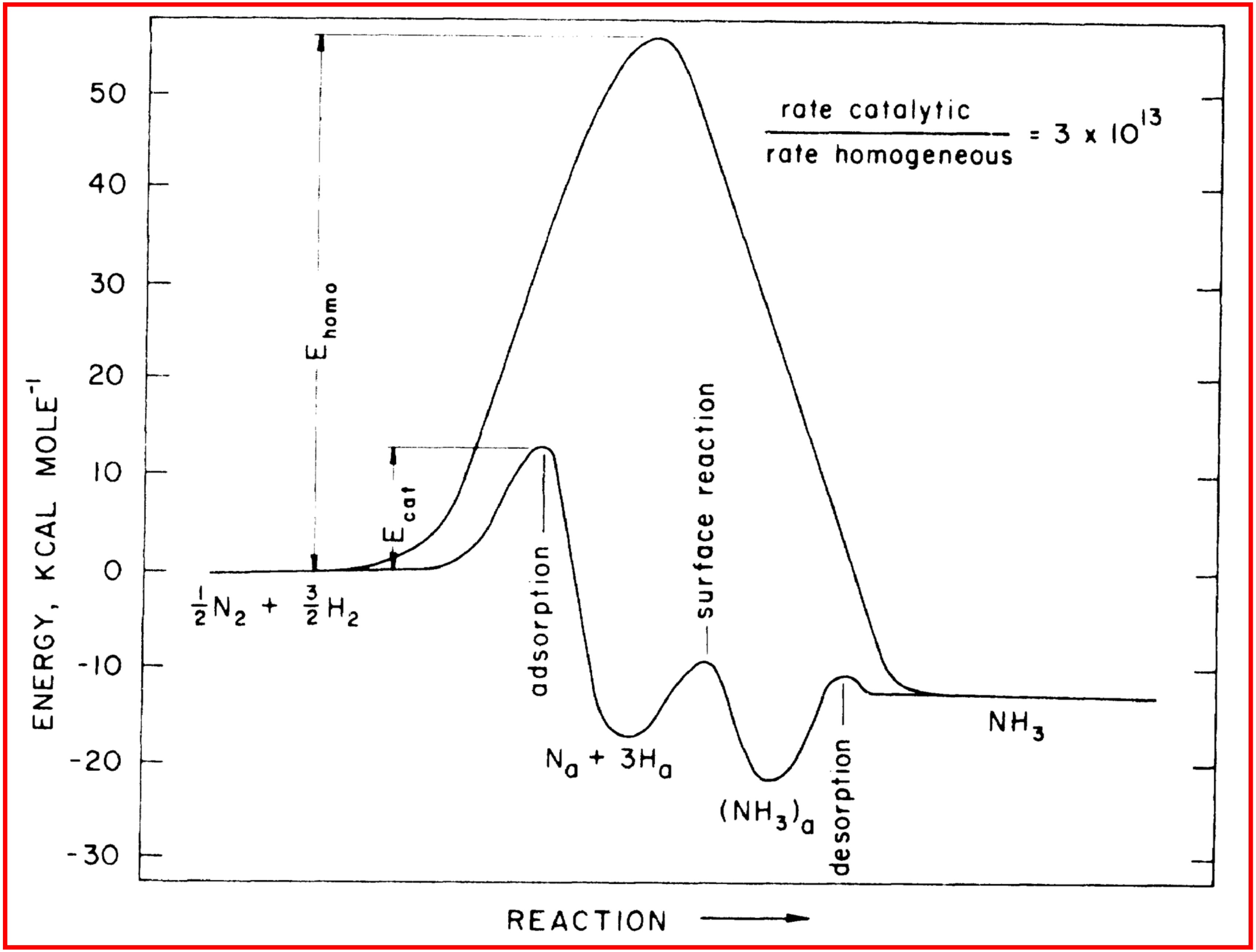
✓In the absence of a catalyst it occurs at extremely low pace. The activation energy, 238.5 kJ/mol [6], associated with the homogenous reaction is quite high

✓The presence of a typical catalyst decreases the activation energy of the rate controlling step (adsorption of nitrogen) to only 50.2 kJ/mol [6]

$$\boxed{N_2 + 3H_2 = 2NH_3}$$

The Nobel Prize in Chemistry 1918

Catalytic reaction path for ammonia synthesis [6]



Principles of catalysis

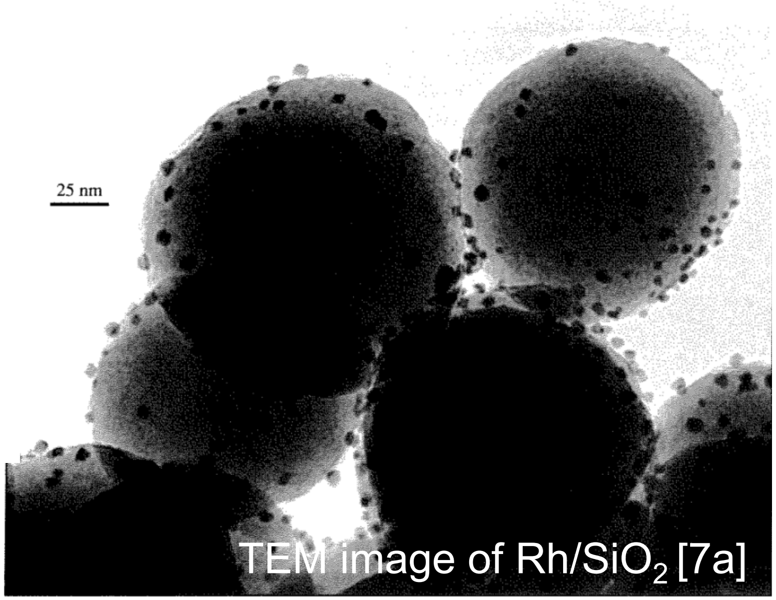
✓As the equilibrium constant is a ratio of forward rate to the reverse rate constants, increasing forward rate of reaction also increases the rate of the reverse reaction (as equilibrium constant is to be unaffected).

✓Principally, the same catalyst is used for forward reaction and reverse reaction. Pt/Al_2O_3 is a good catalyst for dehydrogenation of methylcyclohexane to toluene (an important reforming reaction) as well as for hydrogenation of toluene to methylcyclohexane (reverse reaction). Only the conditions of operation has to be changed. At higher pressures and lower temperatures Pt/Al_2O_3 catalyses hydrogenation of toluene while at lower pressures and higher temperatures it catalyses dehydrogenation.

✓This fact can be used to discover a catalyst for a reaction at mild conditions which can be used for its counter reaction such as synthesis of ammonia requires high pressures whereas its reversible reaction, decomposition of ammonia is carried out at low pressures [6].

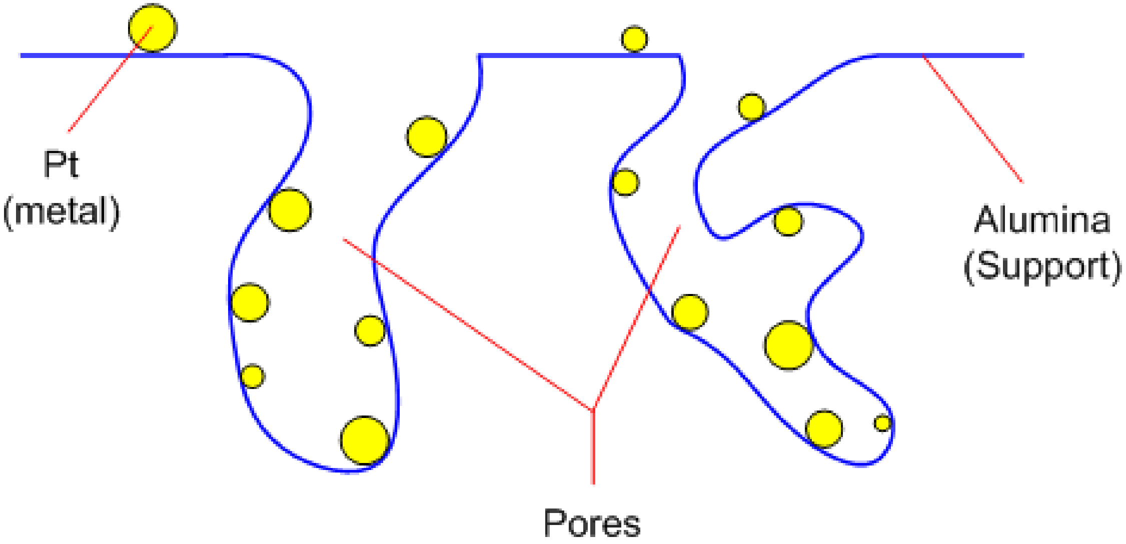
Supported catalysts

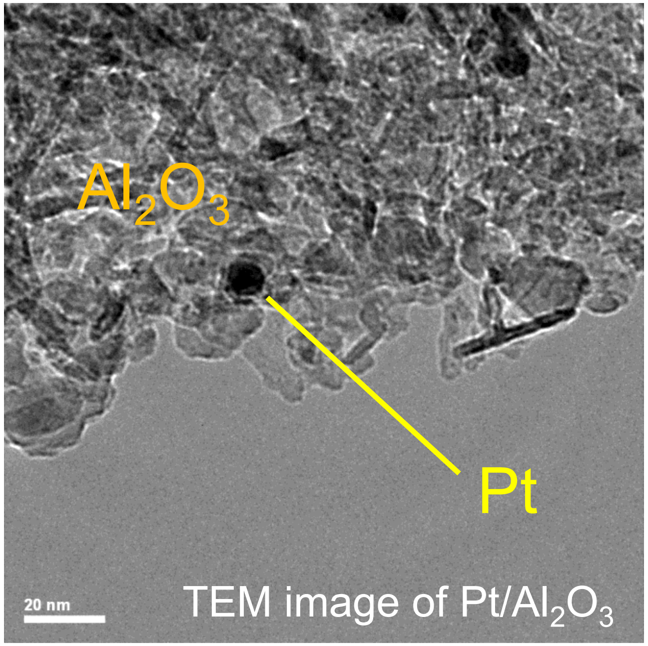
Usually an active component is dispersed over a relatively inactive or less active material which usually has a high surface area. Pt/Al_2O_3, $Ni\text{-}W/Al_2O_3$, Rh/SiO_2 are examples of supported catalysts.



TEM image of Rh/SiO_2 [7a]

Are there any unsupported metal catalysts? Raney catalyst!!!

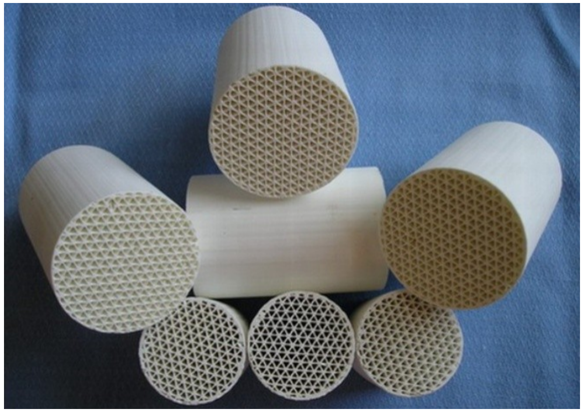




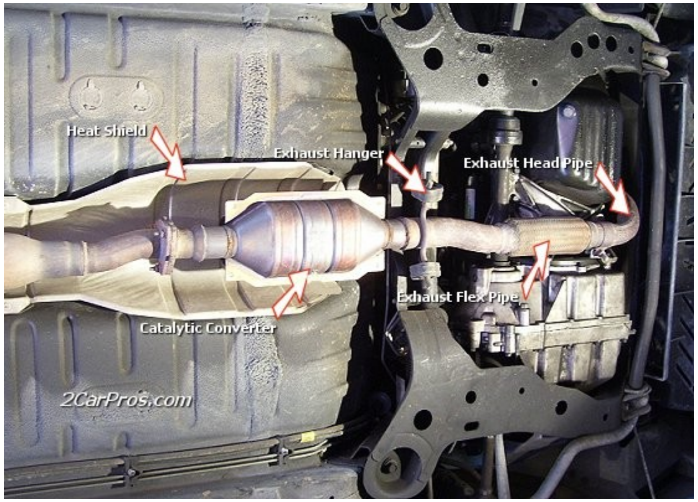
TEM image of Pt/Al_2O_3

Structured catalysts

A structured catalyst is a regular structure free of randomness in reference to the reactor. It is unlike the discrete catalyst particles such as in a conventional fixed bed reactor. Bring to mind the random packing and structured packing in a packed bed.

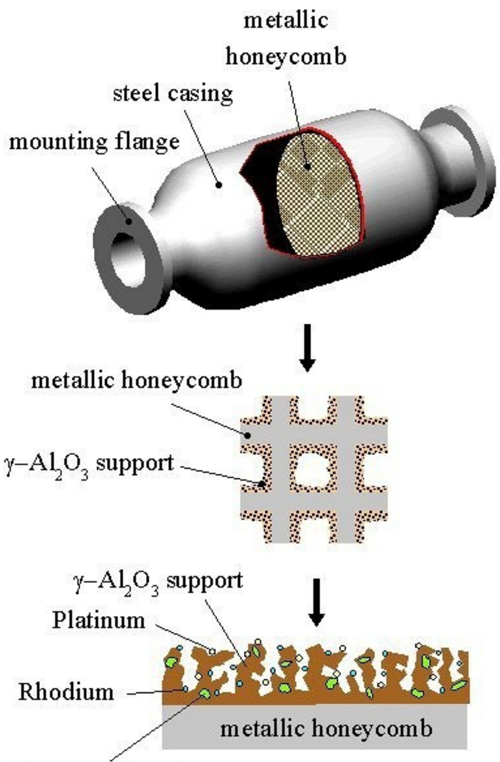


xiaomingdxy.en.made-in-china.com



$$2\,CO + O_2 \longrightarrow 2\,CO_2$$
$$C_mH_n + (m+n/4)\,O_2 \longrightarrow m\,CO_2 + n/2\,H_2O$$
$$2\,NO + 2\,CO \longrightarrow N_2 + 2\,CO_2$$

CATALYTIC CONVERTER



www.tut.fi

en.catalysis.ru

Catalyst support or catalyst carrier

Catalyst support provides surface to the active component of a catalyst. A support is usually a high surface area porous material on which the active component is dispersed and that the support, itself, may be active or inert. A support gives strength, shape, and size to a catalyst. Examples of catalyst supports are alumina, silica, titania, and carbon.

In 1.0wt% Pt over alumina, Pt metal is the active component dispersed over the alumina support.

The same active component when dispersed or supported on a different support may greatly change the activity, selectivity, regenerability, and life of the catalyst.

Bifunctional catalyst

- ✓ It catalyzes two types of catalytic transformations
- ✓ Pt metal loaded on an acid support such as silica-alumina or zeolite is a bifunctional catalyst
- ✓ The Pt metal cares for the dehydrogenation and hydrogenation reactions while acid support facilitates cracking and isomerization reactions
- ✓ A catalytic cracking process requires only an acidic catalyst such as zeolite while hydrocracking process requires a bifunctional catalyst such as Pt/zeolite catalyst or Ni-W/silica-alumina catalyst.

Zeolite

Cracking catalyst

Pt/Al_2O_3

Reforming catalyst

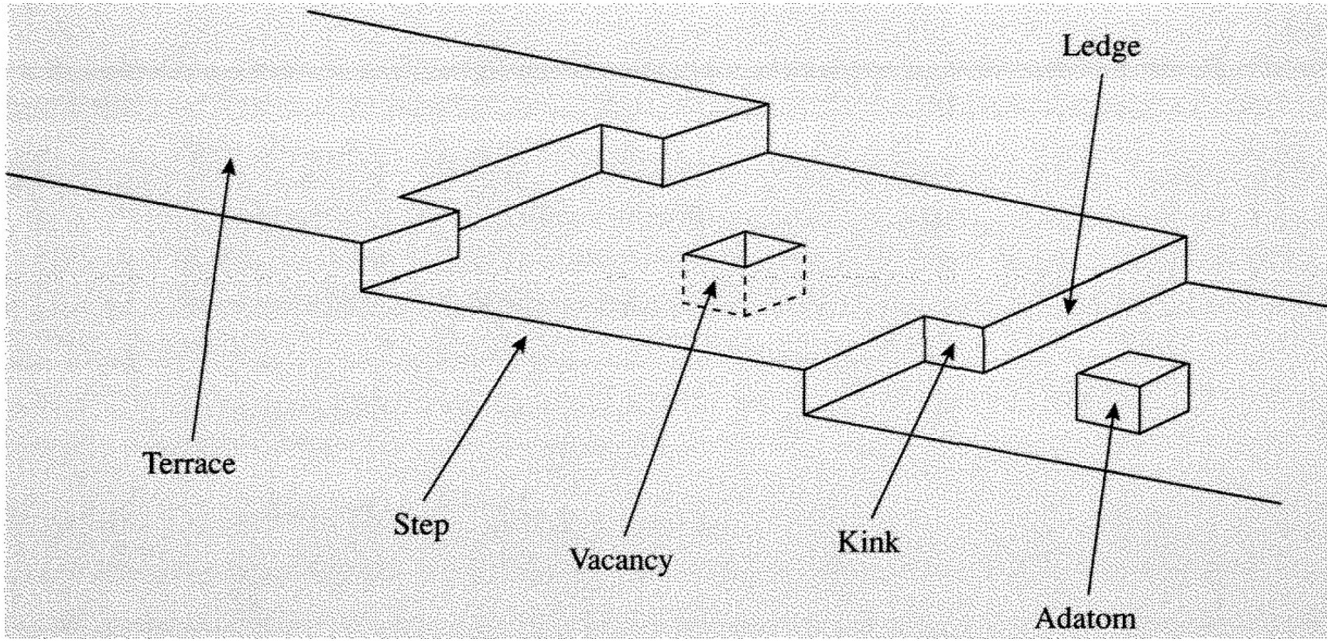
Pt/zeolite

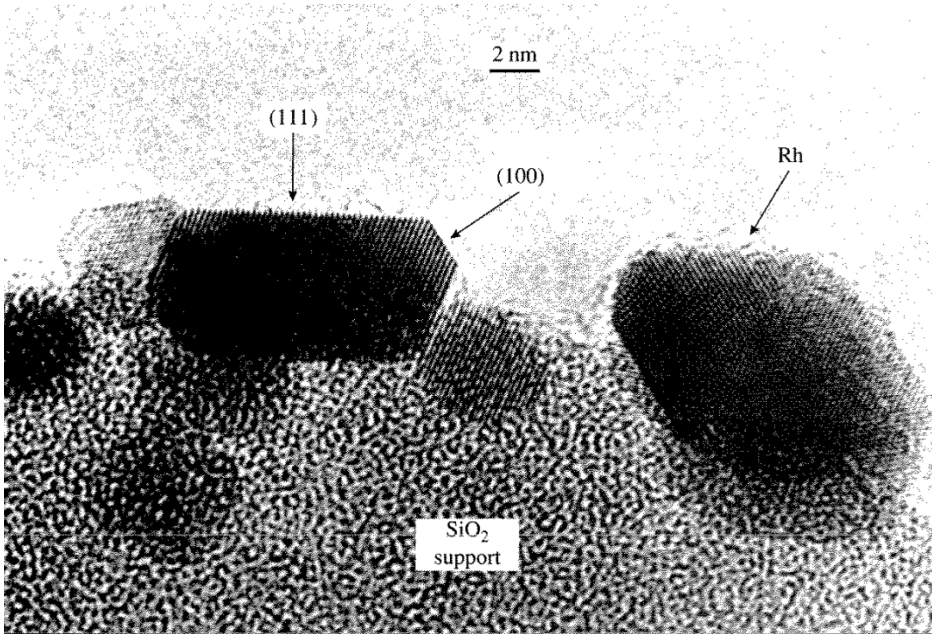
Hydrocracking catalyst

Active sites or active centers [2]

"In a landmark contribution to catalytic theory, Taylor suggested that a reaction is not catalyzed over the entire solid surface but only at certain *active sites* or *centers*. He visualized these sites as unsaturated atoms in the solids that resulted from surface irregularities, dislocations, edges of crystals, and cracks along grain boundaries. Other investigators have taken exception to this definition, pointing out that other properties of the solid surface are also important. The active sites can also be thought of as places where highly reactive intermediates (i.e., chemisorbed species) are stabilized long enough to react. However, for our purposes we will define an *active site as a point on the catalyst surface that can form strong chemical bonds with an adsorbed atom or molecule*."

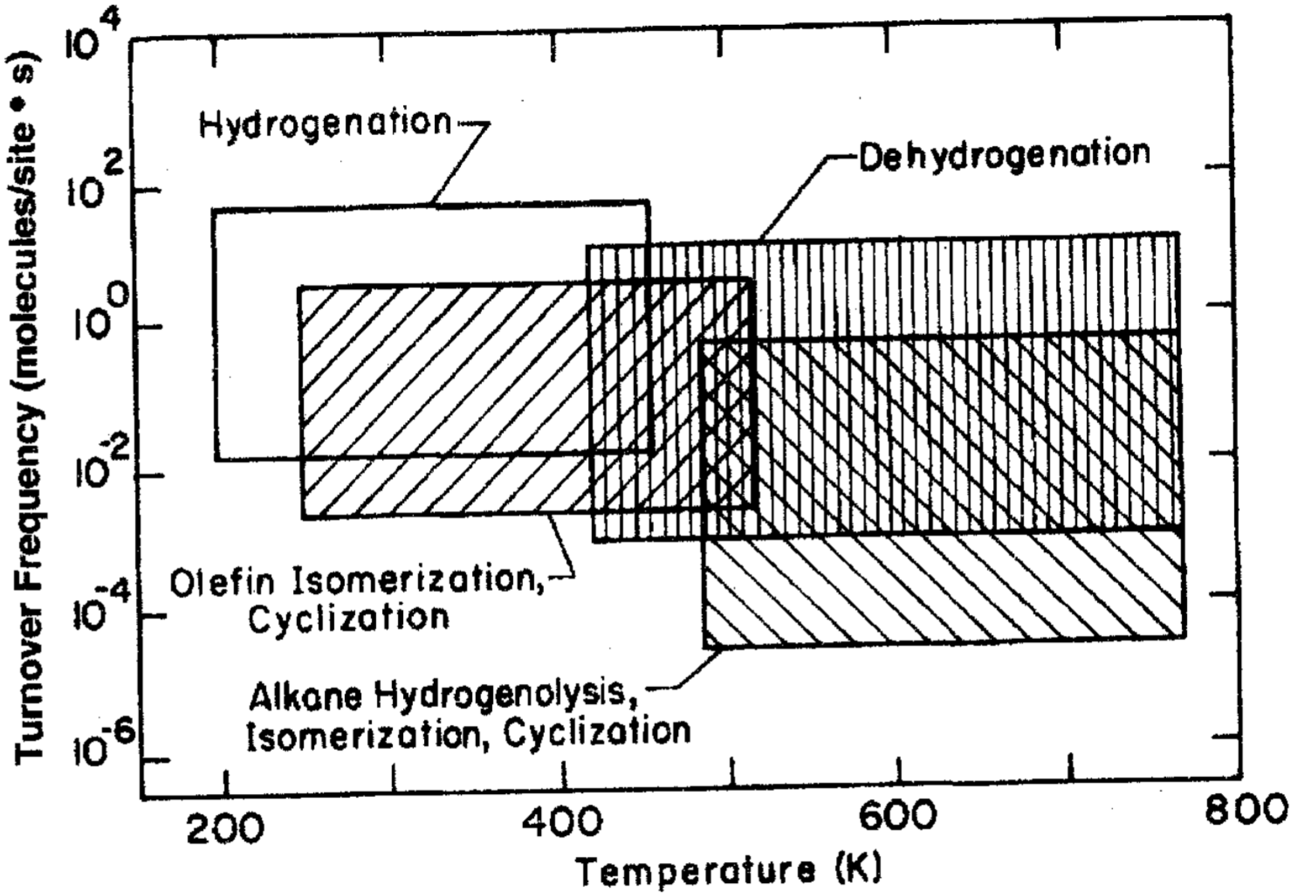
Schematic representation of a single crystal surface [7a]





Turnover frequency (TOF) [2]

It is the number of molecules converted per unit time per active site.



Activity, selectivity, stability, and regenerability of a catalyst

The selection of a suitable catalyst for a process usually demands the knowledge regarding the

- ✓ Activity
- ✓ Selectivity
- ✓ Stability, and
- ✓ Regenerability

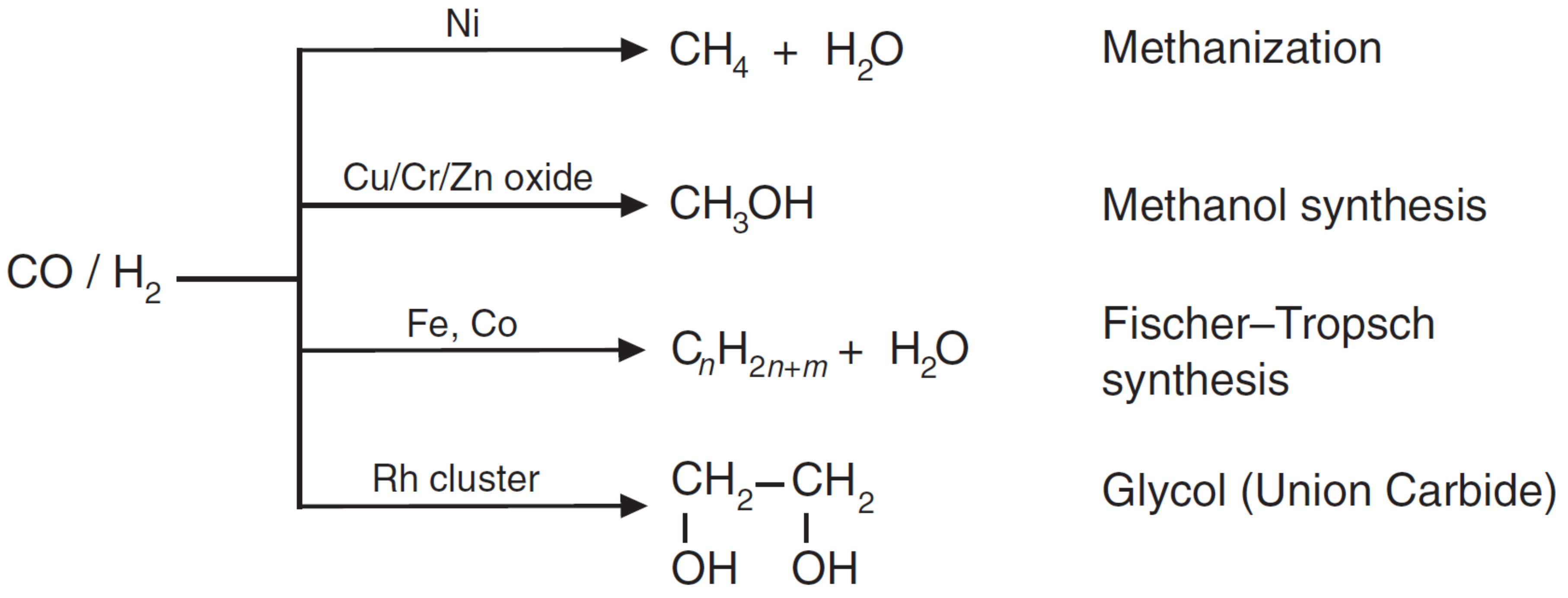
of a catalyst.

Activity, selectivity, stability, and regenerability of a catalyst

Activity: Activity of a catalyst controls the extent of a chemical reaction involved and describes the effectiveness of a catalyst towards the rate of the chemical reaction and conversion of the reactant. It has no concern with the product distribution (selectivity).

Selectivity: Selectivity refers to the efficacy of a catalyst towards producing the desired product. For both the parallel and consecutive reactions, the selectivity is important and a catalyst is required to produce the desired product in greater amounts (increased selectivity).

Selectivity of a catalyst



$CO / H_2 \xrightarrow{Ni} CH_4 + H_2O$ Methanization

$CO / H_2 \xrightarrow{Cu/Cr/Zn\ oxide} CH_3OH$ Methanol synthesis

$CO / H_2 \xrightarrow{Fe,\ Co} C_nH_{2n+m} + H_2O$ Fischer–Tropsch synthesis

$CO / H_2 \xrightarrow{Rh\ cluster} \underset{OH}{\underset{|}{CH_2}}-\underset{OH}{\underset{|}{CH_2}}$ Glycol (Union Carbide)

$$C_2H_5OH \xrightarrow[catalyst]{acid} C_2H_4 + H_2O \quad \text{(dehydration)}$$

$$C_2H_5OH \xrightarrow[catalyst]{metal} C_2H_4O + H_2 \quad \text{(dehydrogenation)}$$

Activity, selectivity, stability, and regenerability of a catalyst

Stability: For a catalyst, it refers to the life of the catalyst. If the activity and selectivity of a catalytic system remains unchanged during the course of a given period of time, under the same conditions of temperature, pressure, and space time, the catalyst gives the same product composition for the same feed composition, the catalyst is said to have stable characteristics for that period of time.

Regenerability: It refers the ability of a catalyst to be reactivated to more or less to its original conditions.

Activity, selectivity, stability, and regenerability of a catalyst

Richardson [6] suggests the order of importance of the activity, selectivity, and stability as:

Selectivity

Stability

Activity

Characterization of catalysts

- ✓ XRD: Stands for x-ray diffraction. It is commonly used for phase identification and to observe bulk crystal structure. Diffraction lines widen as crystallite size decreases. A broader peak may show distortion and less degree of crystallinity. It helps to make sure the presence of the desired material.
- ✓ SEM: Stands for scanning electron microscopy. It is used to see the topography of the catalyst surface. It gives an information regarding surface features such as surface irregularities and particle shape, size, and distribution. Lower resolutions compared to TEM.
- ✓ TEM: Stands for transmission electron microscopy. Electrons have to be passed or transmitted through the sample. Sample should be very thin and very high resolutions are obtained. Atomic arrangement in crystals and crystalline defects at nano-level can be detected.

Characterization of catalysts

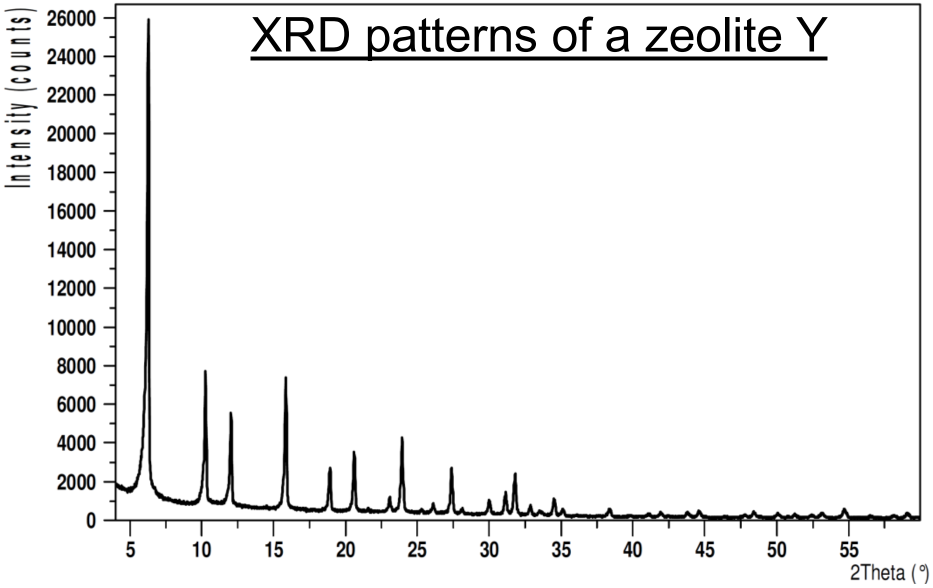
✓ N_2-BET surface area: Surface area of catalytic materials is measured by N_2 adsorption using BET isotherm. Pore size and pore volume of the pores present within the catalyst are also measured.

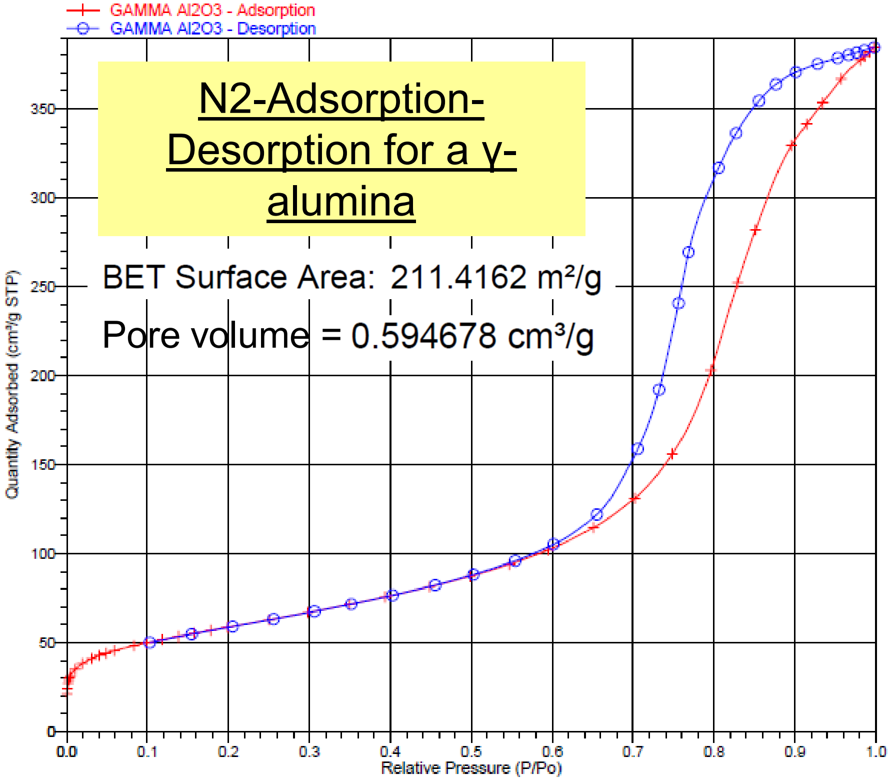
✓ Porosimetry: Helium or mercury intrusion porosimetry can be used to measure the pore size, pore volume, and skeletal and particle densities of the material.

✓ Elemental composition: Atomic absorption spectroscopy (AAS), Inductively coupled plasma (ICP) spectroscopy, Energy dispersive X-ray (EDX) analysis with SEM can be used for the elemental identification and composition.

✓ Temperature programmed techniques: Py-TPD (Pyridine-temperature programmed desorption) or NH_3-TPD is used to measure the acidity of a catalyst. Other temperature programmed techniques such as TPR (temperature programmed reduction), TPO (temperature programmed oxidation), TGA (thermogravimetric analysis), and DTA (differential thermal analysis) are also used for various other purposes.

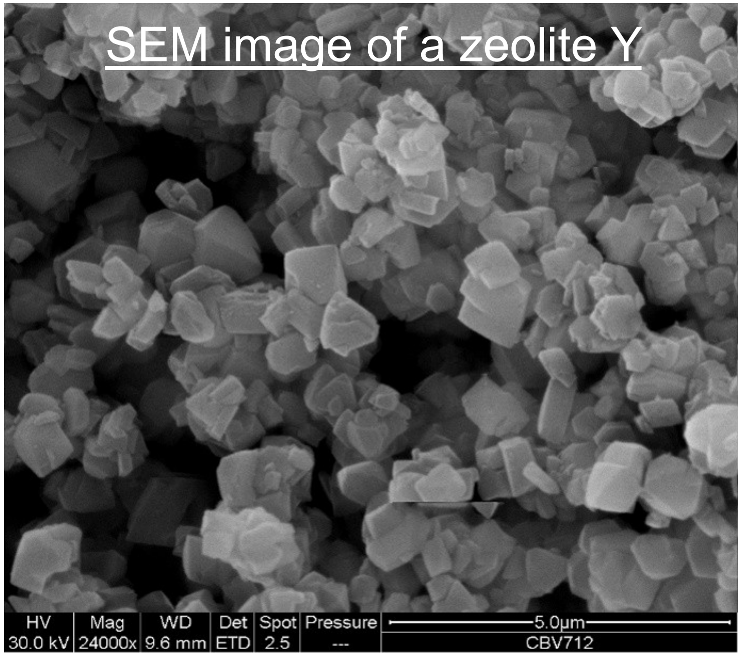
Catalyst Characterization

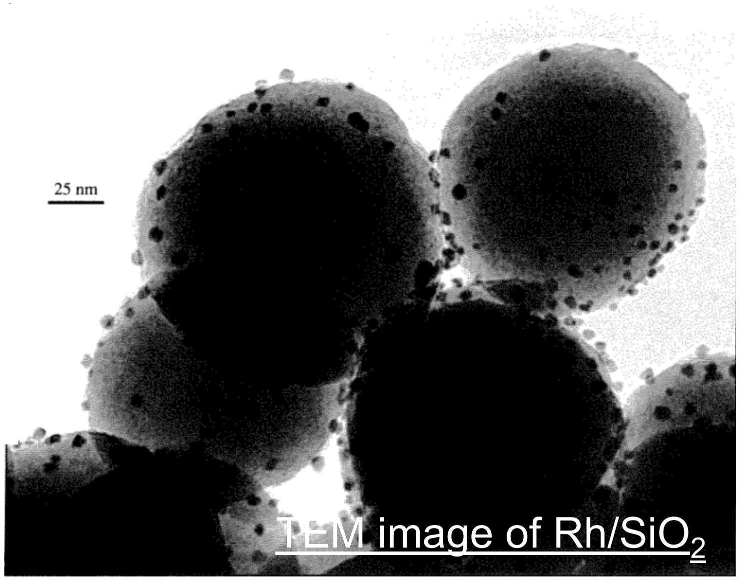

XRD patterns of a zeolite Y


N2-Adsorption-Desorption for a γ-alumina

BET Surface Area: 211.4162 m²/g

Pore volume = 0.594678 cm³/g


SEM image of a zeolite Y


TEM image of Rh/SiO_2

Source of many chemical engineering related terms

Muhammad Rashid Usman is Associate Professor at the Institute of Chemical Engineering and Technology, University of the Punjab, Lahore. He spent most of his career working at the institute. He completed his PhD in Chemical Engineering and Analytical Science from the University of Manchester, UK and resumed his job at the institute in 2010. He is currently teaching undergraduate and graduate students and involved in research activities regarding catalysis and reaction engineering. He has received several performance awards and research grants and has more than 25 research publications to his name. He is a member of PEC, PIChE, and NCQT Pakistan.

