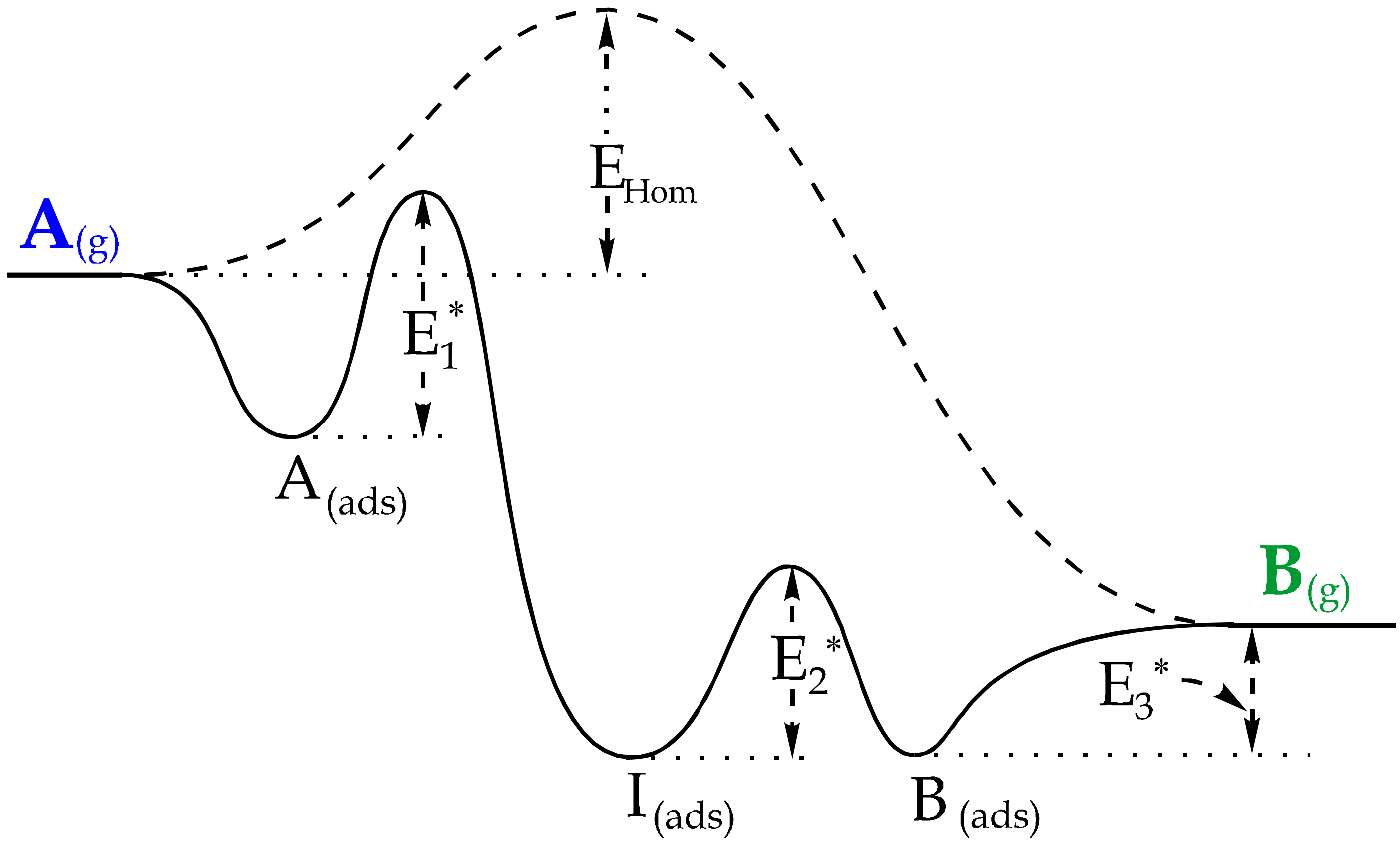
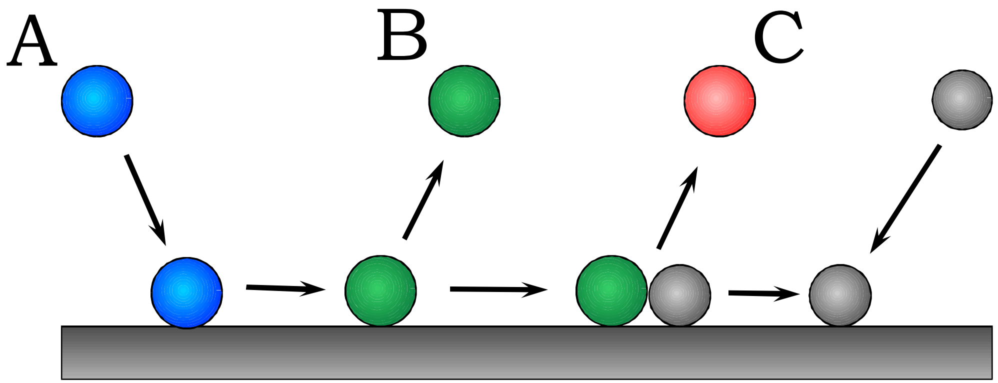
Experimental Aspects of Catalytic Kinetics Investigations

