How to build a catalytic test reactor

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how to build a catalytic test reactor

- i.e.:
  guidelines for building a set-up to investigate solid catalysts for gas phase reactions using a fixed bed pfr (plug flow reactor)
- commercial set-ups preferred for other reactions

overview

three sections of a set-up:

- gas delivery system
  - permanent gases
  - vapors of condensable substances
  - mixing unit
  - pressure controller (if needed)
- reactor with temperature control
  - reactor tube
  - oven/cryostat
- analytics with sampling device
  - GC
  - MS

overview

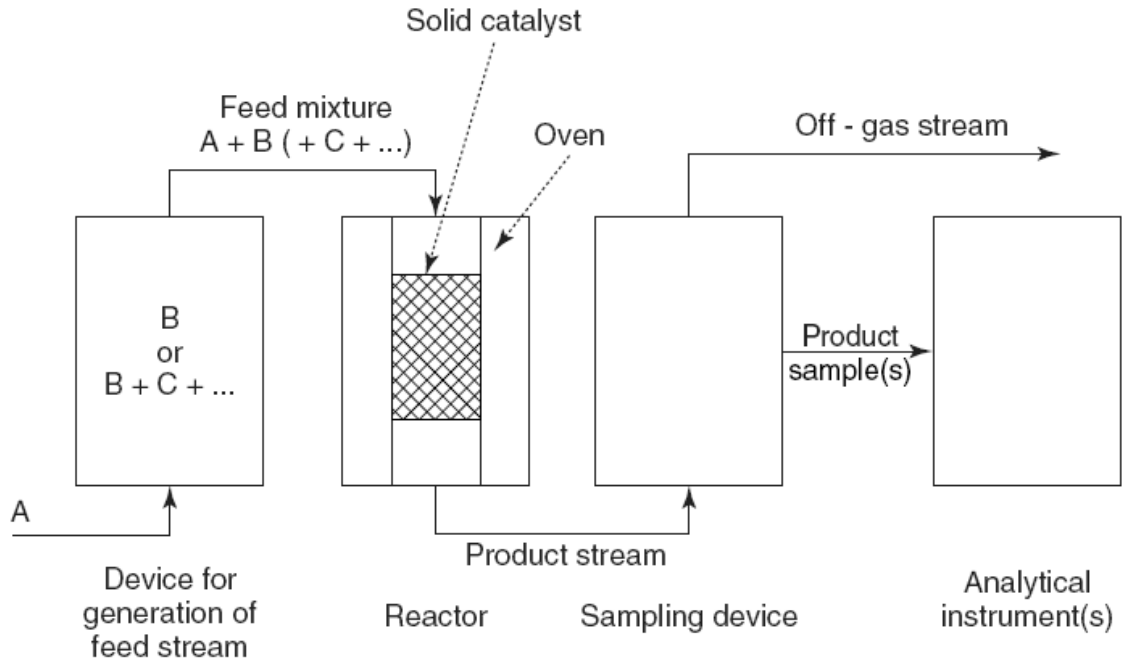


Fig. 1 Scheme of a continuously operated flow-type unit with a fixed-bed reactor for studying a gas-phase reaction on a solid catalyst. A is the carrier gas; B and C are solids or liquids at room temperature and vaporizable at elevated temperature.

gas delivery system: permanent gases

- if possible from central gas supply:
  He, N_2, Ar, H_2, O_2 (p<10 bar)
- special gases from cylinder in cabinet:
  Hydrocarbons, NH_3, calibration mix
- high pressure gas from cylinder in cabinet

gas delivery system: permanent gases

parts of a typical gas line in usual order:

- pressure reducing valve
- check valve
- filter
- mass flow controller
- shut-off valve

connect by stainless steel tubing (1/8”)

stainless steel parts preferred

brass or Cu cheaper, but less robust

gas delivery system: permanent gases

parts of a typical gas line:

- pressure reducing valve
  - if part of central gas supply: no problems
  - in case of gas cylinder:
    - gas type (toxic, corrosive, oxygen …)
    - gas purity
    - inlet pressure
    - outlet pressure
    - one stage/two stage

gas delivery system: permanent gases

parts of a typical gas line:

- check valve
  - to prevent mixing of gases
  - dangerous mixtures (H_2/O_2)
  - contamination
  - mandatory

gas delivery system: permanent gases

parts of a typical gas line:

- filter
  - to protect mass flow controller
  - suitable filter size: 2 µm
  - pressure drop normally no problem

gas delivery system: permanent gases

parts of a typical gas line:

- mass flow controller
  - generally (AC, FHI): EL-FLOW, Bronkhorst
  - thermal MFC, linear range: 2 - 98 %
  - nominal range depends on gas
  - gas change possible
  - calibrated for several gases
  - calibration factors from database (fluidat.com)
  - special version for high pressure

gas delivery system: permanent gases

parts of a typical gas line:

- shut-off valve
  - closed MFC not 100 % tight
  - in position to minimize dead volume
  - working pressure
  - gas purity

gas delivery system: permanent gases

problems with hydrocarbon gas lines:

- flow often not stable
- sensitive to pressure changes

possible solutions:

- adjust MFC parameters (S. Engelschalt)
- buffer volume
- flow restrictor (capillary)
- special pressure reducing valve

gas delivery system: permanent gases

problems with gas purity:

- impurities in cylinder:
  use cleaning traps
  hydrosorb, oxisorb

- impurities due to leaks:
  check connections
  exchange valves
  (diffusion along concentration gradient)

gas delivery system: condensable substances

two possibilities:

- saturators
  - cheap and easy to use
  - no mixtures
  - atmospheric pressure
- evaporators
  - mixtures and high pressure possible
  - hard to control

heating of all downstream parts

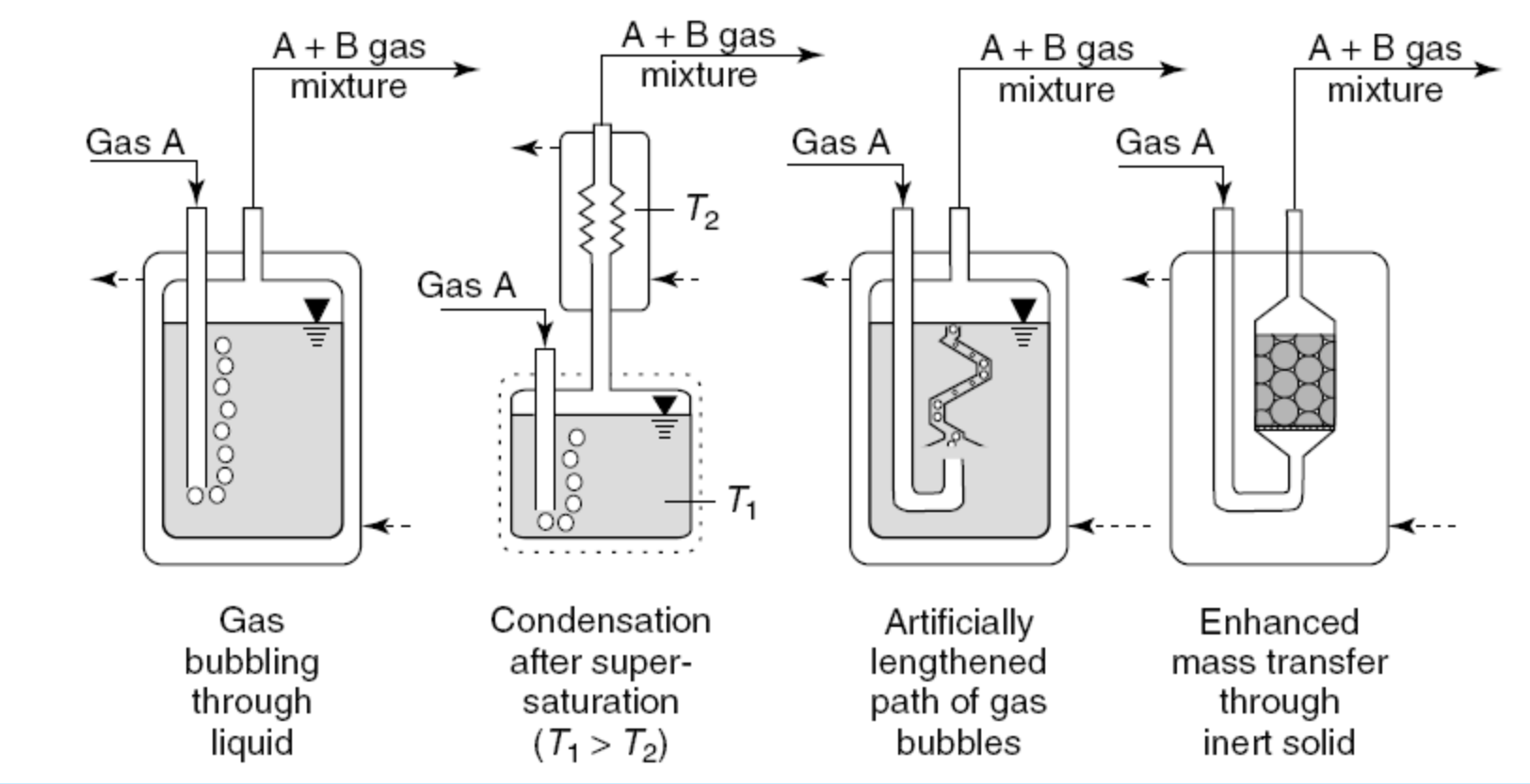
gas delivery system: condensable substances

saturators:

- based on thermodynamic equilibrium
- p_{vap} (p_i)as function of T in databases
- p_i/p_{tot} = molar fraction
- $p_{tot} = p_{atmospheric}$ + pressure drop
- errors:
  wrong p_{tot}, T
  incomplete saturation (τ too short)
  cold/hot spots

gas delivery system: condensable substances

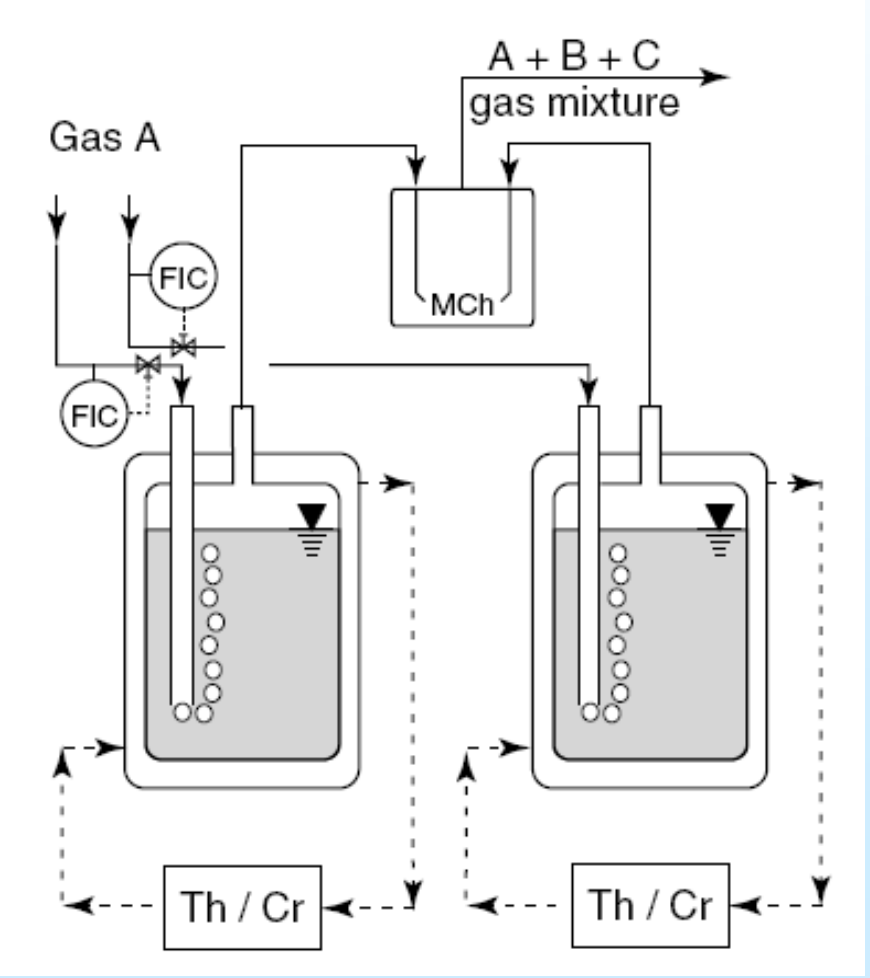
saturator designs:



gas delivery system: condensable substances

mixing two vapors using saturators:

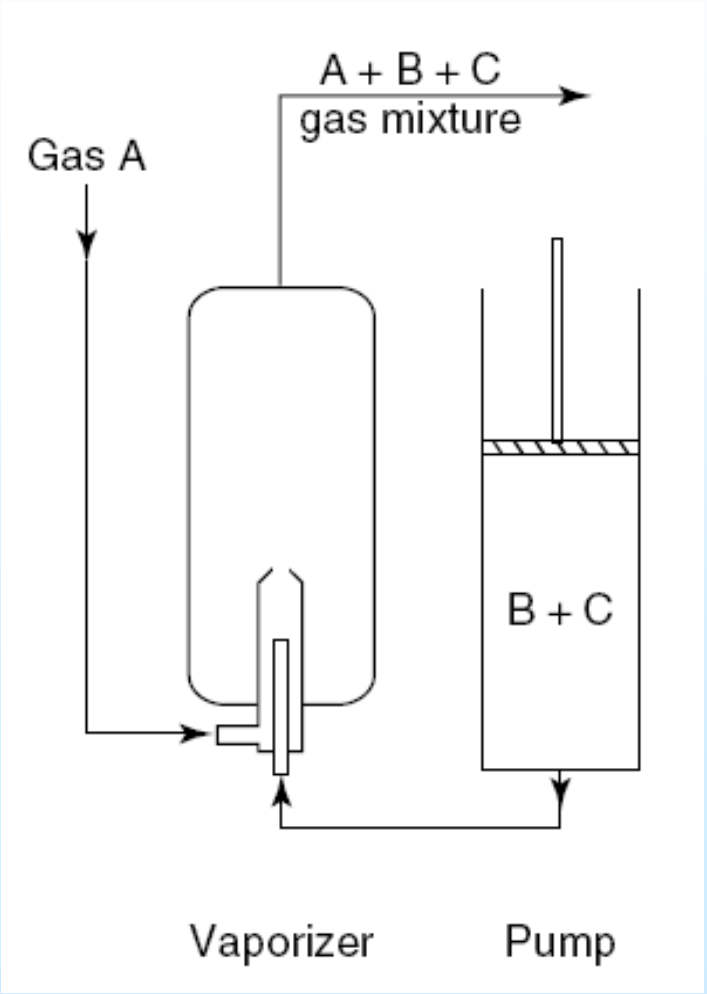
- hard to control
- not recommended



gas delivery system: condensable substances

evaporators:

- molar fractions calculated from flows
- often oscillations due to
  - pulsation of feed
  - droplets at nozzle
  - evaporation in feed line
  - bad temperature control



gas delivery system: mixing unit

- simple:
  tee pieces and shut-off valves
- advanced:
  valco switching valves
- in case of condensable substances:
  avoid condensation/adsorption (heating)
- filter before reactor as static mixer