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Comprehensive Dictionary of Chemical Engineering

Muhammad Rashid Usman

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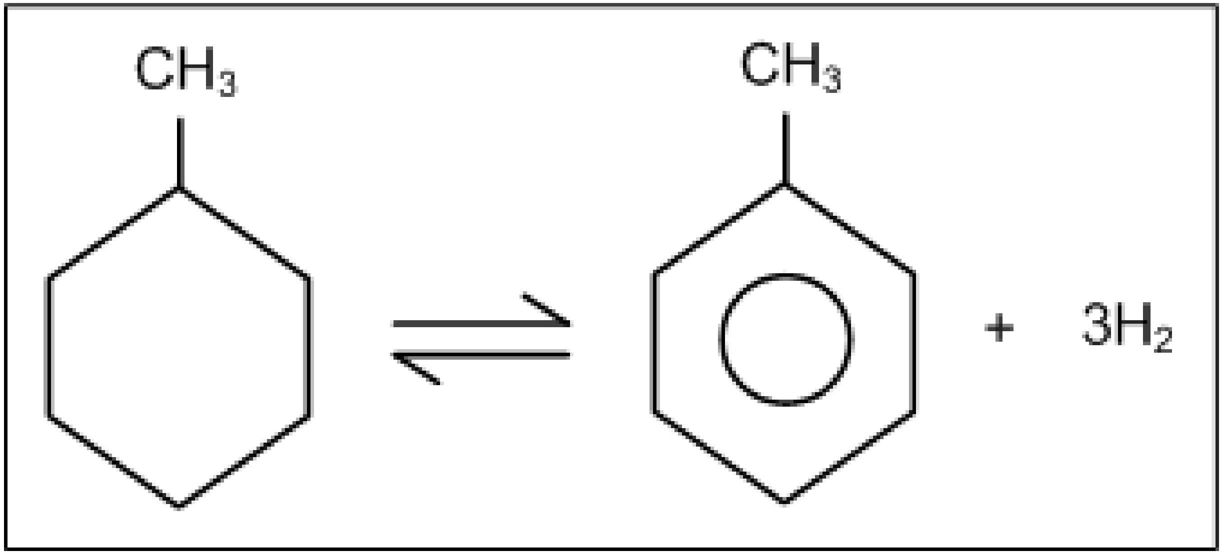
(576 pages)

The dehydrogenation of methylcyclohexane (MCH)



$$C_7H_{14} \rightleftharpoons C_7H_8 + 3H_2$$

Methylcyclohexane Toluene Hydrogen

Importance of the dehydrogenation of methylcyclohexane (MCH) reaction

- ✓ Dehydrogenation of methylcyclohexane is an important reforming reaction
- ✓ Dehydrogenation of methylcyclohexane may be useful in the conversion of naphthenic base heavy oils
- ✓ Dehydrogenation of methylcyclohexane is involved in the hydrogen storage applications in the MTH (methylcyclohexane-toluene-hydrogen) system
- ✓ Dehydrogenation of methylcyclohexane may be used as a fuel to absorb energy in high speed air craft engines

Requirements for the realization of MCH as organic hydride

The dehydrogenation reaction is highly endothermic and occurs at a high temperature

- ✓The minimum *T* of 306.9°C is required for 90% equilibrium conversion at 2.0 bar with pure MCH as feed
- ✓Heat of reaction at 1 bar and 25°C is 205 kJ/mol

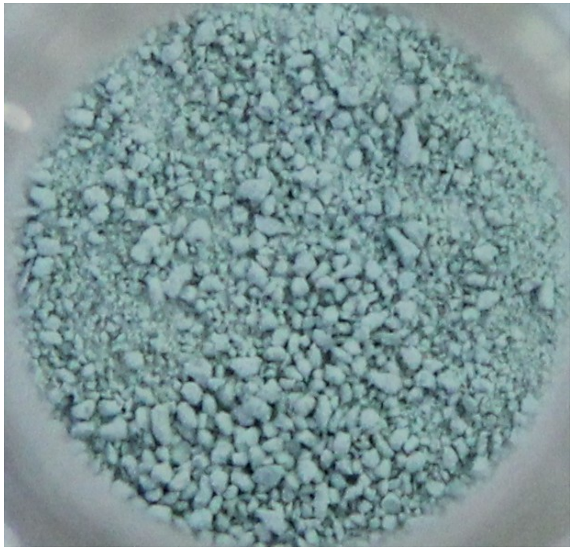
A highly active, selective, and stable catalyst is required (Catalyst Development)

Various commercial and In-house catalysts [7]

Catalyst	**Assay**	**Supplier**	**Dispersion type**	**Method of preparation**	**BET ($m^2 \cdot g^{-1}$)**	**Pore volume (cm^3/g)**	**Median pore diameter (Å)**	**Reference**
CAT-A	0.3 wt% Pt/Al_2O_3	Commercial	Egg-shell	—	—	—	—	This study
CAT-B	x wt% $Pt/\theta\text{-}Al_2O_3$	Commercial	Egg-shell	—	—	—	—	This study
CAT-C	1.0 wt% $Pt/\gamma\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	208	0.58	69	This study
CAT-D	1.0 wt% $Pt/\theta\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	99.1	0.84	291.3	This study
CAT-E	20.0 wt% $Ni/\gamma\text{-}Al_2O_3$	Development	Uniform	Dry impregnation	208	0.58	69	This study
CAT-F	1.0 wt% Pt/β-zeolite	Development	Uniform	Ion exchange	509.8	0.38	33.3	This study
CAT-G	1.0 wt% $Pt/\gamma\text{-}Al_2O_3$	Commercial	Uniform	—	302.3	0.51	67.2	Tsakiris [2007] Alhumaidan [2008]
CAT-H	0.5 wt% $Pt/\gamma\text{-}Al_2O_3$	Commercial	Egg-shell	—	124.6	0.35	110.3	Tsakiris [2007] Alhumaidan [2008]
CAT-I	0.3 wt% $Pt/\gamma\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	220	0.62	70	Alhumaidan [2008]
CAT-J	0.3 wt% $Pd/\gamma\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	220	0.62	70	Alhumaidan [2008]
CAT-K	0.1 wt% $Pt/\gamma\text{-}Al_2O_3$	Commercial	—	—	172.7	0.58	131.4	Tsakiris [2007]
CAT-L	0.3 wt% $Pt/\alpha\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	14.2	0.05	133	Tsakiris [2007]
CAT-M	1.0 wt% $Pt/\alpha\text{-}Al_2O_3$	Development	Uniform	Wet impregnation	14.3	0.05	127.7	Tsakiris [2007]

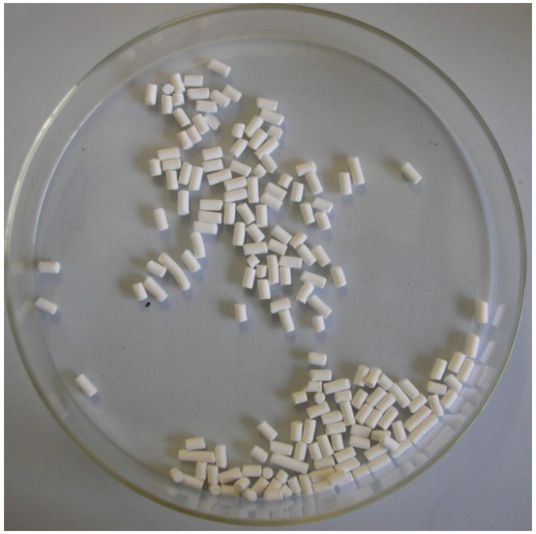
Various commercial and in-house dehydrogenation catalysts


Commercial Pt/alumina catalysts


Ni/γ-alumina


1.0wt%Pt/γ-alumina

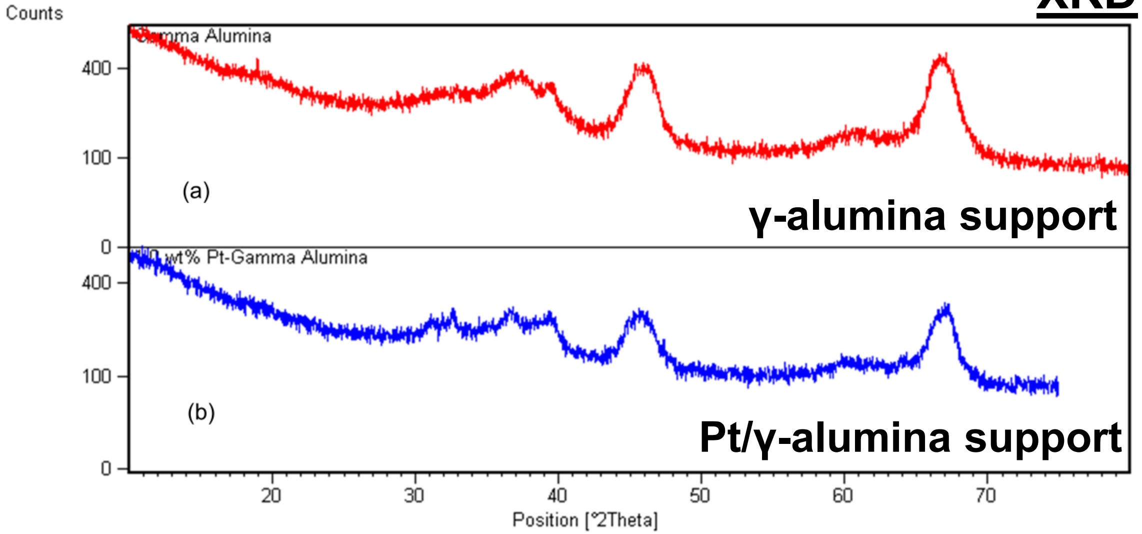
Commercial γ-alumina support



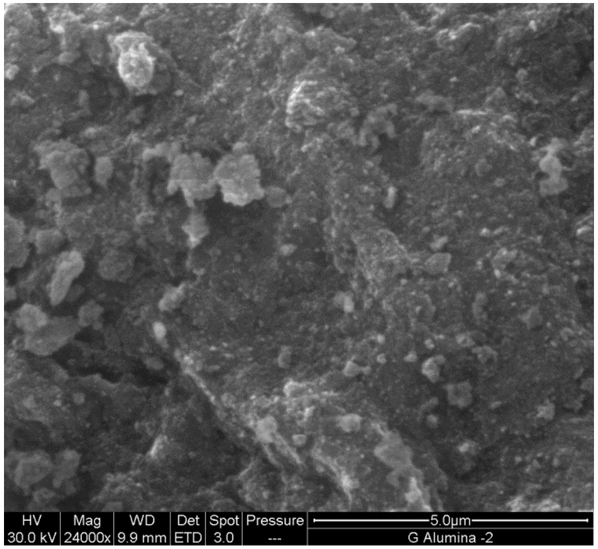
Commercial zeolite beta support

1.0 wt% Pt/γ-Al_2O_3 catalyst

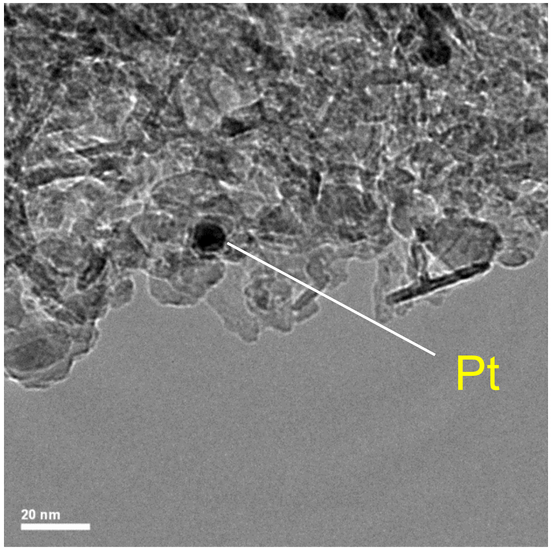
XRD

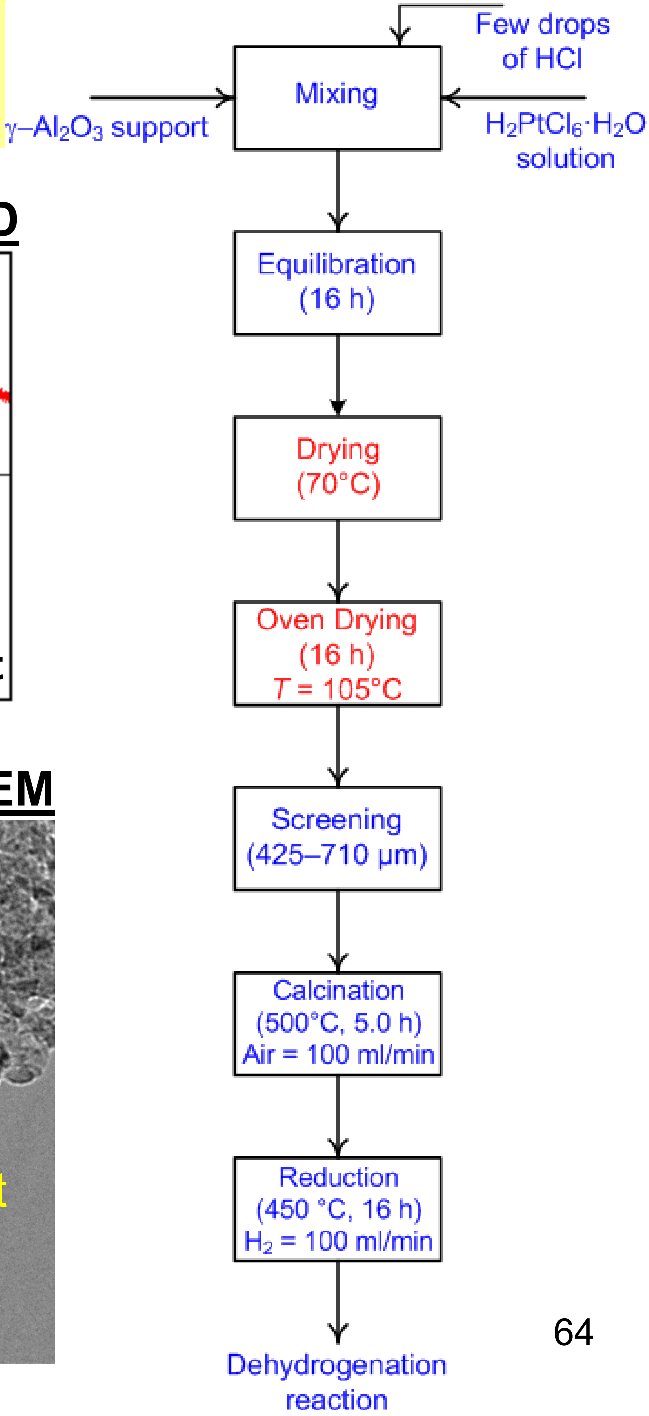


SEM



TEM





γ–Al_2O_3 support

Few drops of HCl

$H_2PtCl_6 \cdot H_2O$ solution

Mixing

Equilibration (16 h)

Drying (70°C)

Oven Drying (16 h) T = 105°C

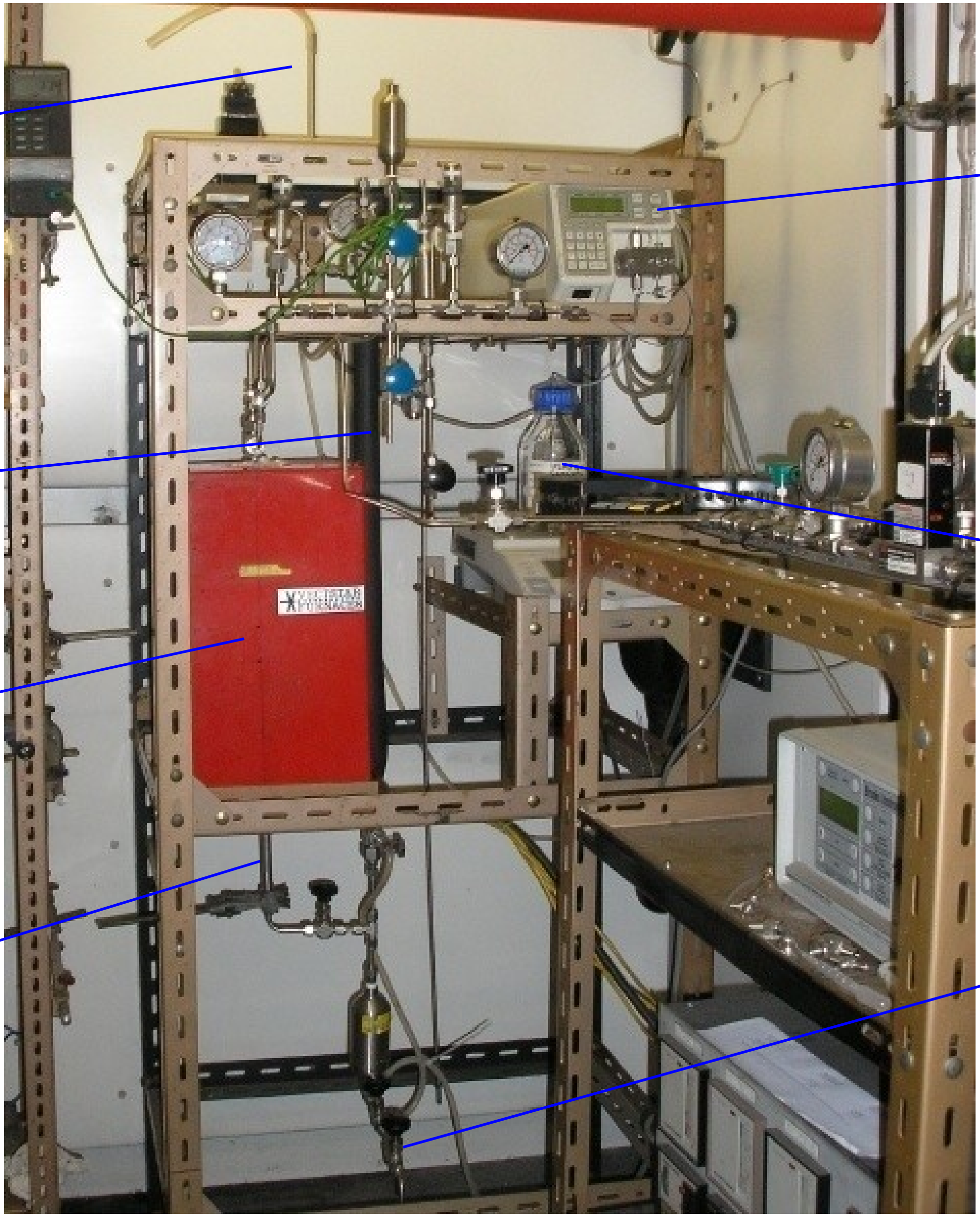
Screening (425–710 µm)

Calcination (500°C, 5.0 h) Air = 100 ml/min

Reduction (450 °C, 16 h) H_2 = 100 ml/min

Dehydrogenation reaction

High pressure (upto 30 bar) experimental rig



Product gas outlet

Condenser

Furnace

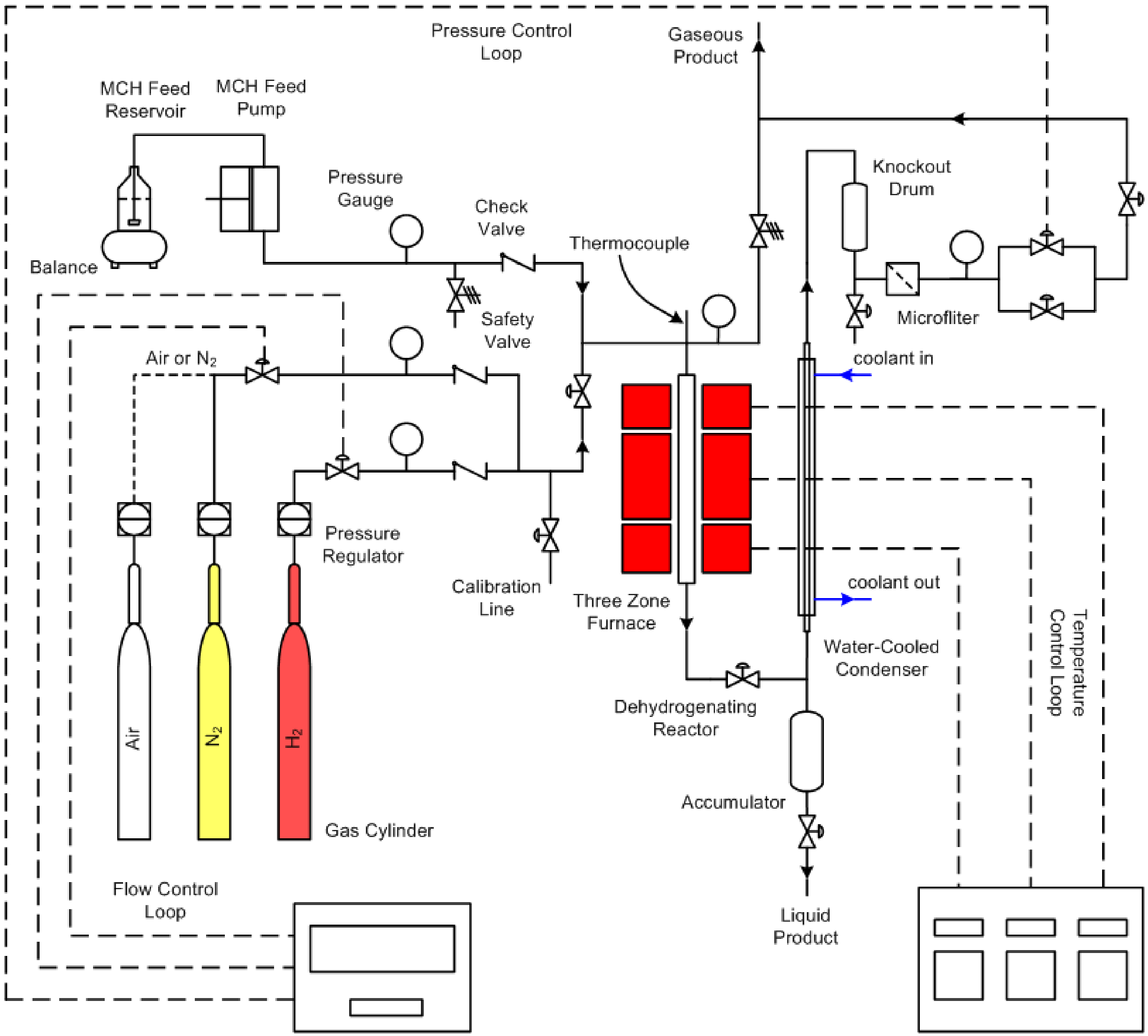
Reactor tube

HPLC Pump

MCH feed reservoir

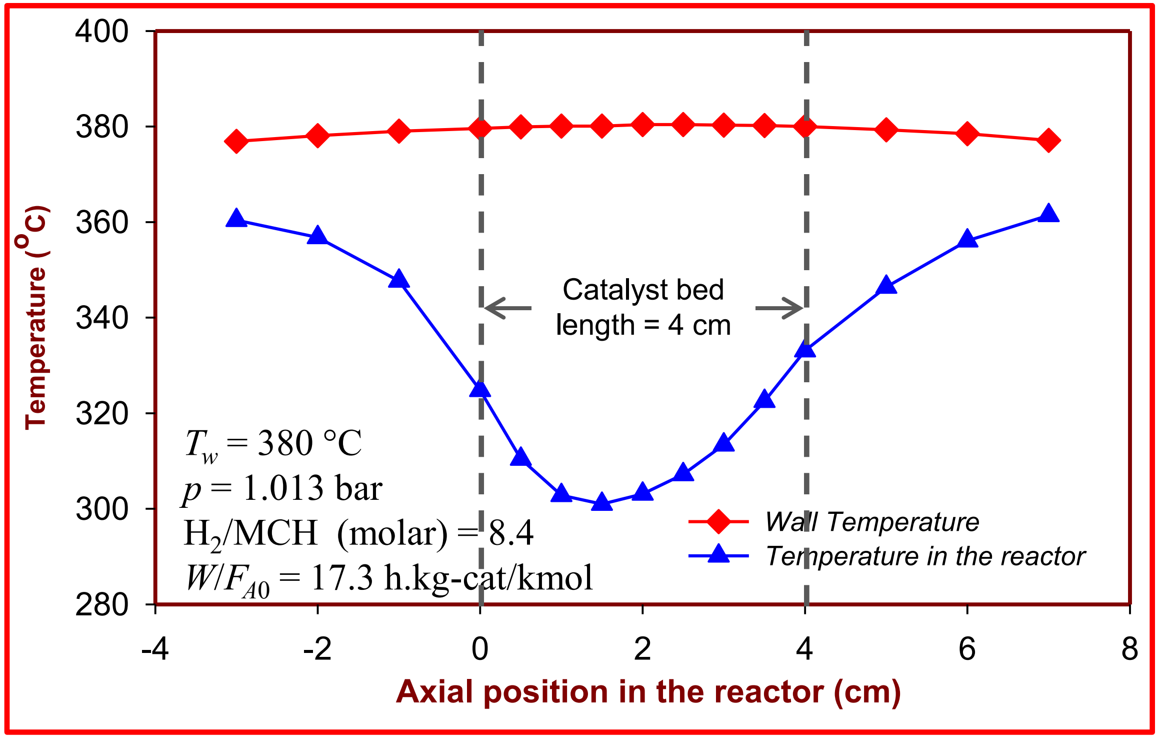
Liquid product outlet

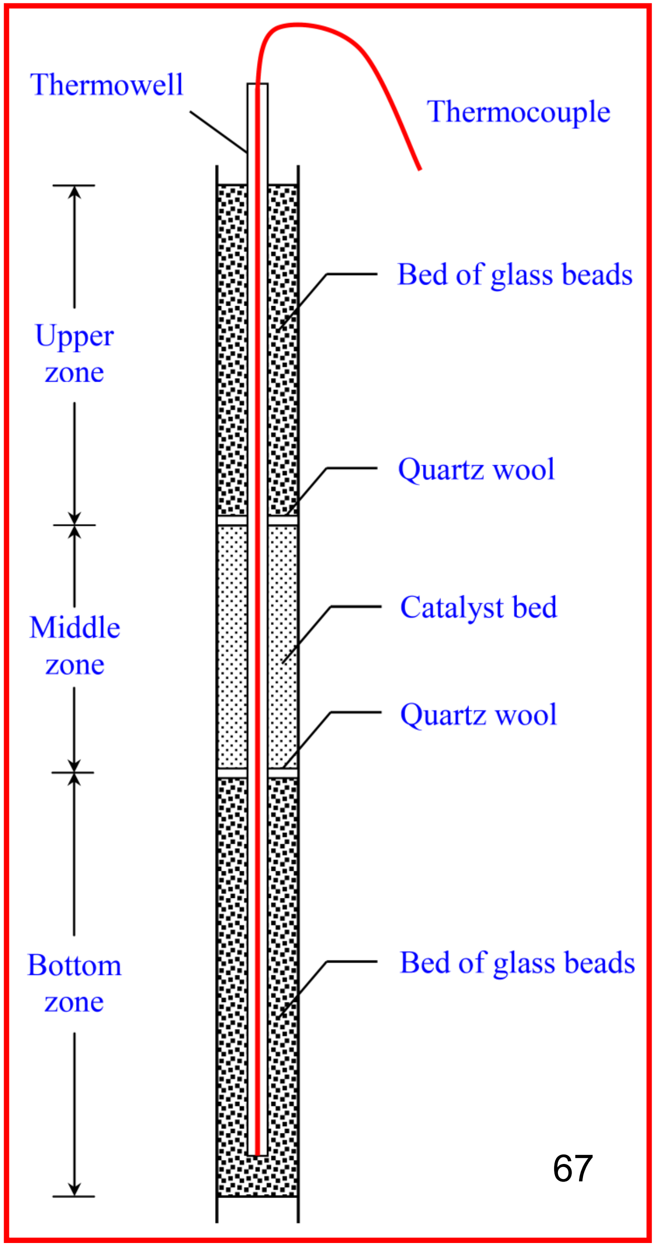
High pressure (upto 30 bar) experimental rig



High pressure (upto 30 bar) experimental rig

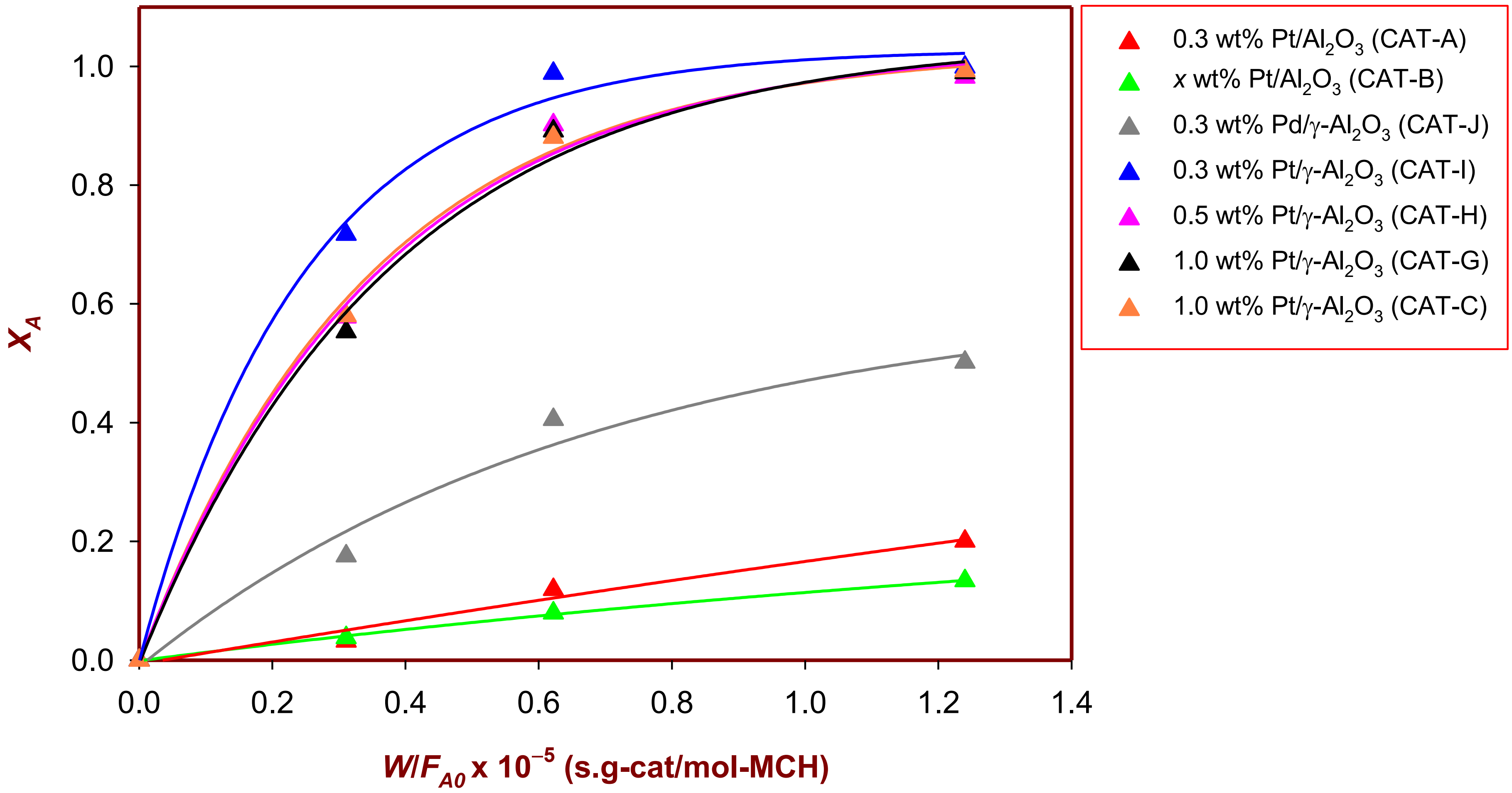
Description	Specification
Body material	SS-316
Reactor tube length (cm)	66
Reactor bed length (cm)	55
Tube outside diameter (cm)	1.27
Tube inside diameter (cm)	1.02
Tube wall thickness (cm)	0.1245
Thermowell material	Al_2O_3
Thermowell outside diameter (cm)	0.2880–0.3175





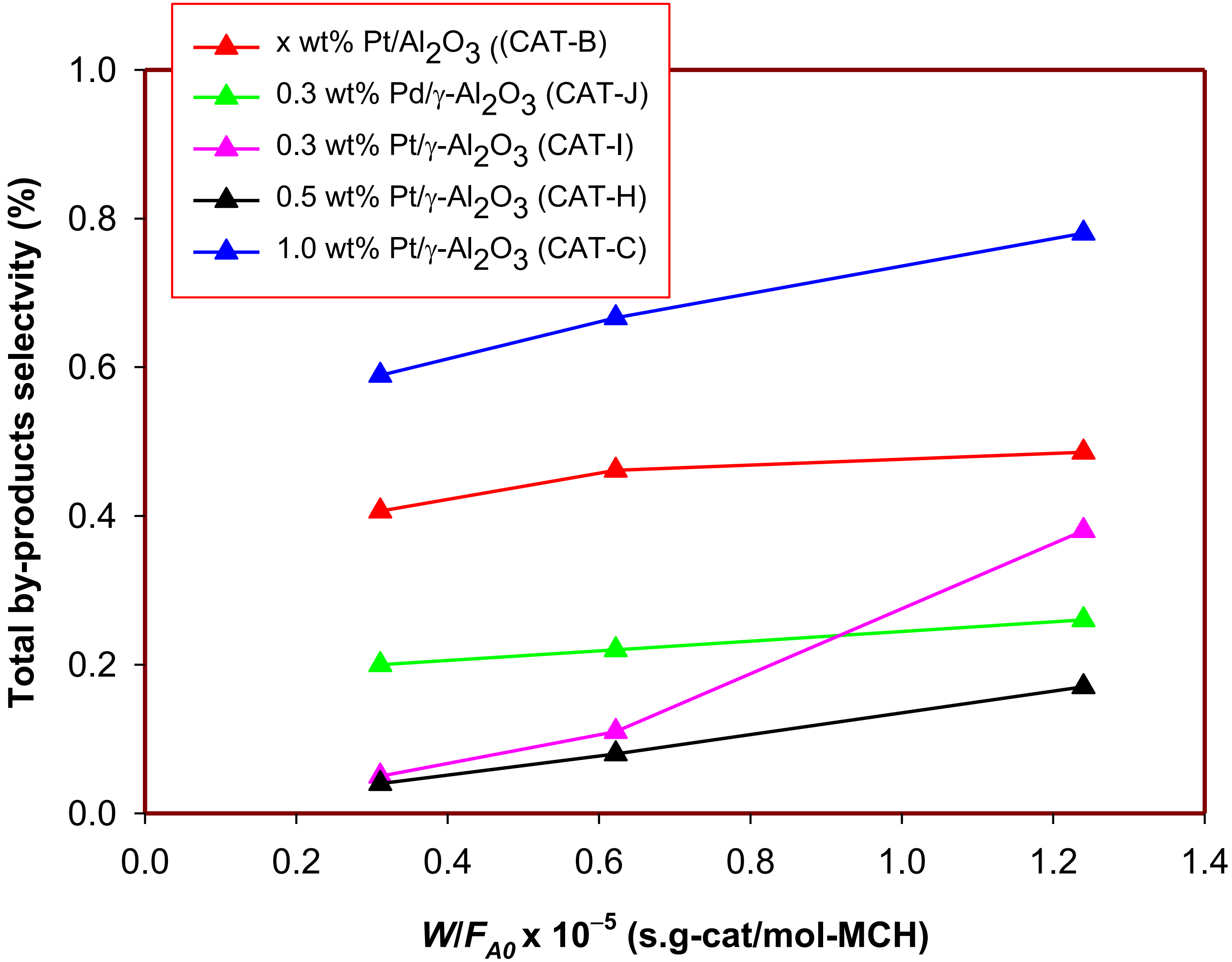
Activity results [7]

p = 1 bar; T_w = 380 °C; H_2 to MCH (molar)= 8.4



Selectivity results [7]

p = 5 bar; T_w = 380 °C; H_2 to MCH (molar)= 8.4

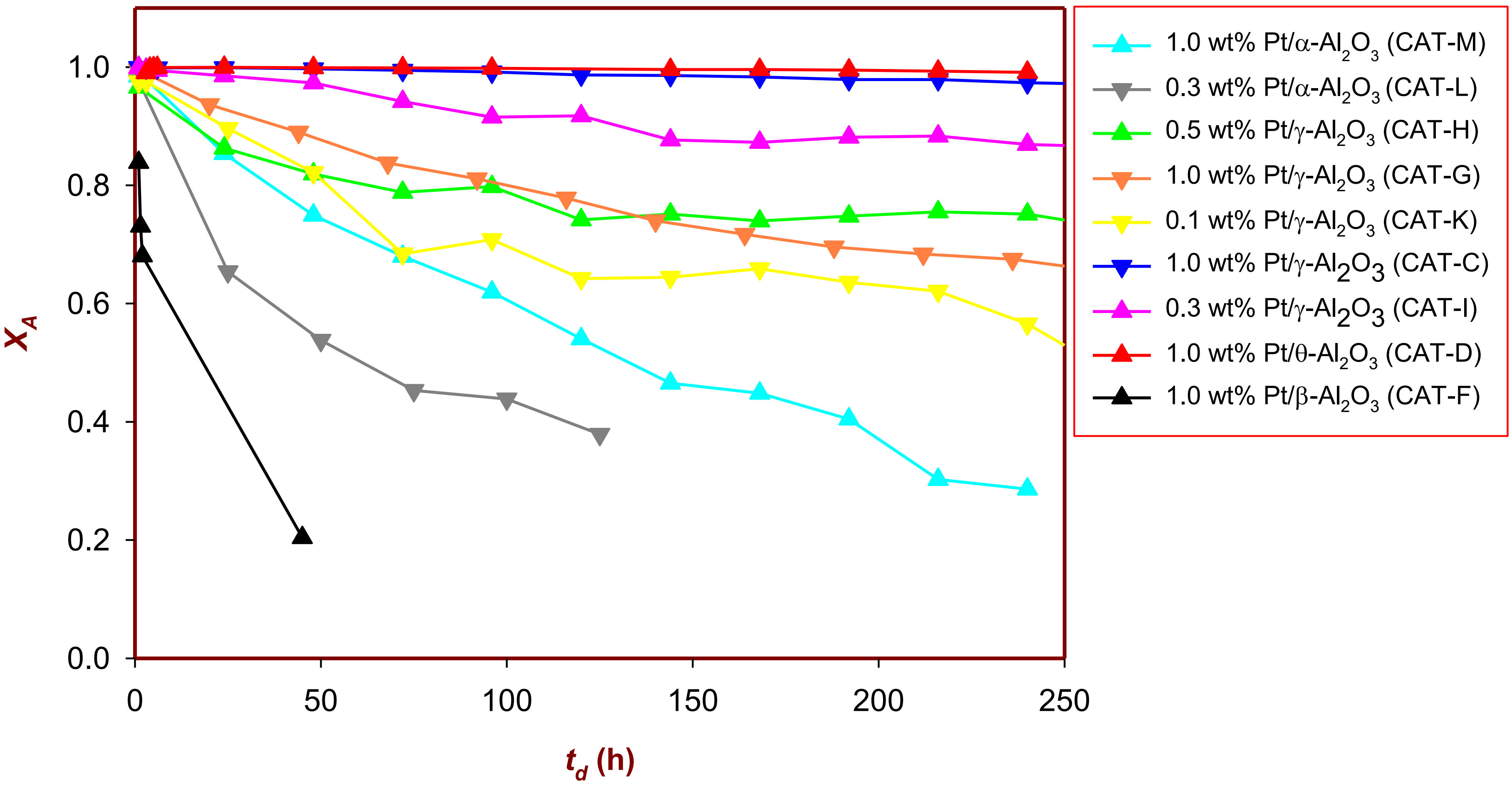


Comparative activity and selectivity for in-house development catalysts [7]

W/F_{A0} = 0.62 × 10^5 s·g-cat/mol MCH, T_w = 360 °C, p = 1.0 bar, H_2 to MCH molar ratio = 1.0

Catalyst	**Assay**	**MCH conversion (%)**	**By-product selectivity (%)**
CAT-C	1.0 wt% Pt/γ-Al_2O_3	92.0	0.63
CAT-D	1.0 wt% Pt/θ-Al_2O_3	91.0	0.10
CAT-E	20.0 wt% Ni/γ-Al_2O_3	31.0	7.87
CAT-F	1.0 wt% Pt/β-zeolite	73.0	22.48

Deactivation behavior of catalysts [7]



p = 1 bar; T_w = 380 °C; Pure MCH; W/F_{A0} = 34.5 h·kg-cat/kg

Hydroisomerization of heavy naphtha

✓Isomerization is used to improve the octane number of the n-paraffinic feeds by converting them into iso-paraffins.

✓n-pentane has RON (research octane number) of 61.7 while isopentane has an octane rating of 92.3.