Julie L. d’Itri
University of Pittsburgh

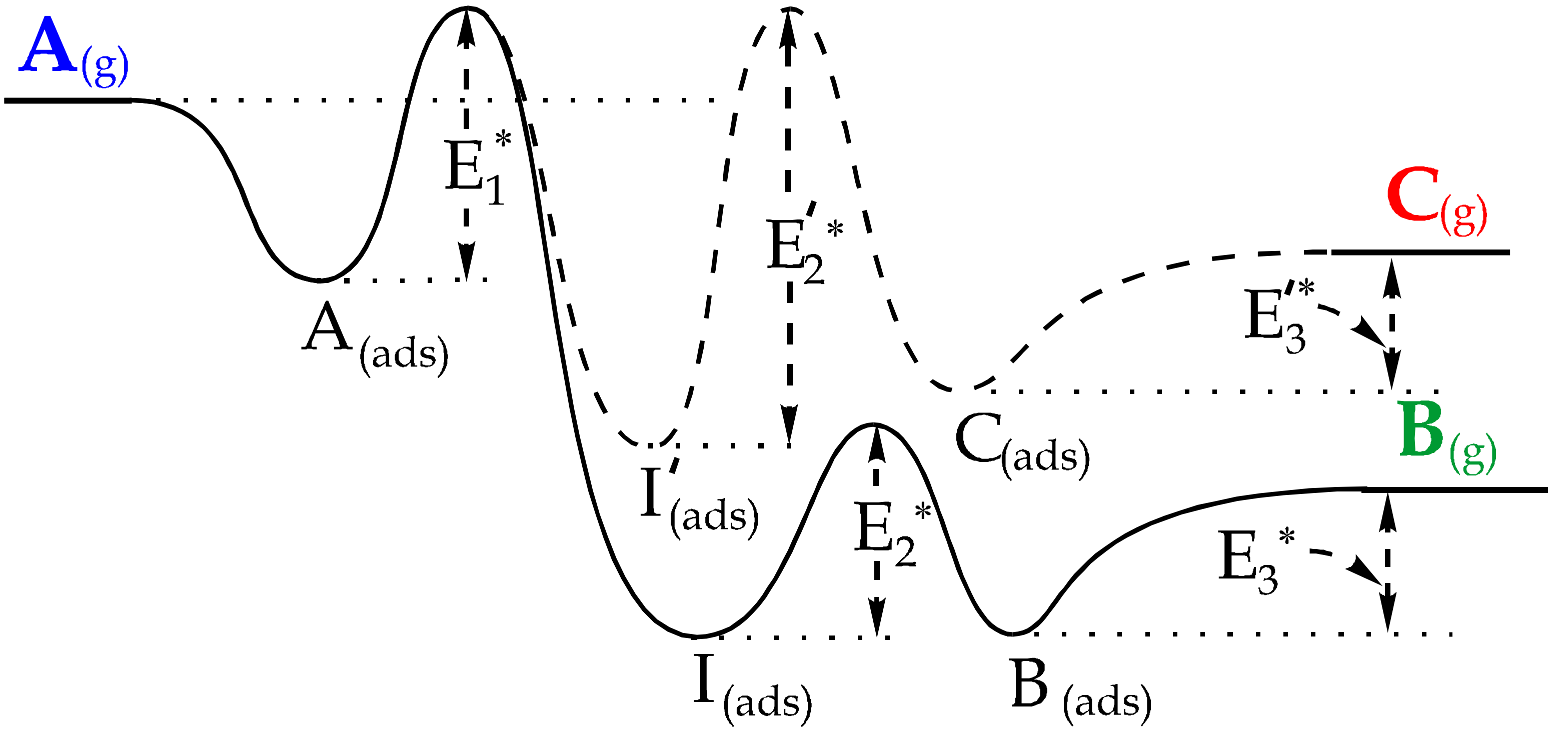
What a Surface Can Do

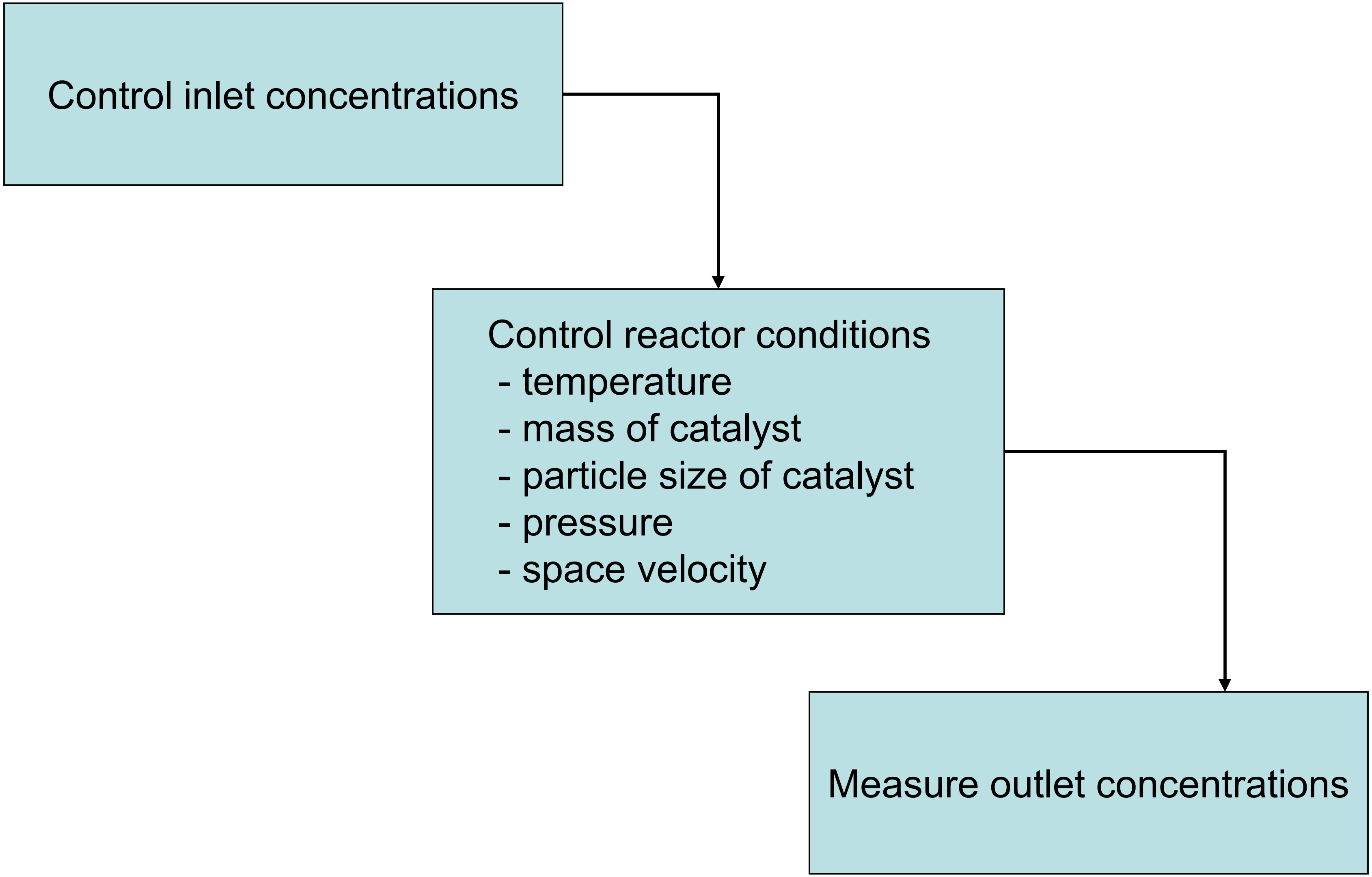


Real-Word Reactions Are Not So Simple



- Adsorption
- Surface Diffusion
- Reaction
- Desorption


$A_{(g)}$
E_1^*
$E_2'^*$
$C_{(g)}$
$A_{(ads)}$
$E_3'^*$
$C_{(ads)}$
$B_{(g)}$
$I'_{(ads)}$
E_2^*
E_3^*
$I_{(ads)}$
$B_{(ads)}$

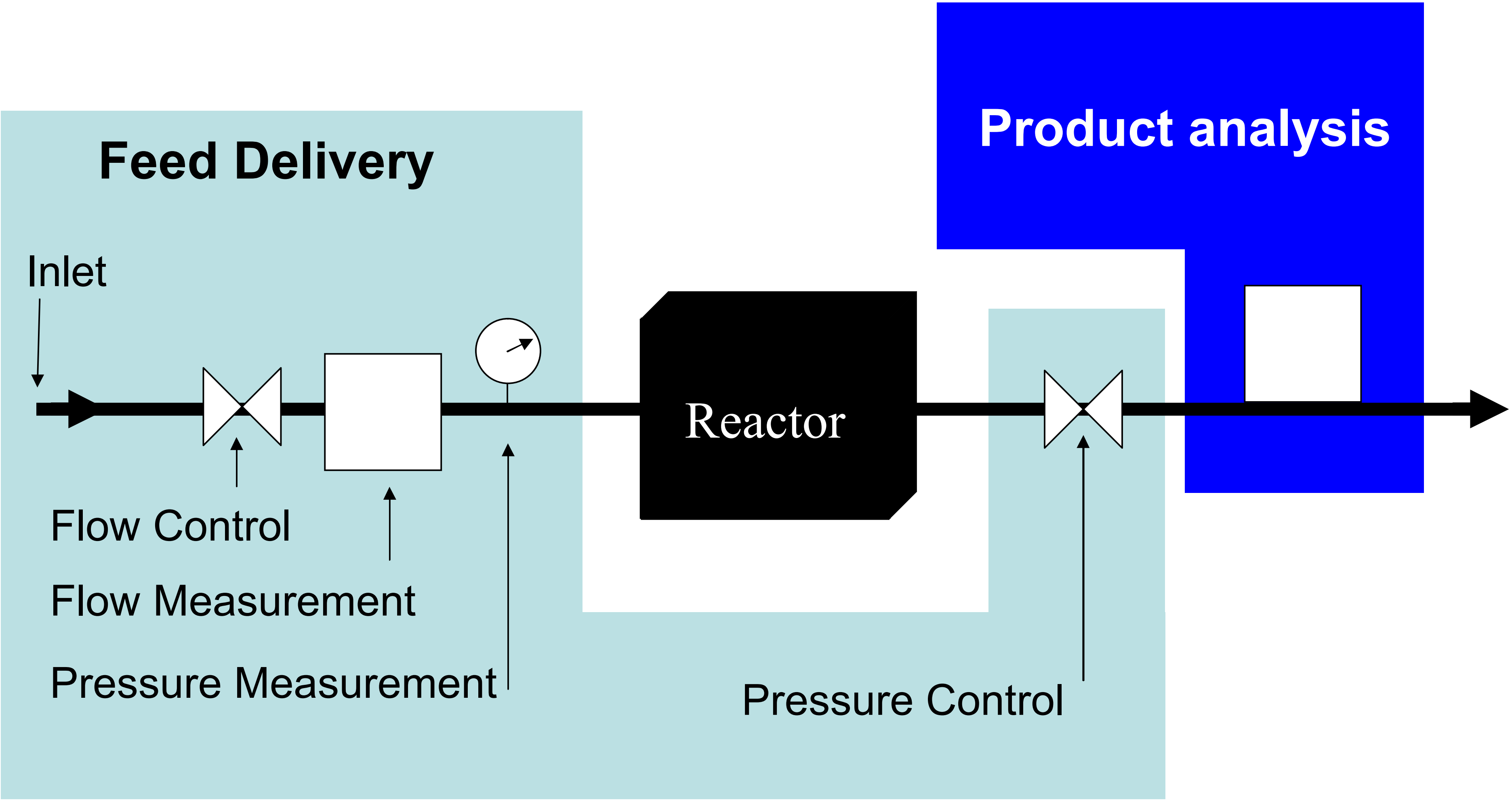


Control inlet concentrations

Control reactor conditions
- temperature
- mass of catalyst
- particle size of catalyst
- pressure
- space velocity

Measure outlet concentrations

Classical Flow System



First and Foremost

Thermodynamics must be established first.

Simplest Terms

- You measure what goes in…

and

- You measure what goes out.