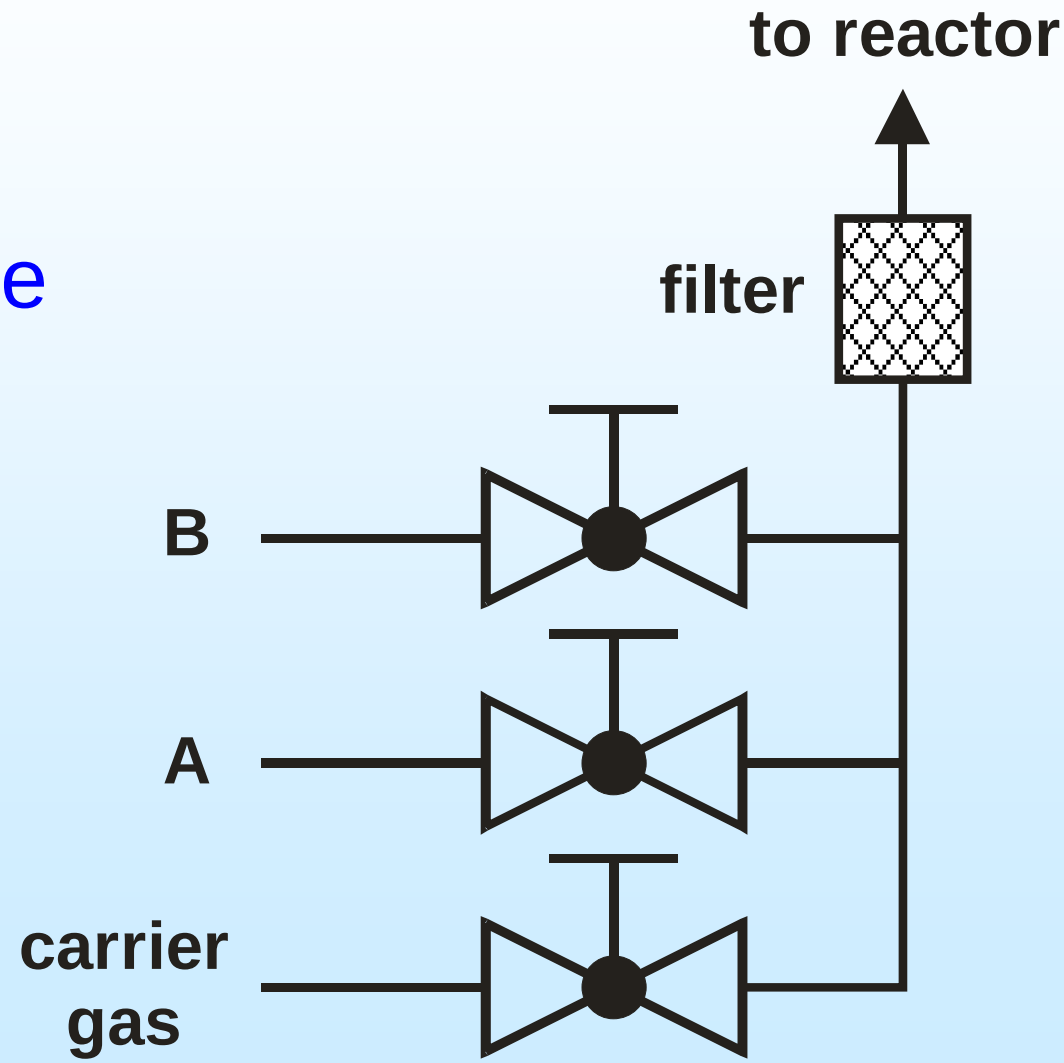
gas delivery system: mixing unit

- simple:
  tee pieces and shut-off valves
- advanced:
  valco switching valves
- in case of condensable substances:
  avoid condensation/adsorption (heating)
- filter before reactor as static mixer

gas delivery system: mixing unit

simple:

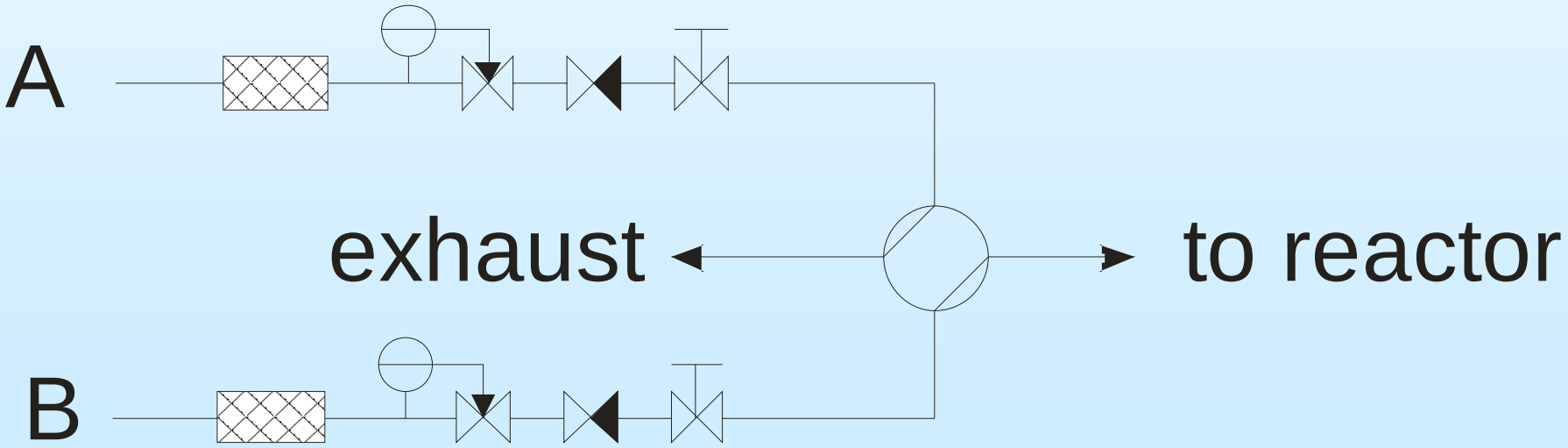
- purging time after gas change
- minimize dead volume



gas delivery system: mixing unit

advanced:

- 4 port valve for fast switching
- purging before switching

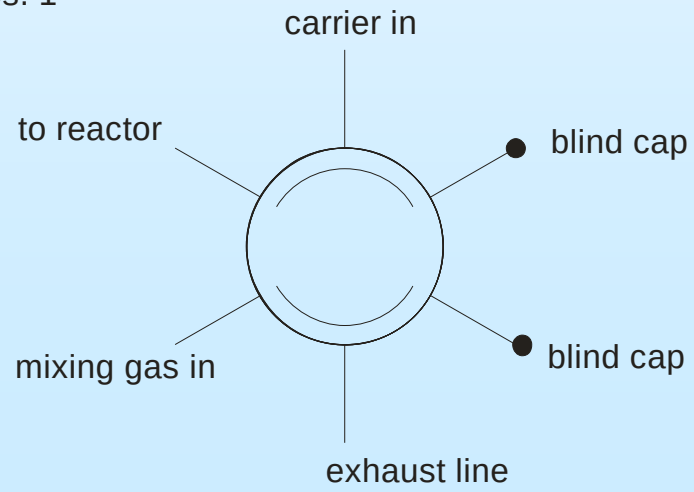


gas delivery system: mixing unit

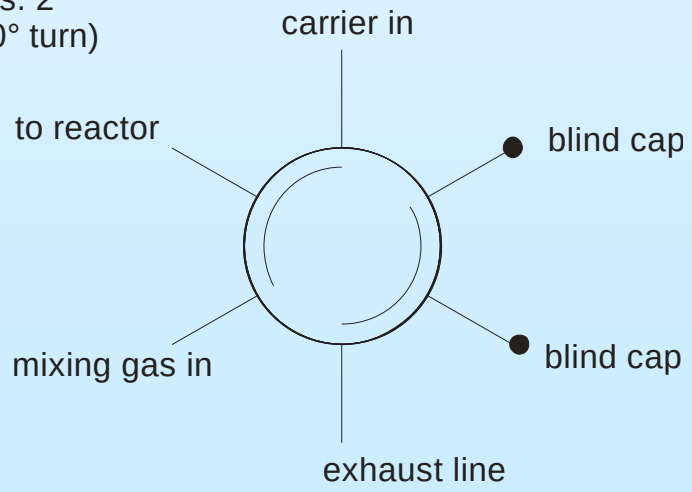
advanced:

- special 6 port valve for mixing
- fast switching
- purging before switching

Pos. 1



Pos. 2
(60° turn)



gas delivery system: mixing unit

heating:

- to avoid condensation or adsorption
- including reactor connections and exhaust lines
- heating tape coiled around all lines
- large drying oven (recommended)

gas delivery system: pressure controller

experiments at high pressure:

- needle valve and pressure gauge in exhaust line
  - cheap, but not controlled
  - change with time and RT
- back-pressure regulator in exhaust line
  - stable pressure
  - can be monitored
  - expensive

gas delivery system

- check all parts used
- suitable for
  - applied temperature
  - applied pressure
  - educts and products
  - desired gas purity
- if possible use parts with Swagelok connectors (1/8”, ¼”, 6 mm)

gas delivery system: metal connection

Swagelok connection

- standard metal connection at AC, FHI
- many parts available
- no workshop needed
- reusable
- safe and leak tight
- widely used

gas delivery system: swagelok connection

preswaging

Fig. 1

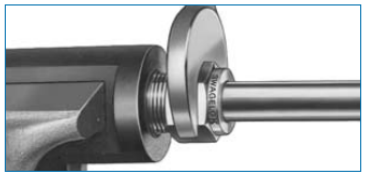


Fig. 2

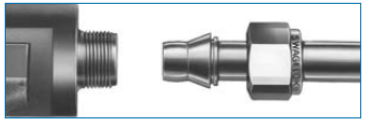
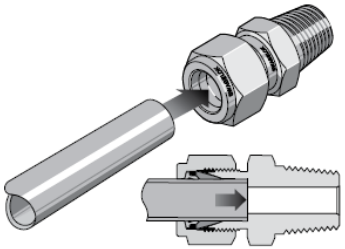


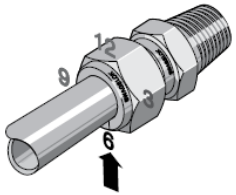
Fig. 3

first assembly

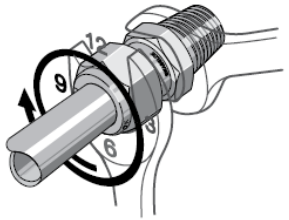


Fully insert the tube into the fitting and against the shoulder; rotate the nut finger-tight.

High-pressure applications and high safety-factor systems: *Further tighten the nut until the tube will not turn by hand or move axially in the fitting.*



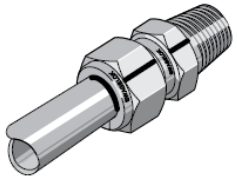
Mark the nut at the 6 o'clock position.



While holding the fitting body steady, tighten the nut one and one-quarter turns to the 9 o'clock position.

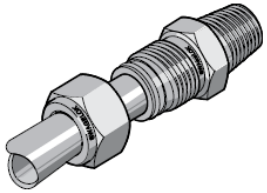
For 1/16, 1/8, and 3/16 in.; 2, 3, and 4 mm tube fittings, tighten the nut only three-quarters turn to the 3 o'clock position.

reassembly



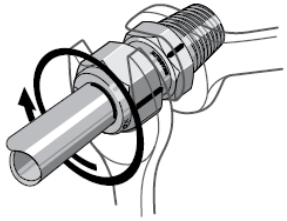
Prior to disassembly, mark the tube at the back of the nut; mark a line along the nut and fitting body flats.

Use these marks to ensure that you return the nut to the previously pulled-up position.