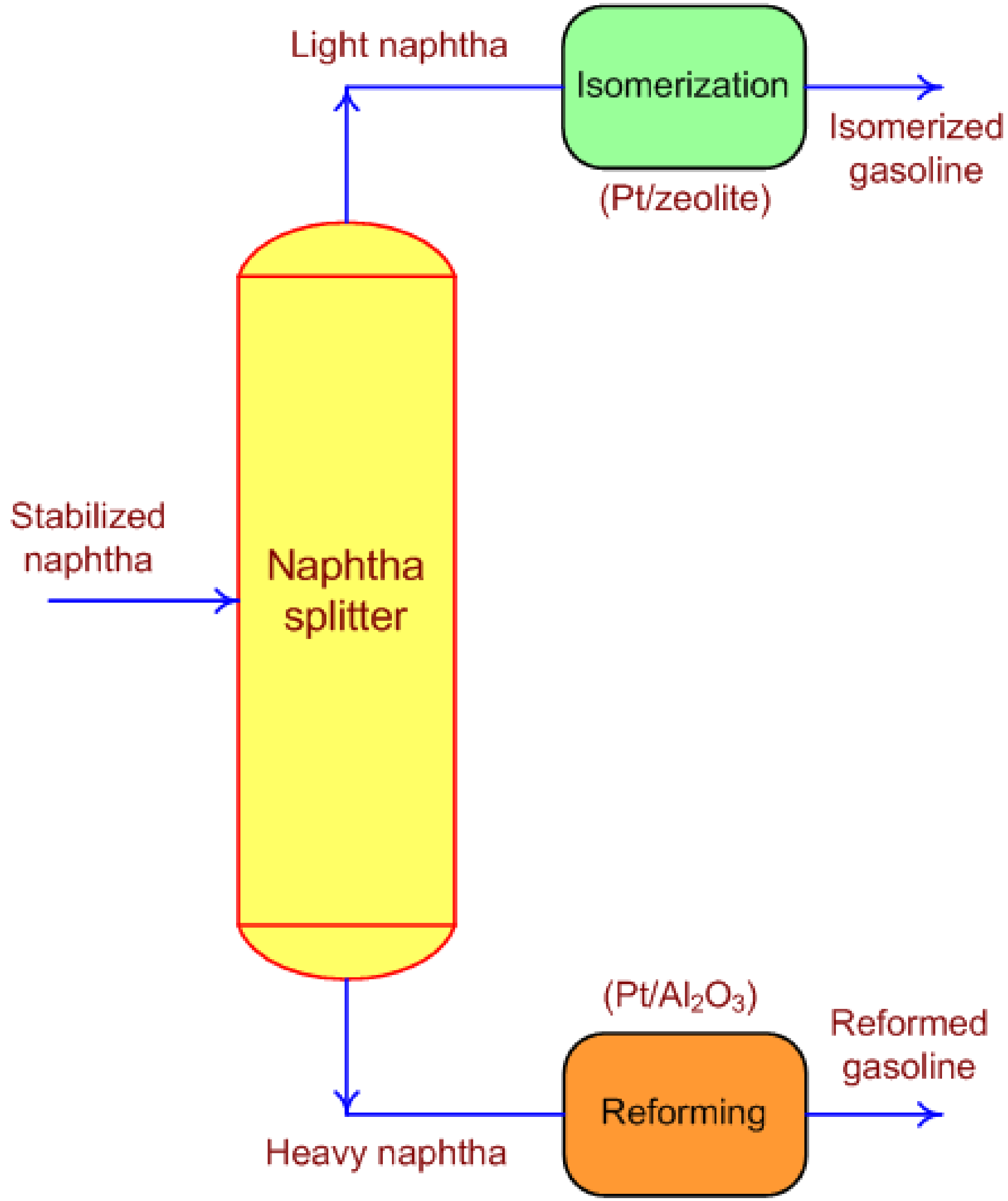
Hydrogen is added to the feed to avoid the deposition of coke on the catalyst surface and consumption of hydrogen is negligible. Due to hydrogen presence in the feed, the process is frequently called as hydroisomerization.

Hydroisomerization of heavy naphtha

Benzene is toxic and therefore we do not want benzene in a gasoline. If present in gasoline, the spillage of gasoline and incomplete combustion of gasoline in an engine may add benzene to the atmosphere we breath in.

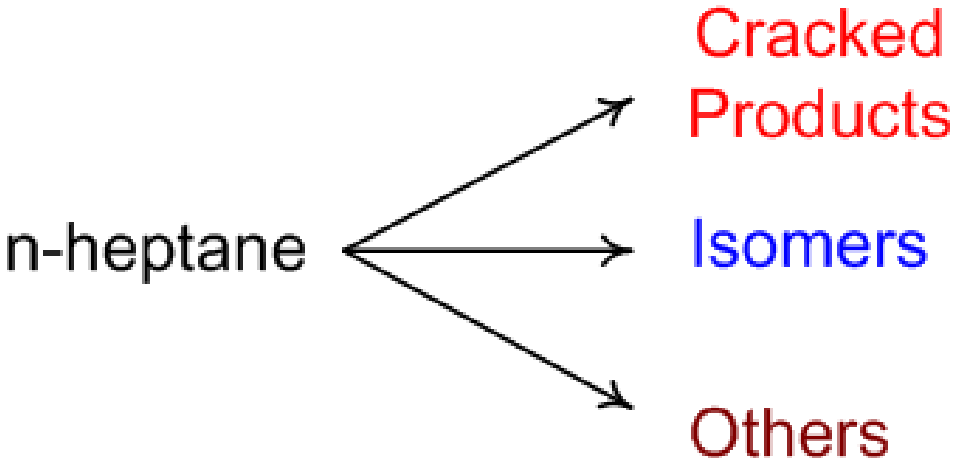
For a naphtha feed, how can we reduce the concentration of benzene in a gasoline while virtually keeping the same octane rating? By isomerizating naphtha.

Hydroisomerization of heavy naphtha



Hydroisomerization of n-heptane

Isoms	Cracks	Others
2,2-Dimethylpentane	n-Propane	1,2-Dimethylcyclopentane
2,4-Dimethylpentane	n-Butane	Methylcyclopentane
2,2,3-Trimethylbutane	i-butane	Ethylcyclopentane
3,3-Dimethylpentane	n-Pentane	Toluene
2-Methylhexane	2-Methylpentane	2-Methylheptane
2,3-Dimethylpentane	3-Methylpentane	3-Methylheptane
3-Methylhexane	2,2-Dimethylbutane	1,3-Dimethycyclohexane
3-Ethylpentane	n-Hexane	



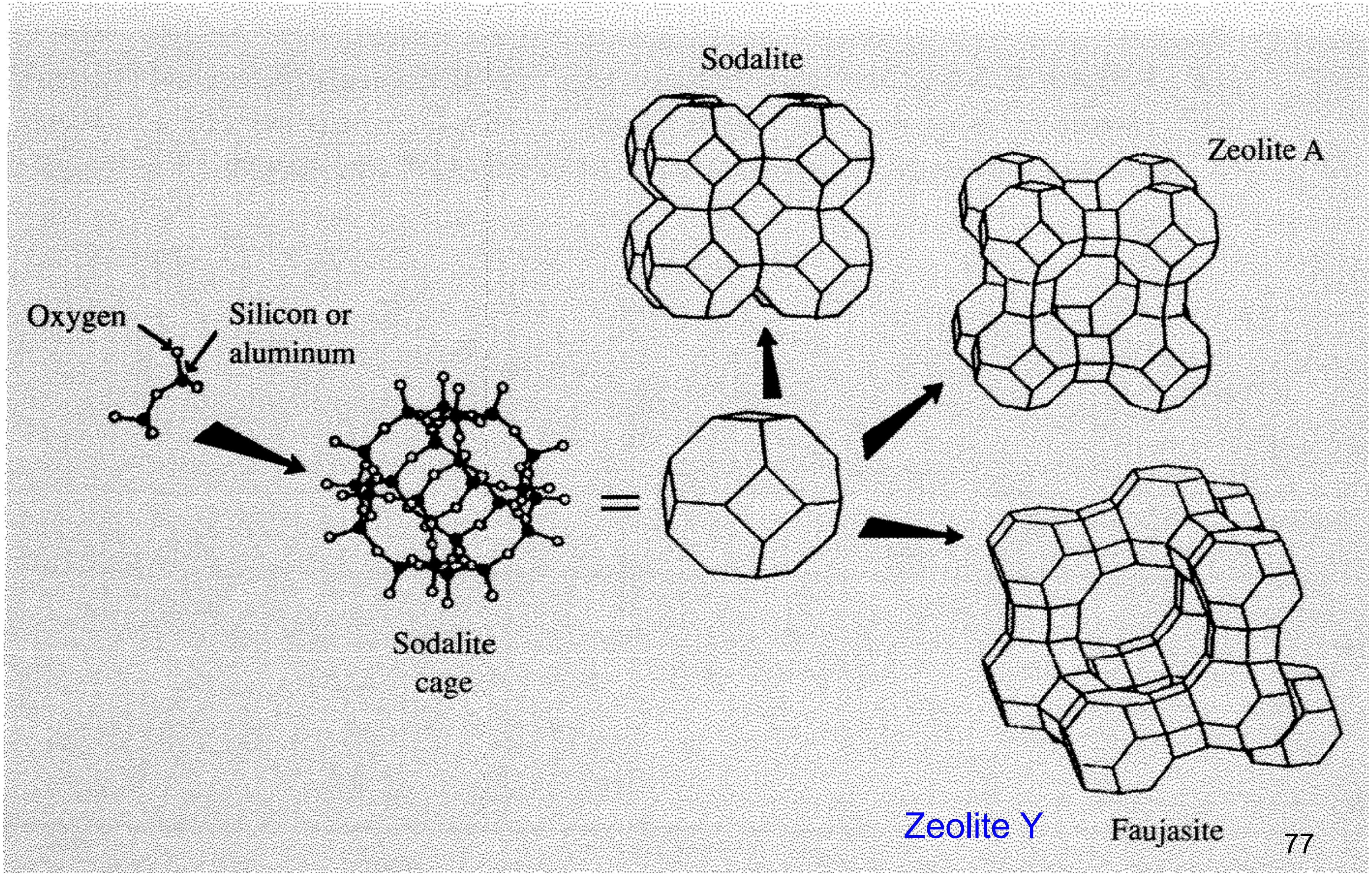
Catalysts studied [8]

Catalyst	Catalyst type	Zeolite trade name	Nominal cation form	Post-synthesis modification	Zeolite supplier
CAT-1	1.0 wt% Pt/USY	320 HOA	Sodium and ammonium	As received	Tosoh Corporation
CAT-2	1.0 wt% Pt/USY	350HOA	Ammonium	As received	Tosoh Corporation
CAT-3	1.0 wt% Pt/USY	320 HOA	Sodium and ammonium	AHFS treatment*	Tosoh Corporation
CAT-4	2.0 wt% Pt/USY	350HOA	Ammonium	As received	Tosoh Corporation
CAT-5	1.0 wt% Pt/Beta	CP814E	Ammonium	As received	Zeolyst International
CAT-6	1.0 wt% Pt/Beta	CP814C	Ammonium	As received	Zeolyst International

*0.6 g of ammonium hexafluorosilicate solution (AHFS, 99.999 wt% trace metal basis, Sigma-Aldrich) added in 2.0 g of zeolite and 50 ml of water is added. The contents are mixed for 1 h at a temperature of 25 °C. The solution is filtered and dried.

Catalyst	Si/Al (bulk molar)	N_2-BET (m^2/g)	Pore vol. (cm^3/g)	Pore size (Å)	Pt content (wt%)	Metal dispersion	NH_3-TPD (mmol/g)
CAT-1	2.90	735.87	0.39	34.52	0.83	0.149	0.30±0.01
CAT-2	5.55	872.97	0.47	26.10	0.90	–	0.76±0.01
CAT-3	5.65	818.98	0.45	31.43	0.94	–	1.05±0.01
CAT-4	5.55	872.97	0.47	26.10	1.46	–	0.76±0.01
CAT-5	13.21	577.48	0.85	72.70	1.07	0.307	0.63±0.01
CAT-6	20.10	643.24	0.32	22.22	1.03	0.501	0.30±0.01

Concept of zeolite structures [7a]

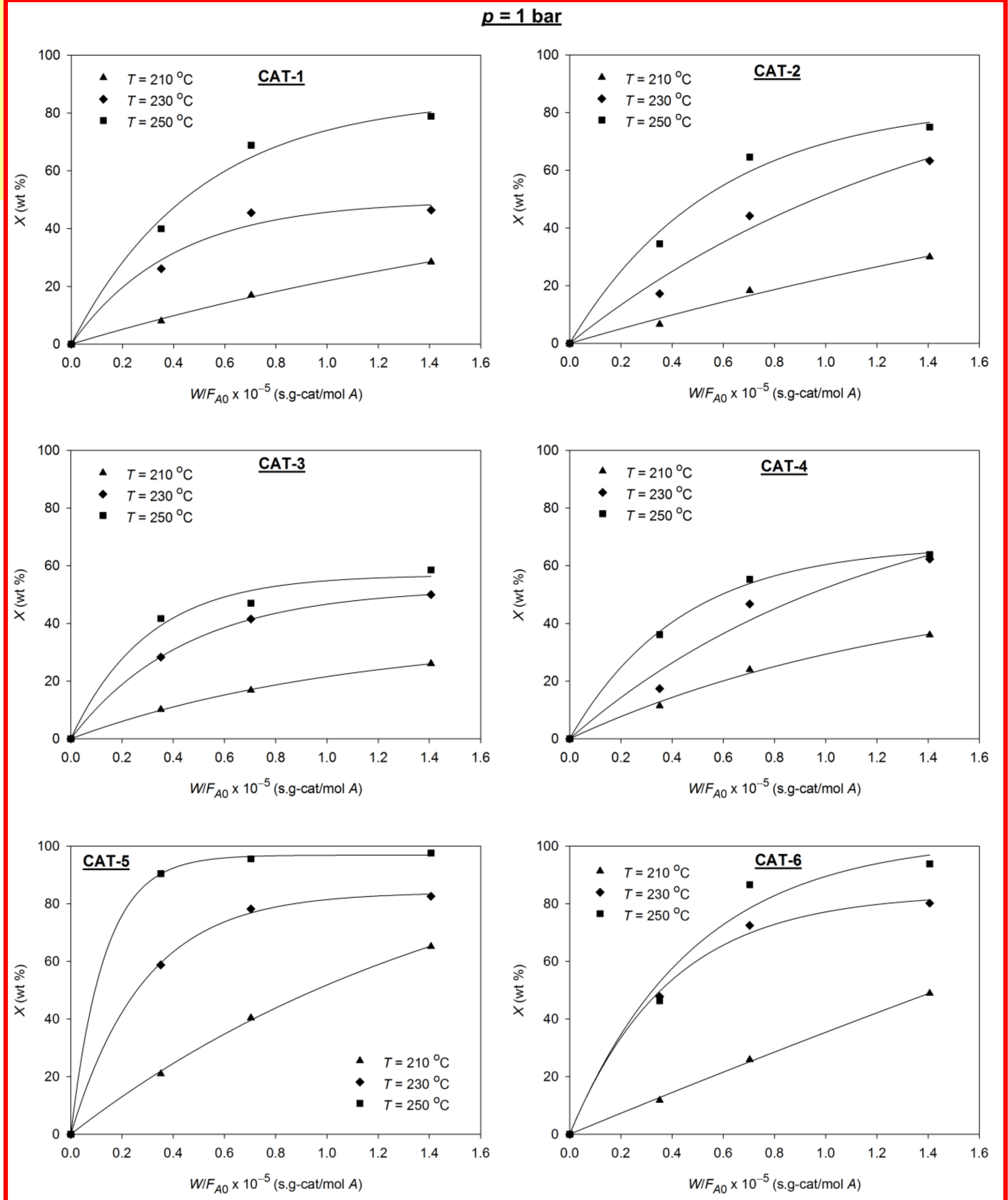


Zeolite Y

Activity results [8]

p = 1.0 bar

H_2/C_7H_{16} molar ratio = 9:1



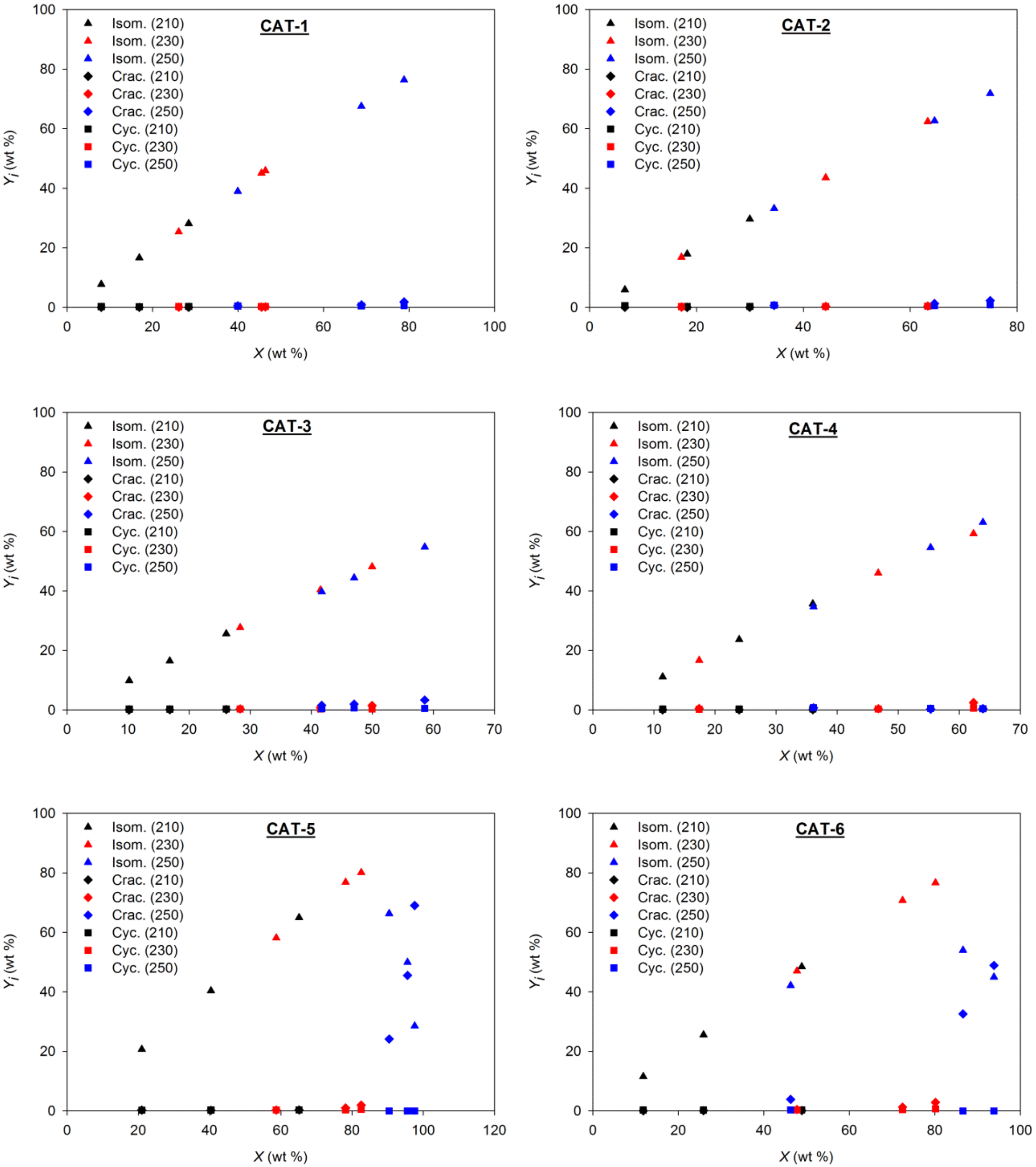
Selectivity results [8]

p = 1.0 bar

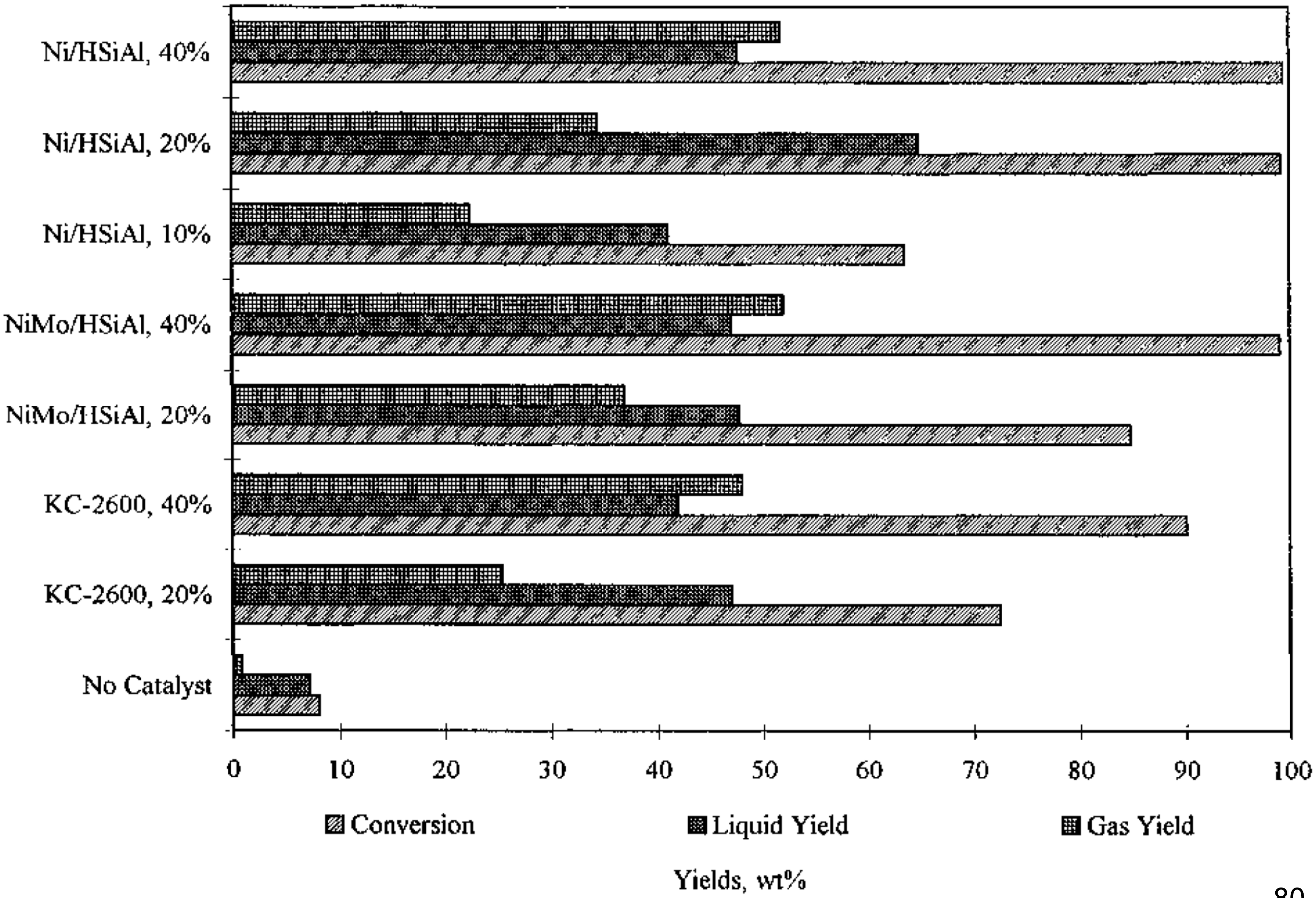
H_2/C_7H_{16} molar ratio = 9:1

Values in parentheses are temperatures in degrees Celsius

p = 1 bar

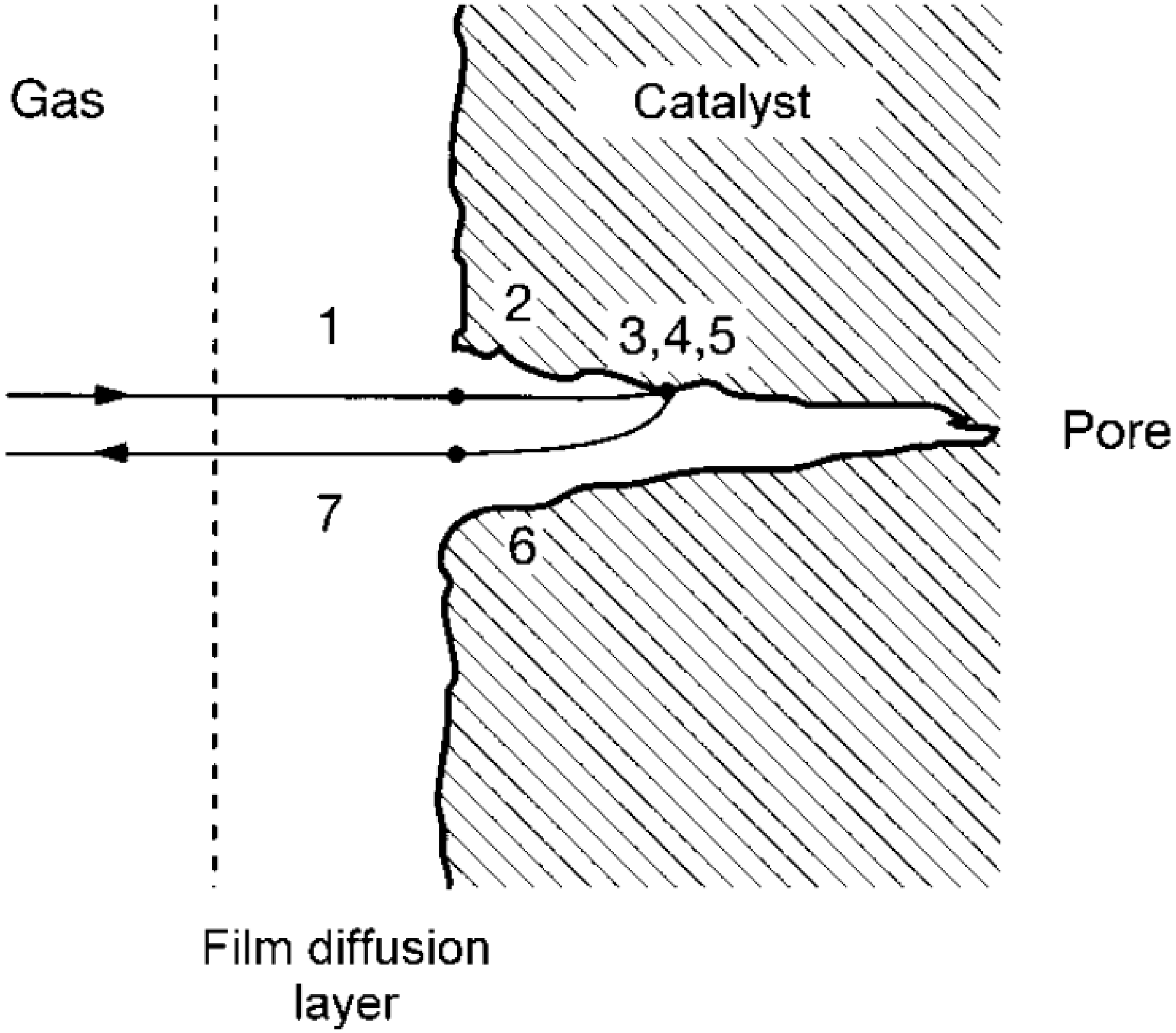


Hydrocracking of waste plastics [8a]



T = 375 ^{o}C, $p_{H2,0}$ = 7.0 MPa, t = 60 min, Reactor volume = 27 mL

Steps involved in a heterogeneous catalytic gas-solid reaction



Steps involved in a heterogeneous catalytic gas-solid reaction

1. Diffusion of reactant/s through external gas film to the catalyst surface.
2. Diffusion through pores of the catalysts.
3. Adsorption of the reactants on the surface of the catalyst (within the pores).
4. Surface chemical reaction on the catalytic surface.
5. Desorption of the reaction products from the catalyst surface.
6. Diffusion of the reaction products through the pores back to the external surface.
7. Diffusion of the products into the gas phase.

Intrinsic and global rates of reaction

✓When mass transfer resistances are also considered in the development of a rate equation, the rate of the corresponding chemical reaction is known as global rate.

✓When the external and internal diffusions are removed or highly reduced, the rate of a gas-solid reaction is based only on the intrinsic kinetics.

The intrinsic kinetics of a gas-solid reaction involves only the following three steps as outlined in the previous slide.

✓Adsorption of the reactants on the surface of the catalyst (within the pores)

✓Surface chemical reaction on the catalytic surface

✓Desorption of the reaction products from the catalyst surface

Common kinetic models

- ✓ The power law (PL) kinetics
- ✓ The Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics
- ✓ The Eley-Rideal (ER) kinetics

The power law kinetics

The power law is an empirical kinetic model and assumes homogenous gas-solid reaction.

See the following article in favor of the power law.

Weller, S. (1956). Analysis of kinetic data for heterogeneous reactions. AIChE J. 2, 59–62.

The power law kinetics

For the reaction

$$aA + bB \rightarrow cC + dD$$

According to the law of mass action, a rate equation can be written as:

$$(-r_A) = k \cdot C_A^a \cdot C_B^b$$

The sum of *a* and *b* is called overall order of the reaction.

Eq. 3 (from the law of mass action) seldom represents the true rate of a reaction and in most of the cases, rate equation has to be found empirically.

The power law kinetics

For the power law, the empirical rate equation my be of the type

$$(-r_A) = k \cdot C_A^{n1} \cdot C_B^{n2}$$

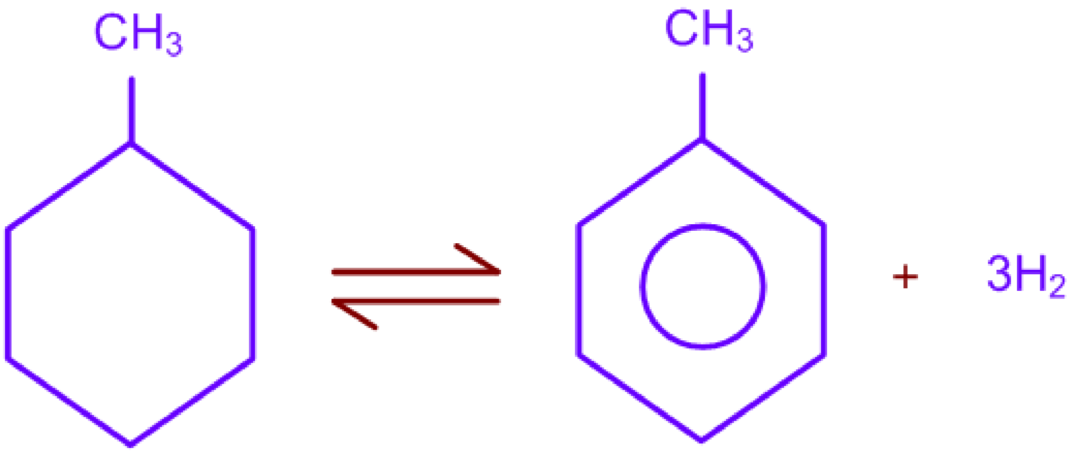
Where, sum of n_1 and n_2 is called the overall order of the reaction and may be denoted as n.

n_1 and n_2 are not necessarily be equal to a and b in the above equation. It happens rarely when reaction is elementary in nature.

What are elementary and non-elementary reactions?

The power law kinetics

For the dehydrogenation of methylcyclohexane to toluene



$$A = B + 3C$$

Assuming irreversible reaction (for the forward reaction only), the power law rate equation may be written as:

$$(-r_A) = k \cdot C_A^n$$

The power law kinetics

As the reaction is a gas-phase chemical reaction:

$$(-r_A) = k \cdot p_A^n$$

The parameter *k* and *n* are the regression parameters to be found (fitted) against the experimental data.

Rate constant *k* is described as a function of temperature and usually represented by the Arrhenius equation, the above equation will be used with Arrhenius equation and additional parameters (Arrhenius parameters) are also to be fitted.

Arrhenius equation

Arrhenius equation is frequently applied to approximate the temperature dependency of reaction rate and the rate constant or velocity constant, *k*, is related to temperature, *T*, by the following expression:

$$\boxed{\frac{d\ln k}{dT} = \frac{E_a}{RT^2}}$$

$$\boxed{k = k_0 \cdot e^{-\frac{E_a}{RT}}}$$

en.wikipedia.org

k_0 = pre-exponential factor and has units similar to that of k
E_a = activation energy, $\mathrm{J \cdot mol^{-1}}$

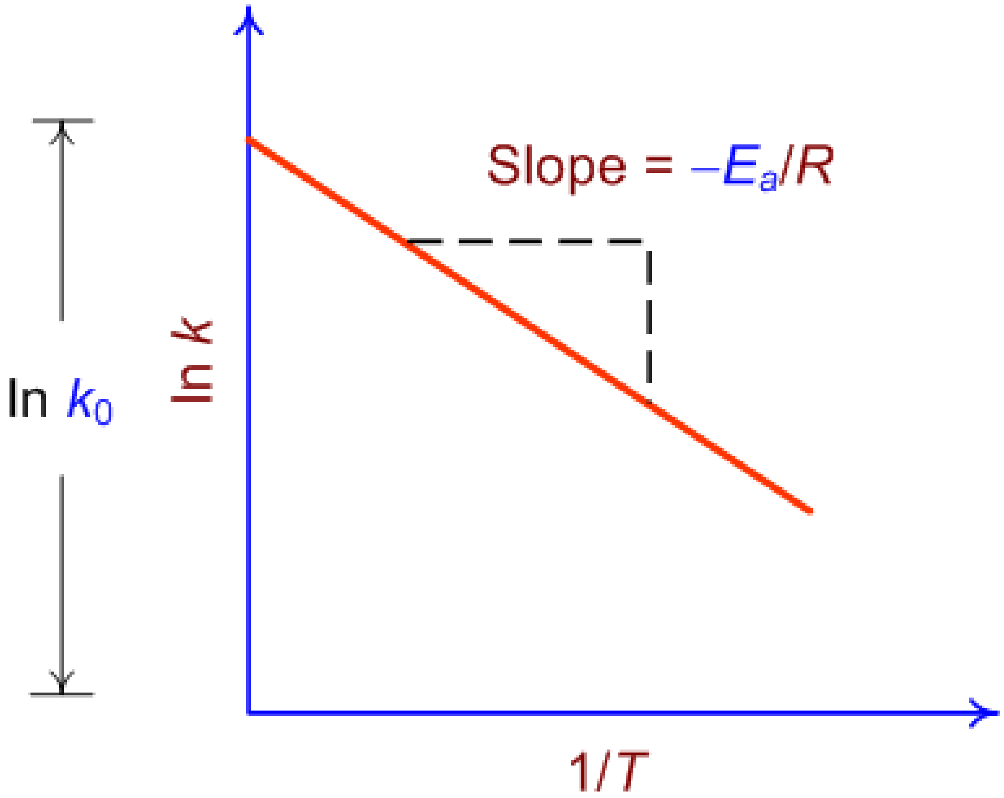
Arrhenius equation

- ✓ Reactions having large value of E_a are more temperature sensitive while with low value of E_a are less temperature dependent
- ✓ E_a and k_0 are called Arrhenius parameters. To estimate the effect of temperature on the rate of a chemical reaction, the values of Arrhenius parameters are to be known, otherwise experimental data of rate vs temperature can be used to calculate the parameters.
- ✓ Arrhenius equation may be written in terms of two rate constants and two temperatures:

$$\boxed{\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\cdot\left(\frac{1}{T_1} - \frac{1}{T_2}\right)}$$

Arrhenius plot

A plot of ln$k$ vs 1/T will be straight line, the slope of which is E_a/R. The SI unit of the slope is K. A large slope of Arrhenius plot means large value of E_a and vice versa.



Developing a rate equation

- ✓Experimental data is required where experiments may be carried out in a batch reactor, semi-batch reactor, CSTR, or a tubular reactor system
- ✓Data can be obtained under differential or integral conditions
- ✓A small enough particle size is used so as to minimize the diffusion limitations (intrinsic kinetics). External diffusion limitations are also required to be eliminated
- ✓For simplicity of calculations and more reliable results, attempts are made to have an isothermal reactor. This may be done in PFR by diluting the catalyst bed with inert particles. Gradientless reactors may be required
- ✓Experiments are performed over a stable catalyst, otherwise the effect of time is to be incorporated in the rate equation

Go to the laboratory to generate some experimental reaction data or obtain from a reliable source

Developing a rate equation

The experimental data is fitted against the appropriate rate model

✓The basic performance equation as that of a batch reactor, CSTR, or PFR is required. The solution of the performance equation requires a rate expression

✓A rate equation is assumed and the experimental data is fitted to obtain the model parameters

✓Various rate equations based on various kinetic models, e.g., the power law model, LHHW kinetics, and ER kinetics are assumed. Each rate equation is fitted with the experimental data and the kinetically and statistically best-fit equation is the rate equation for the experimental data.

Developing a rate equation

✓Sum of squares of the errors (SSE) is the common objective function to be minimized. F-value, residual plot, t-values of the parameters, 95% confidence intervals of the parameters, and correlation matrix of the parameters are the common statistical tools required to discriminate the rival models.

✓Both linear and non-linear regressions may be applied

✓Excel using the Solver tool, Polymath (available in a CD with book of Elements of Chemical Reaction Engineering, by H. S. Fogler, 3rd ed., Prentice-Hall, 1999), SigmaPlot, TableCurve 2D, and subroutines made in FORTRAN and MATLAB may be used for the regression of the data.