Real – World Problems

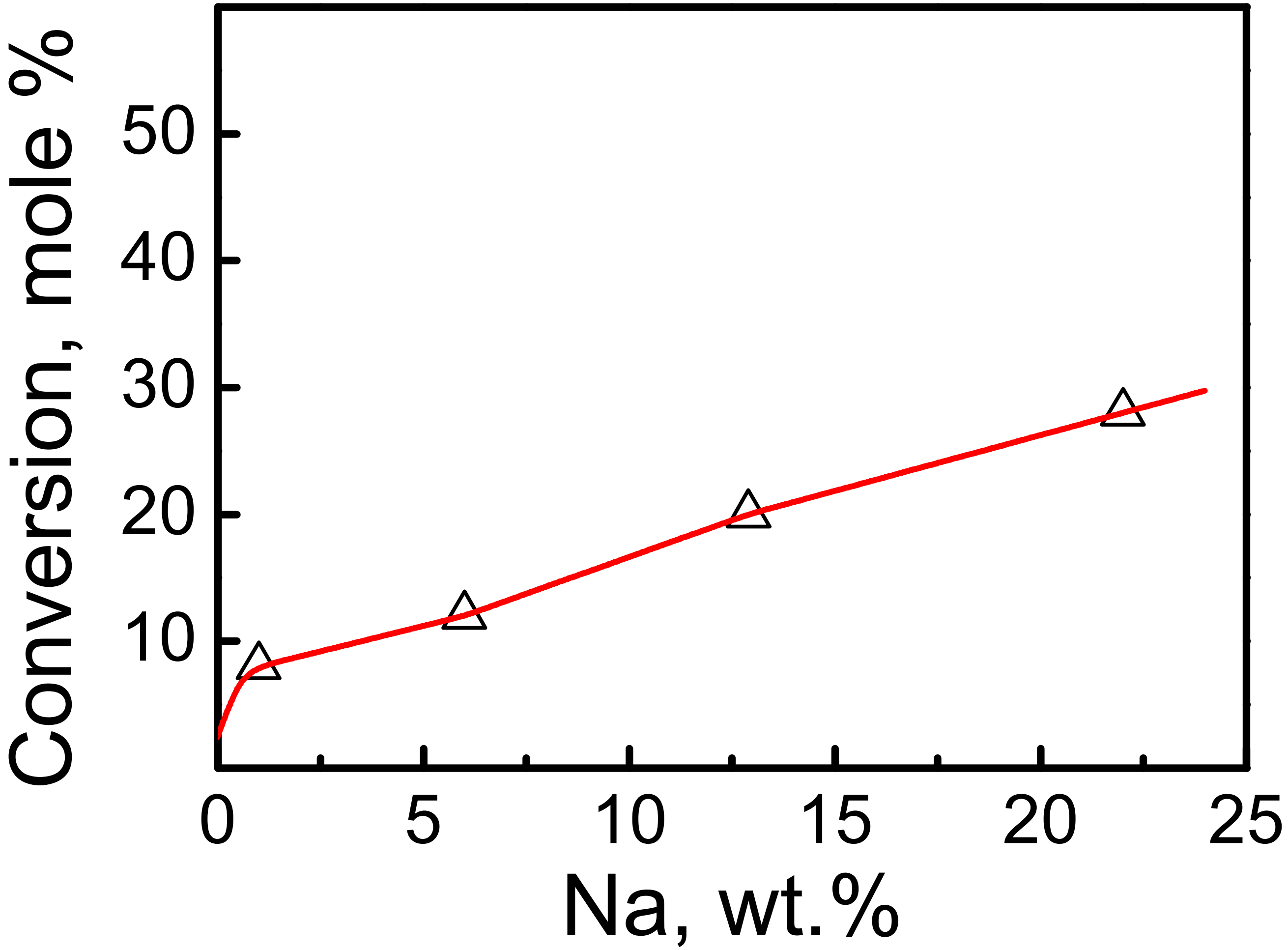
Most Active Catalyst?

A series of acidic molecular sieve catalysts were evaluated in a recent cumene process optimization study. The experiments were carried out in a tubular flow reactor at 543 K, 1.05 bar, with a benzene:propylene ratio of 2.4, and with 2.1 benzene liquid hourly space velocity. The reactor held 2.0 ml 40/60 mesh catalyst particles diluted with an equal volume of 60 mesh quartz particles to approximate isothermal conditions. Products were analyzed by gas chromatograph equipment with flame ionization detector and thermal conductivity detectors. An on-line sampling valve delivered the samples from the reactor to the GC instrument. The on-line samples were taken 60 minutes after start-up.

HNaY Zeolite for Benzene Alkylation with Propylene

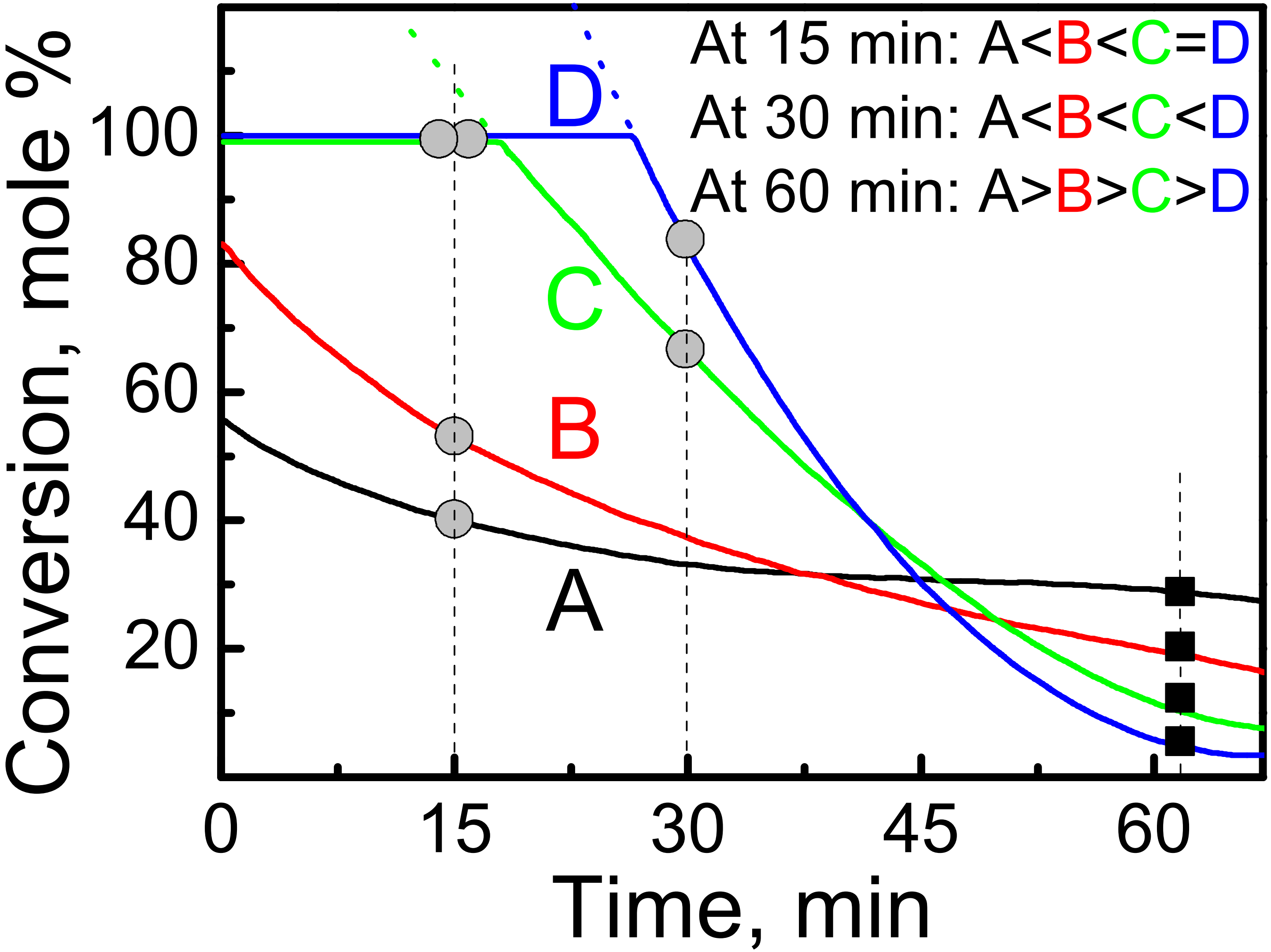
Preparation	Na, Wt%	Conversion to Cumene, Mol%
A. Single Exchange with NH4NO3	2.11	29.3
B. Two Exchanges with NH4NO3	1.28	20.6
C. Ultrastabilization	0.53	12.4
D. Ultrastabilization & Dealumination	0.08	6.6

C_6H_6 Alkylation with C_3H_6 over HNaY Molecular Sieve



Is the single exchange NaY the most active catalyst for benzene alkylation?