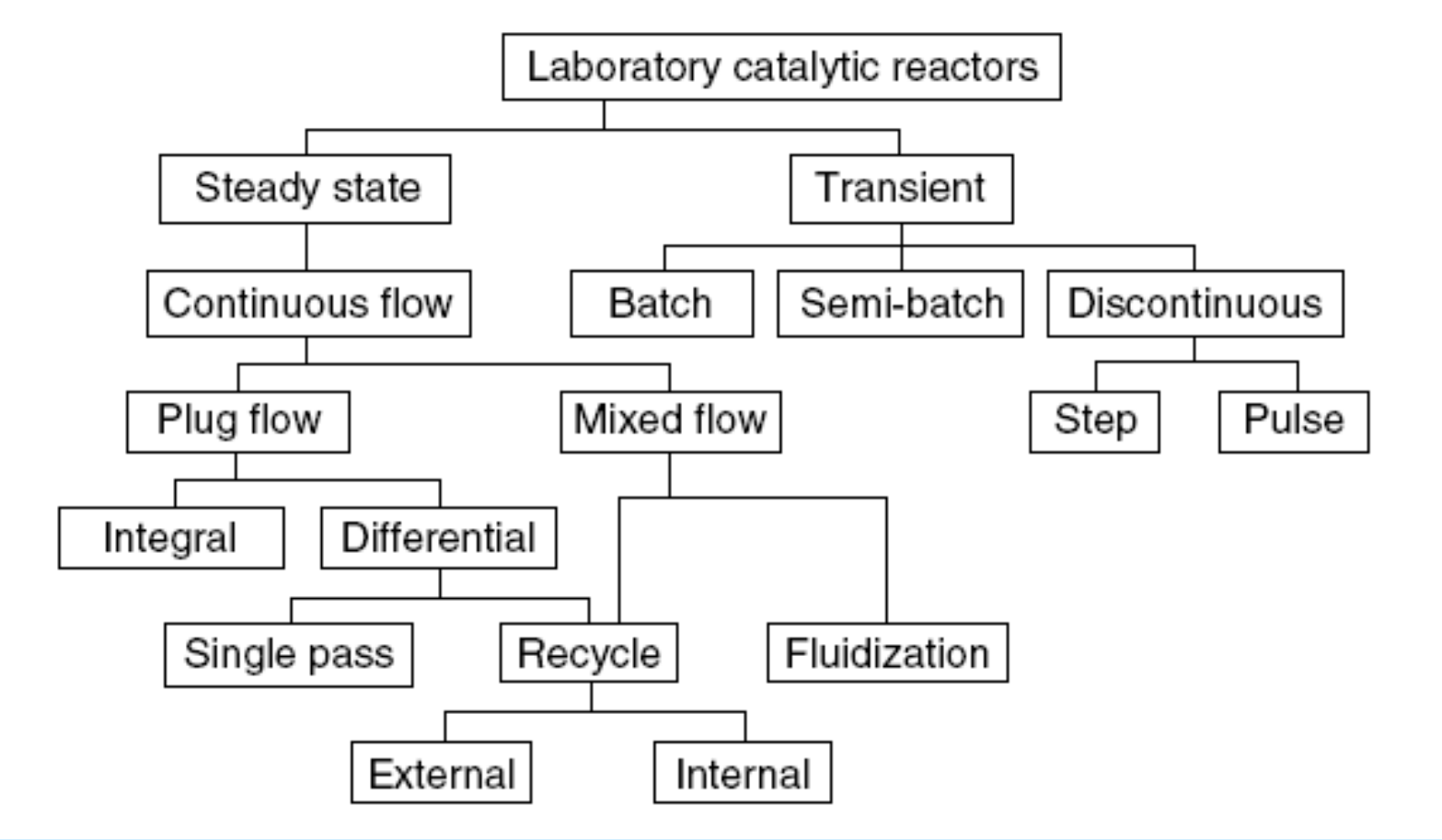
Insert the tube with preswaged ferrules into the fitting until the front ferrule seats against the fitting body.

Over 1 in./25 mm sizes: *If needed, reapply lubricant lightly to the body threads and the rear surface of the back ferrule.*



While holding the fitting body steady, rotate the nut with a wrench to the previously pulled-up position, as indicated by the marks on the tube and flats. At this point, you will feel a significant increase in resistance. Tighten the nut slightly.