Basic performance equations of flow reactors

CSTR (100% backmixed reactor) system

PFR (one-dimensional pseudo-homogeneous reactor) system

$$\frac{W}{F_{A0}} = \frac{X_A}{(-r_A)}$$

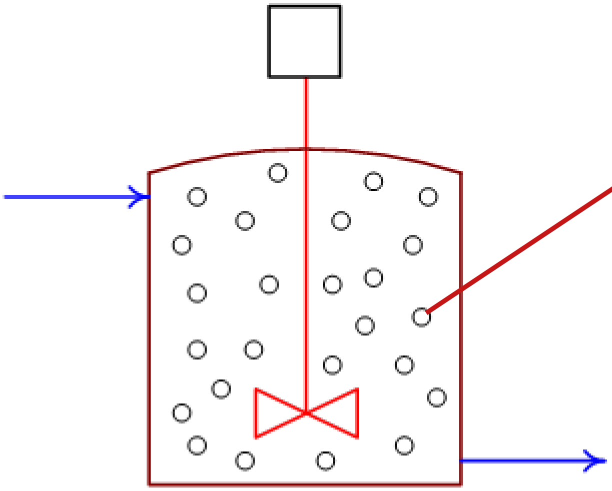
Fractional conversion of *A*

$$\frac{dX_A}{d\left(\frac{W}{F_{A0}}\right)} = (-r_A)$$

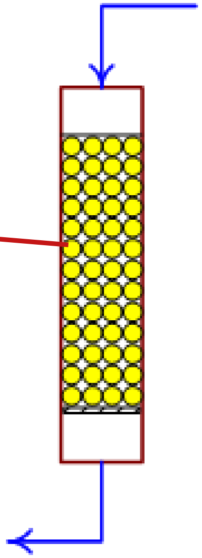
Weight of catalyst, kg

Initial molar flowrate of the limiting reactant, mol/s

Weight of catalyst, kg



Catalyst



$$\frac{W}{F_{A0}} = \int_0^{X_A} \frac{dX_A}{(-r_A)}$$

Example 1: Fitting the experimental data in a CSTR

The experimental data given below for the dehydrogenation of methylcyclohexane (MCH) is generated in a catalytic continuous stirred tank reactor (CSTR) under integral conditions. Using power law kinetics for the irreversible reaction, fit the experimental data and find out the kinetic parameters.

$$\frac{W}{F_{A0}} = \frac{X_A}{(-r_A)} \quad \longrightarrow \quad X_A = \frac{W}{F_{A0}}(-r_A)$$

Example 1: Laboratory experimental data

RUN No.	Fmch,0	Fhyd,0	Fhyd,0/Fmch,0	W/Fmch,0	(W/Fmch,0) $\times 10^{-5}$	Target T	Tave	Tave	*Xave*
	mol/min	mol/s	—	(g·s)/mol	(g·s)/mol	°C	°C	K	—
1	0.25	2.74E-04	8.3774	61875.8	0.6187584	380	377.72	650.87	0.119
2	0.125	1.37E-04	8.3774	123752	1.2375168	380	378.93	652.08	0.2005
3	0.5	5.47E-04	8.3774	30937.9	0.3093792	380	374.53	647.68	0.032
4	0.25	2.74E-04	8.3774	61875.8	0.6187584	380	378.73	651.88	0.063
5	0.25	0	0	61875.8	0.6187584	380	369.46	642.61	0.3405
6	0.125	0	0	123752	1.2375168	380	373.54	646.69	0.4895
7	0.5	0	0	30937.9	0.3093792	380	366.11	639.26	0.2135
8	0.063	0	0	245539	2.4553906	380	376.28	649.43	0.644
9	0.25	0	0	61875.8	0.6187584	430	412.57	685.72	0.6145
10	0.125	0	0	123752	1.2375168	430	418.44	691.59	0.855
11	0.5	0	0	30937.9	0.3093792	430	407.61	680.76	0.3845
12	0.063	0	0	245539	2.4553906	430	423.87	697.02	0.9745

Fitting of experimental data

Using the power law of the following form

$$(-r_A) = k \cdot p_A^n$$

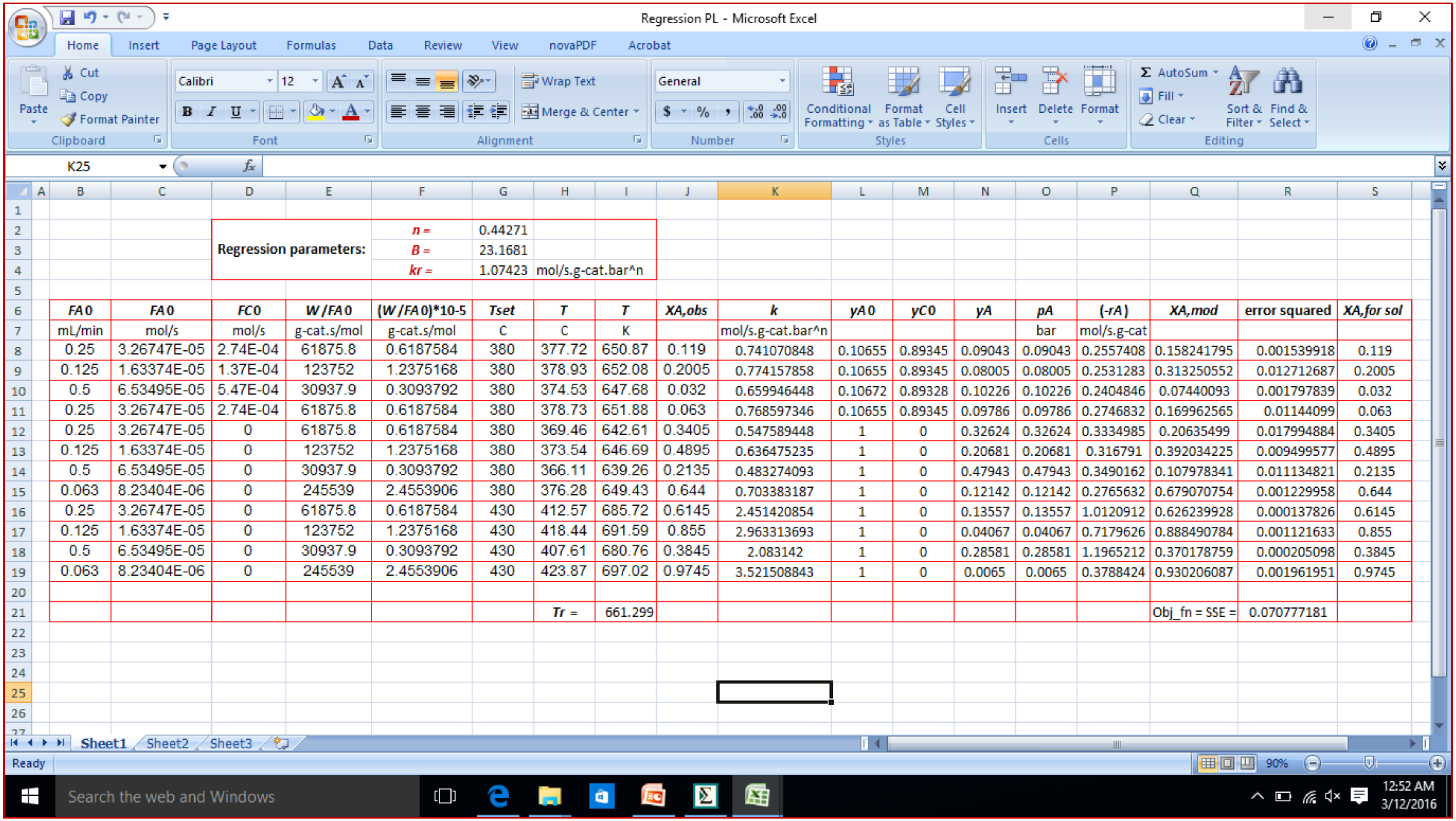
$$k = k_r \cdot \exp\left(B \cdot \left(1 - \frac{T_r}{T} \right) \right)$$

$$B = \frac{E}{R \cdot T_r}$$

Mole fractions in the vapor phase (reaction mixture) at conversion X_A

Component	Representation	Mole fraction
Methylcyclohexane	A	$\dfrac{y_{A0}\cdot(1-X_A)}{1+3\cdot y_{A0}\cdot X_A}$
Toluene	B	$\dfrac{y_{B0}+y_{A0}\cdot X_A}{1+3\cdot y_{A0}\cdot X_A}$
H_2	C	$\dfrac{y_{C0}+3\cdot y_{A0}\cdot X_A}{1+3\cdot y_{A0}\cdot X_A}$
Inert	I	$\dfrac{y_{I0}}{1+3\cdot y_{A0}\cdot X_A}$

Regression in MS Excel Solver Tool



Regression parameters:

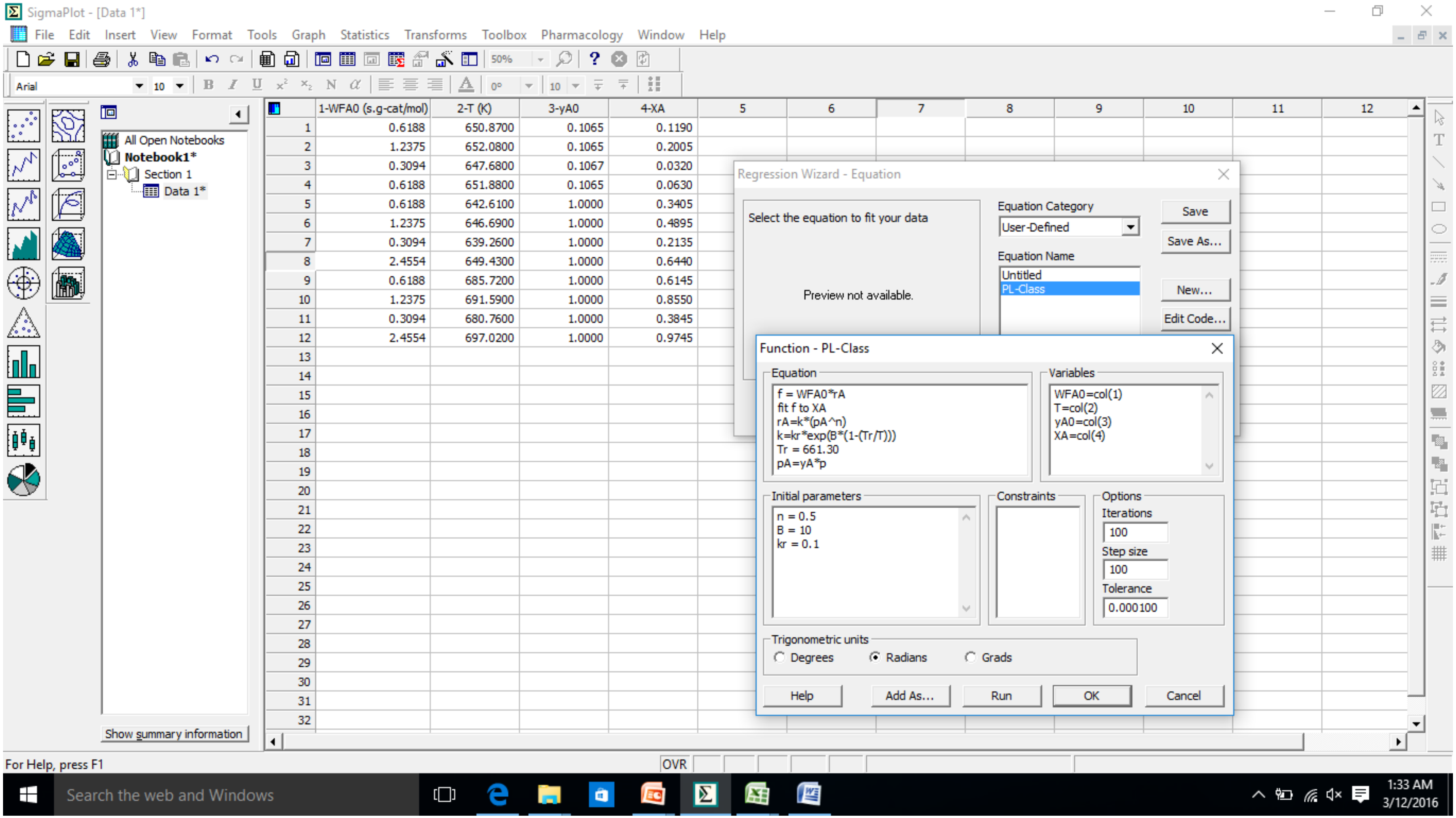
n = 0.44271

B = 23.1681

kr = 1.07423 mol/s.g-cat.bar^n

FA0	FA0	FC0	W/FA0	(W/FA0)*10-5	Tset	T	T	XA,obs	k	yA0	yC0	yA	pA	(-rA)	XA,mod	error squared	XA,for sol
mL/min	mol/s	mol/s	g-cat.s/mol	g-cat.s/mol	C	C	K		mol/s.g-cat.bar^n				bar	mol/s.g-cat			
0.25	3.26747E-05	2.74E-04	61875.8	0.6187584	380	377.72	650.87	0.119	0.741070848	0.10655	0.89345	0.09043	0.09043	0.2557408	0.158241795	0.001539918	0.119
0.125	1.63374E-05	1.37E-04	123752	1.2375168	380	378.93	652.08	0.2005	0.774157858	0.10655	0.89345	0.08005	0.08005	0.2531283	0.313250552	0.012712687	0.2005
0.5	6.53495E-05	5.47E-04	30937.9	0.3093792	380	374.53	647.68	0.032	0.659946448	0.10672	0.89328	0.10226	0.10226	0.2404846	0.07440093	0.001797839	0.032
0.25	3.26747E-05	2.74E-04	61875.8	0.6187584	380	378.73	651.88	0.063	0.768597346	0.10655	0.89345	0.09786	0.09786	0.2746832	0.169962565	0.01144099	0.063
0.25	3.26747E-05	0	61875.8	0.6187584	380	369.46	642.61	0.3405	0.547589448	1	0	0.32624	0.32624	0.3334985	0.20635499	0.017994884	0.3405
0.125	1.63374E-05	0	123752	1.2375168	380	373.54	646.69	0.4895	0.636475235	1	0	0.20681	0.20681	0.316791	0.392034225	0.009499577	0.4895
0.5	6.53495E-05	0	30937.9	0.3093792	380	366.11	639.26	0.2135	0.483274093	1	0	0.47943	0.47943	0.3490162	0.107978341	0.011134821	0.2135
0.063	8.23404E-06	0	245539	2.4553906	380	376.28	649.43	0.644	0.703383187	1	0	0.12142	0.12142	0.2765632	0.679070754	0.001229958	0.644
0.25	3.26747E-05	0	61875.8	0.6187584	430	412.57	685.72	0.6145	2.451420854	1	0	0.13557	0.13557	1.0120912	0.626239928	0.000137826	0.6145
0.125	1.63374E-05	0	123752	1.2375168	430	418.44	691.59	0.855	2.963313693	1	0	0.04067	0.04067	0.7179626	0.888490784	0.001121633	0.855
0.5	6.53495E-05	0	30937.9	0.3093792	430	407.61	680.76	0.3845	2.083142	1	0	0.28581	0.28581	1.1965212	0.370178759	0.000205098	0.3845
0.063	8.23404E-06	0	245539	2.4553906	430	423.87	697.02	0.9745	3.521508843	1	0	0.0065	0.0065	0.3788424	0.930206087	0.001961951	0.9745
						Tr =	661.299								Obj_fn = SSE =	0.070777181	

Regression in SigmaPlot Software



	1-WFA0 (s.g-cat/mol)	2-T (K)	3-yA0	4-XA
1	0.6188	650.8700	0.1065	0.1190
2	1.2375	652.0800	0.1065	0.2005
3	0.3094	647.6800	0.1067	0.0320
4	0.6188	651.8800	0.1065	0.0630
5	0.6188	642.6100	1.0000	0.3405
6	1.2375	646.6900	1.0000	0.4895
7	0.3094	639.2600	1.0000	0.2135
8	2.4554	649.4300	1.0000	0.6440
9	0.6188	685.7200	1.0000	0.6145
10	1.2375	691.5900	1.0000	0.8550
11	0.3094	680.7600	1.0000	0.3845
12	2.4554	697.0200	1.0000	0.9745

Regression Wizard - Equation

Select the equation to fit your data

Preview not available.

Equation Category: User-Defined

Equation Name: Untitled, PL-Class

Function - PL-Class

Equation

```
f = WFA0*rA
fit f to XA
rA=k*(pA^n)
k=kr*exp(B*(1-(Tr/T)))
Tr = 661.30
pA=yA*p
```

Variables

```
WFA0=col(1)
T=col(2)
yA0=col(3)
XA=col(4)
```

Initial parameters

```
n = 0.5
B = 10
kr = 0.1
```

Constraints

Options

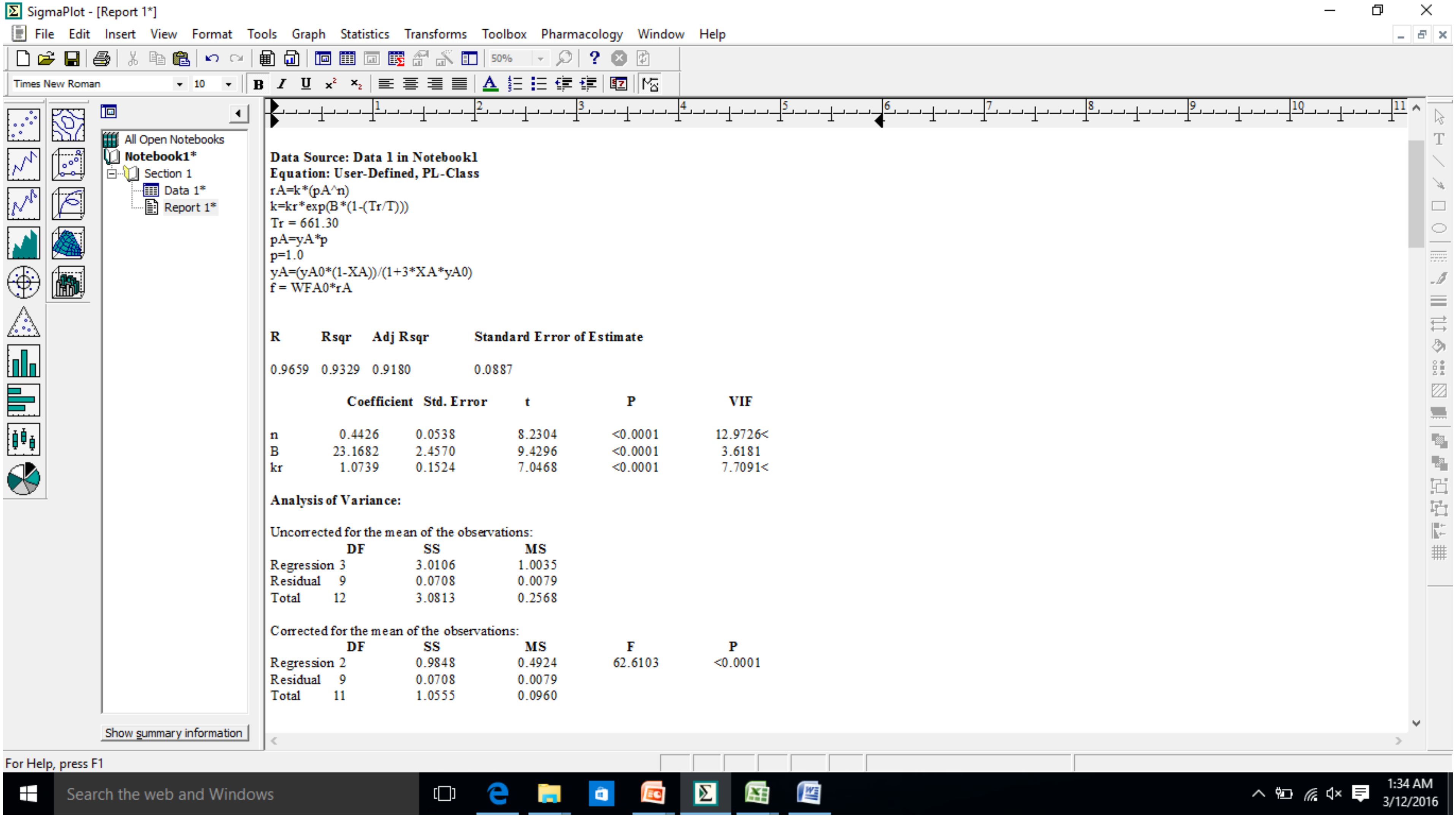
Iterations: 100

Step size: 100

Tolerance: 0.000100

Trigonometric units: ○ Degrees ● Radians ○ Grads

Regression in SigmaPlot Software



```
Data Source: Data 1 in Notebook1
Equation: User-Defined, PL-Class
rA=k*(pA^n)
k=kr*exp(B*(1-(Tr/T)))
Tr = 661.30
pA=yA*p
p=1.0
yA=(yA0*(1-XA))/(1+3*XA*yA0)
f = WFA0*rA


R        Rsqr     Adj Rsqr         Standard Error of Estimate

0.9659   0.9329   0.9180           0.0887

               Coefficient  Std. Error       t              P              VIF

n              0.4426       0.0538           8.2304         <0.0001        12.9726<
B              23.1682      2.4570           9.4296         <0.0001        3.6181
kr             1.0739       0.1524           7.0468         <0.0001        7.7091<

Analysis of Variance:

Uncorrected for the mean of the observations:
               DF           SS               MS
Regression 3                3.0106           1.0035
Residual   9                0.0708           0.0079
Total      12               3.0813           0.2568

Corrected for the mean of the observations:
               DF           SS               MS             F              P
Regression 2                0.9848           0.4924         62.6103        <0.0001
Residual   9                0.0708           0.0079
Total      11               1.0555           0.0960
```

Fitting of experimental data

Now assume the reversible reaction is also important, therefore, reversible kinetics are also included which is mostly true when high conversions are obtained during the experimentation. Including reversibility the following power law form may be used with the experimental data:

$$(-r_A) = k \cdot \left(p_{\mathrm{A}} - \frac{p_{\mathrm{B}} \cdot p_{\mathrm{C}}^3}{K_e} \right)^n$$

Where, K_e is reaction equilibrium constant. Only rate equation is changed, the rest of the procedure of fitting the data is the same.

Repeat Example 1 using the power law form shown above. Use SigmaPlot and compare the results with Example 1.

Example 2: Fitting the experimental data in a PFR

The experimental data given in the next slide for the dehydrogenation of methylcyclohexane (MCH) is generated in a plug flow reactor (PFR) under integral conditions. Using power law kinetics for the irreversible reaction, fit the experimental data and find out the kinetic parameters.

$$\frac{dX_A}{d\left(\frac{W}{F_{A0}}\right)} = (-r_A) \longrightarrow \frac{dX_A}{dW} = \frac{(-r_A)}{F_{A0}}$$

Example 2: Laboratory experimental data

Twall (°C)	*Tave* (°C)	*Tave* (K)	*p* (bar)	*Fmch0* (mol/s)	*Fhyd0* (mol/s)	*Fhyd0/ Fmch0*	*W/Fmch0* (s.g/gmol)	*ymch0*	*yhyd0*	*yimp0*	*Xmche*	*%Xmch*
360.6	324.6	597.786	1.013	3.23E-05	2.72E-04	8.428431	62185.22	0.106	0.893	0.0011	0.992	93.676
360.6	321.7	594.864	1.013	6.46E-05	5.45E-04	8.428431	31092.61	0.106	0.893	0.0011	0.991	62.878
360.6	338.1	611.2	1.013	1.62E-05	1.36E-04	8.428431	124370.4	0.106	0.893	0.0011	0.997	98.349
360.6	328.3	601.457	2	3.23E-05	3.41E-05	1.053554	62185.22	0.485	0.5105	0.0049	0.972	87.802
360.6	323	596.121	2	6.46E-05	6.81E-05	1.053554	31092.61	0.485	0.5105	0.0049	0.959	50.802
340.49	312.4	585.571	1.013	3.23E-05	2.72E-04	8.428431	62185.22	0.106	0.893	0.0011	0.982	78.1895
340.5	307.7	580.814	1.013	3.23E-05	3.41E-05	1.053554	62185.22	0.485	0.5105	0.0049	0.983	79.211
360.6	341.5	614.6	2	1.62E-05	1.70E-05	1.053554	124370.4	0.485	0.5105	0.0049	0.989	97.699
360.6	322.5	595.614	1.013	3.23E-05	3.41E-05	1.053554	62185.22	0.485	0.5105	0.0049	0.994	90.57
360.6	337.2	610.329	1.013	1.62E-05	1.70E-05	1.053554	124370.4	0.485	0.5105	0.0049	0.998	99.217
380.44	342.4	615.5	1.013	3.23E-05	2.72E-04	8.428431	62185.22	0.106	0.893	0.0011	0.998	97.622
340.5	312	585.143	1.013	3.23E-05	2.72E-04	8.428431	62185.22	0.106	0.893	0.0011	0.981	78.37
340.5	308.2	581.386	1.013	3.23E-05	3.41E-05	1.053554	62185.22	0.485	0.5105	0.0049	0.983	77.549
360.6	320.1	593.214	1.013	6.46E-05	6.81E-05	1.053554	31092.61	0.485	0.5105	0.0049	0.993	55.609
340.5	307	580.121	1.013	3.23E-05	0	0	62185.22	0.99	0	0.01	0.985	77.653
360.6	318.6	591.793	1.013	6.46E-05	0	0	31092.61	0.99	0	0.01	0.994	54.001
360.6	322.2	595.321	1.013	3.23E-05	0	0	62185.22	0.99	0	0.01	0.995	87.951
360.6	336.4	609.507	1.013	1.62E-05	0	0	124370.4	0.99	0	0.01	0.998	98.507
380.44	339.8	612.979	1.013	3.23E-05	3.41E-05	1.053554	62185.22	0.485	0.5105	0.0049	0.998	97.371
380.44	339.5	612.614	1.013	3.23E-05	0	0	62185.22	0.99	0	0.01	0.999	96.204
340.69	317.1	590.271	1.013	1.62E-05	1.70E-05	1.053554	124370.4	0.485	0.5105	0.0049	0.9914	98.241
340.69	307.9	581.093	1.013	6.46E-05	6.81E-05	1.053554	31092.61	0.485	0.5105	0.0049	0.9828	44.015
319.76	290.1	563.279	1.013	6.46E-05	0	0	31092.61	0.99	0	0.01	0.9453	35.4
340.69	304.5	577.621	1.013	6.46E-05	0	0	31092.61	0.99	0	0.01	0.9817	44.3

Example 2: Fitting the experimental data in a PFR

The regression with PFR requires differential equation to be solved. Euler or 4th order RK method can be used for this purpose. As discussed before subroutines made in FORTRAN and MATLAB may be used for the regression of the data. Try in Excel using Solver..

Chemical reaction equilibrium constant

- ✓ Experimental equilibrium constant may be found in the literature such as in a research article or a handbook

- ✓ When experimental K_e is not available it may be worked out in the laboratory

- ✓ Equilibrium constant can also be calculated using the values of Gibbs free energies of formation

Chemical reaction equilibrium constant

$$\ln K_e = \frac{-\Delta G^{\circ}(T)}{R \cdot T}$$

$$K_e = \exp\left(\frac{-\Delta G^{\circ}(T)}{R \cdot T}\right)$$

$$\Delta G^{\circ}(T) = -\sum \Delta G_i^{\circ}(T)$$

$$\frac{d \ln K_e}{dT} = \frac{\Delta H^{\circ}_{rxn}}{R \cdot T^2}$$

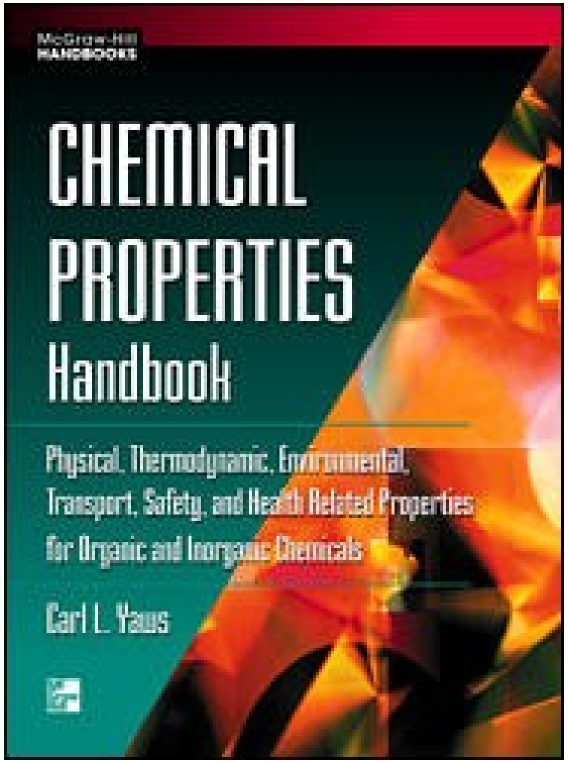
$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^{\circ}_{rxn}}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

G_i^{o} is a property of pure component *i* in its standard state at fixed pressure but depends on temperature

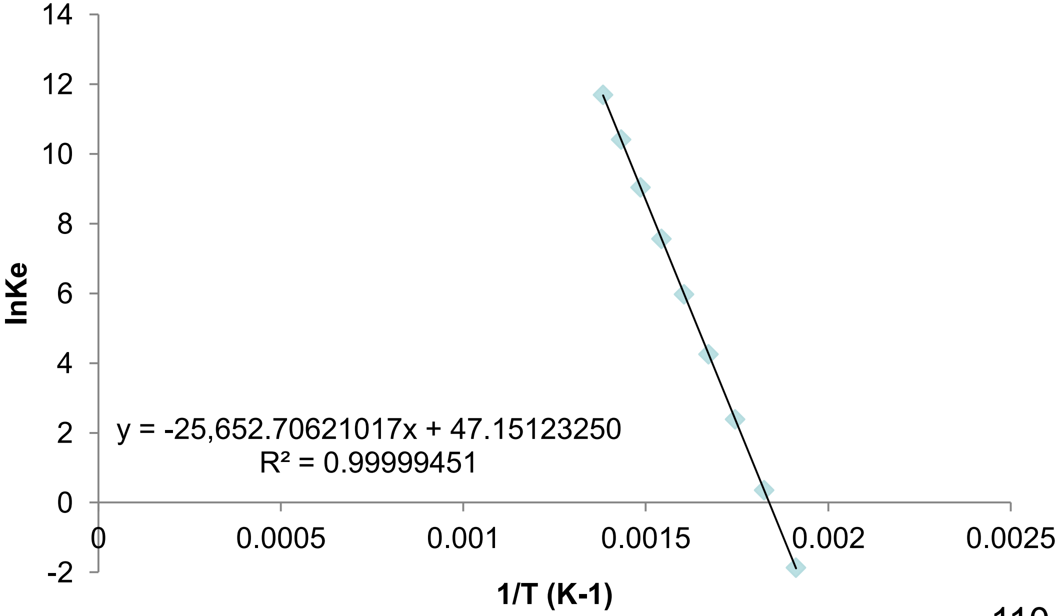
How can one calculate heat of reaction?

Determination of equilibrium constant (Using Gibbs free energies of formation)

When experimental equilibrium constant is not available, one can find from the information of Gibbs free energy of formation of each species. Please see references [10] and [10a].



Equilibrium constant for the dehydrogenation of MCH to toluene using the information of Gibbs free energies of formation from Yaws [10].



N.B.: Some people prefer to plot with 1000/*T* instead of 1/*T*

Example: Calculations for equilibrium composition

Calculate the equilibrium composition of the reaction dehydrogenation of methylcyclohexane carrying out at 5 bar and 380 °C with 50 mol% H_2 in the feed. The experimental equilibrium constant is given below [11a].

$$K_e = 3.60\times10^{3}\cdot\exp\left(\frac{-217650}{R}\left(\frac{1}{T}-\frac{1}{650}\right)\right)$$

K_e in bar^{3}, R in J·mol^{1}·K^{1}, and T in K

How can we find experimental equilibrium constant?

Calculations for equilibrium composition

$$K_e = \frac{p_{Be} \times (p_{Ce})^3}{p_{Ae}} = \frac{y_{Be} \times (y_{Ce})^3}{y_{Ae}} \times p^3$$

Component	Representation	Mole fraction
Methylcyclohexane	A	$\frac{y_{A0} \cdot (1 - X_{Ae})}{1 + 3 \cdot y_{A0} \cdot X_{Ae}}$
Toluene	B	$\frac{y_{B0} + y_{A0} \cdot X_{Ae}}{1 + 3 \cdot y_{A0} \cdot X_{Ae}}$
H_2	C	$\frac{y_{C0} + 3 \cdot y_{A0} \cdot X_{Ae}}{1 + 3 \cdot y_{A0} \cdot X_{Ae}}$
Inert	I	$\frac{y_{I0}}{1 + 3 \cdot y_{A0} \cdot X_{Ae}}$

Calculations for equilibrium composition

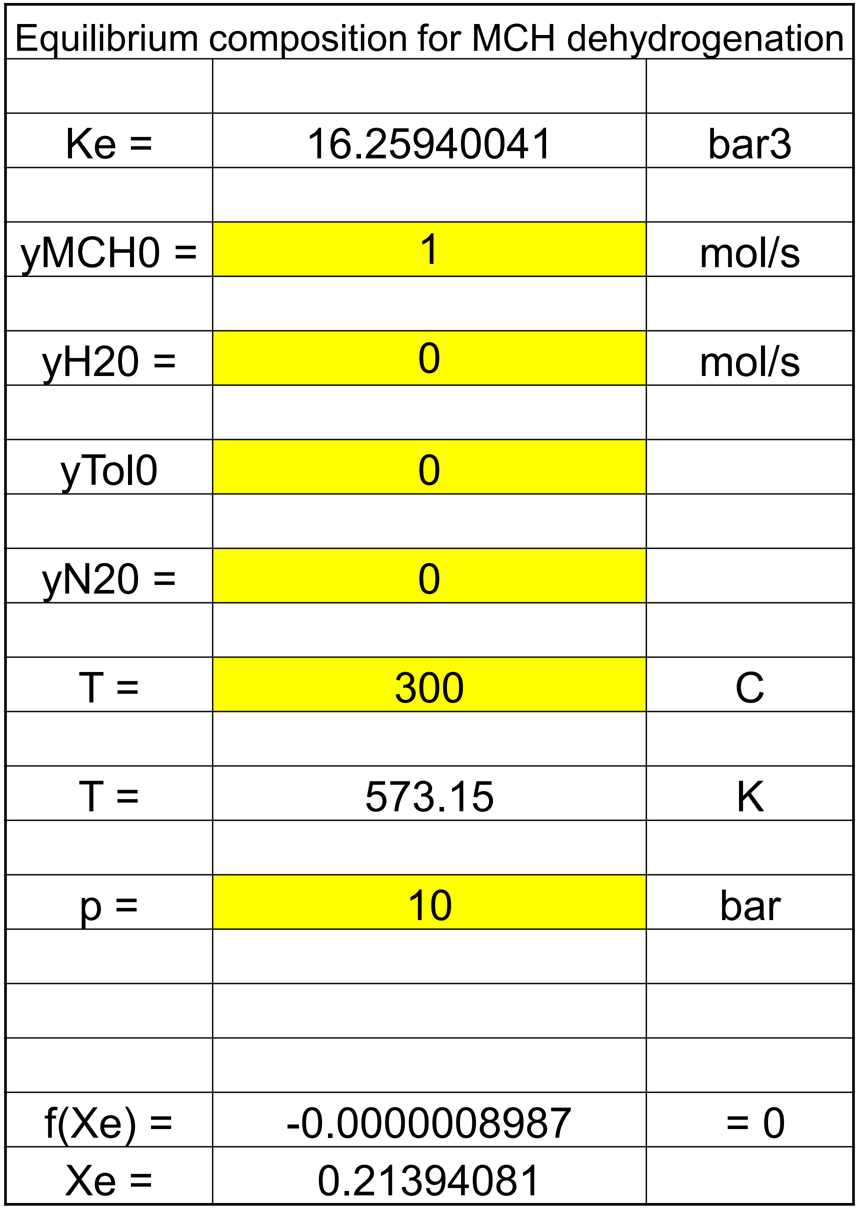
$$\frac{\left(\frac{(y_{B0}+X_{Ae}\cdot y_{A0})}{1}\right)\times\left(\frac{y_{C0}+3\cdot X_{Ae}\cdot y_{A0}}{1+3\cdot X_{Ae}\cdot y_{A0}}\right)^3\times p^3}{\left(\frac{(y_{A0}-X_{Ae}\cdot y_{A0})}{1}\right)}-K_e=0$$

$$\frac{\left(\frac{(y_{B0}+X_{Ae}\cdot y_{A0})}{1}\right)\times\left(\frac{y_{C0}+3\cdot X_{Ae}\cdot y_{A0}}{1+3\cdot X_{Ae}\cdot y_{A0}}\right)^3\times p^3}{\left(\frac{(y_{A0}-X_{Ae}\cdot y_{A0})}{1}\right)}-3600\cdot\exp\left(\frac{-217650}{8.31434}\left(\frac{1}{T}-\frac{1}{650}\right)\right)=0$$

Put p in bar *and T in* K.

We need such a value of X_{Ae} that LHS equals RHS, i.e., LHS becomes equal to zero.

Calculations for equilibrium composition (MS Excel Solver application)



Equilibrium composition for MCH dehydrogenation		
Ke =	16.25940041	bar3
yMCH0 =	1	mol/s
yH20 =	0	mol/s
yTol0	0	
yN20 =	0	
T =	300	C
T =	573.15	K
p =	10	bar
f(Xe) =	-0.0000008987	= 0
Xe =	0.21394081	

Inputs

Class activity

Acetone can be produced from isopropyl alcohol in a fixed bed reactor according to the following gas phase reaction

$$(CH_3)_2CHOH \rightarrow (CH_3)_2CO + H_2$$

For each of the reactant species, find out the mole fraction relationship in terms of initial mole fractions and fractional conversion (X) at any length in the reactor.

You may consider $(CH_3)_2CHO = A$, $(CH_3)_2CO = B$, and $H_2 = C$

Class activity

For the simultaneous gas phase reactions

$$2NO + O_2 \rightarrow 2NO_2$$

$$NO_2 + NO + 2NH_3 \rightarrow 2N_2 + 3H_2O$$

for each of the reactant species, find out the mole fraction (at any length/time in the reactor) relation in terms of initial mole fraction and conversion or yield.

You may consider $NO = A$, $O_2 = B$, $NO_2 = C$, $NH_3 = D$, $N_2 = E$, and $H_2O = F$.

Homework problem

Ethylbenzene is produced by the alkylation of benzene as shown in the following simultaneous chemical reactions. Workout the relationship for mole fraction of each species involved in the reaction in terms of initial mole fractions. Use X_{I} and X_{II} as the fractional conversions for the first and the second chemical reactions, respectively.

$$\underset{\text{benzene}}{C_6H_6} + \underset{\text{ethylene}}{C_2H_4} \rightarrow \underset{\text{ethylbenzene}}{C_6H_5C_2H_5} \qquad \mathrm{I}$$

$$\underset{\text{ethylbenzene}}{C_6H_5C_2H_5} + \underset{\text{ethylene}}{C_2H_4} \rightarrow \underset{\text{diethylbenzene}}{C_6H_4(C_2H_5)_2} \qquad \mathrm{II}$$

Homework problems

1. For the gas phase reaction

$$CO + NO \rightarrow CO_2 + \frac{1}{2} N_2 ,$$

for each of the reactant species, find out the mole fraction (at any length/time in the reactor) relation in terms of initial mole fractions and fractional conversion (X).

You may consider $CO = A$, $NO = B$, $CO_2 = C$, and $N_2 = D$.

Also write down the equilibrium constant in terms of equilibrium conversion and mole fractions of the reacting species.

2. For the gas phase reaction

$$NO + \frac{1}{2} O_2 \rightarrow NO_2 ,$$

for each of the reactant species, find out the mole fraction (at any length/time in the reactor) relation in terms of initial mole fractions and fractional conversion (X).

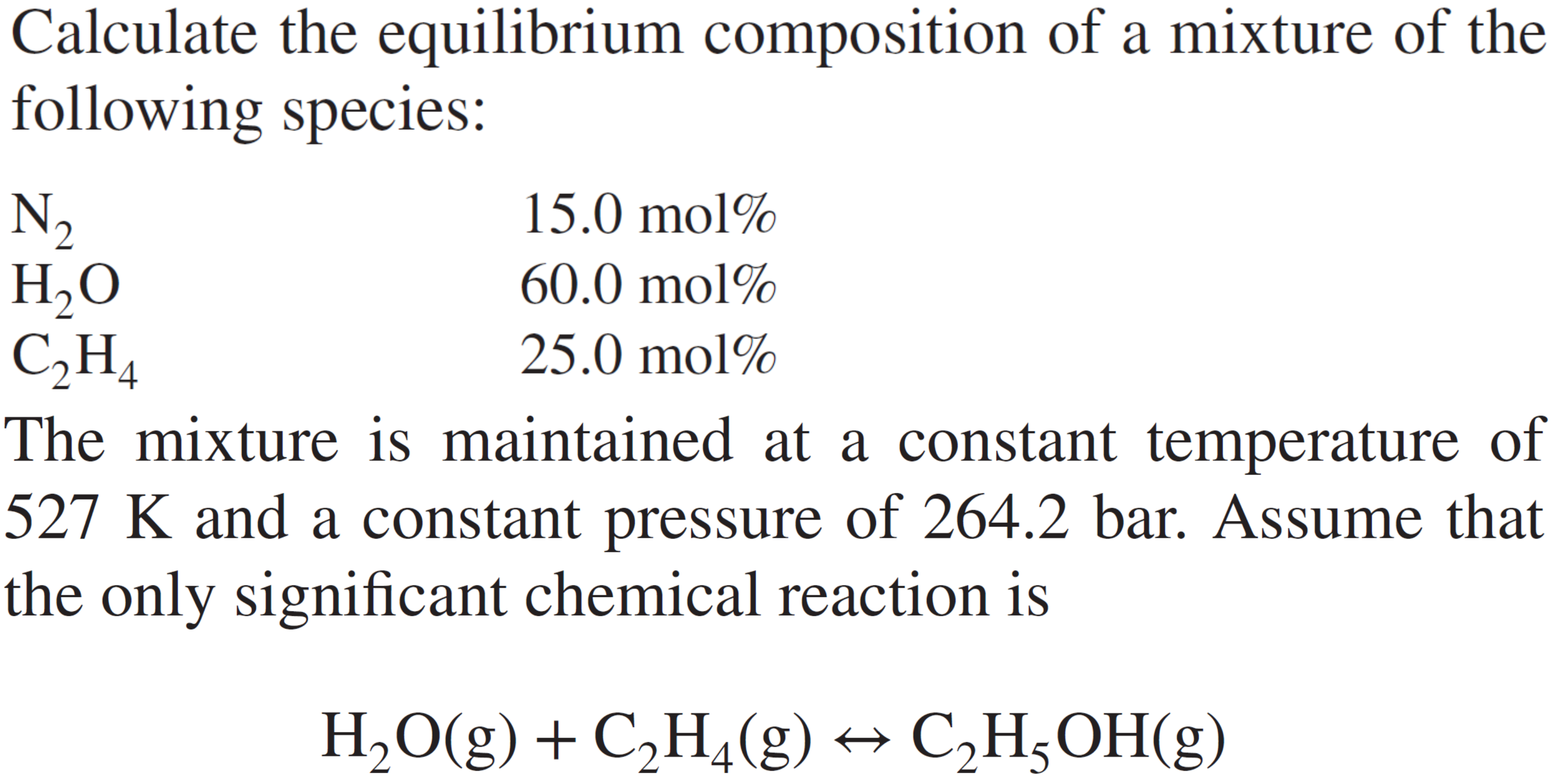
You may consider $NO = A$, $O_2 = B$, and $NO_2 = C$.