C_6H_6 Alkylation with C_3H_6 over HNaY Molecular Sieve



Another “activity” example

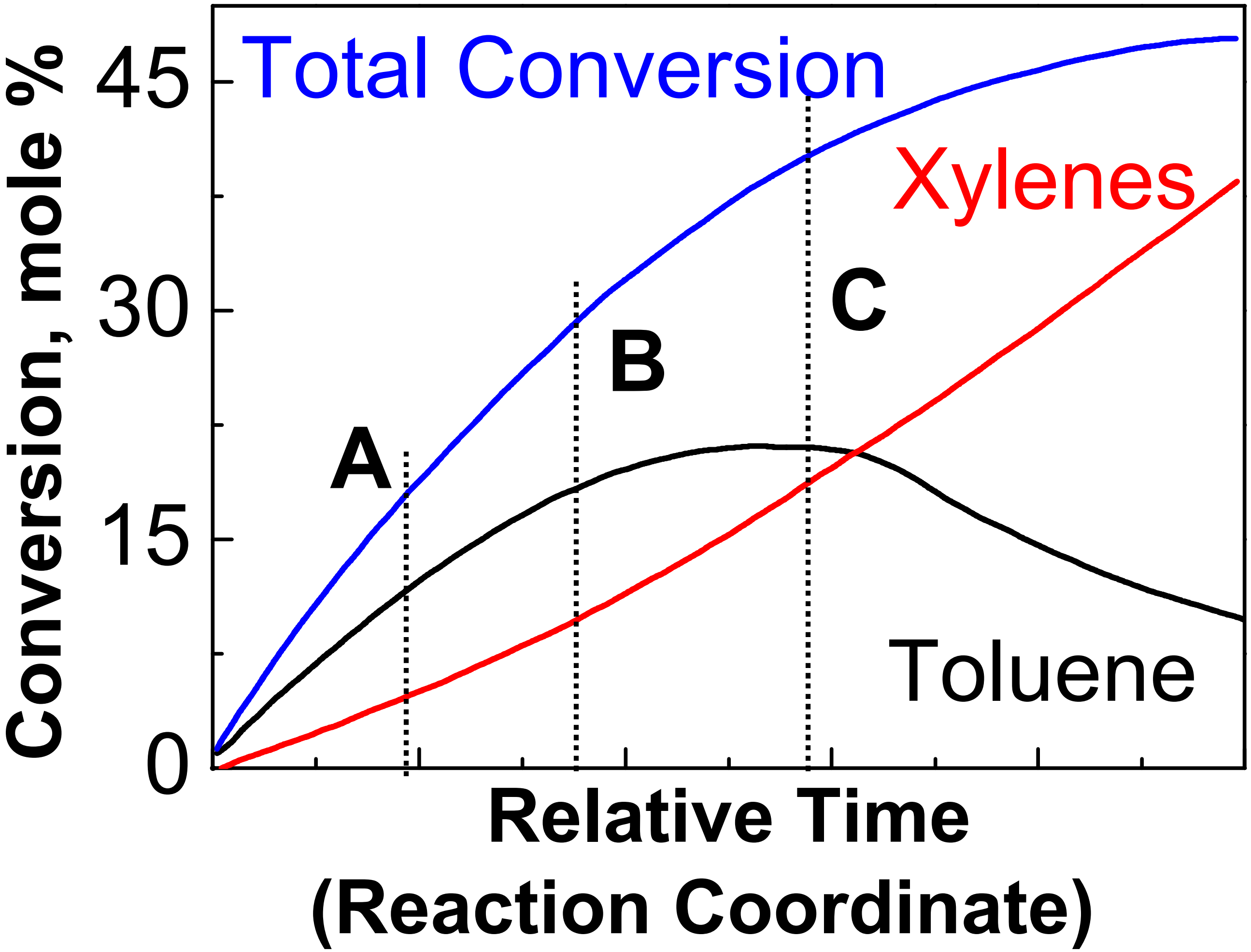
The reaction of benzene with methanol was catalyzed by a series of H-ZSM-5 zeolites in order to understand the effects of the Si/Al ratio on toluene selectivity. The reaction conditions were 683 K, atmospheric pressure, a benzene:methanol mole ratio of 2.0, and a benzene LHSV f 1.8. Liquid samples collected at subsequent one hour periods show that deactivation is negligible. Alkylation products were toluene and xylenes. Toluene selectivity is defined as [toluene]/[toluene + xylenes].

Benzene Alkylation with Methanol catalyzed by H-ZSM-5 Zeolites

Catalyst	Framework Si/Al Ratio	Conversion (Mole %)	Toluene Selectivity (Mole %)
A.	118	29.8	67.1
B.	68	60.6	63.3
C.	37	79.7	52.5

Is the increase in toluene selectivity attributed to the decrease in acid site density?

All three catalysts have exactly the same selectivity!



At constant temperature and pressure in a consecutive reaction system, the ratio of secondary products (xylenes) to primary product (toluene) depends on the ratio of the corresponding rate constants (k_1/k_2). As a consequence, the [toluene]/[toluene + xylenes] ratio will decrease with increasing conversion level.

The different "selectivities" shown in the Table are not real selectivities. They are toluene + xylenes product distributions corresponding at <u>constant selectivity</u> (viz. constant k_1/k_2 ratio) to different conversions (viz., to different points along the reaction profile).

Take Home Messages

- Determine how the catalyst deactivates with time on stream
  - Single on-line samples or single liquid samples per catalyst are acceptable only if stable operation is assured for every one of the catalysts tested.

More Rules

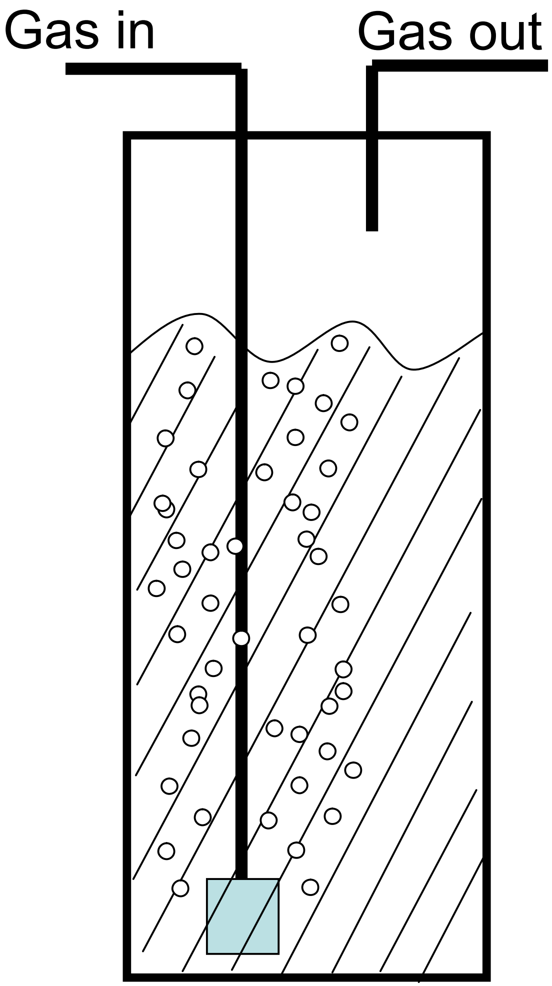
- Compare selectivies at equal conversion levels.

- Do NOT extrapolate.

Feed Delivery System

Saturators

Saturators: carrier gas is bubbled through a volume (height) of the liquid feed



Correct operation: gas in equilibrium with liquid reagent – fully saturated

Degree of saturation is a function of temperature and pressure

Need to control temperature and measure pressure

Saturator Design Aspects

Carrier gas inert to liquid,
(saturates liquid at very low concentration)

Bubbles should be small (frit on bottom of inlet)

Height of liquid must be controlled

No foaming or formation of spray

Analyze to determine saturation and stability

Tubing down stream of saturator must be at
higher temperature than liquid

Example Calculation

What is methanol concentration in a N_2 stream that exits a saturator filled with methanol at 21.2 °C and 1 bar?