Also write down the equilibrium constant in terms of equilibrium conversion and mole fractions of the reacting species.

Homework problems

Calculate the equilibrium composition of the reaction dehydrogenation of cyclohexane to benzene carrying out at 10 bar and 350 °C with 10 mol% H_2 and 30 mol% N_2 in the feed along with cyclohexane.

Hint: Consider ideal gas conditions and avoid fugacity calculations.



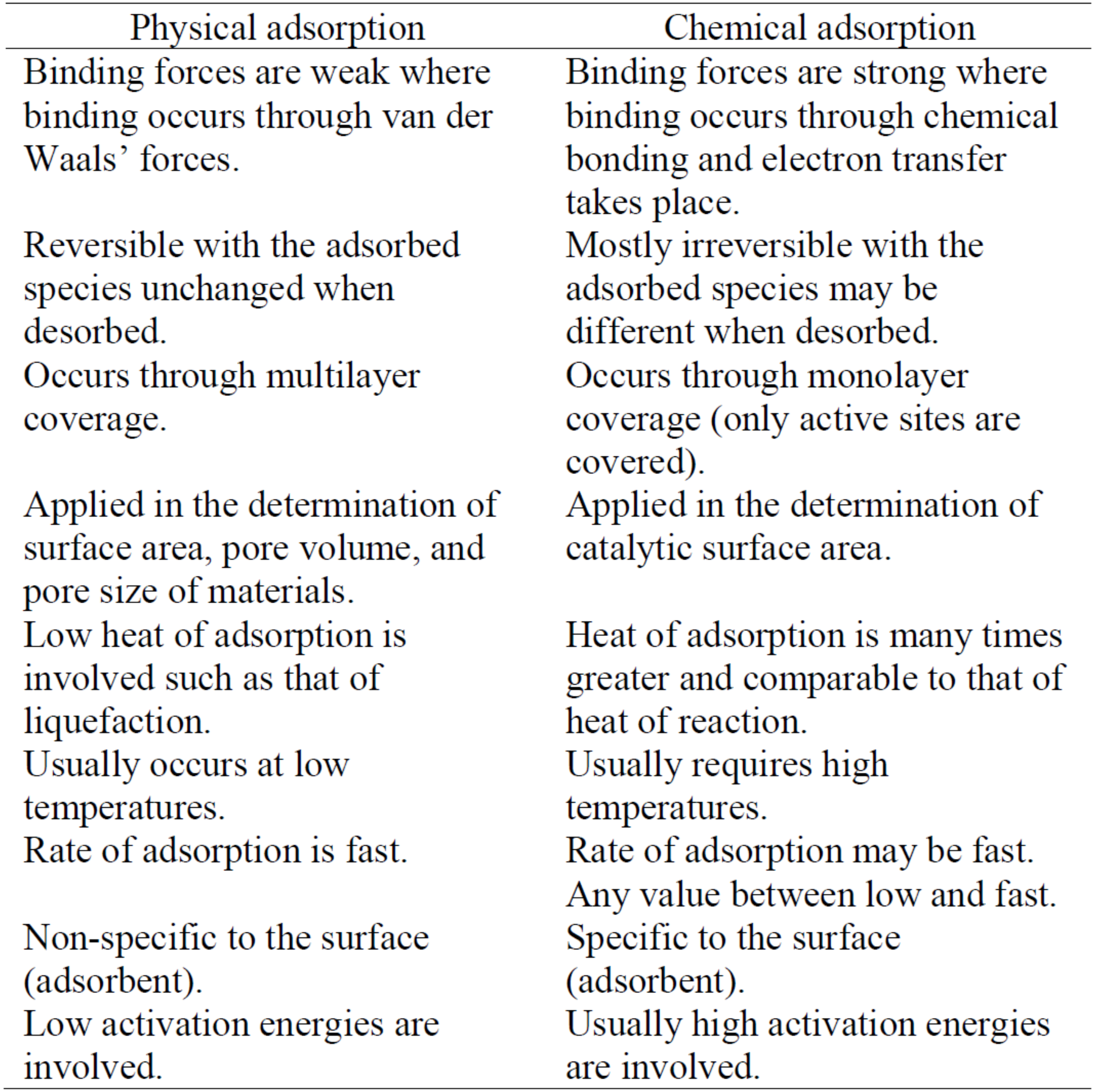
Calculate the equilibrium composition of a mixture of the following species:

N_2	15.0 mol%
H_2O	60.0 mol%
C_2H_4	25.0 mol%

The mixture is maintained at a constant temperature of 527 K and a constant pressure of 264.2 bar. Assume that the only significant chemical reaction is

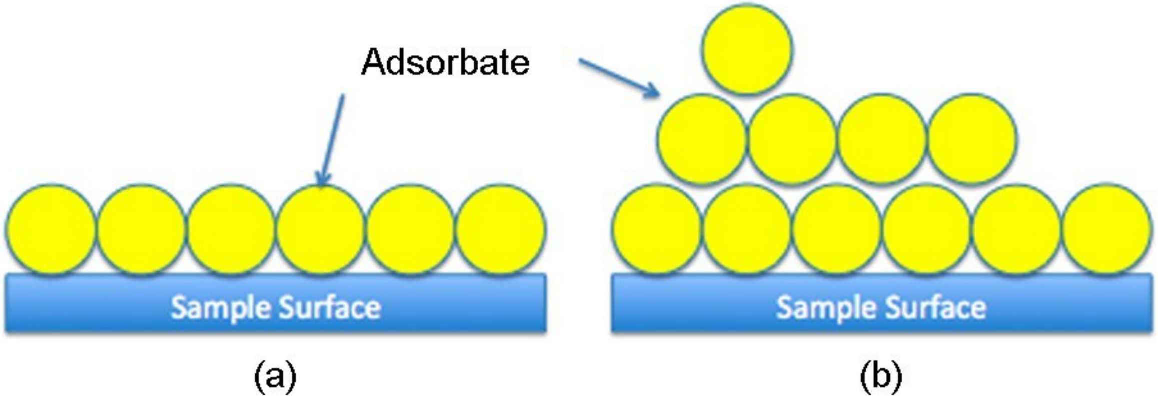
$$H_2O(g) + C_2H_4(g) \leftrightarrow C_2H_5OH(g)$$

Physical and chemical adsorption



Physical adsorption	Chemical adsorption
Binding forces are weak where binding occurs through van der Waals' forces.	Binding forces are strong where binding occurs through chemical bonding and electron transfer takes place.
Reversible with the adsorbed species unchanged when desorbed.	Mostly irreversible with the adsorbed species may be different when desorbed.
Occurs through multilayer coverage.	Occurs through monolayer coverage (only active sites are covered).
Applied in the determination of surface area, pore volume, and pore size of materials.	Applied in the determination of catalytic surface area.
Low heat of adsorption is involved such as that of liquefaction.	Heat of adsorption is many times greater and comparable to that of heat of reaction.
Usually occurs at low temperatures.	Usually requires high temperatures.
Rate of adsorption is fast.	Rate of adsorption may be fast. Any value between low and fast.
Non-specific to the surface (adsorbent).	Specific to the surface (adsorbent).
Low activation energies are involved.	Usually high activation energies are involved.

Concept of multilayer adsorption



(a) Monolayer adsorption

(b) Multilayer adsorption

http://archive.cnx.org/

Dissociative and non-dissociative adsorption

Adsorption of a component may be non-dissociative or dissociative. The previous case is for non-dissociative adsorption.

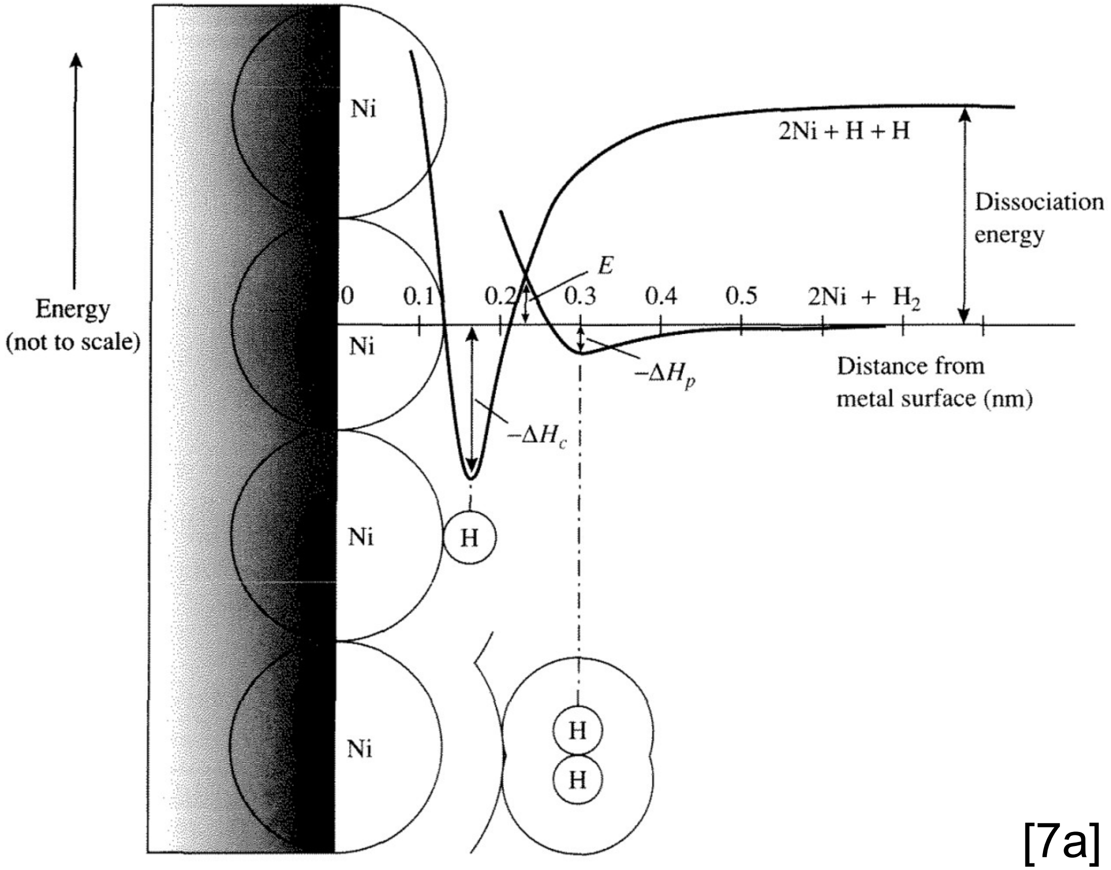
In non-dissociative case, the molecule is adsorbed as a whole and it may be called as molecular adsorption.
In dissociative adsorption, the molecule such as of H_2 is dissociated into H-H form and adsorbed. Of course the dissociative case requires 2 sites for the adsorption.

Non-dissociative: $H_2 + s \Leftrightarrow H_2 \cdot s$

Dissociative: $H_2 + 2s \Leftrightarrow 2H \cdot s$

Activated and non-activated adsorption

For activated adsorption, rate of adsorption is dependent upon temperature. It requires some activation energy before the component is adsorbed. Chemisorption is usually activated adsorption. Non-activated adsorption or ordinary adsorption does not depend upon temperature therefore activation energy is zero.



[7a]

Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics

✓The Langmuir-Hinshelwood-Hougen-Watson (LHHW) approach accounts for the surface concentrations of the species taking part in the reaction.

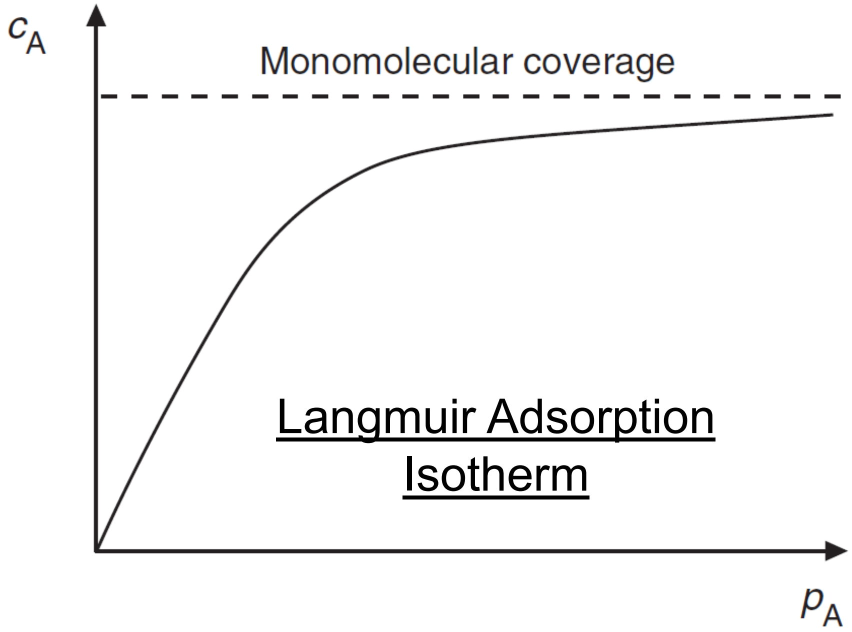
✓Relating surface species to the observed species partial pressures in the gas phase provides equations that can be fitted to the kinetic data.

✓Based on the Langmuir adsorption isotherm, the approach was first developed by Hinshelwood and therefore sometimes termed as Langmuir-Hinshelwood kinetics. Hougen and Watson [1943] developed a similar approach and popularize the Langmuir-Hinshelwood kinetics.

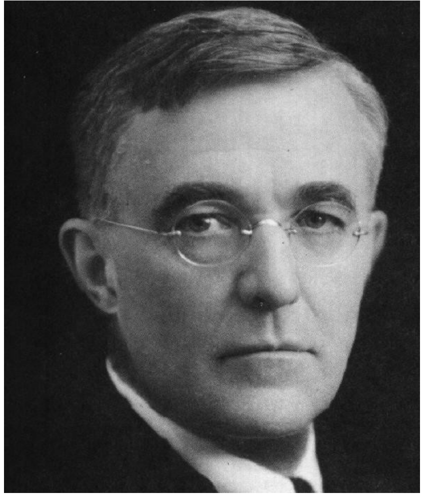
✓The LHHW approach assumes that all active sites are energetically uniform and, upon adsorption, adsorbed species do not interact (except for surface reaction) with species already adsorbed.

Langmuir-Hinshelwood-Hougen-Watson (LHHW) kinetics

- ✓Active sites have similar kinetic and thermodynamic characteristics and the entropy and enthalpy of adsorption are constant and not functions of the adsorbed amount.
- ✓The species adsorption restricts itself to only monolayer coverage and the rate of adsorption is proportional to the concentration of the active sites not occupied (empty) and the partial pressure of the component in the gas phase.



http://langmuir.nmt.edu/

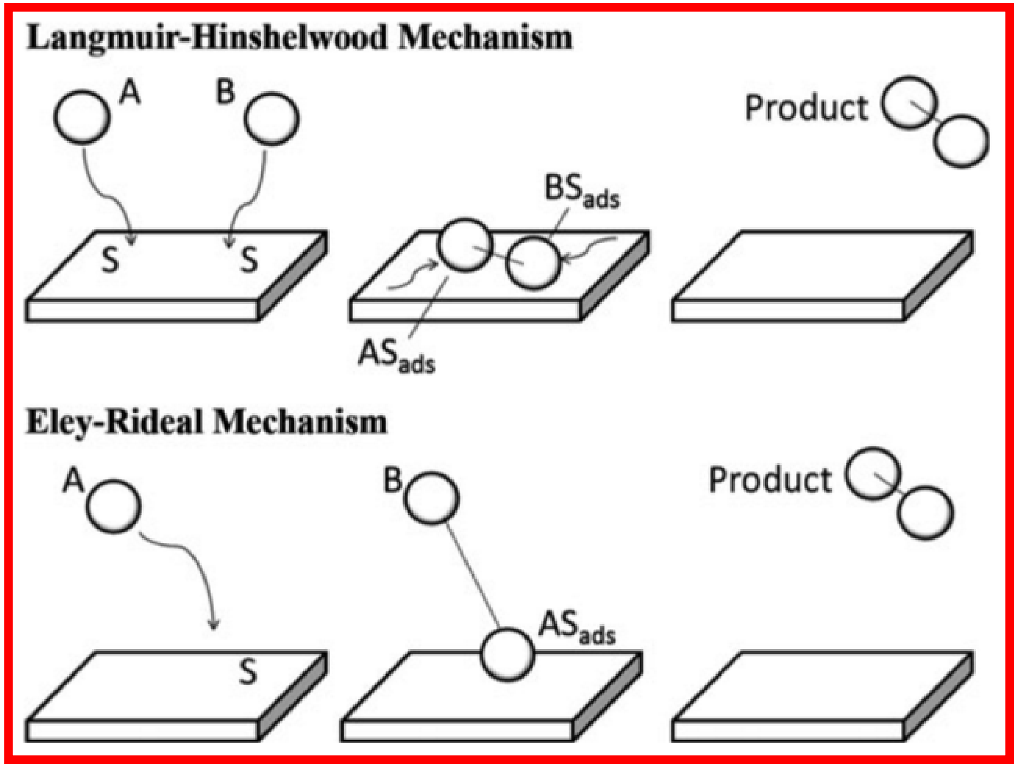


Irving Langmuir

Eley-Rideal kinetics

A gas phase component reacts with an adsorbed species, i.e., a component reacts from the gas phase with an adsorbed component.

$$A \cdot s + B(g) \rightarrow C(g) + s$$



Nanotechnology for Water Treatment and Purification by Anming Hu and Allen Apblett

Langmuir adsorption isotherm

For the adsorption of component *A* on a certain surface

$$A + s \Leftrightarrow A \cdot s$$

Non-dissociative adsorption

$$C_{A \cdot s} = \frac{C_T \cdot K_A \cdot p_A}{1 + K_A \cdot p_A}$$

$$\frac{C_{A \cdot s}}{C_T} = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A}$$

$$\theta_A = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A}$$

Dissociative adsorption

$$C_{A \cdot s} = \frac{C_T \cdot \sqrt{K_A \cdot p_A}}{1 + \sqrt{K_A \cdot p_A}}$$

$$\frac{C_{A \cdot s}}{C_T} = \frac{\sqrt{K_A \cdot p_A}}{1 + \sqrt{K_A \cdot p_A}}$$

$$\theta_A = \frac{\sqrt{K_A \cdot p_A}}{1 + \sqrt{K_A \cdot p_A}}$$

Competitive adsorption

If more than one component competes for the adsorption:

$$A + s \Leftrightarrow A \cdot s$$

$$B + s \Leftrightarrow B \cdot s$$

$$C_{A\cdot s} = \frac{C_T \cdot K_A \cdot p_A}{1 + K_A \cdot p_A + K_B \cdot p_B}, \quad \theta_A = \frac{K_A \cdot p_A}{1 + K_A \cdot p_A + K_B \cdot p_B}$$

$$C_{B\cdot s} = \frac{C_T \cdot K_B \cdot p_B}{1 + K_A \cdot p_A + K_B \cdot p_B}, \quad \theta_B = \frac{K_B \cdot p_B}{1 + K_A \cdot p_A + K_B \cdot p_B}$$

Development of a typical kinetic rate equation

- ✓Assume a reaction mechanism. The mechanism may include single-site or dual-site surface reactions and dissociated or non-dissociated adsorption steps
- ✓Assume the single rate determining step (rds)
- ✓Assume that all the other steps except the rate determining step are in equilibrium (pseudoequilibrium)
- ✓Write down the adsorbed concentration variables in terms of measurable concentrations
- ✓Write down the total site balance, eliminate the variable C_s (concentration of empty sites), and simplify to get the required rate equation.

Development of kinetic rate equation based on LHHW kinetics single-site mechanism

The surface reaction may be single-site or dual-site, i.e., a single site or two sites may be involved:

Single-site

$$A + s \Leftrightarrow A \cdot s$$
$$A \cdot s \Leftrightarrow B \cdot s$$
$$B \cdot s \Leftrightarrow B + s$$

Dual-site

$$A + s \Leftrightarrow A \cdot s$$
$$A \cdot s + s \Leftrightarrow B \cdot s + s$$
$$B \cdot s \Leftrightarrow B + s$$

Development of kinetic rate equation based on LHHW kinetics single-site mechanism: Step-II as RDS

Overall:	$A \Leftrightarrow B$
Adsorption of A:	$A + s \Leftrightarrow A \cdot s$
Surface reaction of A to B:	$A \cdot s \Leftrightarrow B \cdot s$
Desorption of B:	$B \cdot s \Leftrightarrow B + s$

$$\boxed{(-r_A) = \frac{k \cdot K_A \cdot p_A \cdot \left(1 - \dfrac{p_B}{p_A \cdot K_e}\right)}{1 + K_A \cdot p_A + K_B \cdot p_B}}$$

Development of kinetic rate equation based on LHHW kinetics dual-site mechanism: Step-II as RDS

$$A \Leftrightarrow B$$

$$A + s \Leftrightarrow A \cdot s$$

$$A \cdot s + s \Leftrightarrow B \cdot s + s$$

$$B \cdot s \Leftrightarrow B + s$$

$$\boxed{(-r_A) = \frac{k \cdot K_A \cdot p_A \cdot \left(1 - \dfrac{p_B}{p_A \cdot K_e}\right)}{(1 + K_A \cdot p_A + K_B \cdot p_B)^2}}$$

Class activity

Workout for the other possible rate equations based on the mechanisms given earlier, i.e. develop rate equation when

- ✓ First step (adsorption of A) is the rate controlling step for single-site mechanism
- ✓ Third step (desorption of B) is the rate controlling step for dual-site mechanism

Homework problem [2]

Workout the example given in Section 10.3 of the book by Fogler [2]: Decomposition of cumene to form benzene and propylene.

$$C_6H_5CH(CH_3)_2 \longrightarrow C_6H_6 + C_3H_6$$

$C + S \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} C \cdot S$	Adsorption of cumene on the surface
$C \cdot S \underset{k_{-S}}{\overset{k_S}{\rightleftarrows}} B \cdot S + P$	Surface reaction to form adsorbed benzene and propylene in the gas phase
$B \cdot S \underset{k_{-D}}{\overset{k_D}{\rightleftarrows}} B + S$	Desorption of benzene from surface

Eley-Rideal kinetics

For the Eley-Rideal kinetic mechanism shown below, workout the rate equation for the surface reaction rate controlling.

$$A + s \Leftrightarrow A \cdot s$$

$$A \cdot s + B \Leftrightarrow C \cdot s$$

$$C \cdot s \Leftrightarrow B + s$$

General rate equation

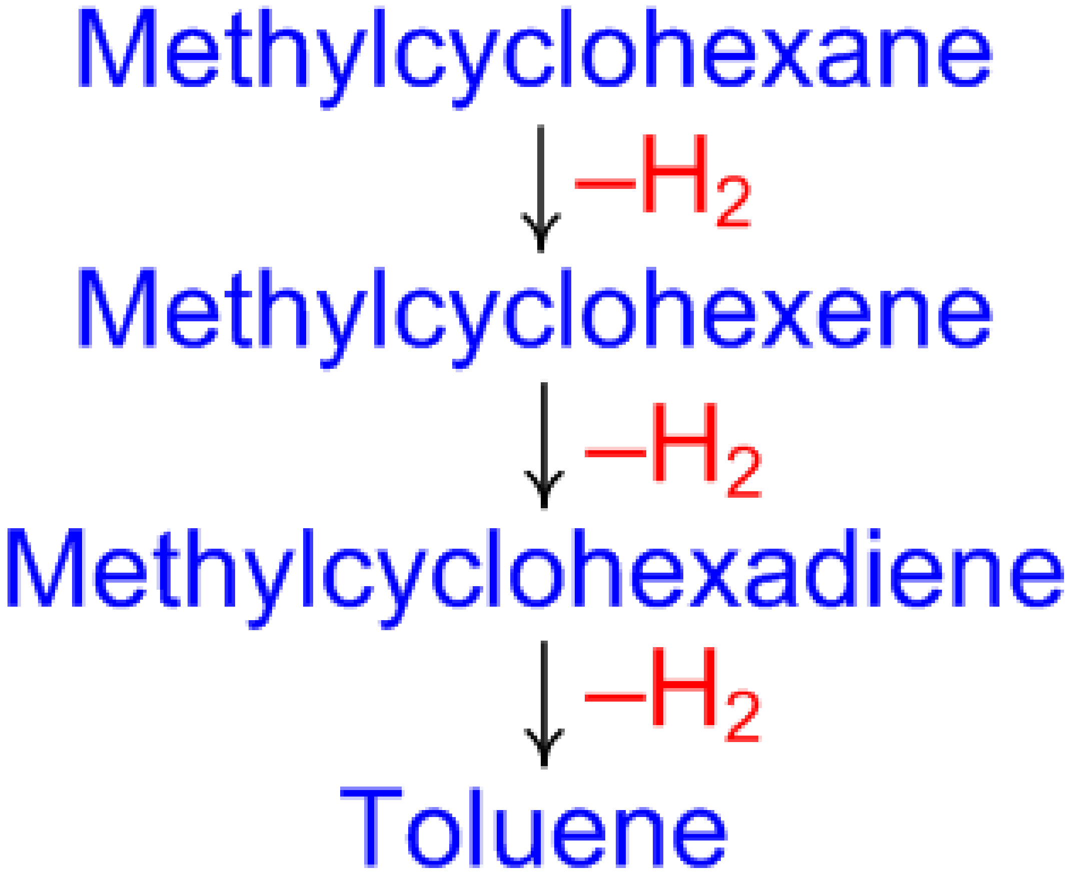
$$\boxed{(-r) = \frac{kinetic\,term \times potential\,term}{adsorption\,term}}$$

✓For intrinsic kinetics, the *kinetic term* contains the reaction velocity constant and may or may not contain adsorption constants.

✓The *potential term* is the simple driving potential and for an essentially irreversible reaction should be equal to unity.

✓The *adsorption term* contains the adsorption coefficients and partial pressures of species and provides a means of quantifying the competition among the species to occupy the active centres. This is useful in the sense that it helps in interpreting the effect of partial pressures of reaction species and even inert and poisons on the rate of reaction.

Successive dehydrogenations in methylcyclohexane dehydrogenation



Methylcyclohexane

$\downarrow -H_2$

Methylcyclohexene

$\downarrow -H_2$

Methylcyclohexadiene

$\downarrow -H_2$

Toluene

Development of kinetic rate equation based on LHHW dual-site surface reaction for the dehydrogenation of methylcyclohexane

Step two (II) is the rate controlling in dual-site surface reaction

$$\mathrm{MCH} + \mathrm{s} \rightleftharpoons \mathrm{MCH{\cdot}s} \qquad \text{(I)}$$

$$\mathrm{MCH{\cdot}s} + \mathrm{s} \rightleftharpoons \mathrm{MCHe{\cdot}s} + \mathrm{H_2{\cdot}s} \qquad \text{(II)}$$

$$\mathrm{MCHe{\cdot}s} + \mathrm{s} \rightleftharpoons \mathrm{MCHde{\cdot}s} + \mathrm{H_2{\cdot}s} \qquad \text{(III)}$$

$$\mathrm{MCHde{\cdot}s} + \mathrm{s} \rightleftharpoons \mathrm{TOL{\cdot}s} + \mathrm{H_2{\cdot}s} \qquad \text{(IV)}$$

$$\mathrm{TOL{\cdot}s} \rightleftharpoons \mathrm{TOL} + \mathrm{s} \qquad \text{(V)}$$

$$\mathrm{H_2{\cdot}s} \rightleftharpoons \mathrm{H_2} + \mathrm{s} \qquad \text{(VI)}$$

A = MCH, B = TOL, C = H_2, D = MCHe, and E = MCHde

Development of kinetic rate equation based on dual-site surface reaction for the dehydrogenation of methylcyclohexane

For Step-I, it may shown that

$$(-r_A) = k_1 \cdot p_A \cdot C_s - k_{-1} \cdot C_{A\cdot s} \tag{1}$$

At equilibrium net rate is zero, so

$$C_{A\cdot s} = K_A \cdot p_A \cdot C_s \tag{2}$$

For Step-II which is the rate controlling step:

$$(-r_A) = k_2 \cdot C_{A\cdot s} \cdot C_s - k_{-2} \cdot C_{D\cdot s} \cdot C_{C\cdot s} \qquad \text{(rate determining step)} \tag{3}$$

Development of kinetic rate equation based on dual-site surface reaction for the dehydrogenation of methylcyclohexane

For Step-III at equilibrium

$$C_{D\cdot s} = \frac{C_{E\cdot s} \cdot C_{C\cdot s}}{K_3 \cdot C_s} \tag{4}$$

For Step-IV at equilibrium

$$C_{E\cdot s} = \frac{C_{B\cdot s} \cdot C_{C\cdot s}}{K_4 \cdot C_s} \tag{5}$$

For Step-V at equilibrium

$$C_{B\cdot s} = K_B \cdot p_B \cdot C_s \tag{6}$$

Development of kinetic rate equation based on dual-site surface reaction for the dehydrogenation of methylcyclohexane

For Step-VI at equilibrium

$$C_{C\cdot s} = K_C \cdot p_C \cdot C_s \tag{7}$$

For Eq. 3, we need the values of $C_{D.s}$ and indirectly $C_{E\cdot s}$ in the known concentration values, i.e. we need to eliminate these two concentrations from Eq. 3.

Inserting Eq. 5 into Eq. 4, it may shown that

$$C_{D\cdot s} = \frac{\dfrac{C_{B\cdot s} \cdot C_{C\cdot s}}{K_4 \cdot C_s} \cdot C_{C\cdot s}}{K_3 \cdot C_s} \tag{8}$$

Development of kinetic rate equation based on dual-site surface reaction for the dehydrogenation of methylcyclohexane

Inserting Eq. 6 and Eq. 7 in Eq. 8, it may be written that

$$C_{D\cdot s} = \frac{\dfrac{K_B \cdot p_B \cdot C_s \cdot (K_C \cdot p_C \cdot C_s)}{K_4 \cdot C_s} \cdot (K_C \cdot p_C \cdot C_s)}{K_3 \cdot C_s}$$

$$C_{D\cdot s} = \frac{K_B \cdot K_C^2 \cdot C_s \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} \qquad (9)$$

From Eq. 5 upon inserting Eq. 6 and Eq. 7, it may shown that

$$C_{E\cdot s} = \frac{K_5 \cdot p_B \cdot C_s \cdot K_6 \cdot p_C}{K_4}$$

Development of kinetic rate equation based on dual-site surface reaction for the dehydrogenation of methylcyclohexane

Inserting Eq. 2 and Eq. 9 in Eq. 3, it may shown that

$$(-r_A) = k_2 \cdot (K_A \cdot p_A \cdot C_s) \cdot C_s - k_{-2} \cdot \left(\frac{K_B \cdot K_C^2 \cdot C_s \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} \right) \cdot (K_C \cdot p_C \cdot C_s)$$

$$(-r_A) = k_2 \cdot K_A \cdot p_A \cdot C_s^2 \cdot \left(1 - \frac{k_{-2} \cdot K_B \cdot K_C^3 \cdot p_B \cdot p_C^3}{k_2 \cdot K_1 \cdot K_3 \cdot K_4 \cdot p_A} \right)$$

$$(-r_A) = k_2 \cdot K_A \cdot p_A \cdot C_s^2 \cdot \left(1 - \frac{p_B \cdot p_C^3}{K \cdot p_A} \right) \tag{10}$$

Where,

$$K = \frac{k_2 \cdot K_1 \cdot K_3 \cdot K_4}{k_{-2} \cdot K_5 \cdot K_6^3}$$

Development of kinetic rate equation based on dual-site surface reaction for the dehydrogenation of methylcyclohexane

Total concentration of the sites is the sum of all the covered sites and the empty sites

$$C_T = C_s + C_{A\cdot s} + C_{B\cdot S} + C_{C\cdot s} + C_{D\cdot s} + C_{E\cdot s} \tag{11}$$

Inserting the corresponding expression in Eq. 11, it may be shown that

$$C_T = C_s + K_A \cdot p_A \cdot C_s + K_B \cdot p_B \cdot C_s + K_C \cdot p_C \cdot C_s + \frac{K_B \cdot K_C^2 \cdot C_s \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} + \frac{K_B \cdot p_B \cdot C_s \cdot K_C \cdot p_C}{K_4}$$

$$C_T = C_s \cdot \left(1 + K_A \cdot p_A + K_C \cdot p_C + K_B \cdot p_B + \frac{K_B \cdot K_C^2 \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} + \frac{K_B \cdot p_B \cdot K_C \cdot p_C}{K_4} \right)$$

$$C_s = C_T \cdot \left(1 + K_A \cdot p_A + K_C \cdot p_C + K_B \cdot p_B + \frac{K_B \cdot K_C^2 \cdot p_B \cdot p_C^2}{K_4 \cdot K_3} + \frac{K_B \cdot p_B \cdot K_C \cdot p_C}{K_4} \right)^{-1} \tag{12}$$

Development of kinetic rate equation based on dual-site surface reaction for the dehydrogenation of methylcyclohexane

Using Eq. 12 with Eq. 10, it may shown that

$$(-r_A)=\frac{k\cdot K_A\cdot p_A\cdot\left(1-\dfrac{p_B\cdot p_C^3}{K\cdot p_A}\right)}{\left(1+K_A\cdot p_A+K_C\cdot p_C+K_B\cdot p_B+\dfrac{K_B\cdot K_C^2\cdot p_B\cdot p_C^2}{K_4\cdot K_3}+\dfrac{K_B\cdot p_B\cdot K_C\cdot p_C}{K_4}\right)^2}$$

Where, $k=k_2\cdot C_T^2$

$$\boxed{(-r_A)=\frac{k\cdot K_A\cdot p_A\cdot\left(1-\dfrac{p_B\cdot p_C^3}{K\cdot p_A}\right)}{\left(1+K_A\cdot p_A+K_C\cdot p_C+K_B\cdot p_B+K''\cdot p_B\cdot p_C^2+K'\cdot p_B\cdot p_C\right)^2}} \tag{13}$$

Eq. 13 is the final and the required equation.

Note that the denominator is squared in dual-site mechanism which is not the case for single-site mechanism.

Homework problems

- ✓ For the mechanisms given on slide 130, work out the rate equations by considering adsorption, surface reaction, and desorption as the rate controlling step.
- ✓ For the Eley-Rideal mechanism,

$$A + s \Leftrightarrow A \cdot s$$

$$A \cdot s + B \Leftrightarrow C \cdot s$$

$$C \cdot s \Leftrightarrow \boldsymbol{C} + s$$

workout the rate equation for the adsorption of *A* and desorption of *C*.

Homework problems

For the oxidation of nitric oxide to produce e, the following Eley-Riedel mechanism is proposed. Derive rate expression assuming surface reaction as rate determining step.

$$O + s \rightleftharpoons O\cdot s \qquad \text{ER-1}$$

$$NO + O.s \rightleftharpoons NO_2\cdot s \qquad \text{ER-2}$$

$$NO_2\cdot s \rightleftharpoons NO_2 + s \qquad \text{ER-3}$$

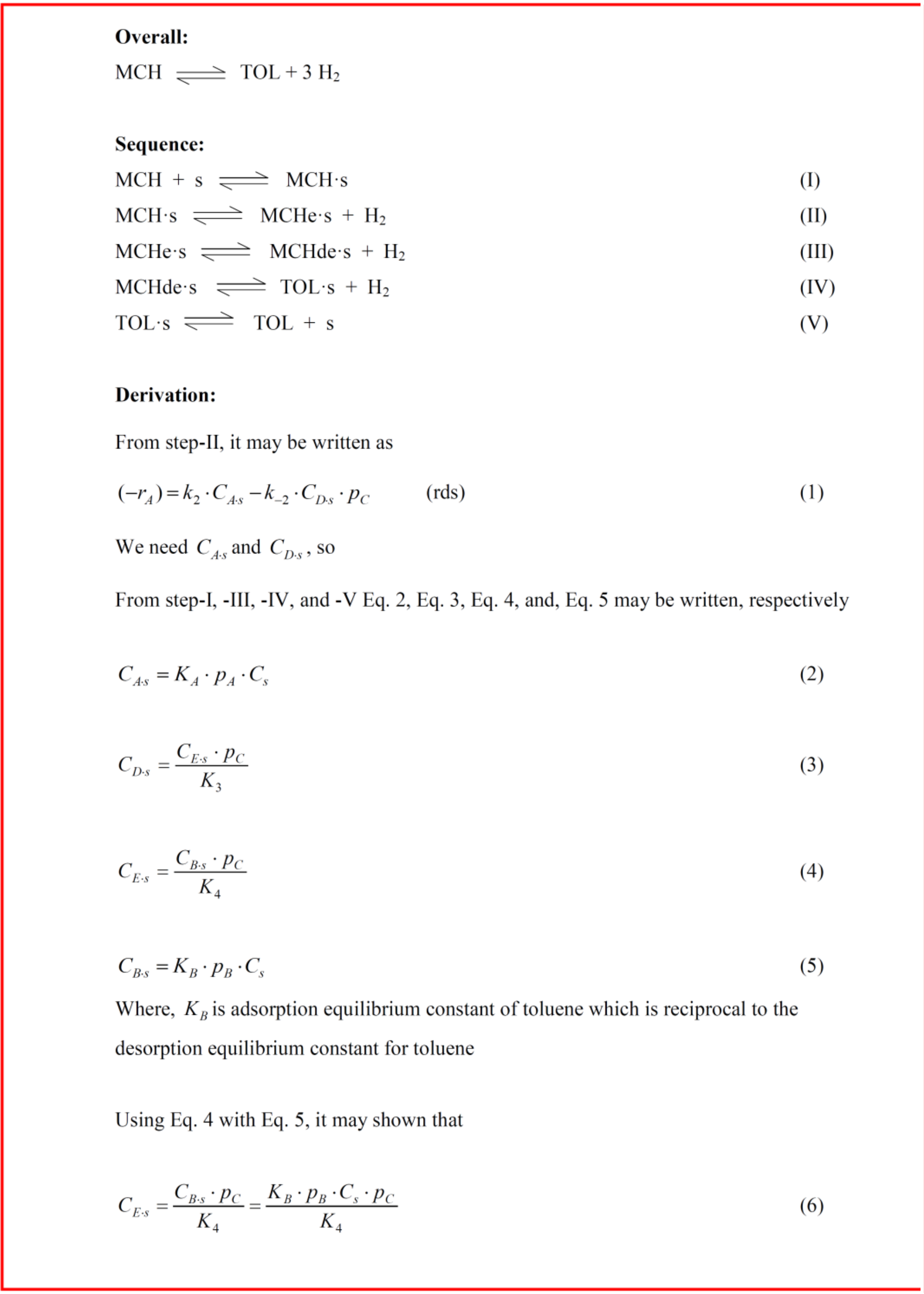
Homework problems

Modify the mechanisms given on slide 137 to single-site surface reaction while neglecting hydrogen adsorption-desorption step, develop kinetic rate equation based on LHHW kinetics when the rate controlling step is:

- Adsorption of methylcyclohexane (Class activity)
- Single-site surface reaction for the loss of first hydrogen
- Single-site surface reaction for the loss of second hydrogen
- Single-site surface reaction for the loss of third hydrogen
- Desorption of toluene

See a few next slides. You may consult Chapter 10 of Fogler [2]. See also Chapter 2 of Froment et al. [11].

Class activity



Overall:

MCH $\rightleftharpoons$ TOL + 3 H_2

Sequence:

MCH + s $\rightleftharpoons$ MCH·s (I)

MCH·s $\rightleftharpoons$ MCHe·s + H_2 (II)

MCHe·s $\rightleftharpoons$ MCHde·s + H_2 (III)

MCHde·s $\rightleftharpoons$ TOL·s + H_2 (IV)

TOL·s $\rightleftharpoons$ TOL + s (V)

Derivation:

From step-II, it may be written as

$$(-r_A) = k_2 \cdot C_{A\cdot s} - k_{-2} \cdot C_{D\cdot s} \cdot p_C \qquad \text{(rds)} \tag{1}$$

We need $C_{A\cdot s}$ and $C_{D\cdot s}$, so

From step-I, -III, -IV, and -V Eq. 2, Eq. 3, Eq. 4, and, Eq. 5 may be written, respectively

$$C_{A\cdot s} = K_A \cdot p_A \cdot C_s \tag{2}$$

$$C_{D\cdot s} = \frac{C_{E\cdot s} \cdot p_C}{K_3} \tag{3}$$

$$C_{E\cdot s} = \frac{C_{B\cdot s} \cdot p_C}{K_4} \tag{4}$$

$$C_{B\cdot s} = K_B \cdot p_B \cdot C_s \tag{5}$$

Where, K_B is adsorption equilibrium constant of toluene which is reciprocal to the desorption equilibrium constant for toluene

Using Eq. 4 with Eq. 5, it may shown that

$$C_{E\cdot s} = \frac{C_{B\cdot s} \cdot p_C}{K_4} = \frac{K_B \cdot p_B \cdot C_s \cdot p_C}{K_4} \tag{6}$$

Using Eq. 6 with Eq. 3, it may shown that

$$C_{D\cdot s} = \frac{C_{E\cdot s} \cdot p_C}{K_3} = \frac{K_B \cdot p_B \cdot C_s \cdot {p_C}^2}{K_3 \cdot K_4} \tag{7}$$

$$(-r_A) = k_2 \cdot K_A \cdot p_A \cdot C_s - k_{-2} \cdot \frac{K_B \cdot p_B \cdot C_s \cdot p_c^3}{K_3 \cdot K_4}$$

$$(-r_A) = k_2 \cdot K_A \cdot p_A \cdot C_s \cdot \left(1 - \frac{k_{-2} \cdot K_B \cdot p_B \cdot {p_C}^3}{k_2 \cdot K_A \cdot K_3 \cdot K_4 \cdot p_A}\right) \tag{8}$$

Now, $K = \dfrac{k_2 \cdot K_A \cdot K_3 \cdot K_4}{k_{-2} \cdot K_B}$, so Eq. 8 becomes as follows

$$(-r_A) = k_2 \cdot K_A \cdot p_A \cdot C_s \cdot \left(1 - \frac{p_B \cdot {p_C}^3}{K \cdot p_A}\right) \tag{9}$$

<u>Site balance:</u>

$$C_T = C_s + C_{A\cdot s} + C_{B\cdot S} + C_{D\cdot s} + C_{E\cdot s} \tag{10}$$

Inserting corresponding expressions in Eq. 10, it may shown that

$$C_T = C_s + K_A \cdot p_A \cdot C_s + K_B \cdot p_B \cdot C_s + \frac{K_B \cdot p_B \cdot C_s \cdot {p_C}^2}{K_3 \cdot K_4} + \frac{K_B \cdot p_B \cdot C_s \cdot p_C}{K_4}$$

$$C_T = C_s \cdot \left(1 + K_A \cdot p_A + K_B \cdot p_B + \frac{K_B \cdot p_B \cdot {p_C}^2}{K_3 \cdot K_4} + \frac{K_B \cdot p_B \cdot p_C}{K_4}\right)$$

$$C_s = C_T \cdot \left(1 + K_A \cdot p_A + K_B \cdot p_B + \frac{K_B \cdot p_B \cdot {p_C}^2}{K_3 \cdot K_4} + \frac{K_B \cdot p_B \cdot p_C}{K_4}\right)^{-1} \tag{11}$$

Inserting Eq. 11 in Eq. 9 and writing $C_T \cdot k_2$ as *k*, it may shown that

$$\boxed{(-r_A) = \frac{k \cdot K_A \cdot p_A \cdot \left(1 - \dfrac{p_B \cdot {p_C}^3}{K \cdot p_A}\right)}{\left(1 + K_A \cdot p_A + K_B \cdot p_B + \dfrac{K_B \cdot p_B \cdot {p_C}^2}{K_3 \cdot K_4} + \dfrac{K_B \cdot p_B \cdot p_C}{K_4}\right)}}$$

<u>(Final form)</u>

Discrimination among the rival models

Now we have a number of rate models developed based on power law, LHHW, and Eley-Rideal. Each of the rate equations developed is to be fitted against the experimental data and the one which is the **most appropriate kinetically and statistically** would be chosen as the best-fit rate equation. "Initial rate" analysis may be used to get a clue of the final form of the equation best suited to the experimental data. Comparing the results to the literature findings and microkinetic analysis may be carried for the final discrimination and for observing the validity of the final rate model. For more on discrimination among the rival models, see Chapter 10 of Fogler [2], Chapter 2 of Froment et al. [11], and Usman et al. [12].

Problem: Design of a fixed bed reactor

A gas phase fixed bed reactor is to be designed for the isothermal dehydrogenation of methylcyclohexane (MCH) to toluene and hydrogen. The feed to the reactor is pure methylcyclohexane flowing at the rate of 100 mol/s. The temperature and pressure conditions are 360°C and 2.0 bar. Assuming the principal reaction is clean and no byproducts are formed, find out the:

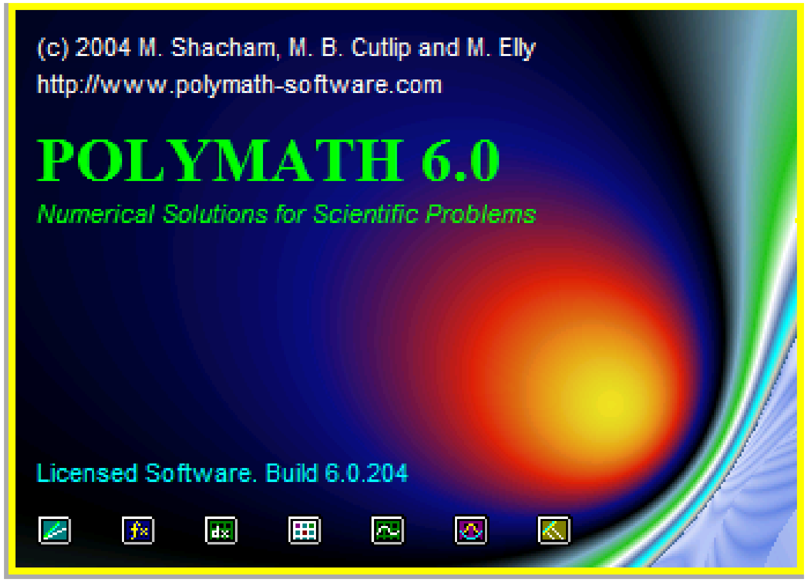
a) weight of the catalyst required for a total of 90% conversion of methylcyclohexane

b) the final conversion if the catalyst weight is 100 kg.

The rate equation for the problem is given below:

Problem: Design of a fixed bed reactor

$$\frac{dX_A}{d\left(\frac{W}{F_{A0}}\right)} = (-r_A)$$



(c) 2004 M. Shacham, M. B. Cutlip and M. Elly
http://www.polymath-software.com

POLYMATH 6.0

Numerical Solutions for Scientific Problems

Licensed Software. Build 6.0.204

The software is an excellent source for solving single and simultaneous ordinary differential equations.

$$(-r_A) = k \cdot \left(p_A - \frac{p_B \cdot p_C^3}{K} \right)$$

$$K = 3600 \cdot \exp\left(\frac{-217650}{8.3143} \left(\frac{1}{T} - \frac{1}{650} \right) \right), \text{ bar}^3$$

$$k = 1.65 \times 10^{-5} \exp\left(B \cdot \left(1 - \frac{661.8}{T} \right) \right), \text{ mol} \cdot \text{s}^{-1} \cdot \text{g-cat}^{-1} \cdot \text{Pa}^{-1}$$

$$B = 18.1$$

Component	Representation	Mole fraction
Methylcyclohexane	A	$\frac{y_{A0} \cdot (1 - X_A)}{1 + 3 \cdot y_{A0} \cdot X_A}$
Toluene	B	$\frac{y_{B0} + y_{A0} \cdot X_A}{1 + 3 \cdot y_{A0} \cdot X_A}$
H_2	C	$\frac{y_{C0} + 3 \cdot y_{A0} \cdot X_A}{1 + 3 \cdot y_{A0} \cdot X_A}$
Inert	I	$\frac{y_{I0}}{1 + 3 \cdot y_{A0} \cdot X_A}$

Homework problems

- ✓Using POLYMATH software, find out the weight of the catalyst for the problem described above, however, use the rate equation as described in Usman et al. 2011 [13]. Solve the problem and see the difference for using two different rate equations. What are your comments?
- ✓Example 10-3 of Fogler [2].

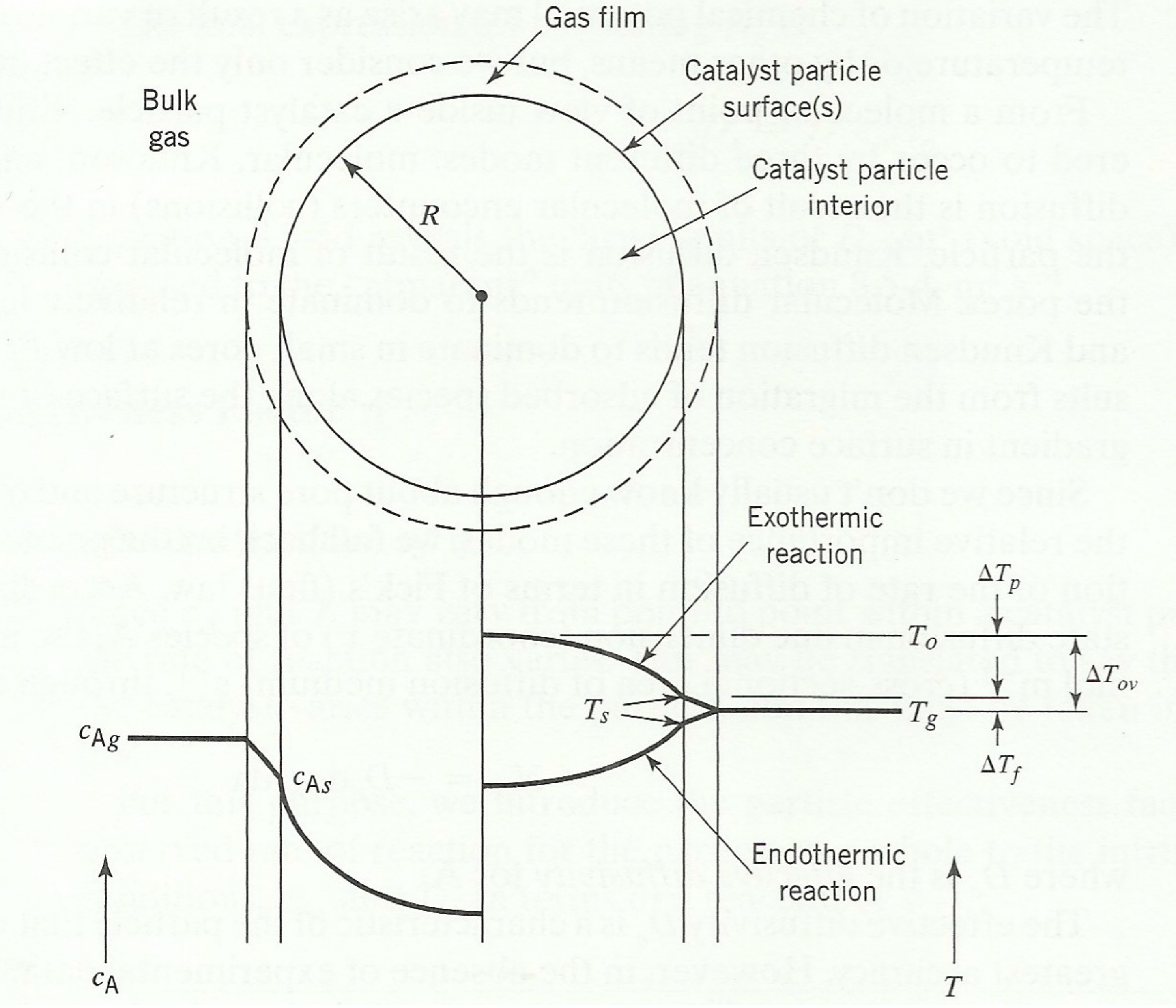
Instead of using POLYMATH software, you can prepare an excel spreadsheet using Euler's method or Runge-Kutta method for finding the weight of the catalyst, etc.

Diffusion and reaction for porous catalysts

Solid catalysts are usually porous structures in order to have high surface area (m^2) per unit gram. Due to the porous nature, the inner surface is many times greater than the outer particle surface. Now as the reactants have to reach the inner surface through small pores, there may be significant resistance to mass and heat diffusion (transfer). Due to the reason, concentration and temperature profiles may be developed across the particle, i.e., within the particle.

For temperature distribution, if a reaction is exothermic, higher temperatures are possible at the center of the particle than at the outer surface and vice versa for an endothermic reaction.

Concentration and temperature distributions in a gas-solid catalytic reaction [14]



Diffusion and reaction for porous catalysts: Effectiveness factor

The rate (kinetics) of a chemical reaction are dependent on the concentration of the reactant, say A, and temperature at any point of the catalyst. Now as concentration and temperature may vary from point to point so does the rate of the reaction. Therefore, it is required to account for these variations (diffusional resistances) to define the rate which represents the particle as whole. It may be interpreted that the effectiveness of the catalyst towards the rate of reaction varies within the catalyst particle and this effectiveness has to be considered in the final rate law. A factor known as effectiveness factor is required.

Effectiveness factor is defined as the ratio of the observed or overall rate of reaction to the intrinsic rate of reaction at the outer surface of the particle where there are no diffusional limitations.

Diffusion and reaction for porous catalysts: Effectiveness factor

$$\eta = \frac{(-r_A)_{obs}}{(-r_A)_{int}}$$

$(-r_A)_{int}$ is the rate of the reaction at the conditions at the outside surface, i.e., c_{AS} and T_s.

$(-r_A)_{obs}$ is the rate of the reaction actually observed.

η is effectiveness factor

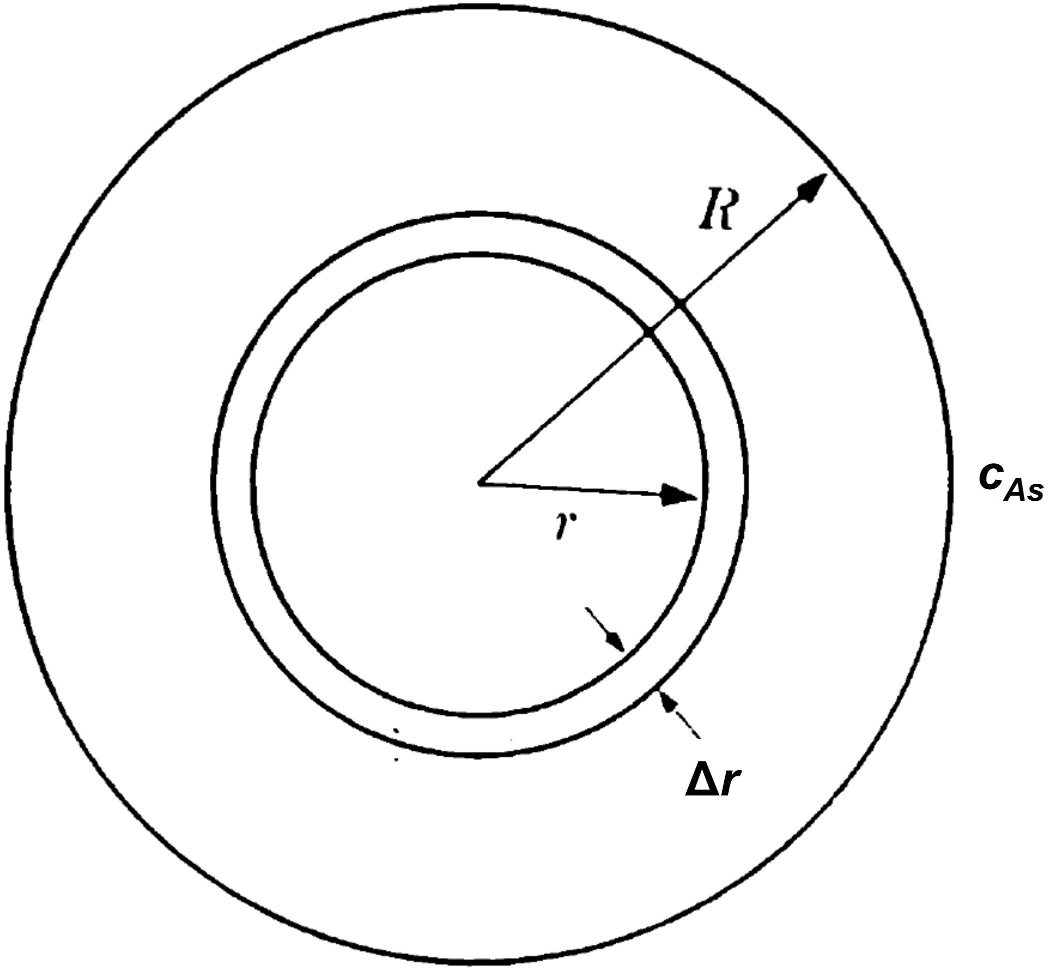
Diffusion and reaction for porous catalysts: Effectiveness factor

Satterfield [15] defines the effectiveness factor as

“the ratio of the actual reaction rate to that which would occur if all of the surface throughout the inside of the catalyst particle were exposed to reactant of the same concentration and temperature as that existing at the outside surface of the particle”.

Diffusion and reaction for porous catalysts: Effectiveness factor

Consider, now, a spherical catalyst particle of radius *R* as shown in the figure below:



Diffusion and reaction for porous catalysts: Effectiveness factor

Considering a thin spherical shell within the catalyst particle and apply mass balance across the thin shell for the following assumptions:

1) Porous particle is spherical;
2) Porous particle is isothermal
3) Reaction is $A \rightarrow Products$ (irreversible)
4) Kinetics are represented by $(-r_A) = k \cdot c_A^n$
5) Steady-state conditions
6) Reactants are transported through diffusion and there is no turbulence. The diffusion is described by Fick's law with mass diffusivity defined as effective diffusivity.

Diffusion and reaction for porous catalysts: Effectiveness factor

Applying boundary conditions:

BC-I: $c_A = c_{As}$ at $r = R$

BC-II: $\dfrac{dc_A}{dr} = 0$ at $r = 0$

And defining Thiele modulus, ϕ, as

$$\phi = R\sqrt{\frac{k \cdot c_{As}^{n-1}}{D_{eff}}}$$

and for $n = 1$, it may shown that

$$\frac{c_A}{c_{As}} = \frac{\sinh\left(\phi \cdot \frac{r}{R}\right)}{\left(\frac{r}{R}\right) \cdot \sinh \phi}$$ (This is for sphere and first order reaction, when $n = 1$)

The above equation describes the concentration profile in the spherical particle.

Diffusion and reaction for porous catalysts: Effectiveness factor

The rate of reaction throughout one spherical porous particle is:

$$Rate = 4\phi\pi \cdot R \cdot D_{eff} \cdot c_{As}\left(\frac{1}{\tanh\phi} - \frac{1}{\phi}\right) \text{mol/s}$$

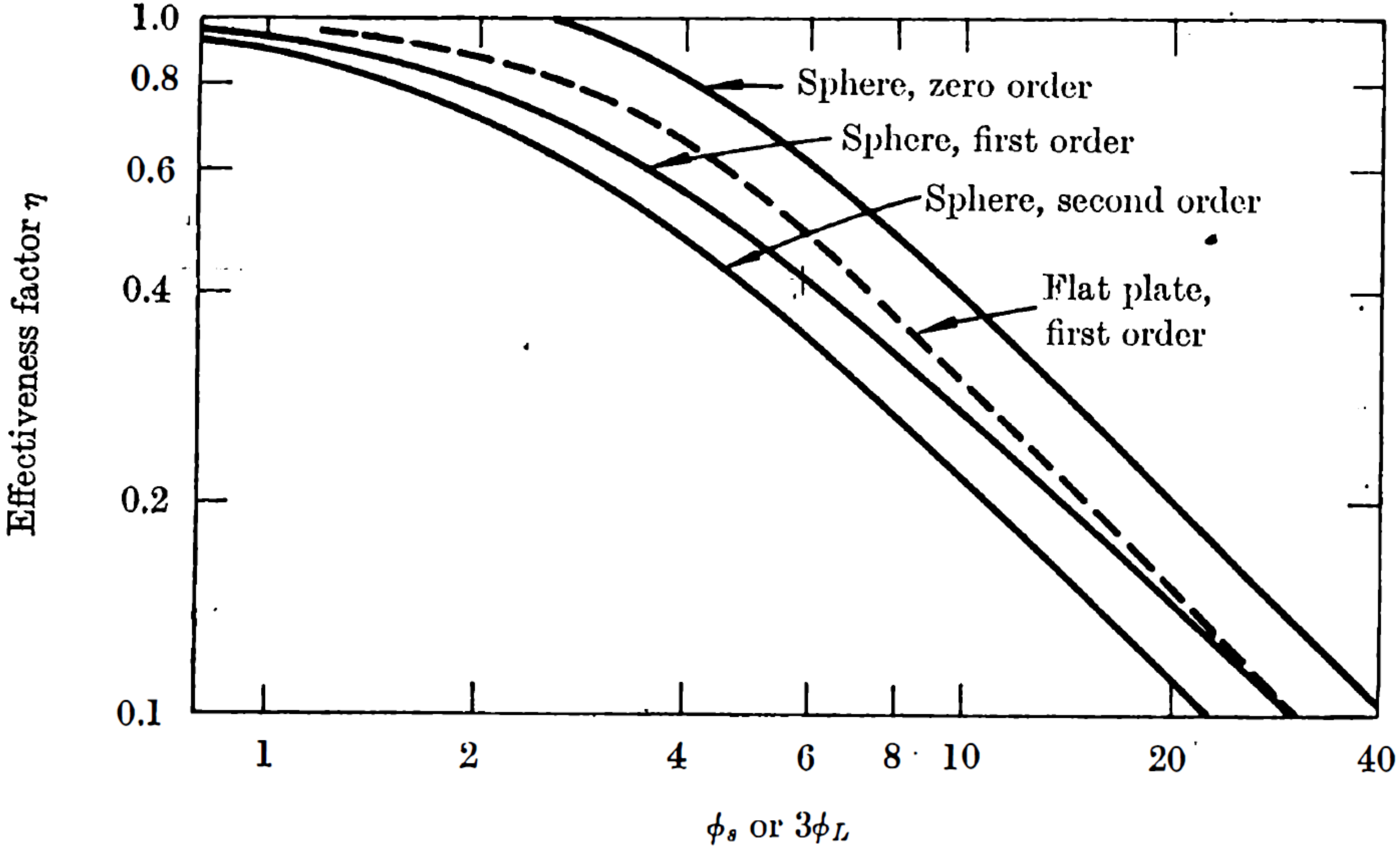
If all the internal surface is at the concentration outside the surface, i.e., c_{As}, then:

$$Rate = \frac{4}{3}\pi \cdot R^3 \cdot k \cdot c_{As} \text{ mol/s}$$

By the definition of effectiveness factor, η

$$\eta = \frac{3}{\phi}\left(\frac{1}{\tanh\phi} - \frac{1}{\phi}\right)$$

Diffusion and reaction for porous catalysts [15]



Effectiveness factor with power-law kinetics.

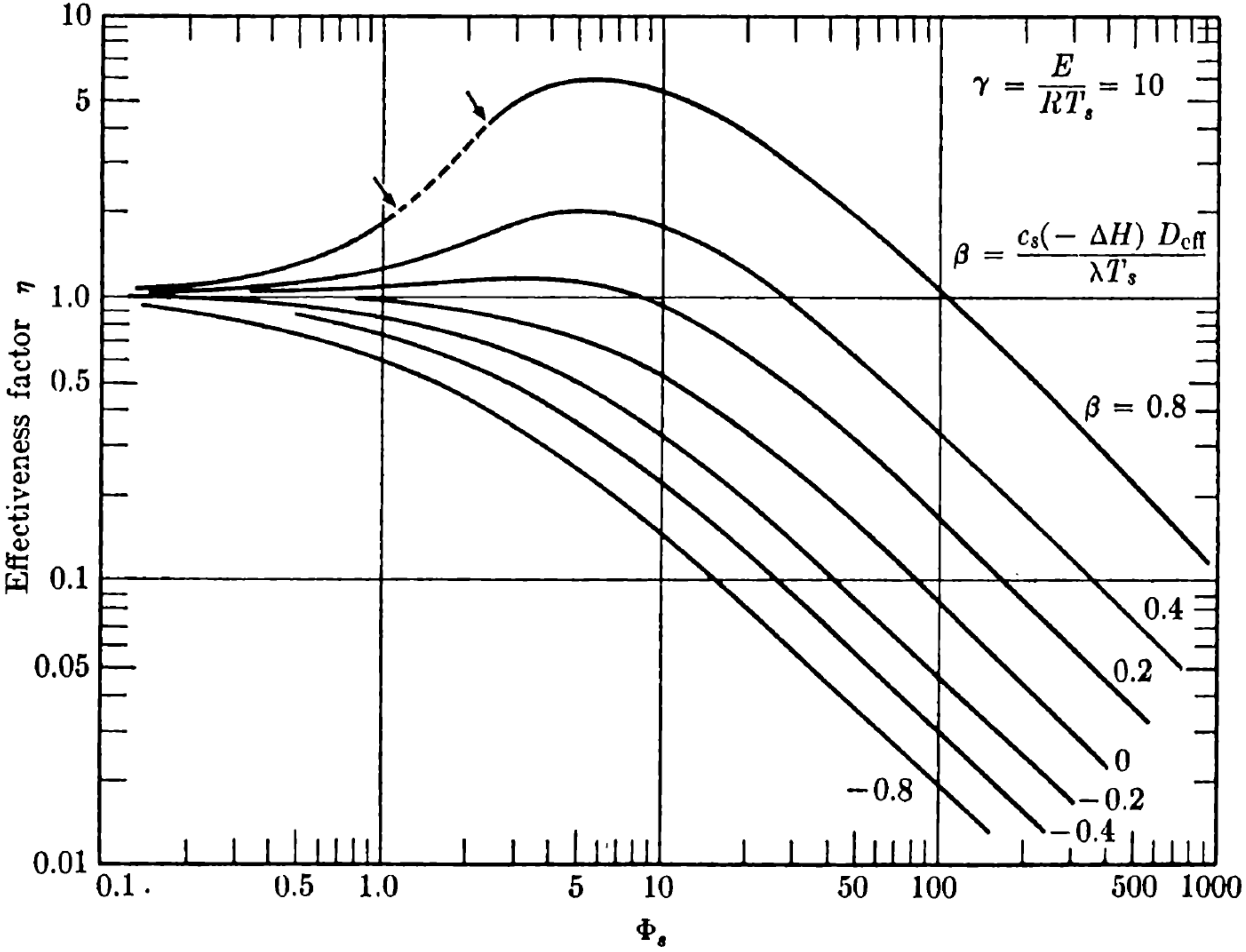
Diffusion and reaction for porous catalysts: Effectiveness factor

A modified Thiele modulus can be defined which is based on observed values

$$\Phi = \frac{R^2}{D_{eff}}\left(-\frac{1}{V_c}\frac{dn}{dt}\right)\frac{1}{c_{As}}$$

This modified Thiele modulus is related for various values of heat generation function, β, and dimensionless Arrhenius number to include the effect of temperature while determining the effectiveness factor. One such relationship (graph) is shown in the figure on the next slide.

Diffusion and reaction for porous catalysts [15]



Effective diffusivity

The effectiveness diffusivity can be calculated by the following equation

$$\frac{1}{D_{eff}} = \frac{1}{D_{Kn,eff}} + \frac{1}{D_{A,eff}}$$

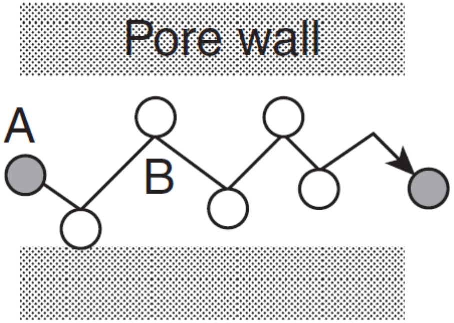
Where,

D_{eff}	effective mass diffusvity, m^2/s
$D_{A,eff}$	ordinary or bulk effective mass diffusivity, m^2/s
$D_{Kn,eff}$	effective Knudsen mass diffusvity, m^2/s

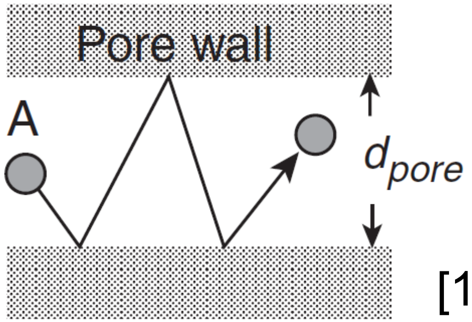
Knudsen diffusivity

“If the gas density is low, or if the pores are quite small, or both, the molecules collide with the pore wall much more frequently than with each other, This is known as Knudsen flow or Knudsen diffusion. The molecules hitting the wall are momentarily adsorbed and then given off in random directions (diffusively reflected). The gas flux is reduced by the wall resistance. Knudsen diffusion is not observed in liquids.” [15]

Pure molecular diffusion



Pure knudsen diffusion



[16]

Knudsen diffusivity

Based on kinetic theory of gases, Knudsen diffusivity can be obtained as

$$D_{Kn} = 9700 \cdot r_p \cdot \sqrt{\frac{T}{M}} \text{ , cm}^2\text{/s}$$

Where,

T	absolute temperature, K
M	molecular weight
r_p	pore radius, cm

The pore radius r_p is for a round straight pore, the actual pore geometry is complex and the therefore including the effect of pore geometry, the following relationship can be written for the effective Knudsen diffusivity [15].

Effective Knudsen and ordinary diffusivities

Effectiveness Knudsen diffusivity

$$D_{Kn,eff} = 19400 \frac{\theta^2}{\tau_m \cdot S_g \cdot \rho_p} \sqrt{\frac{T}{M}} \quad , \mathrm{cm^2/s}$$

Where,

θ	particle voidage
ρ_p	desnity of particle, g/cm^3
τ_m	tortuosity factor when D_{Kn} is calculated based on mean pore radius
S_g	surface are of the article, cm^2/g

Effectiveness bulk diffusivity

$$D_{A,eff} = \frac{D_A \cdot \theta}{\tau_m}$$

D_A	ordinary diffusion , cm^2/s
θ	particle voidage
τ_m	tortuosity factor when D_A is calculated based on mean pore radius

Bulk diffusion coefficient for gases at low pressure

Based on the Chapman-Enskog theory, the following equation using ideal gas law for the determination of total concentration "*c*" may be written [17]

$$\mathcal{D}_{AB} = \frac{3}{16}\sqrt{\frac{2(RT)^3}{\pi}\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\frac{1}{\tilde{N}p\sigma_{AB}^2\Omega_{\mathcal{D},AB}}$$

$$= 0.0018583\sqrt{T^3\left(\frac{1}{M_A}+\frac{1}{M_B}\right)}\frac{1}{p\sigma_{AB}^2\Omega_{\mathcal{D},AB}}$$

Here, D_{AB} is in cm^2/s, σ_{AB} is Å, and p in atm.

The mass diffusivity D_{AB} for binary mixtures of non-polar gases is predictable within about 5% by kinetic theory.

Bulk diffusion coefficient for gases at low pressure

✓The parameters σ_{AB} and ε_{AB} could, in principle, be determined directly from accurate measurement of D_{AB} over a wide range of temperatures.

✓Suitable data are not yet available for many gas pairs, one may have to resort to using some other measurable property, such as the viscosity of a binary mixture of A and B.

✓In the event that there are no such data, then we can estimate them from the following combining rules for non-polar gas pairs.

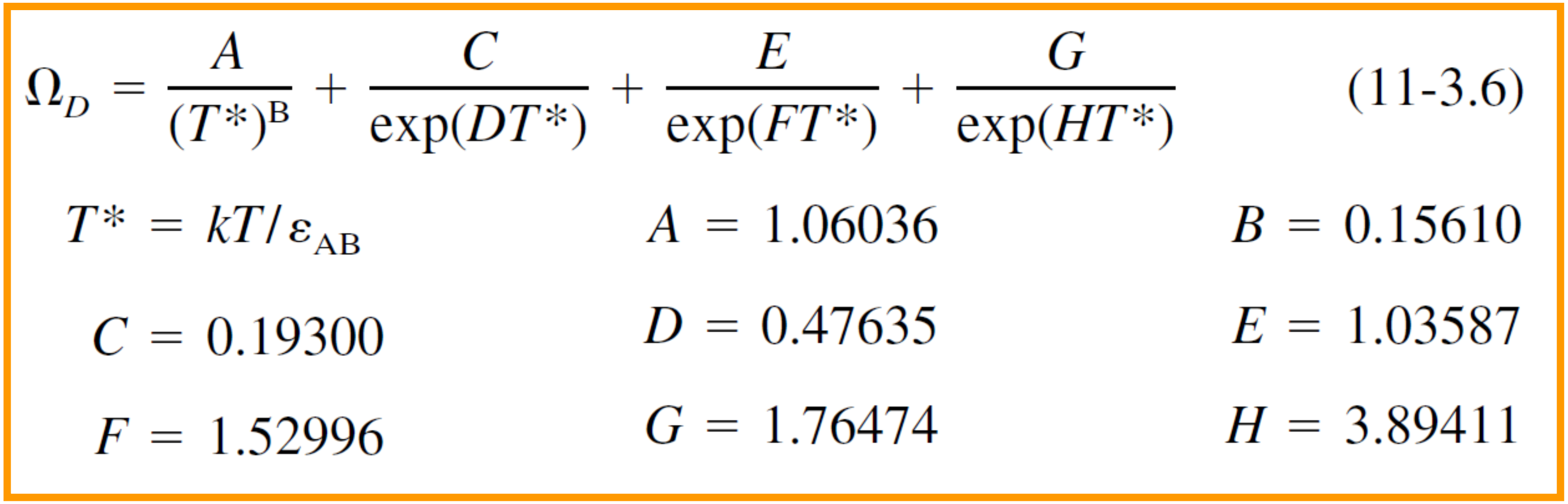
$$\boxed{\varepsilon_{AB} = \sqrt{\varepsilon_A \varepsilon_B}} \qquad \boxed{\sigma_{AB} = \tfrac{1}{2}(\sigma_A + \sigma_B)}$$

✓Use of these combining rules enables us to predict values of D_{AB} within about 6% by use of viscosity data on the pure species A and B, or within about 10% if the Lennard-Jones parameters for A and B are estimated from boiling point data as discussed in Chapter 1 of Bird et al. 2002 [17].

Bulk diffusion coefficient for gases at low pressure

✓The Lennard-Jones parameters can be obtained from the Appendix of the book [17] and in cases when not known can be estimated as described in first chapter of the book [17]. To avoid interpolation, a graphical relationship for collision integral is given on the next slide.

✓A mathematical relationship by Neufeld is recommended for computational (spreadsheet) work [18].



$$\Omega_D = \frac{A}{(T^*)^{B}} + \frac{C}{\exp(DT^*)} + \frac{E}{\exp(FT^*)} + \frac{G}{\exp(HT^*)} \qquad (11\text{-}3.6)$$

$T^* = kT/\varepsilon_{AB}$ $\quad A = 1.06036$ $\quad B = 0.15610$

$C = 0.19300$ $\quad D = 0.47635$ $\quad E = 1.03587$

$F = 1.52996$ $\quad G = 1.76474$ $\quad H = 3.89411$

Bulk diffusion coefficient for mixture of gases and gases at high pressure

✓The behavior of gases at high pressures (dense gases) and of liquids is not well understood and difficult to interpret to a mathematical evaluation. The following approach can be used for estimating the mass diffusivity of gases at high pressures. The method is very good for gases at low pressures. At high pressures, due to the lack of large number of experimental data, a comparison is difficult to make.

✓For the diffusivity of gases at high pressure and mixture of gases, see "Poling, B.E.; Prausnitz, J.H.; O'Connell, J.P. 2000. The properties of gases and liquids. 5th ed. McGraw-Hill" and Chapter 1 of the book by Bird et al. [17].

Class activity

For the exothermic reaction (methanol formation: $CO + 2H_2 \rightarrow CH_3OH$), calculate the effective binary diffusion of CO in H_2, effective Knudsen diffusion, effective diffusivity, and effectiveness factor for the following conditions. Use attached tables and charts where required. Some equations which may helpful are also given along with the data.

$T = 400$K, $p = 5.0$ bar absolute, and $y_{CO} = 0.2$ and $y_{\mathrm{H2}} = 0.8$.