Flow N_2 = $Q_{N_2} =$ 20 sccm/min

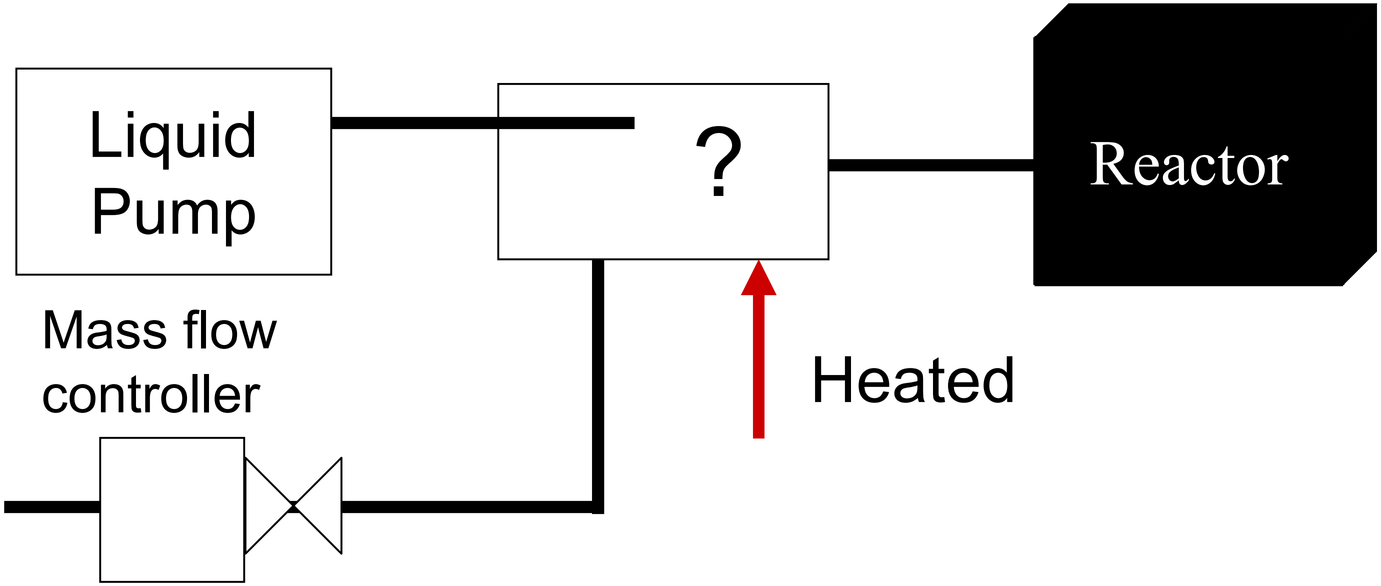
Vapor pressure methanol = p_m = 0.132 bar

$$p_{N_2} = p_{total} - p_m = 0.868 \text{ bar}$$

$$Q_{total} = Q_{N_2}\left(\frac{P_{total}}{P_{N_2}}\right) = 23.0 \text{ sccm/min}$$

Vaporizers

Vaporizers: liquid flow is controlled and liquid is mixed with carrier gas and evaporated



Liquid flow are very low (5 microliters methanol / minute)

Configuration of vaporizer is not trivial

The vaporization process more unstable at low flows

Remember This!

- Connect the feed line directly to a TCD of a gas chromatograph
  - A straight horizontal line shows complete mixing
  - A wavy line shows poor mixing or uneven evaporation of a liquid feed.

More Problems with Liquid Feeds

- Excessive evaporator temperature will cause uneven boiling.
- At low liquid space velocities differences between daytime and nighttime temperatures can seriously disturb flowrates.
- Feed delivery systems have long “memories.”

Classification of Reactors

- Batch
- Continuous plug-flow
- Pulse plug-flow
- Stirred tank
- Single pass or recycle
- Isothermal or adiabatic
- Atmospheric, high-pressure, vacuum

General Operation Requirements for a Reaction System

- Steady state
- Isothermal (unless adiabatic reactor)
- Ideal flow pattern
- Isobaricity
- No concentration gradient

Recommendations about Reactors

- Use the smallest possible size, especially the smallest width.
- Use down flow.
- Use a preheater

Why Use Differential Reactors?

- When conversion is low (0-5%)

$$\text{Rate} = \frac{\text{(initial feed concentration)(conversion)}}{\text{(catalyst bed volume)/(feed rate)}}$$

- Knowledge of rate expression required for integral reactor

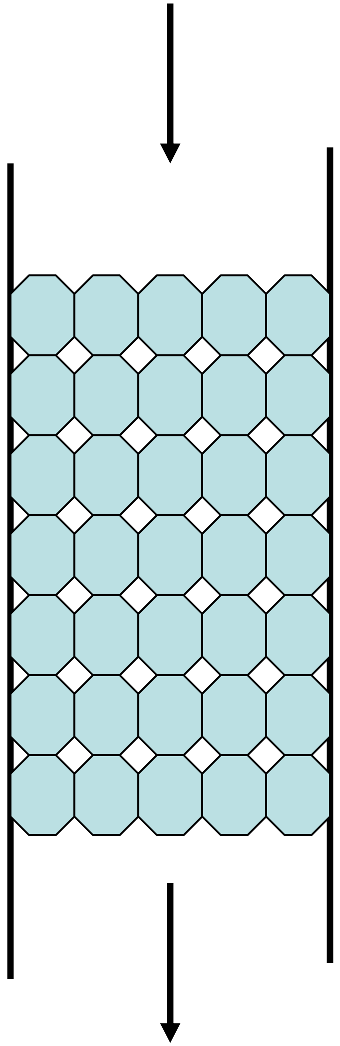
Disadvantages of Differential Reactors

- Rates are frequently measured at initial conversions, where rates are much faster than at higher conversions.
  - Solution: Use a feed that contains product.

- When conversions are small, experimental errors can be large.

Don’t Trust Pulse Reactors

- A distorted Gaussian distribution of feed partial pressures (and after encountering the first catalyst particles, product partial pressures) proceed through the catalyst bed.
- Chromatographic effects can distort results even more if intermediates or products are adsorbed either stronger or weaker than the starting reactant.

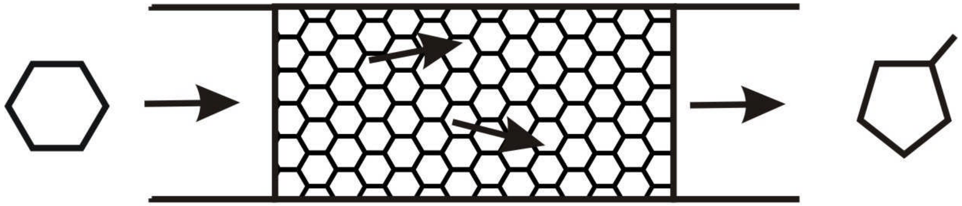


Temperature-Programmed Reactions can be dangerous

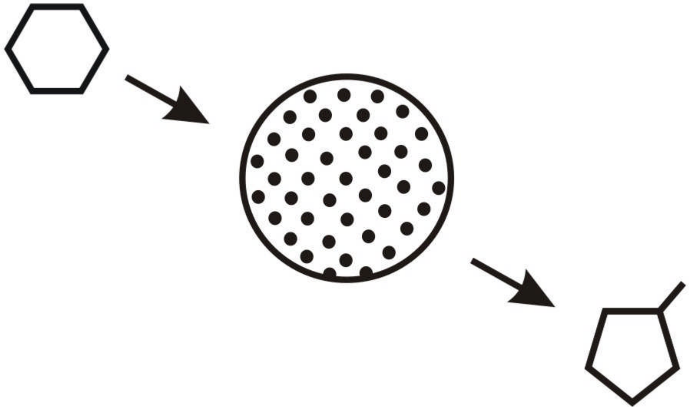
- One more than one parameter changing at a time.
- Equilibrium shifts with temperature.
- Catalyst itself can be changing, in ways unrelated to interactions with the active site.