Particle diameter = 2.0 mm,

Heat of reaction = –90.84 kJ/mol

Thermal conductivity of particle = 0.20 W/m·K

$(-r_{\mathrm{CO}}) = 1.5 \times 10^{-5}$ mol/g-cat·s

Dimensionless activation energy or Arrhenius number = 20

Particle voidage = 0.50

Surface area of the particle = 150 m^2/g

Density of the particle = 1.20 g/cm^3

Tortuosity factor = 4.0

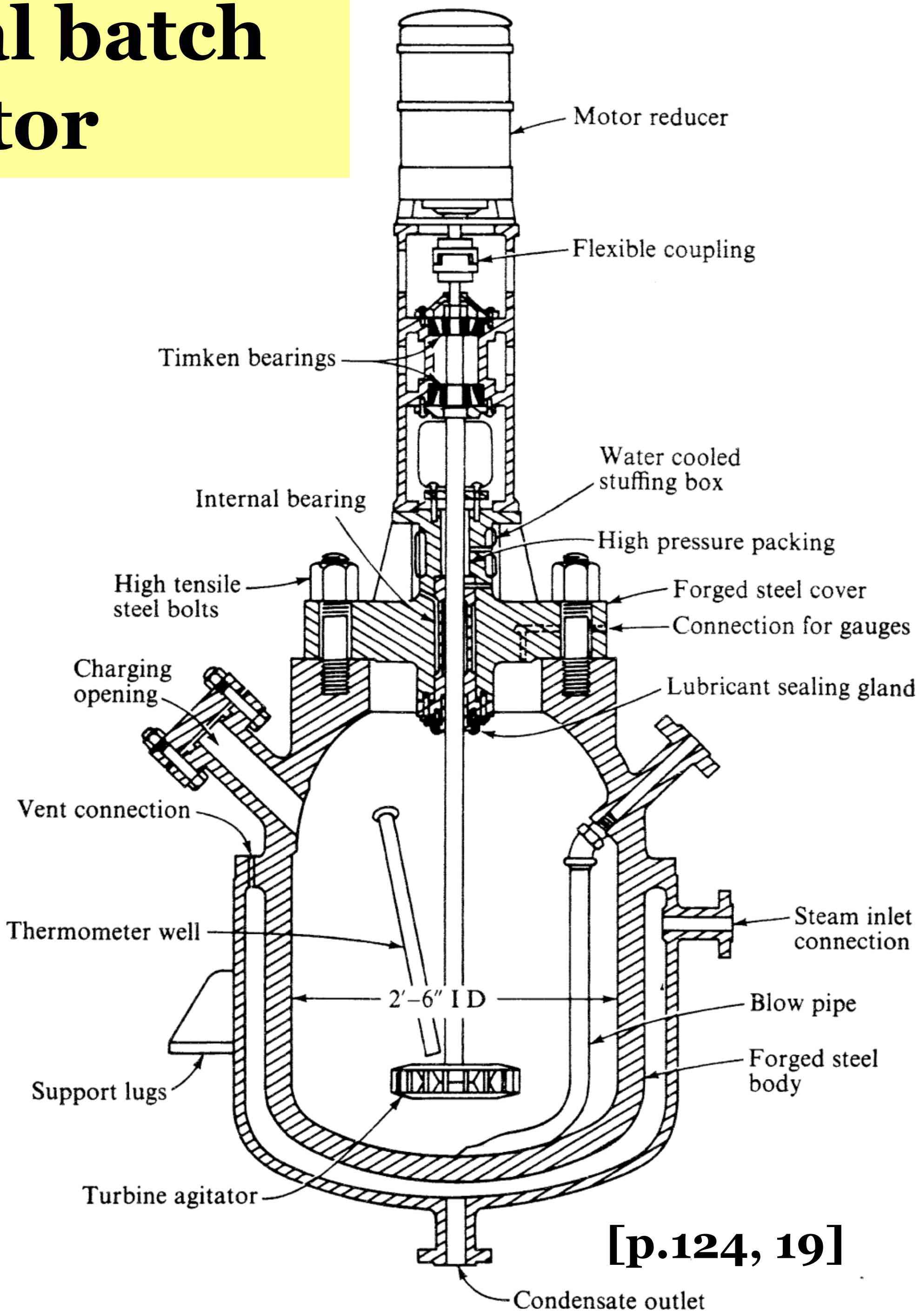
Homework problem

For the isothermal dehydrogenation of methylcyclohexane over Pt/Al_2O_3 catalyst, the following information is available:

$T = 600$ K, $p = 5.0$ bar, $y_{A0} = 0.2$, $y_{C0} = 0.8$
Catalyst particle size = 1.5 mm
Heat of reaction = 205 kJ/mol
Dimensionless activation energy or Arrhenius number = 10
Thermal conductivity of the catalyst particle = 0.16 W/m·K
Particle voidage = 0.55
Surface area of the particle = 208 m^2/g
Density of the particle = 1.5 g/cm^3
Tortuosity factor = 3.0
Use the rate equation given on slide 152 and use initial rate with $p_A = p_{A0}$, $p_B = p_{B0}$, and $p_C = p_{C0}$ to find out the rate of the reaction under the given conditions.

Calculate the effective binary diffusivity (of methylcyclohexane in hydrogen), effective Knudsen diffusivity, effective diffusivity, and effectiveness factor at the given conditions. Observe the effect of temperature (vary between 575 and 675), pressure (vary between 1 and 15 bar), and tortuosity factor (vary between 3 and 7) on the effectiveness factor.
Note: You may prepare an excel spreadsheet but the assignment is to be submitted in the hard form. Late submission will carry not more than half of the marks.

Industrial batch reactor



[p.124, 19]

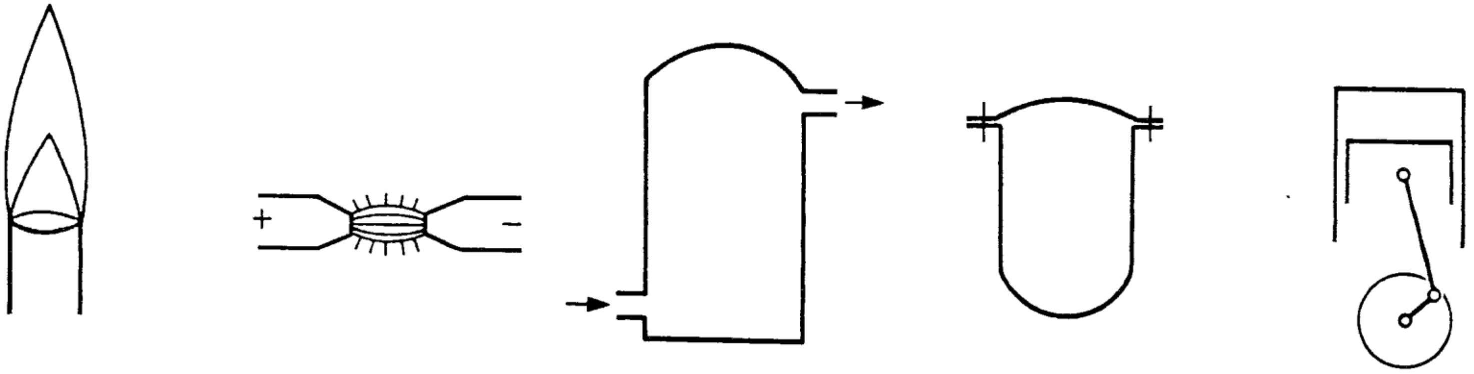
Various design of reactors

Based on the phases involved, reactors may adopt various shapes and designs depending upon the process requirements.

Reactors for gas phase only [20]

✓If rate of the reaction is high, the reaction can be carried out in small reaction spaces, e.g., in flames and arcs.

✓For slower reaction larger reaction space is required.



Flame

Examples: combustion of chlorine detonating gas, dissociation of methane

Electric arc

Examples: acetylene from methane, combustion of nitrogen

Large reaction vessel

Example: nitrogen oxidation

Autoclave

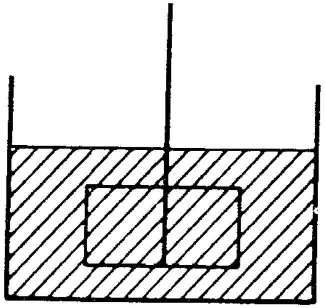
Example (laboratory): acetylene decomposition to acetylene black

Reaction engine

Example (laboratory): combustion of chlorine detonating gas

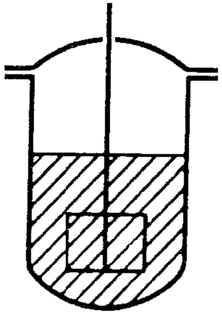
Reactors for liquid phase only [20]

Tank



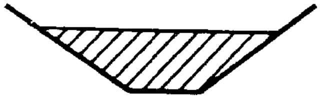
Examples:
diazotization,
dye coupling,
potash recovery,
benzene refining

Autoclave



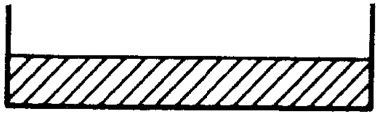
Example:
numerous
organic
processes

Crucible



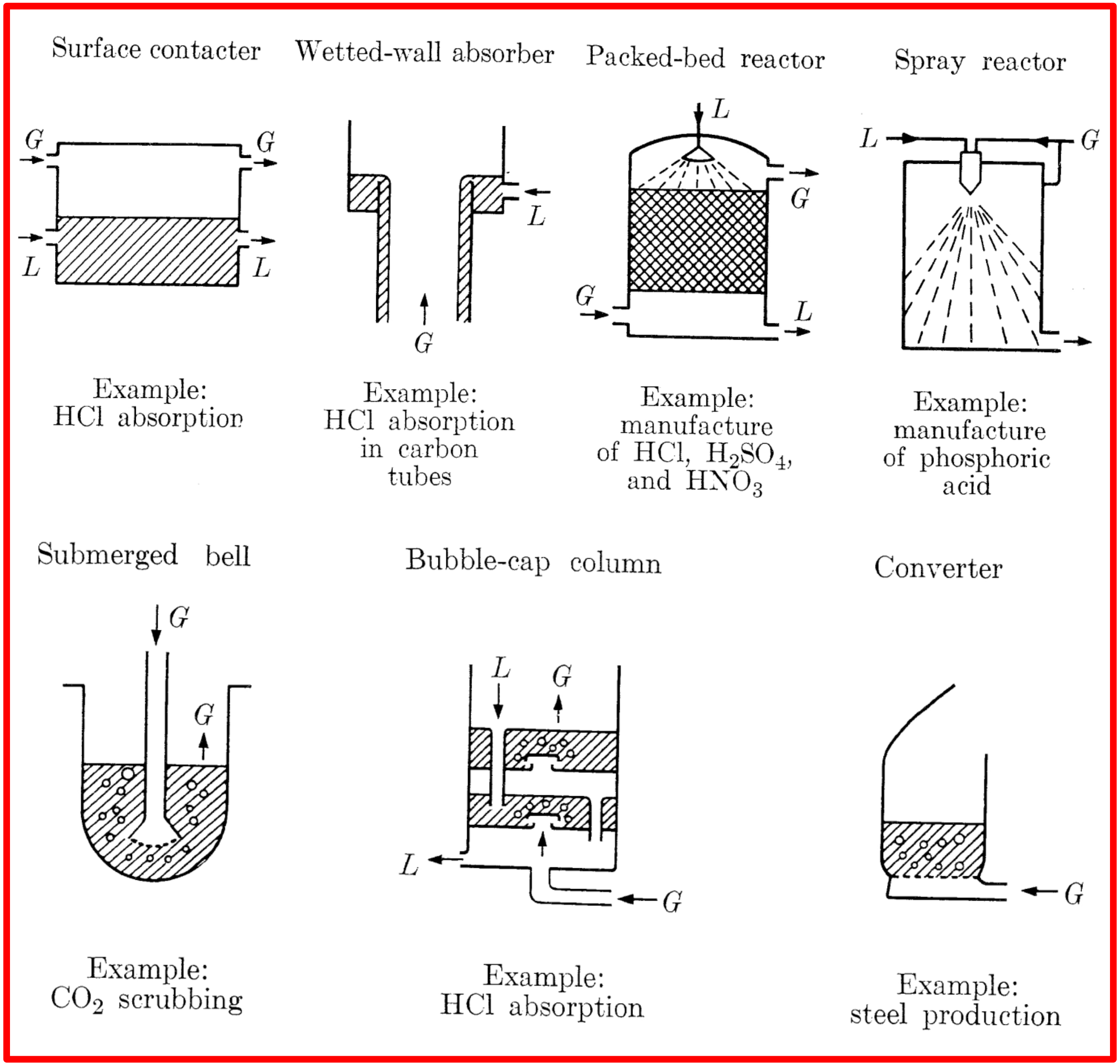
Examples:
glass melting,
Siemens-Martin
furnace

Vat



Example:
glass melting

Gas-liquid reactors only [20]



Surface contacter

Example:
HCl absorption

Wetted-wall absorber

Example:
HCl absorption
in carbon
tubes

Packed-bed reactor

Example:
manufacture
of HCl, H_2SO_4,
and HNO_3

Spray reactor

Example:
manufacture
of phosphoric
acid

Submerged bell

Example:
CO_2 scrubbing

Bubble-cap column

Example:
HCl absorption

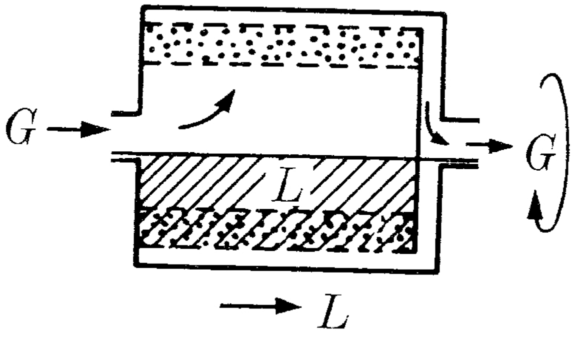
Converter

Example:
steel production

Gas-liquid reactors [20]

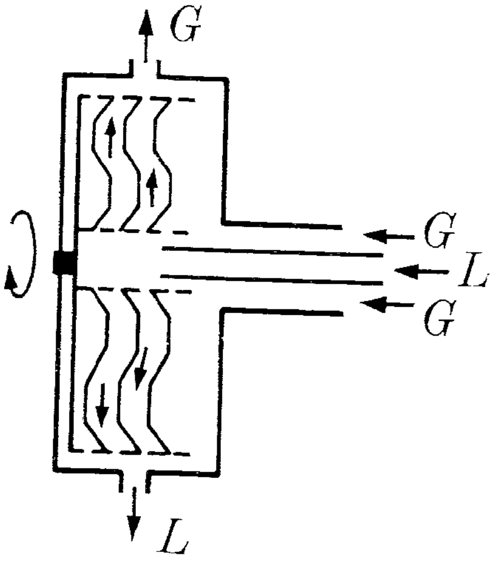
Mechanical absorbers

Drum scrubber



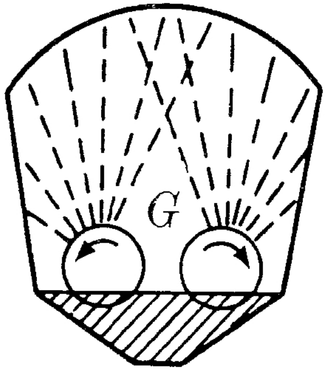
Example:
ammonia
scrubbing

Plate scrubber



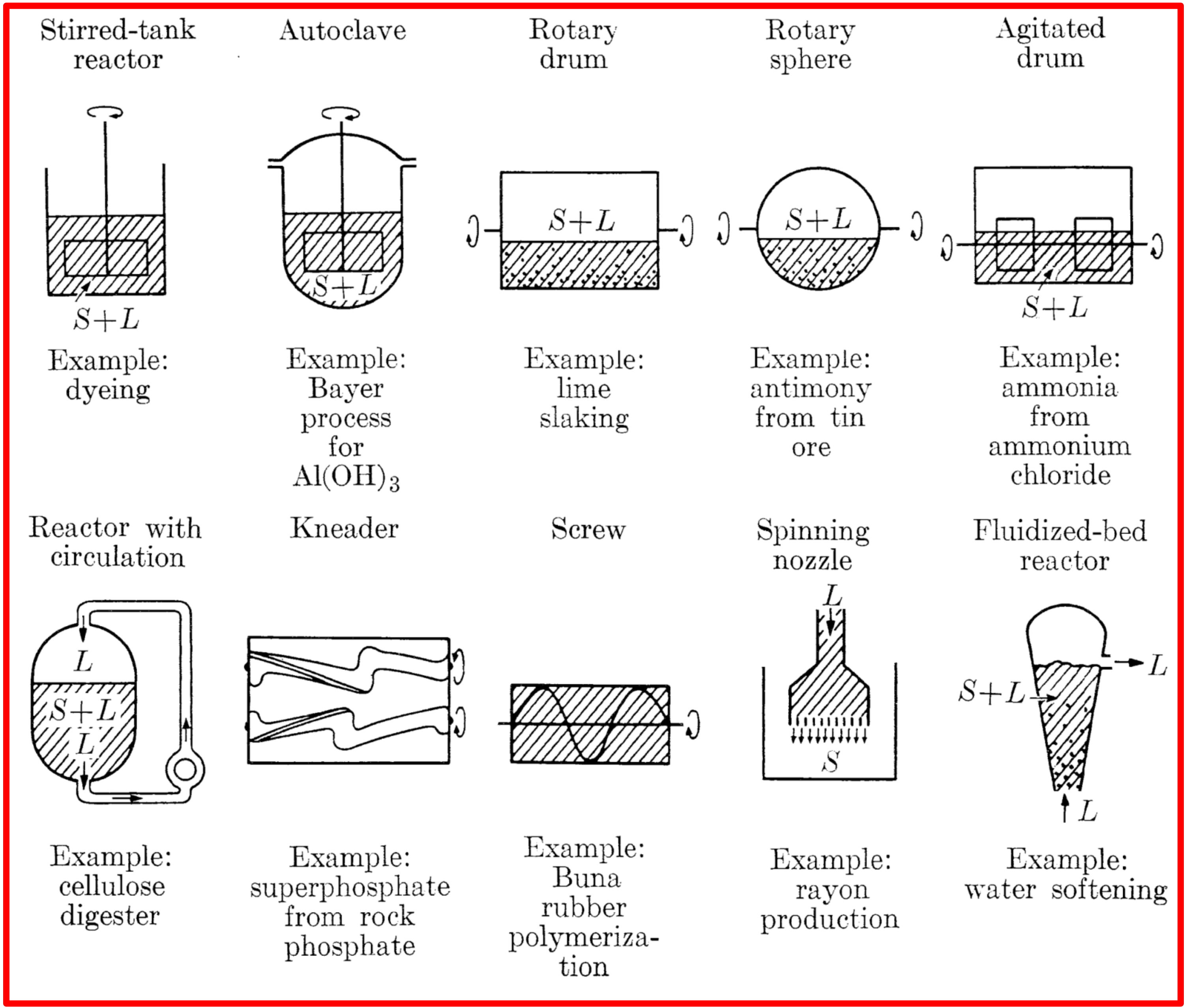
Example:
separation of tar
from coke-oven gas

Rotary scrubber



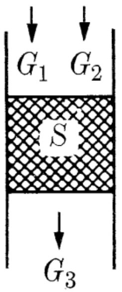
Example:
SO_3 absorption

Liquid-solid reactors [20]



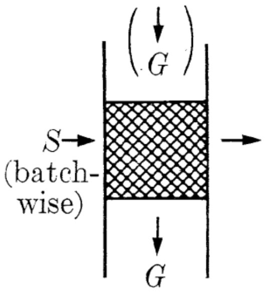
Gas-solid reactors [20]

Reactor with fixed solids



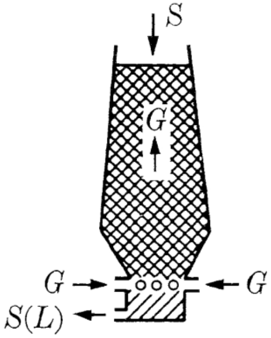
Examples:
$N_2 + 3H_2 \rightarrow 2NH_3$
(with catalyst),
heat regenerator
(with refractory material)

Batch reactor



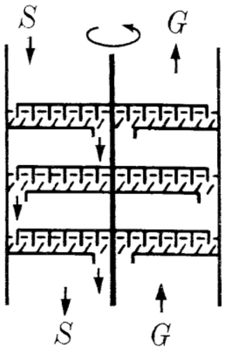
Example:
coking of coal

Moving-bed reactor



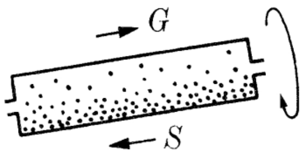
Examples:
iron smelting,
calcination of limestone

Multicompartment reactor



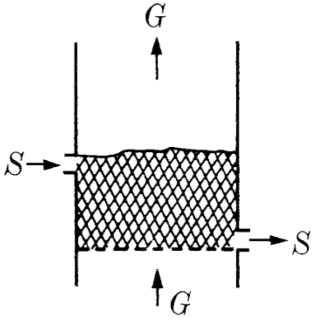
Example:
roasting of ore

Rotary kiln



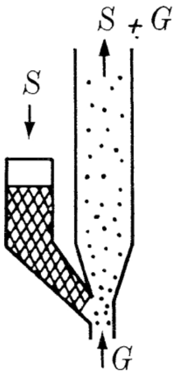
Examples:
roasting of ore,
cement manufacture

Fluidized-bed reactor



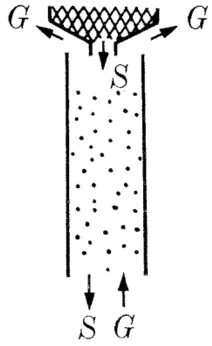
Examples:
coal gasification,
cracking,
roasting of ore

Dilute-phase, cocurrent-flow reactor



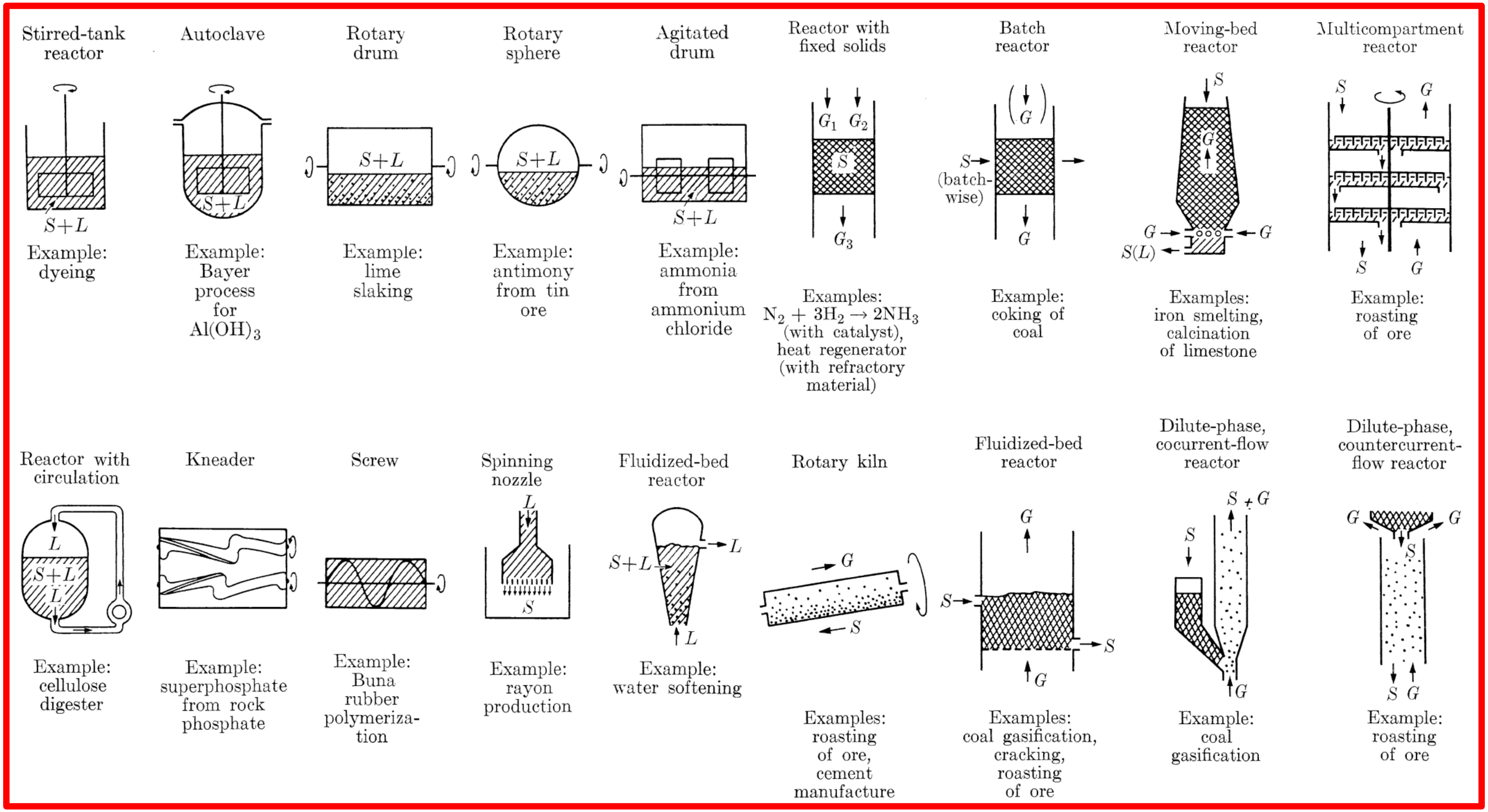
Example:
coal gasification

Dilute-phase, countercurrent-flow reactor



Example:
roasting of ore

Gas-Liquid-solid reactors [20]



Think other designs.

You may have a **novel** idea.

Design of a fixed bed reactor

A commonly used fixed bed reactor has the following features:

✓The reactor is used for a fluid-solid contact though gas-solid systems are more common.

✓The solid catalyst particles are arranged randomly in a cylindrical shell or tube, where the solid particles remain fixed with respect to each other as well with respect to the reactor wall.

How will you define moving bed reactor and fluidized bed reactor?

Design of a fixed bed reactor

✓The gas or liquid flows from top to the bottom. The flow in upward direction may loosen the bed giving rise to attrition and fine particles may increase the pressure drop and may possibly be fluidized.

✓Sulfuric acid production (SO_2 oxidation), methanol production, ammonia synthesis, manufacture of styrene by the dehydrogenation of ethylbenzene are some of the industrial examples that require a fixed bed reactor.

✓The catalytic bed may be arranged in a single shell, single shells adjacent to one another (multibed), or multitubular reactor.

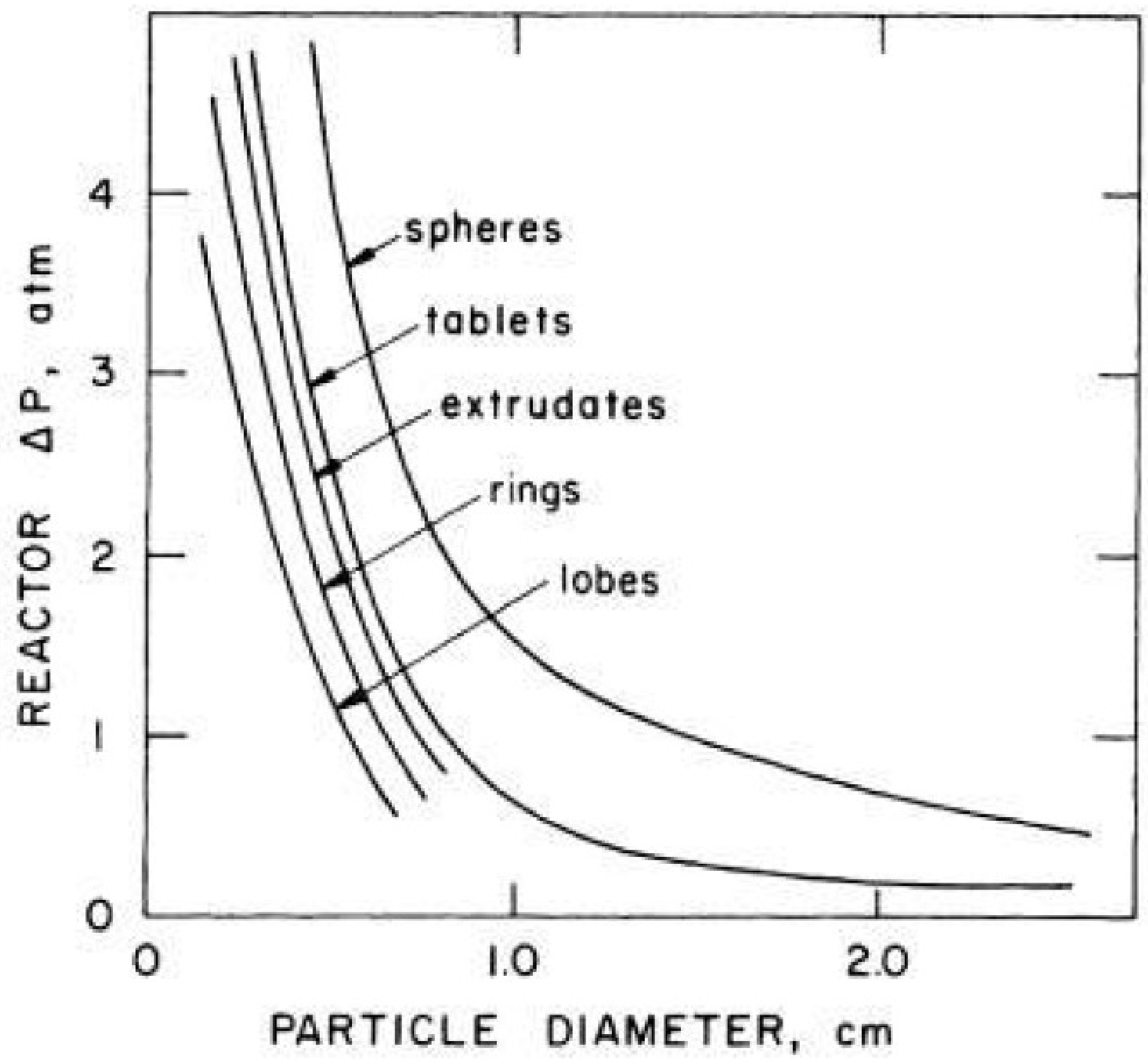
Design of a fixed bed reactor

✓The catalyst bed may be arranged in a multitubular geometry in which a set of tubes are placed inside a shell. This conforms to a shell and heat exchanger type assembly. The catalyst may be packed inside or outside of the tubes.

✓A radial flow reactor may also be used where pressure drop is an issue.

✓The usual catalyst particle size ranges between 2-6 mm. Various shapes of catalysts may be used. Spherical, solid cylindrical, hollow cylindrical (Raschig ring type), Lessing ring type, extrudates, etc., are the different kinds of shapes of catalyst that may be employed.

Variety of catalysts: pressure drop [6]

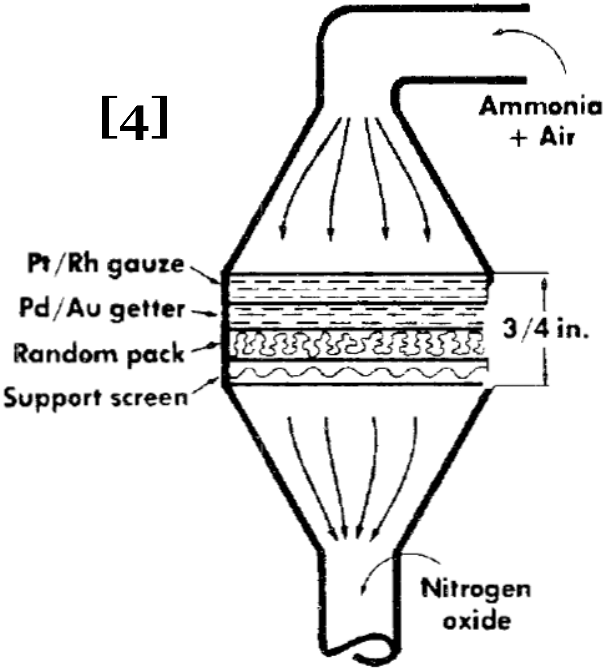


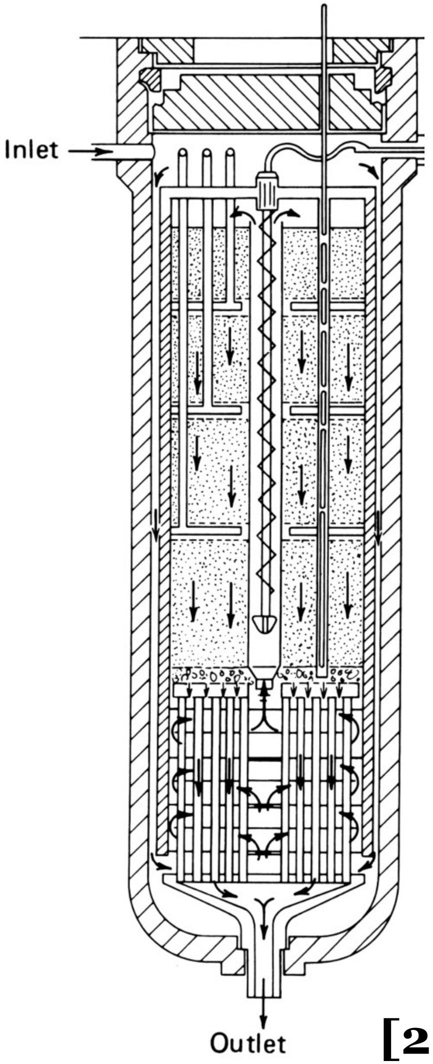
Design of a fixed bed reactor

- ✓ Thermodynamics of the reaction (heat of reaction and chemical reaction equilibrium consideration)
- ✓ Reaction reversibility
- ✓ Kinetics (rate) of the given reaction
- ✓ Feed composition and product specifications
- ✓ Flow requirement
- ✓ Thermal energy requirement
- ✓ Bed arrangement
- ✓ Properties of catalytic particles and catalytic bed
- ✓ Catalyst weight (size of the reactor)
- ✓ Length to diameter ratio
- ✓ Pressure drop
- ✓ Temperature and composition distributions
- ✓ One or more of these requirements may be dependent on each other.

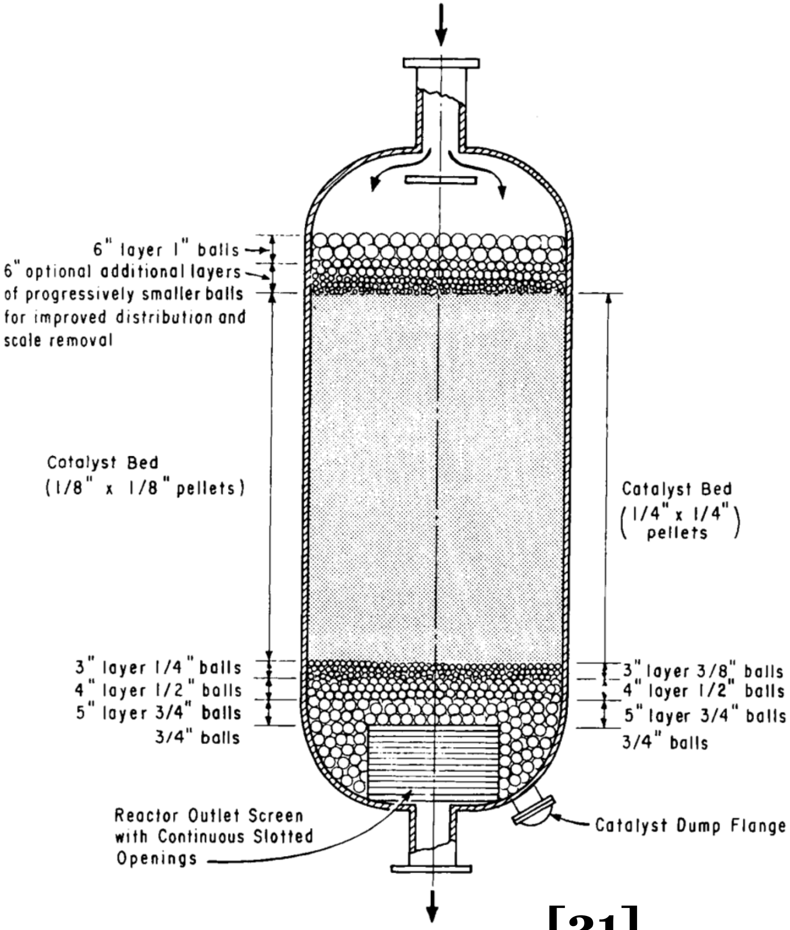
Fixed bed reactors

[4]



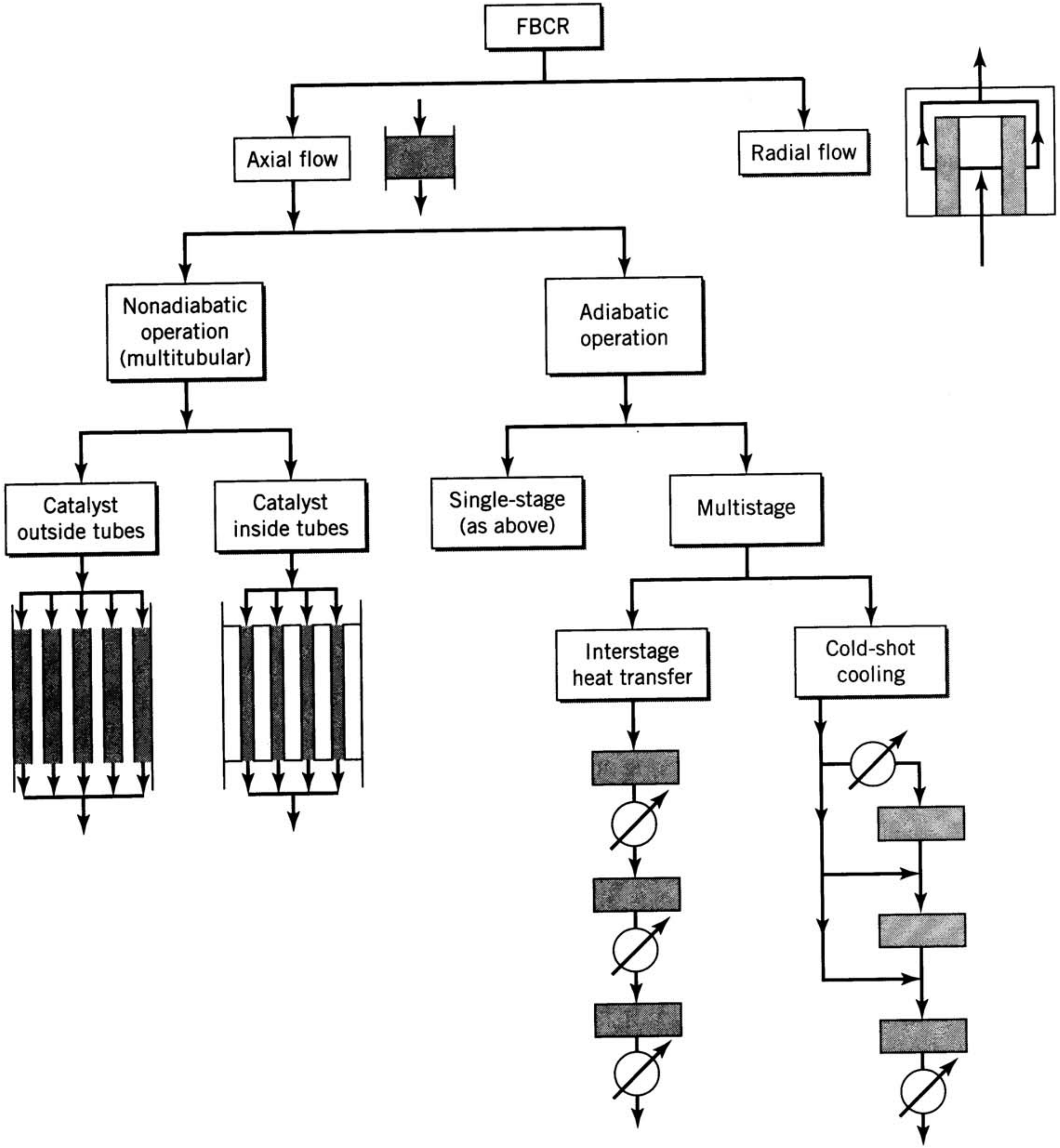


[21a]

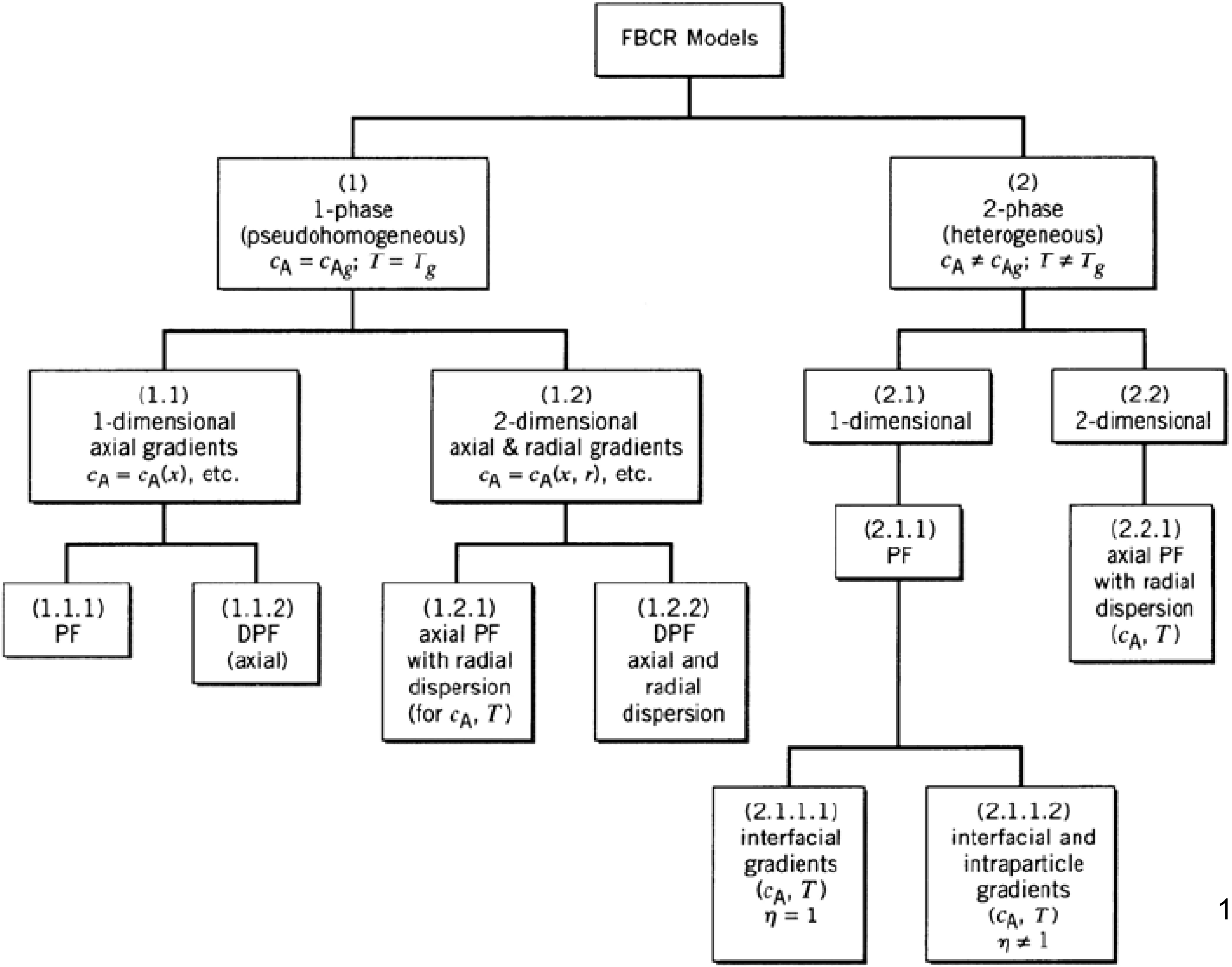


[21]

Types of fixed bed reactors [14]



Fixed bed reactor models [14]



FBCR Models

(1)
1-phase
(pseudohomogeneous)
$c_A = c_{Ag};\ T = T_g$

(2)
2-phase
(heterogeneous)
$c_A \neq c_{Ag};\ T \neq T_g$

(1.1)
1-dimensional
axial gradients
$c_A = c_A(x)$, etc.