Mass Transport Phenomena in a Reactor

Intrareactor Transport

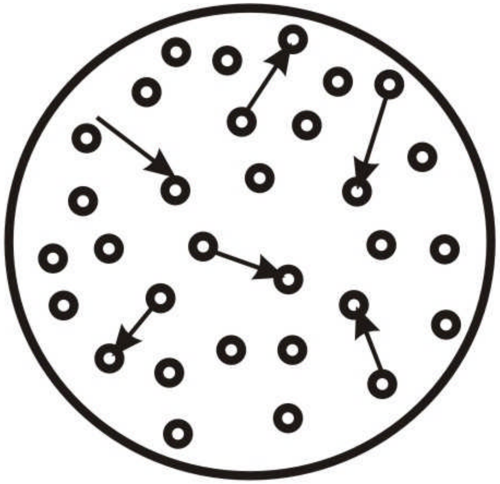


Interphase Transport

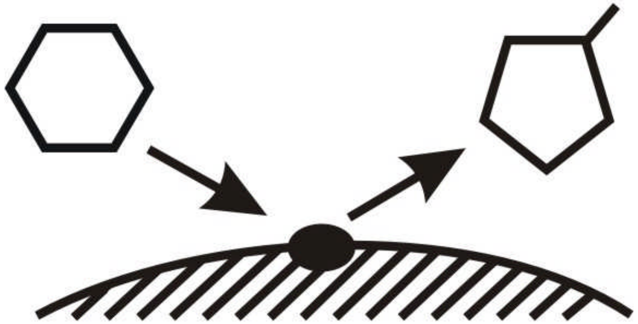


Mass Transport Phenomena in a Reactor

Intraparticle Transport



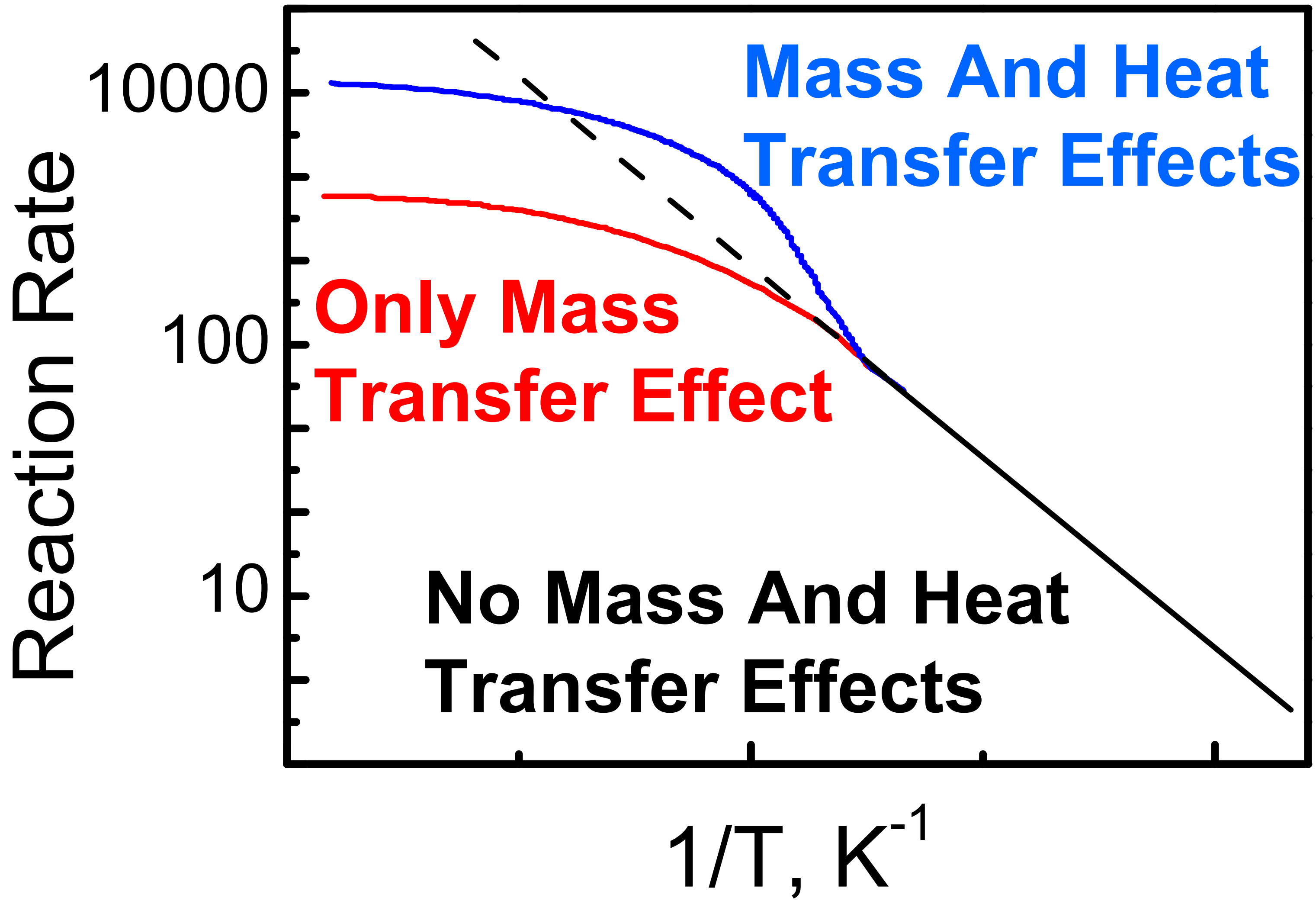
Surface Reaction



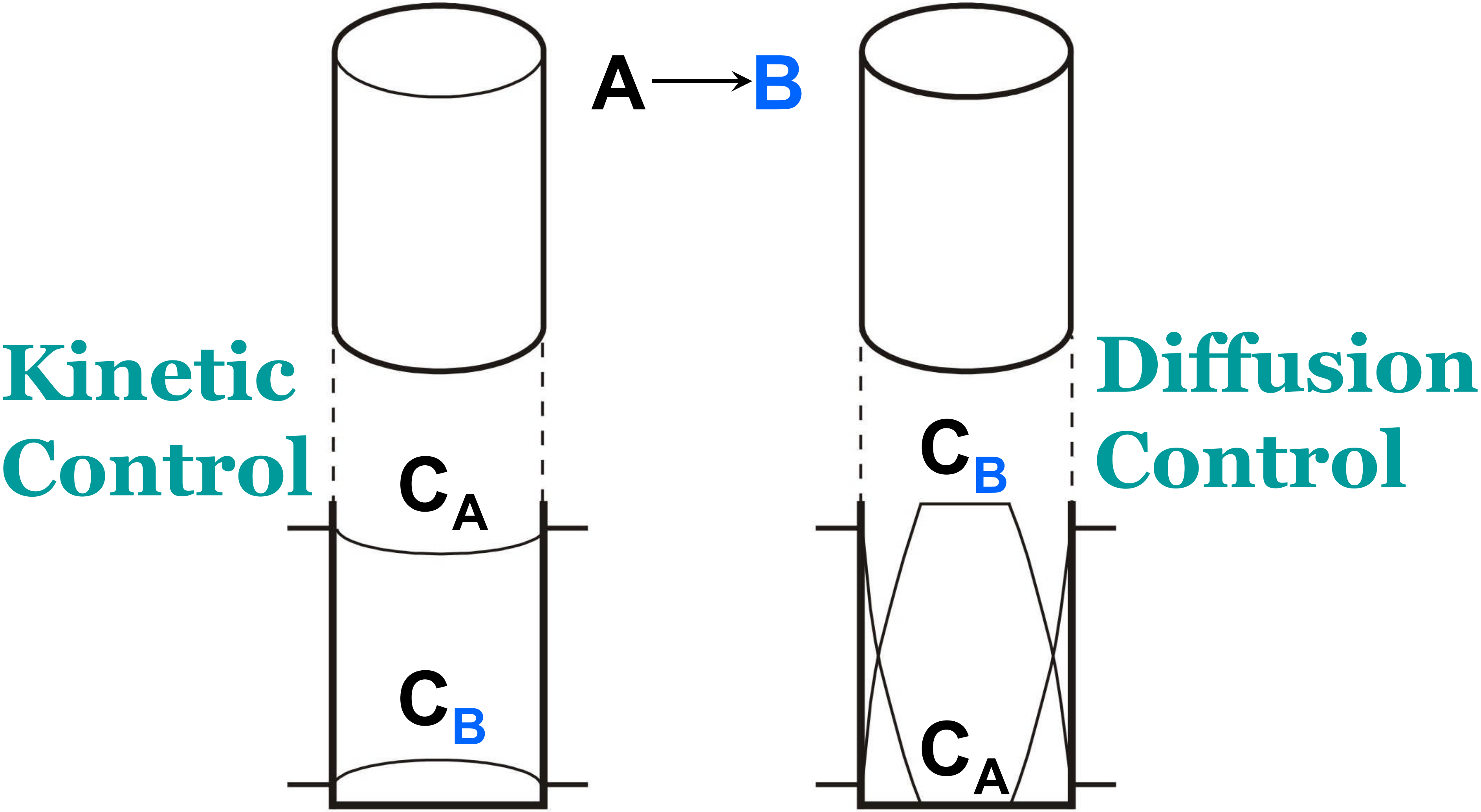
Remember This!

- Mass transfer becomes rate limiting when the surface reaction is faster than the supply of reactants and/or the removal of the products by any one of several diffusion step.
- Chemical reactions increase exponentially with increasing temperature.
- Diffusion increases linearly with temperature

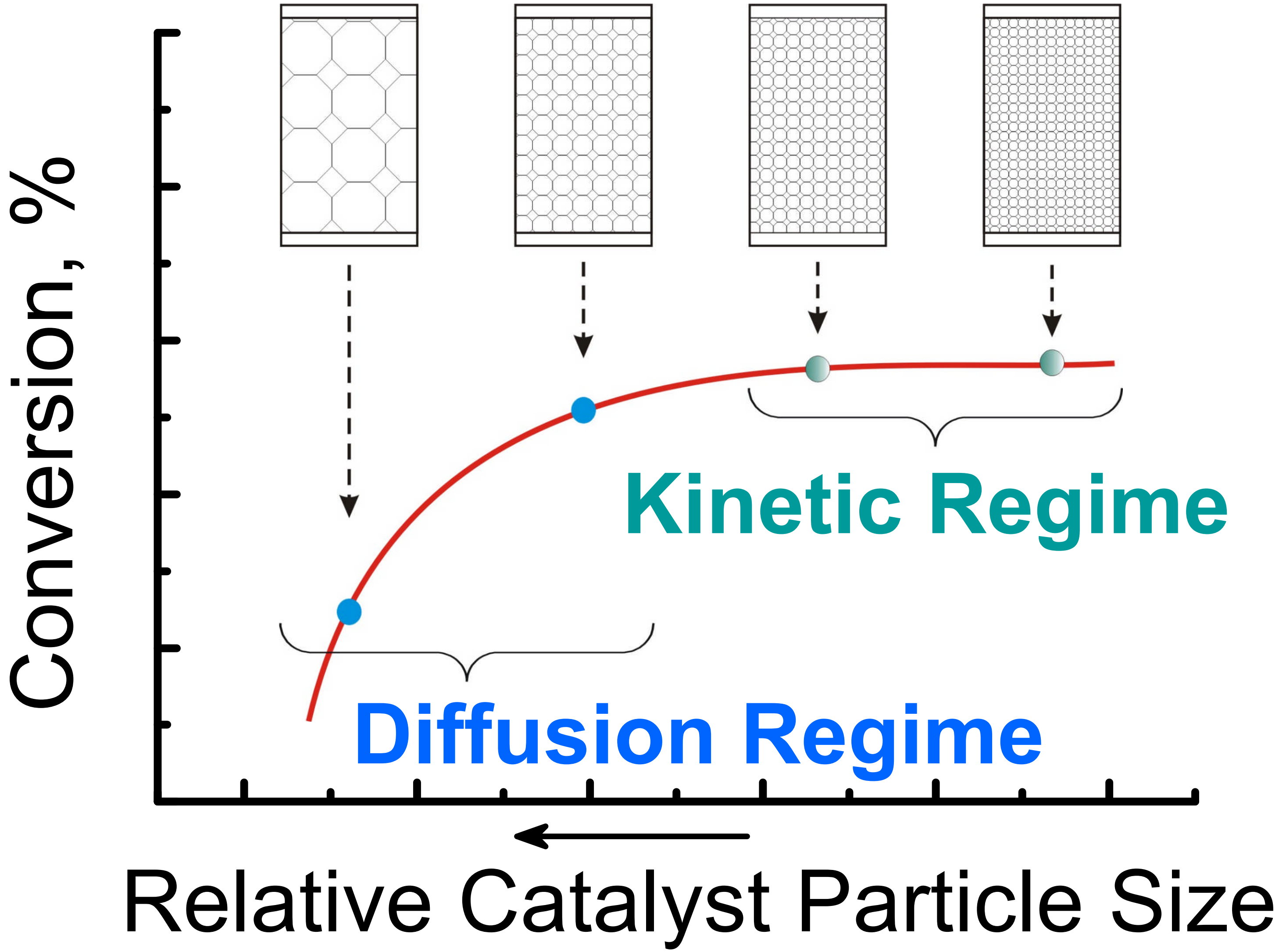
Intraparticle Mass and Heat Transfer Affects Reaction Rates



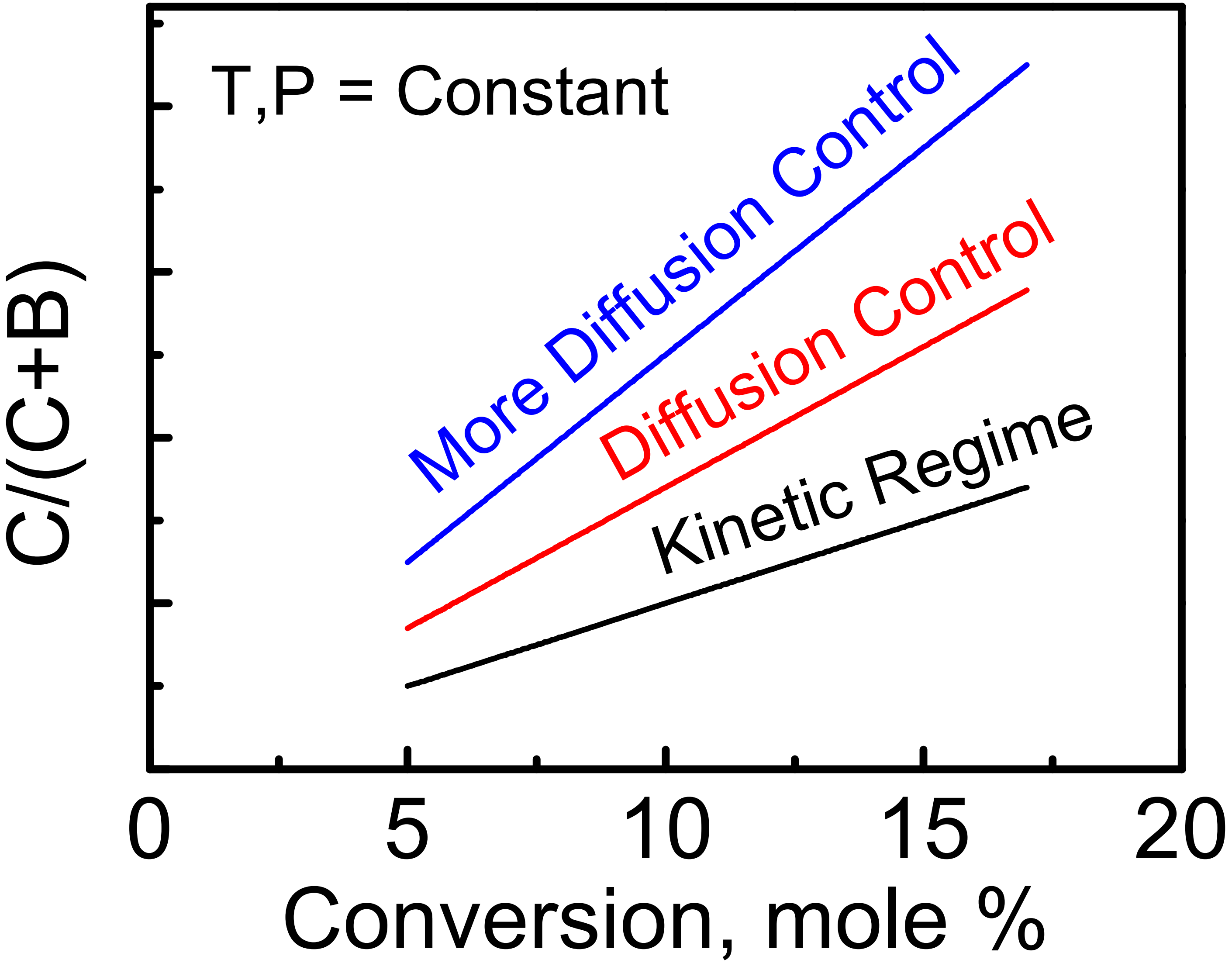
Concentration Profiles in a Catalyst Pellet



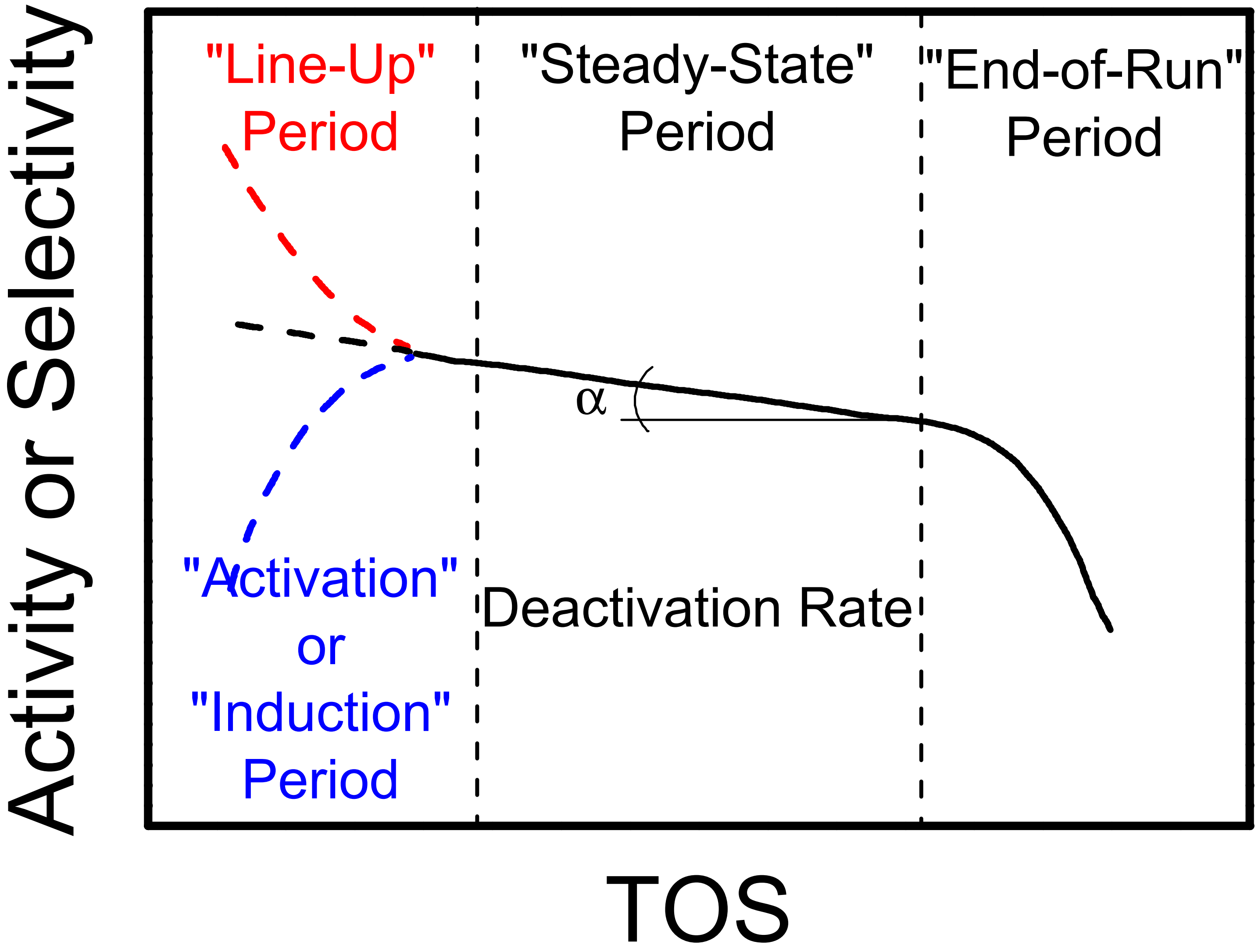
Are We in the Kinetic or in the Diffusion Regime?