(1.2)
2-dimensional
axial & radial gradients
$c_A = c_A(x, r)$, etc.

(2.1)
1-dimensional

(2.2)
2-dimensional

(1.1.1)
PF

(1.1.2)
DPF
(axial)

(1.2.1)
axial PF
with radial
dispersion
(for c_A, T)

(1.2.2)
DPF
axial and
radial
dispersion

(2.1.1)
PF

(2.2.1)
axial PF
with radial
dispersion
(c_A, T)

(2.1.1.1)
interfacial
gradients
(c_A, T)
$\eta = 1$

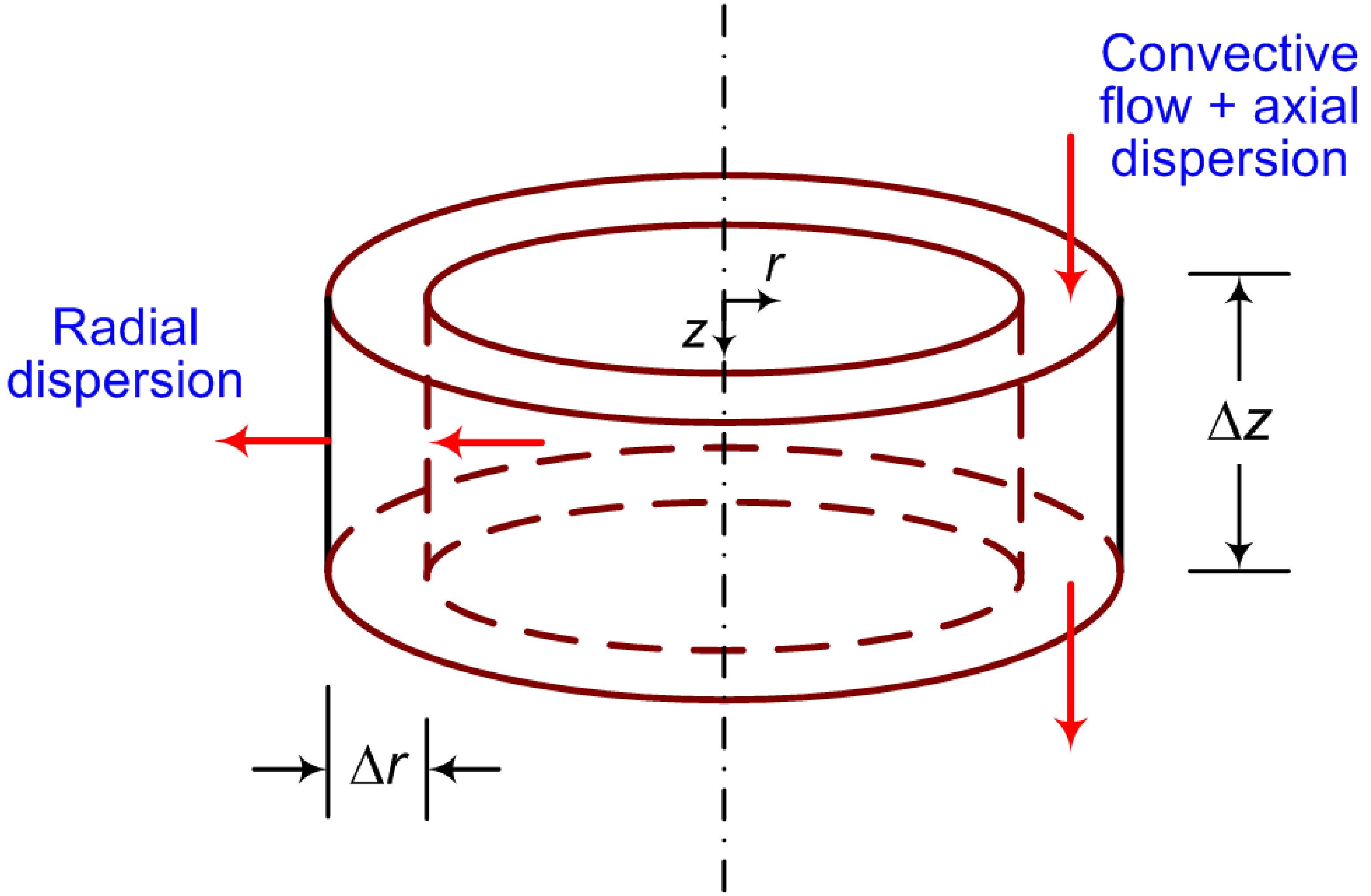
(2.1.1.2)
interfacial and
intraparticle
gradients
(c_A, T)
$\eta \neq 1$

Fixed bed reactor models [14]

(1) In a "one-phase" or pseudohomogeneous model, intraparticle gradients are ignored, so that everywhere in the catalyst bed, the value of concentration (c_A) or temperature (T) is the same as the local value for bulk fluid (c_{Ag} or T_g). The actual two-phase system (fluid and catalyst) is treated as though it were just one phase. In a two-phase or heterogeneous model, intraparticle gradients are allowed, so that, locally, within the particle, $c_A \neq c_{Ag}$ and $T \neq T_g$. The effects of these gradients are reflected in the particle effectiveness factor, η (Section 8.5.4), or an overall effectiveness factor, η_o (Section 8.5.6). If the reactor operates nearly isothermally, a single value of η or η_o may be sufficient to describe thermal and concentration gradients. However, if operation is nonisothermal, η and/or η_o may vary along the length of the vessel, and it may be necessary to account explicitly for this behavior within the reactor model. A further discussion of the effects of interparticle and intraparticle gradients is presented in Section 21.6.

(2) In a one-dimensional model, gradients of c_A and T at the bed level are allowed only in the axial direction of bulk flow. In a two-dimensional model, gradients at the bed level in both the axial and radial directions are taken into account.

Steady-state two-dimensional pseudo-homogeneous model



Steady-state two-dimensional pseudo-homogeneous model

$$
\begin{aligned}
&\mathit{Mass\ balance}:\\
&\left(\mathit{Rate\ of\ mass\ in}\right)-\left(\mathit{Rate\ of\ mass\ out}\right)+\left(\mathit{Rate\ of\ mass\ generation}\right)\\
&-\left(\mathit{Rate\ of\ mass\ consumption}\right)=\left(\mathit{Rate\ of\ accumulation\ of\ mass}\right)
\end{aligned}
$$

$$
\begin{aligned}
&\mathit{Energy\ balance}:\\
&\left(\mathit{Rate\ of\ energy\ in}\right)-\left(\mathit{Rate\ of\ energy\ out}\right)+\left(\mathit{Rate\ of\ energy\ generation}\right)\\
&-\left(\mathit{Rate\ of\ energy\ consumption}\right)=\left(\mathit{Rate\ of\ accumulation\ of\ energy}\right)
\end{aligned}
$$

Steady-state two-dimensional pseudo-homogeneous model

Continuity equation (Constant D_{ea} and D_{er}):

$$D_{ea}\frac{\partial^2 c_A}{\partial z^2}+D_{er}\left(\frac{\partial^2 c_A}{\partial r^2}+\frac{1}{r}\frac{\partial c_A}{\partial r}\right)-\frac{\partial(uc_A)}{\partial z}-\rho_B\cdot(-r_A)=0$$

Energy equation (Constant $c_{p,}$ Δh_{rxn} and k_{er}):

$$k_{ea}\frac{\partial^2 T}{\partial z^2}+k_{er}\left(\frac{\partial^2 T}{\partial r^2}+\frac{1}{r}\frac{\partial T}{\partial r}\right)-Gc_p\frac{\partial T}{\partial z}+\rho_B\cdot(-r_A)(-\Delta h_{rxn})=0$$

For the derivations, see class notes and book by Missen, Ref. 14.

Peclet numbers

Peclet number for mass transfer

$$Peclet\,number = \frac{Mass\,trasnferrate\,by\,convection}{Mass\,transferrate\,by\,conduction}$$

$$\boxed{Pe_{a,m} = \frac{u \cdot d_p}{D_a} = \frac{G \cdot d_p}{\rho \cdot D_a}}$$

$$\boxed{Pe_{r,m} = \frac{u \cdot d_p}{D_r} = \frac{G \cdot d_p}{\rho \cdot D_r}}$$

Peclet number for heat transfer

$$Peclet\,number = \frac{Heat\,trasnferrate\,by\,convection}{Heat\,transferrate\,by\,conduction}$$

$$\boxed{Pe_{a,h} = \frac{u \cdot d_p}{k_a} = \frac{G \cdot c_p \cdot d_p}{k_a}}$$

$$\boxed{Pe_{r,h} = \frac{u \cdot d_p}{k_r} = \frac{G \cdot c_p \cdot d_p}{k_r}}$$

Boundary conditions

$$F'_{A0} = F'_A + \left(-D_a \frac{dc_A}{dz} \right) \qquad \text{at } z = 0$$

$$Gc_p(T_o - T) = -k_a \frac{dT}{dz} \qquad \text{at } z = 0$$

$$\frac{\partial c_A}{\partial z} = \frac{\partial T}{\partial z} = 0 \qquad \text{at } z = L$$

$$\frac{\partial c_A}{\partial r} = \frac{\partial T}{\partial r} = 0 \qquad \text{at } r = 0$$

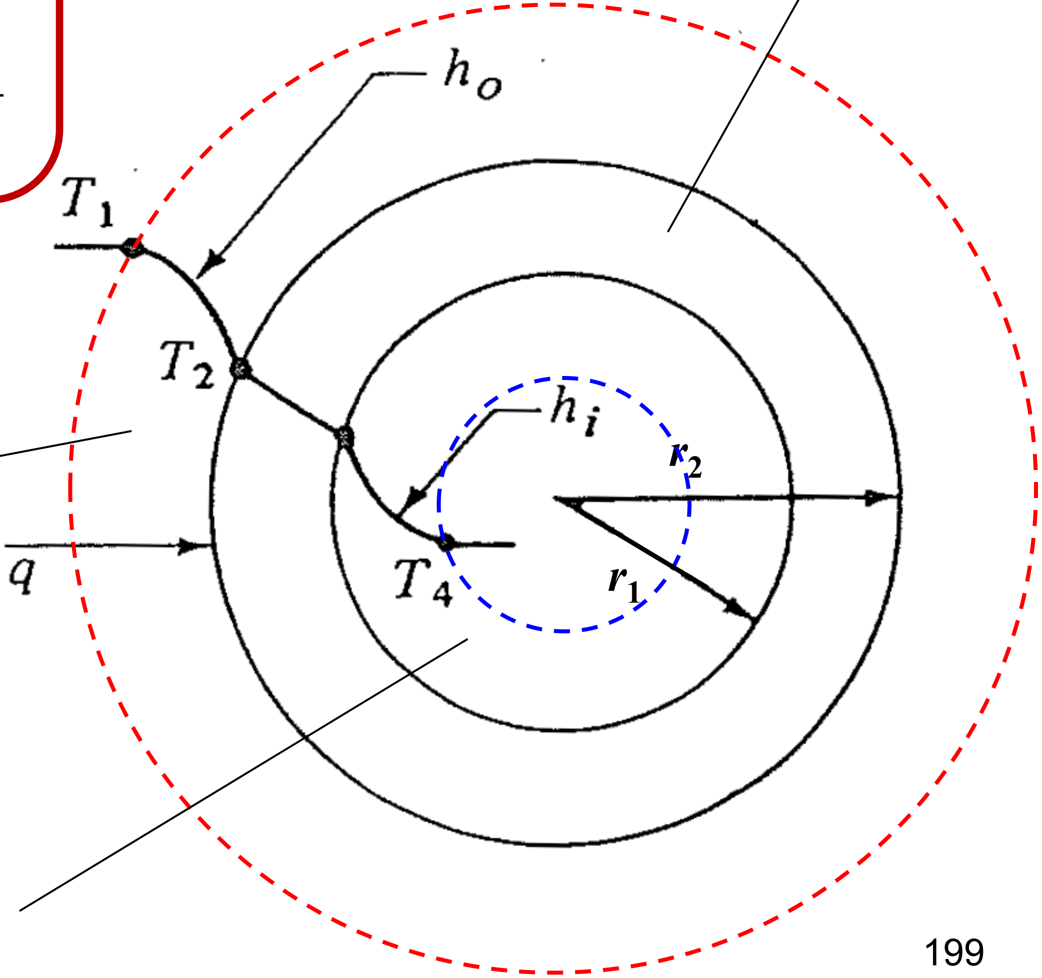
$$\frac{\partial c_A}{\partial r} = 0 \qquad \text{at } r = R_i$$

$$-k_r \left(\frac{dT}{dr} \right) = U_i(T_{r=R_i} - T_f) \qquad \text{at } r = R_i$$

Overall heat transfer coefficients: hollow cylinder

$$\frac{1}{U_i} = \frac{1}{h_i} + \frac{A_i \cdot \ln(r_2 / r_1)}{2 \cdot \pi \cdot k \cdot L} + \frac{A_i}{h_o \cdot A_o}$$

$$\frac{1}{U_o} = \frac{A_o}{h_i \cdot A_i} + \frac{A_o \cdot \ln(r_2 / r_1)}{2 \cdot \pi \cdot k \cdot L} + \frac{1}{h_o}$$



Pipe wall resistance

Outside fluid film resistance

Inside fluid film resistance

Bed properties and Ergun equation for pressure drop calculations

$$Particle\,density = \rho_p = \frac{\rho_s}{(\rho_s \times v_{\mathrm{P}}) + 1} \qquad Bulk\,voidage = \varepsilon_B = 1 - \frac{\rho_B}{\rho_p}$$

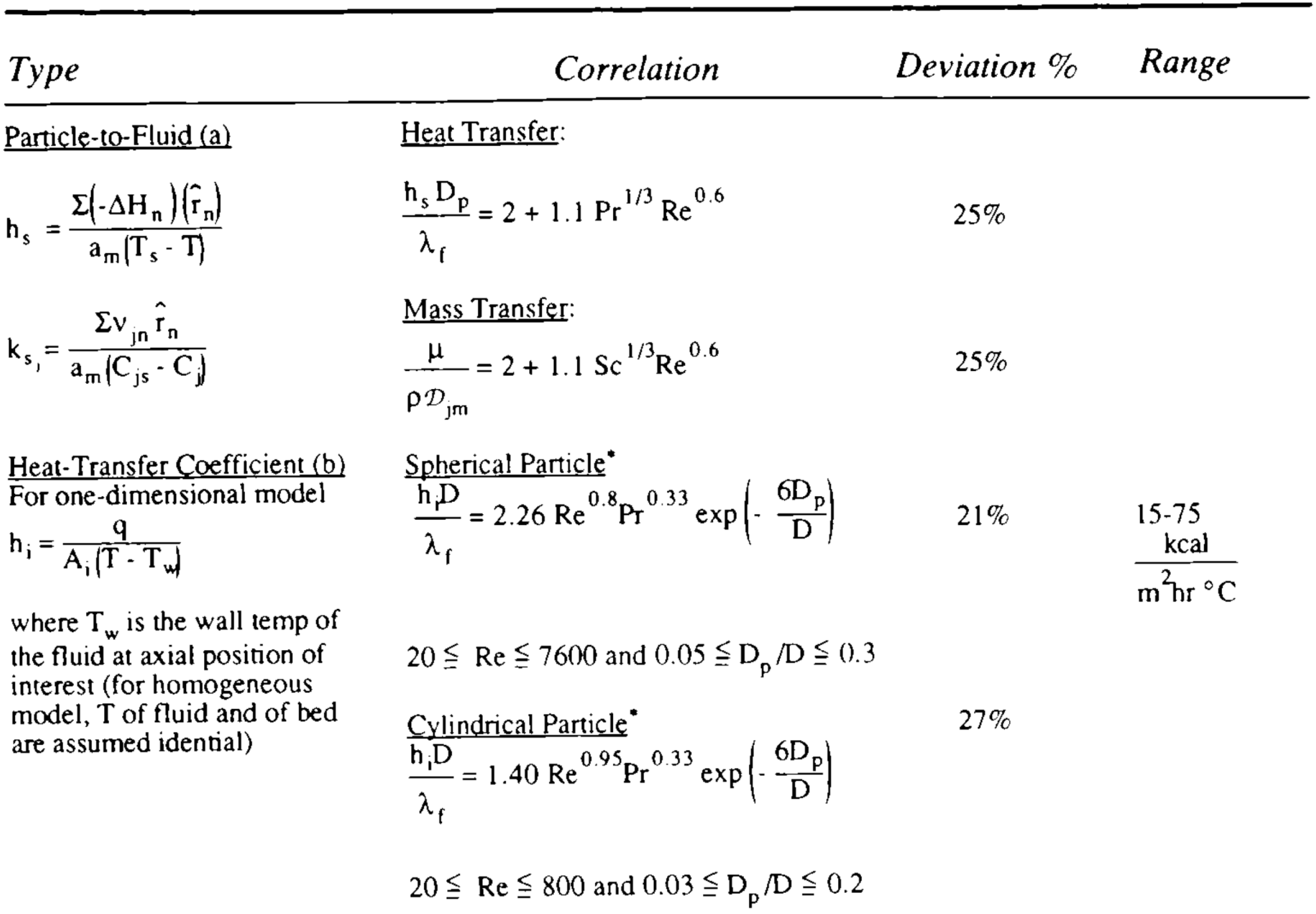
$$Bulk\,density = \rho_B = \rho_p \cdot (1 - \varepsilon_p) \cdot (1 - \varepsilon_B)$$

$$Particle\,Reynolds\,number = Re_p = \frac{d_p \cdot G}{\mu}$$

Ergun equation

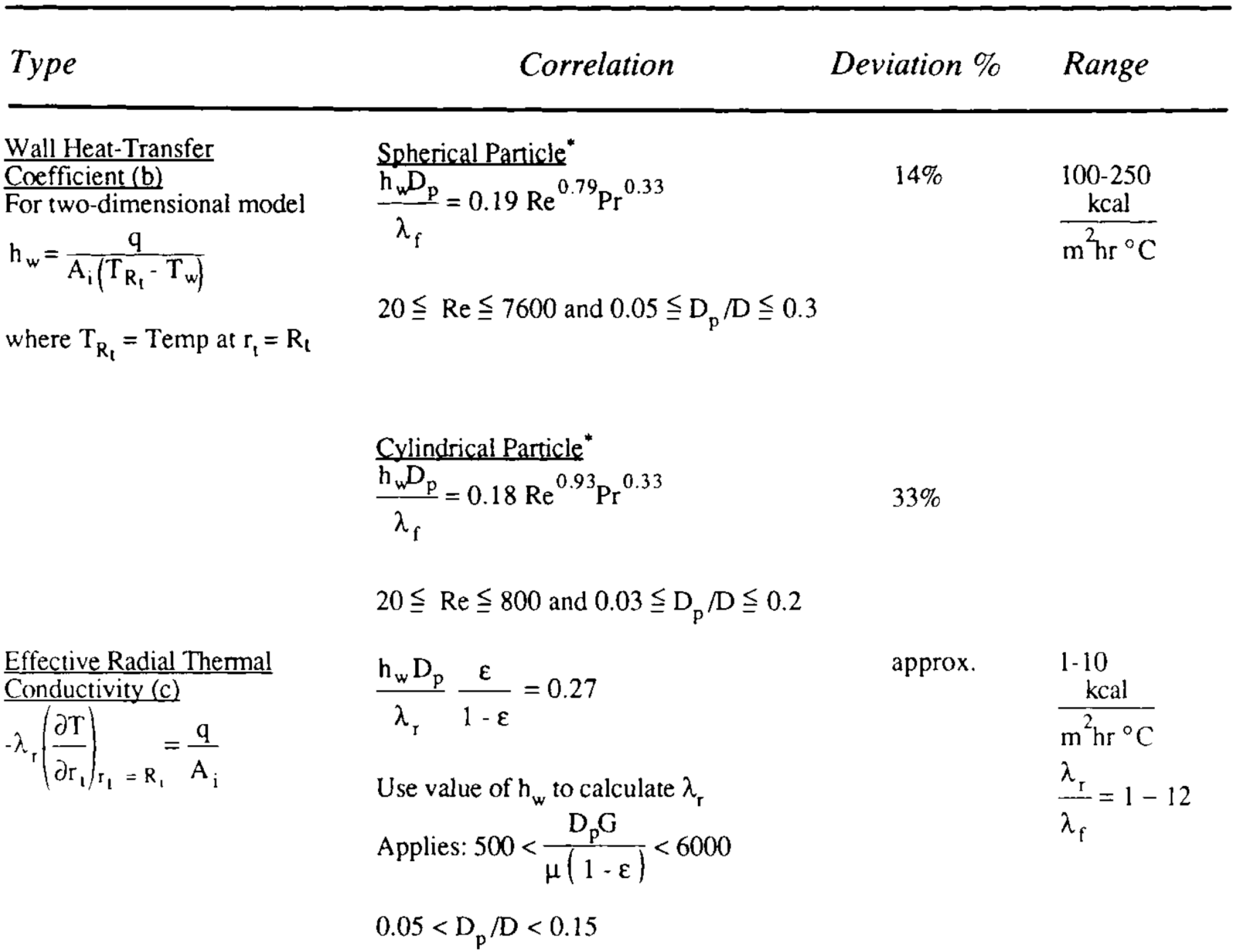
$$\boxed{-\frac{dp}{dz} = \frac{150 \cdot G \cdot \mu}{\rho \cdot \phi_s{}^2 \cdot d_v{}^2} \cdot \frac{(1 - \varepsilon_B)^2}{\varepsilon_B^3} + \frac{1.75 \cdot G^2}{\rho \cdot \phi_s \cdot d_v} \cdot \frac{1 - \varepsilon_B}{\varepsilon_B^3}}$$

Recommended correlations for fixed bed reactors [21]



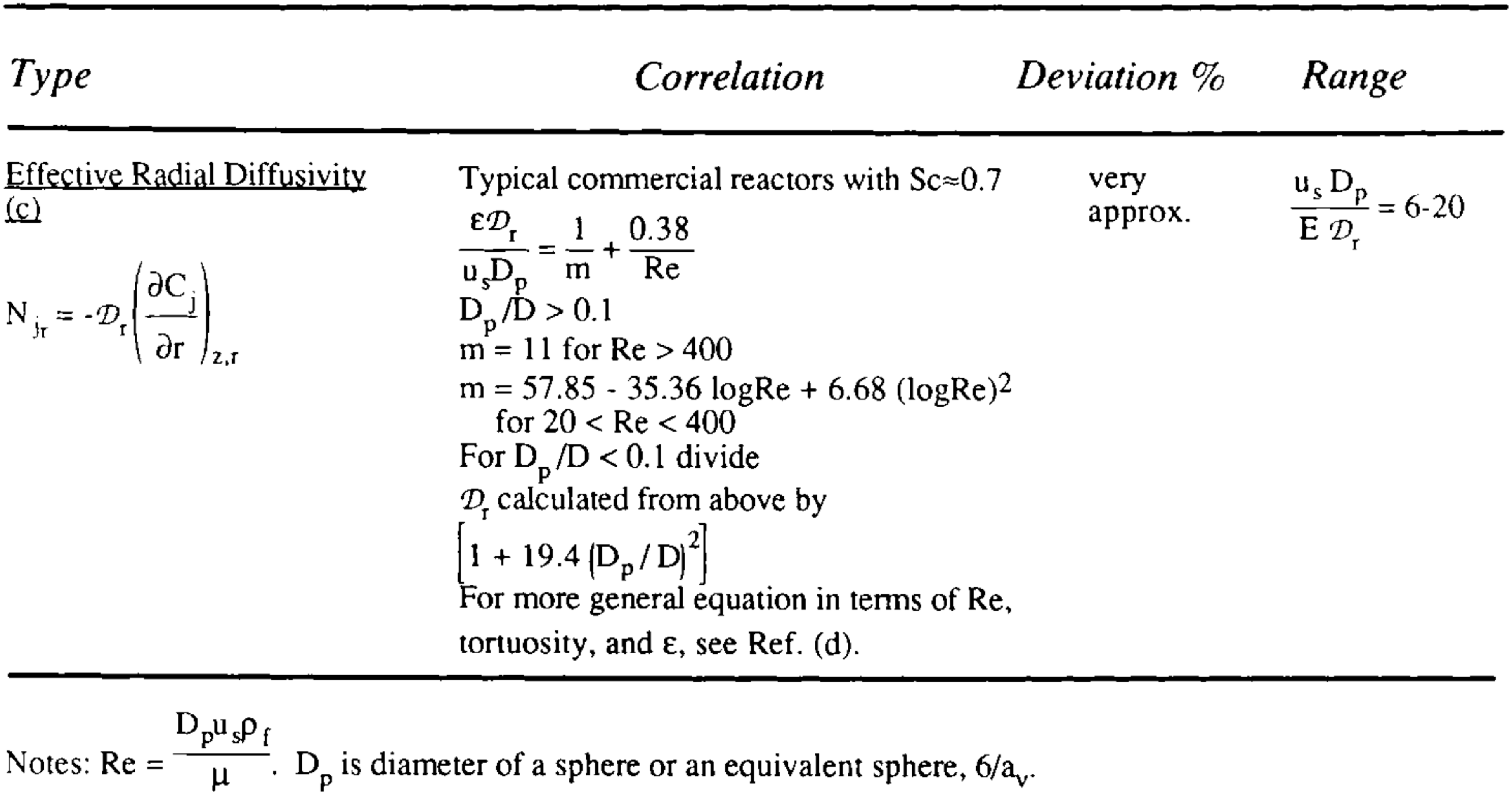
Type	*Correlation*	*Deviation %*	*Range*
Particle-to-Fluid (a)	Heat Transfer:		
$h_s = \frac{\Sigma(-\Delta H_n)(\hat{r}_n)}{a_m(T_s - T)}$	$\frac{h_s D_p}{\lambda_f} = 2 + 1.1\ Pr^{1/3}\ Re^{0.6}$	25%	
	Mass Transfer:		
$k_{s,} = \frac{\Sigma \nu_{jn} \hat{r}_n}{a_m(C_{js} - C_j)}$	$\frac{\mu}{\rho \mathcal{D}_{jm}} = 2 + 1.1\ Sc^{1/3} Re^{0.6}$	25%	
Heat-Transfer Coefficient (b) For one-dimensional model $h_i = \frac{q}{A_i(T - T_w)}$	Spherical Particle* $\frac{h_i D}{\lambda_f} = 2.26\ Re^{0.8} Pr^{0.33}\ \exp\left(-\frac{6D_p}{D}\right)$	21%	15-75 $\frac{\text{kcal}}{\text{m}^2\text{hr}\ {}^\circ\text{C}}$
where T_w is the wall temp of the fluid at axial position of interest (for homogeneous model, T of fluid and of bed are assumed idential)	$20 \leqq Re \leqq 7600$ and $0.05 \leqq D_p/D \leqq 0.3$		
	Cylindrical Particle* $\frac{h_i D}{\lambda_f} = 1.40\ Re^{0.95} Pr^{0.33}\ \exp\left(-\frac{6D_p}{D}\right)$	27%	
	$20 \leqq Re \leqq 800$ and $0.03 \leqq D_p/D \leqq 0.2$		

Recommended correlations for fixed bed reactors [21]



Type	*Correlation*	*Deviation %*	*Range*
Wall Heat-Transfer Coefficient (b) For two-dimensional model $h_w = \frac{q}{A_i\left(T_{R_t} - T_w\right)}$ where T_{R_t} = Temp at $r_t = R_t$	Spherical Particle* $\frac{h_w D_p}{\lambda_f} = 0.19\ Re^{0.79} Pr^{0.33}$ $20 \leqq Re \leqq 7600$ and $0.05 \leqq D_p/D \leqq 0.3$	14%	100-250 $\frac{\text{kcal}}{\text{m}^2\text{hr}\ ^\circ\text{C}}$
	Cylindrical Particle* $\frac{h_w D_p}{\lambda_f} = 0.18\ Re^{0.93} Pr^{0.33}$ $20 \leqq Re \leqq 800$ and $0.03 \leqq D_p/D \leqq 0.2$	33%	
Effective Radial Thermal Conductivity (c) $-\lambda_r \left(\frac{\partial T}{\partial r_t}\right)_{r_t = R_t} = \frac{q}{A_i}$	$\frac{h_w D_p}{\lambda_r} \frac{\varepsilon}{1 - \varepsilon} = 0.27$ Use value of h_w to calculate λ_r Applies: $500 < \frac{D_p G}{\mu(1 - \varepsilon)} < 6000$ $0.05 < D_p/D < 0.15$	approx.	1-10 $\frac{\text{kcal}}{\text{m}^2\text{hr}\ ^\circ\text{C}}$ $\frac{\lambda_r}{\lambda_f} = 1 - 12$

Recommended correlations for fixed bed reactors [21]



Type	*Correlation*	*Deviation %*	*Range*
Effective Radial Diffusivity (c) $N_{jr} = -\mathcal{D}_r \left(\frac{\partial C_j}{\partial r}\right)_{z,r}$	Typical commercial reactors with Sc≈0.7 $\frac{\varepsilon \mathcal{D}_r}{u_s D_p} = \frac{1}{m} + \frac{0.38}{Re}$ $D_p/D > 0.1$ $m = 11$ for $Re > 400$ $m = 57.85 - 35.36 \log Re + 6.68 (\log Re)^2$ for $20 < Re < 400$ For $D_p/D < 0.1$ divide $\mathcal{D}_r$ calculated from above by $\left[1 + 19.4 (D_p/D)^2\right]$ For more general equation in terms of Re, tortuosity, and ε, see Ref. (d).	very approx.	$\frac{u_s D_p}{E\, \mathcal{D}_r} = 6\text{-}20$

Notes: $Re = \frac{D_p u_s \rho_f}{\mu}$. D_p is diameter of a sphere or an equivalent sphere, $6/a_v$.

Physical properties of mixtures

Average molecular weight:

$$M_{ave} = y_A \cdot M_A + y_B \cdot M_B + y_C \cdot M_C + y_I \cdot M_I$$

Density (applicable at low pressure):

$$\rho = \frac{p \cdot M_{ave}}{R \cdot T}$$

Heat capacity:

$$c_p = y_A \cdot c_{p,A}(T) + y_B \cdot c_{p,B}(T) + y_C \cdot c_{p,C}(T) + y_I \cdot c_{p,I}(T)$$

Transport properties such as mass diffusivity, thermal conductivity, viscosity should not be taken as additive. Recommended mixing rules should be applied for such calculations. See Poling et al. [18] and Bird et al. [17] Chapters 1, 9, and 17.

Steady-state one-dimensional pseudo-homogeneous model with negligible axial diffusion for adiabatic operation

Continuity equation:

$$\frac{dX_A}{dz} = \frac{\pi \cdot D_i^2 \cdot \rho_B \cdot (-r_A)}{4 \cdot F_{A0}}$$

or

$$\frac{dX_A}{dz} = \frac{\rho_B \cdot (-r_A) \cdot M_0}{G \cdot y_{A0}}$$

Energy equation (Constant c_p and Δh_{rxn}):

$$\frac{dT}{dz} = \frac{\rho_B \cdot (-r_A) \cdot (-\Delta h_{rxn})}{G \cdot c_p}$$

Steady-state one-dimensional pseudo-homogeneous model with negligible axial diffusion for non-adiabatic operation

Energy equation (Constant c_p and Δh_{rxn}):

$$\frac{dT}{dz} = \frac{\rho_B \cdot (-r_A) \cdot (-\Delta h_{rxn})}{G \cdot c_p} - \frac{4 \cdot U_i \cdot (T - T_f)}{G \cdot c_p \cdot D_i}$$

What would be the boundary conditions for each case?

Fixed bed: A few rules of thumb

1. Usually d_p is chosen so that the ratio $D_i/d_p > 10$ to avoid flow problems. A very small particle, on the other hand, will cause excessive pressured drop.
2. In one of the criteria, the effect of axial dispersion depends on the ratio of the length of the reactor to the particle size. If the ratio is 100 or more, the effect is usually negligible compared to convective mass transfer.
3. Carman-Kozeny equation is suitable for fine particles. Ergun equation works well for both laminar and turbulent regions.

Solution of partial differential equations

- ✓ Finite difference approach
- ✓ Finite element approach

Finite difference:

- ✓ Explicit methods

  (Easy to put but beware of convergence and stability)
- ✓ Implicit methods

  The Crank-Nicolson method

Finite element:

- ✓ Comsol Multiphysics (old name Femlab).

Problem

A gas phase adiabatic fixed bed reactor is to be designed for the dehydrogenation of methylcyclohexane (MCH) to toluene and hydrogen. The feed to the reactor is 80 mol% methylcyclohexane and 20 mol% hydrogen flowing at the rate of 20 mol/s. The inlet temperature and pressure conditions are 340°C and 5.0 bar. Assume the principal reaction is clean and no byproducts are formed. Also assume constant pressure drop, specific heat capacity, and heat of reaction. By applying one-dimensional plug flow model,

a) determine the variation of temperature, partial pressures of each components, fractional conversion, and rate of reaction along the length of the reactor (effective factor is unity),

b) redo Part (a) if the effectiveness factor is 0.9,

c) redo Part (a) for the 80% deactivated catalyst. What are new conditions required for having the same outlet conversion as that obtained in Part (a).

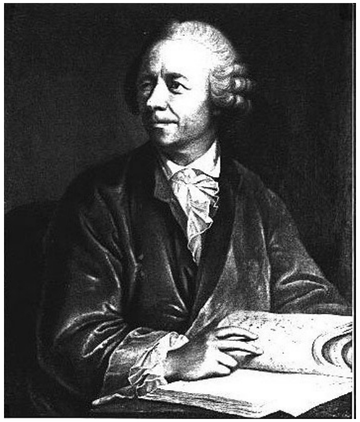
Take W/F_{A0} = 30,000 s·g-cat/mol, catalyst particle size = 4.0 mm, L/D of bed = 3.0, bed density = 900 kg/m^3, and bed voidage = 0.6.

Use the rate equation given on Slide 152.

Solution of one-dimensional pseudo-homogeneous model

Euler’s method is employed for approximate solution of ordinary differential equations with initial value problems.

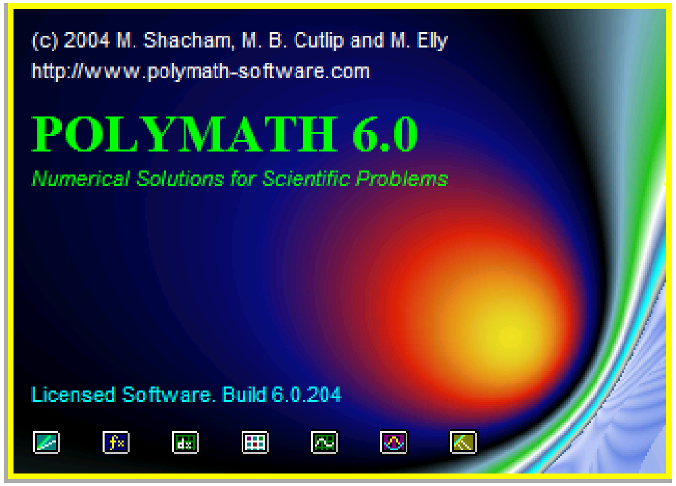
$$\boxed{\begin{gathered} y_{n+1} = y_n + h \cdot f(x_n, y_n) \\ h = x_{n+1} - x_n \end{gathered}}$$



Euler (1707-1783)

Take interval “*h*” as low as possible. Take large number of steps to avoid numerical instability.

Runge-Kutta 4th order method has better efficiency than Euler’s method.



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POLYMATH 6.0

Numerical Solutions for Scientific Problems

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Assignment (Last date: 09-May-2016)
Total marks: 12.5

A gas phase fixed bed reactor is to be designed for an adiabatic dehydrogenation of ethylbenzene. The feed to the reactor is pure reactant flowing at the rate of 20 mol/s. Assume the principal reaction is clean, i.e., no byproducts are formed. Using Euler's method (Excel spreadsheet) to find out the weight (W) of the catalyst for 30% conversion for constant value of effectiveness factor as 0.9. Take heat of reaction and specific heat capacity as constant. While doing this, workout the concentration (X_A), temperature (T), and total pressure (p) profiles along the flow direction (T vs W, p vs W, and X_A vs W). Plot T vs W, p vs W, and X_A vs W.

Note: You may prepare an excel spreadsheet but the assignment is to be submitted in the hard form. You need to find the reaction conditions and intrinsic rate equation from the literature.

Submit **hand written assignment** attached with it print of the part of the actual excel spreadsheet.

Reading materials

R-1	Pages 2 and 3 of Hill and Root [1]
R-2	Pages 591 to 594 of Couper et al. [4]
R-3	Complete article by Usman et al. [7]
R-4	Complete article by Ding et al. [8a]
R-5	Pages 1 to 11 of Richardson [6]
R-6	Complete article by Usman et al. [8]
R-7	Chapter 10 of Fogler [2]
R-8	Complete article by Weller, 1956
R-9	Pages 129 to 147 of Satterfield [15]
R-10	Pages 512 to 517 and 523 to 531 of Missen et al. [14]

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