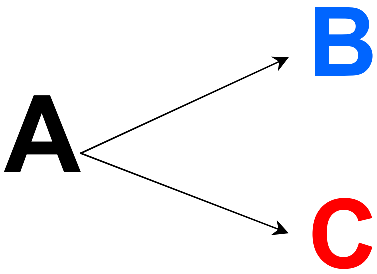
A Test for Mass Transfer Limitation in Irreversible Consecutive Reactions



Life Cycles of a Catalyst
Useful Lifetime of the Catalyst



Reaction Systems



Parallel

$$A \longrightarrow B \longrightarrow C$$

Consecutive

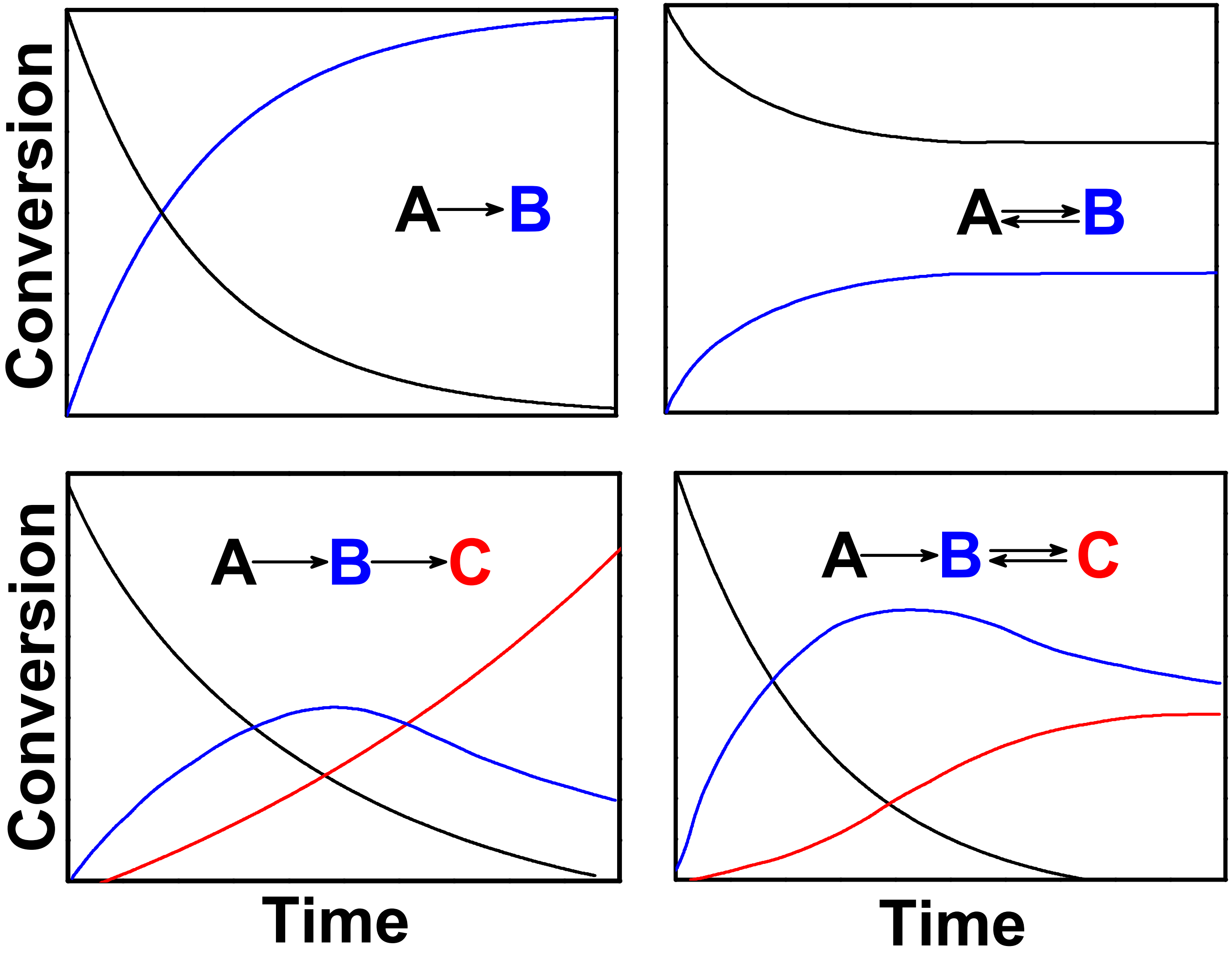
$$A \longrightarrow B$$

Irreversible

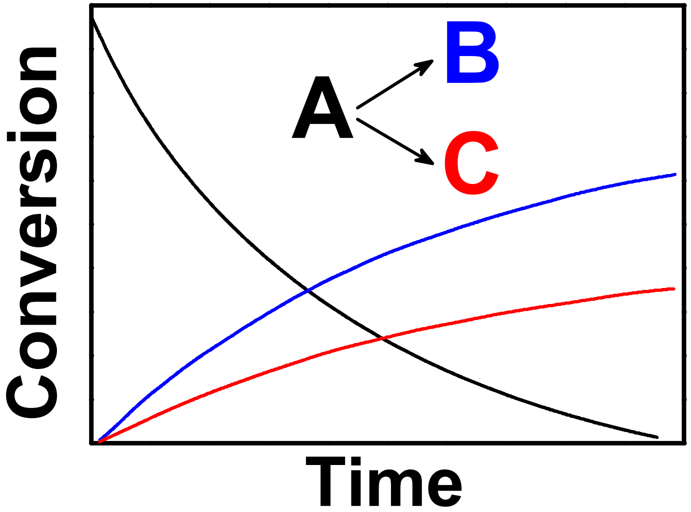
$$A \rightleftarrows B$$

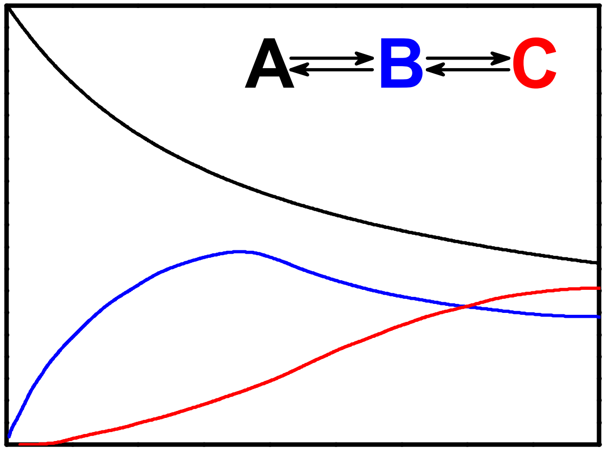
Reversible

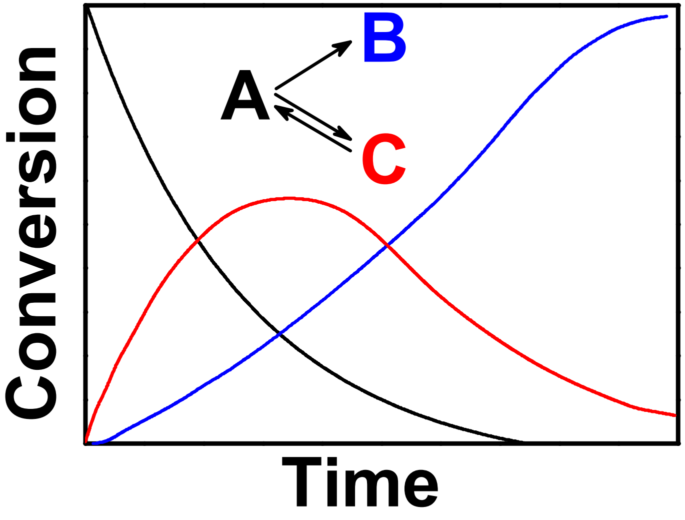
Reaction Systems



Reaction Systems







Acknowledgements

My thanks to Dr. Sigmund Csicsery for providing information and real-world examples used in this presentation.