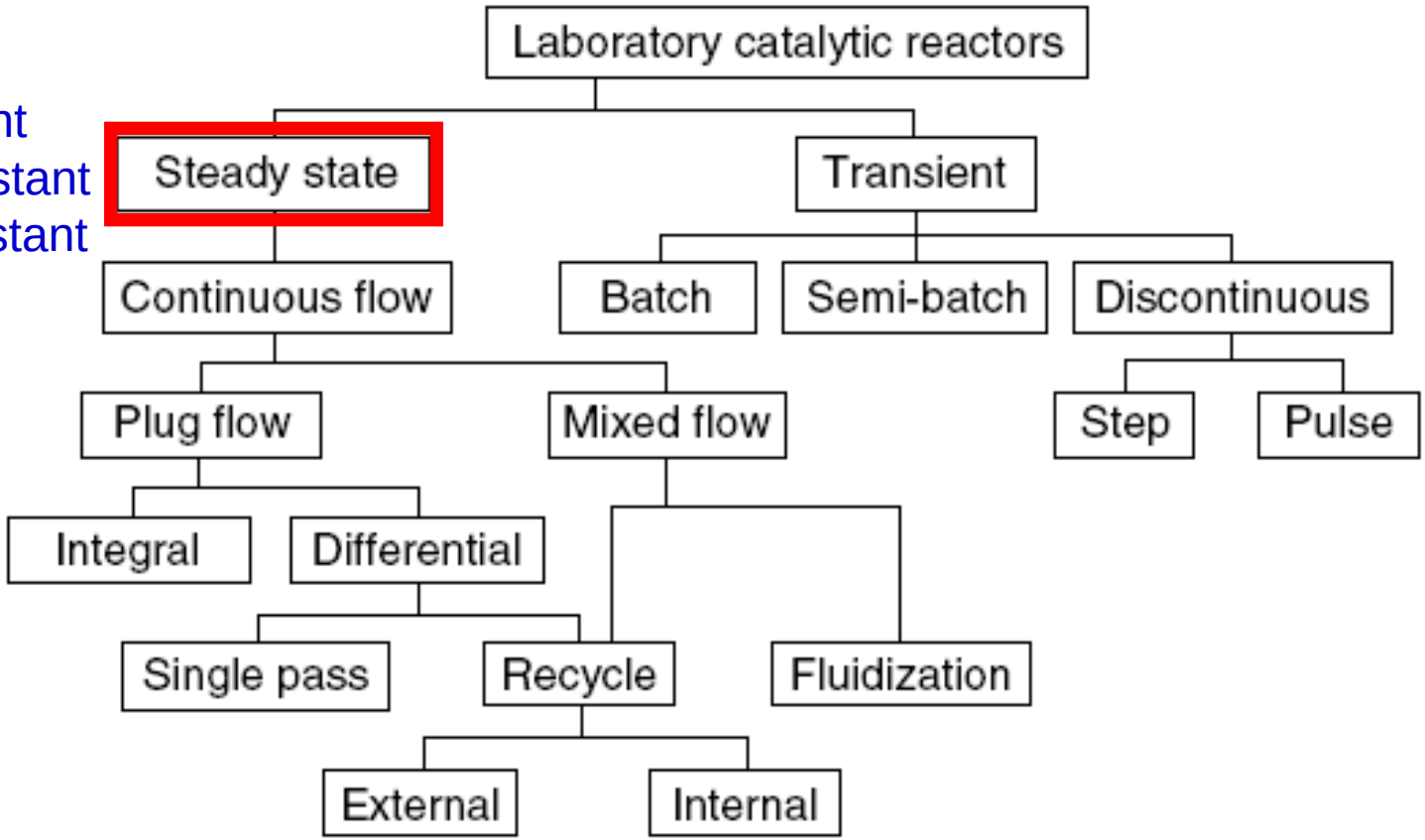
reactor: classification



classification of laboratory reactors according to mode of operation

reactor: classification

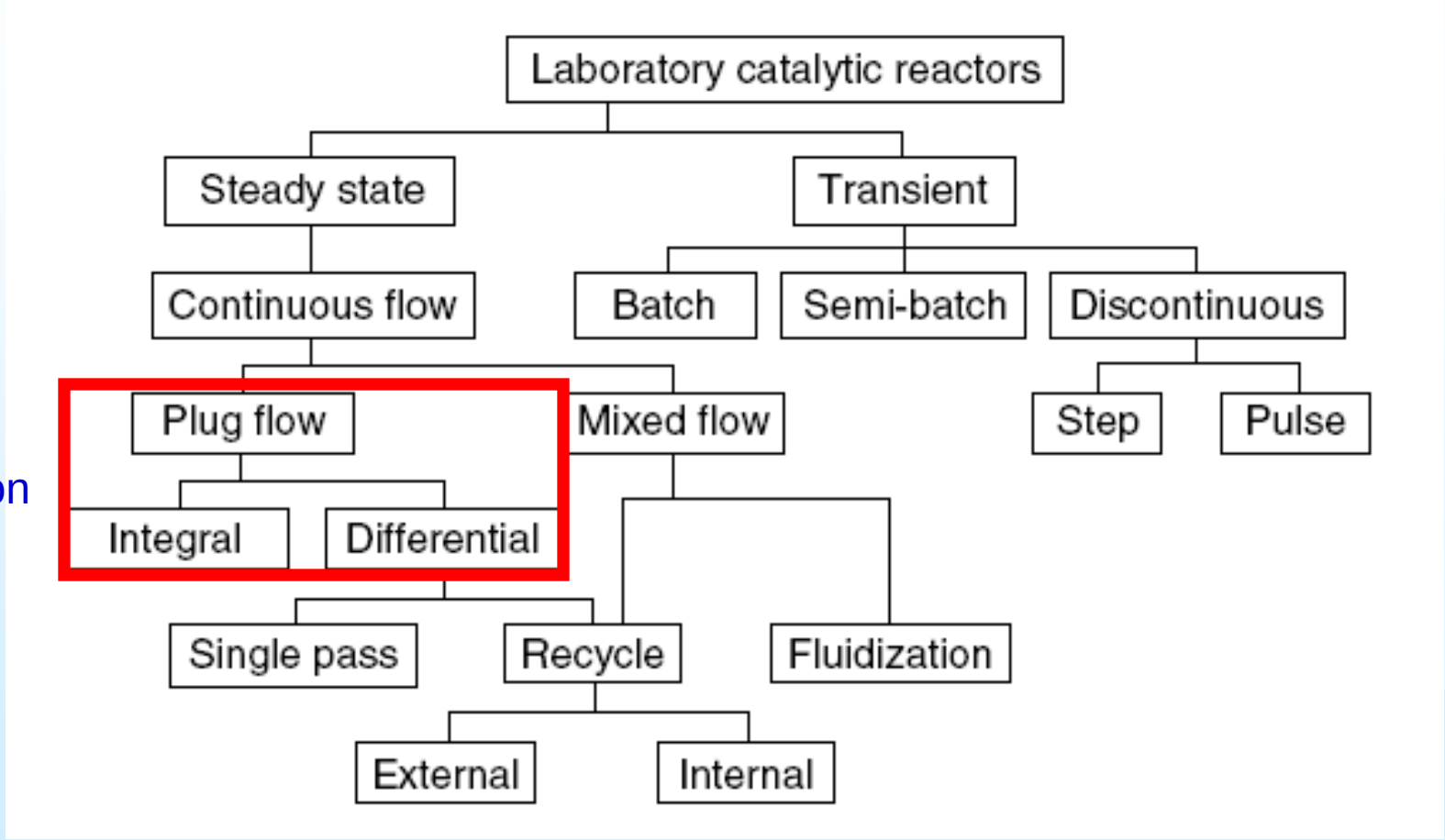
T constant
feed constant
X, S constant



classification of laboratory reactors according to mode of operation

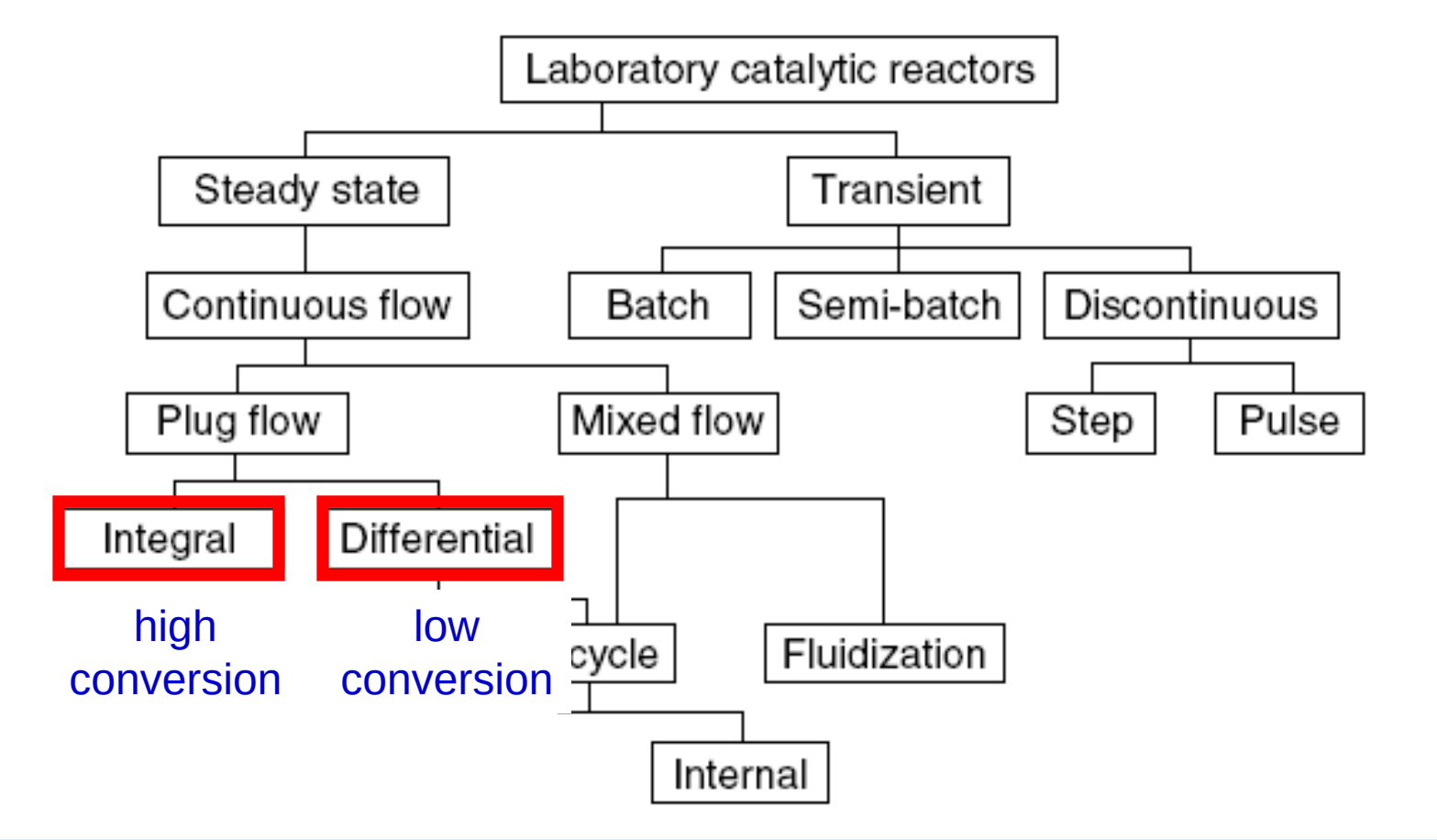
reactor: classification

most common types



classification of laboratory reactors according to mode of operation

reactor: classification



classification of laboratory reactors according to mode of operation

reactor types

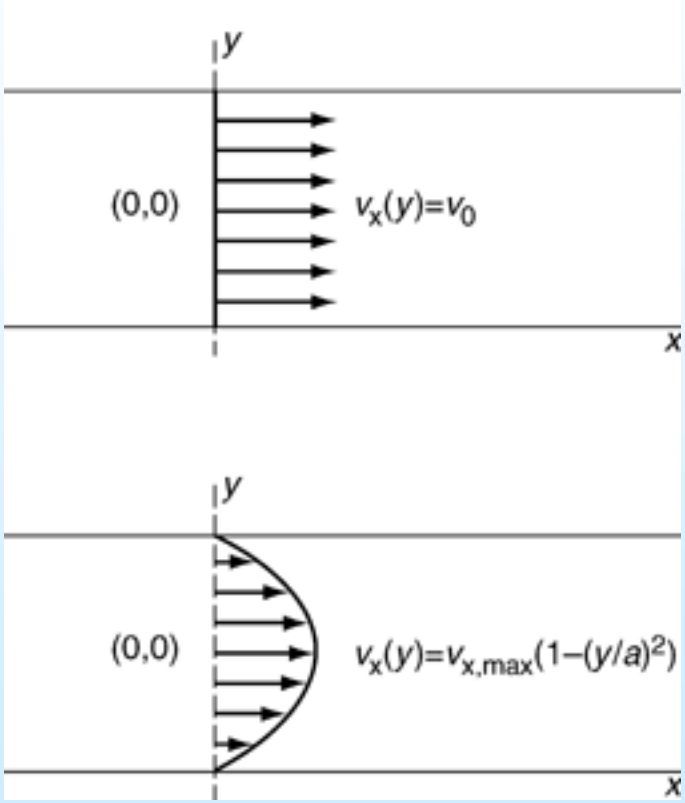
Tab. 1 Summary of relative reactor ratings (L = low, M = medium, H = high)

Aspect	*Reactor type*						
	PFR Differential fixed bed	*PFR Integral fixed bed*	*PFR Solids transport (riser)*	*CSTR External recirculation*	*CSTR Internal fluid recirculation*	*CSTR Spinning catalyst basket*	*Batch Internal fluid recirculation*
Ease of use	H	H	H	M–H	M	L–M	M
Ease of construction	H	H	L	M	M	L–M	M
Cost	L	L	H	L–M	M–H	M–H	M
Ease of sampling and analysis	M	H	L	H	H	H	M
Approach to ideal type	H	H	M	H	M–H	L–M	H
Fluid–catalyst contact	H	H	M	H	M–H	L–M	H
Isothermicity	H	M–H	H	M–H	H	M	H
Temperature measurement	H	H	H	H	M–H	L	H
Kinetics	H	H	M	M	M–H	L–M	M
Deactivation noticed	H	H	L	M	M	M	L
GLS use	L–M	M–H	L	M–H	M–H	M	H

reactor: plug flow reactor

- ideal reactor
- tube reactor
- continuous flow
- turbulent flow
- no velocity gradients
- perfect mixing
  in radial direction
- no mixing
  in axial direction

turbulent flow



laminar flow

reactor: Reynolds number

$$\mathrm{Re} = \frac{\rho \cdot u \cdot L}{\mu}$$

ρ: fluid density
u: fluid velocity
μ: fluid viscosity
L: characteristic length

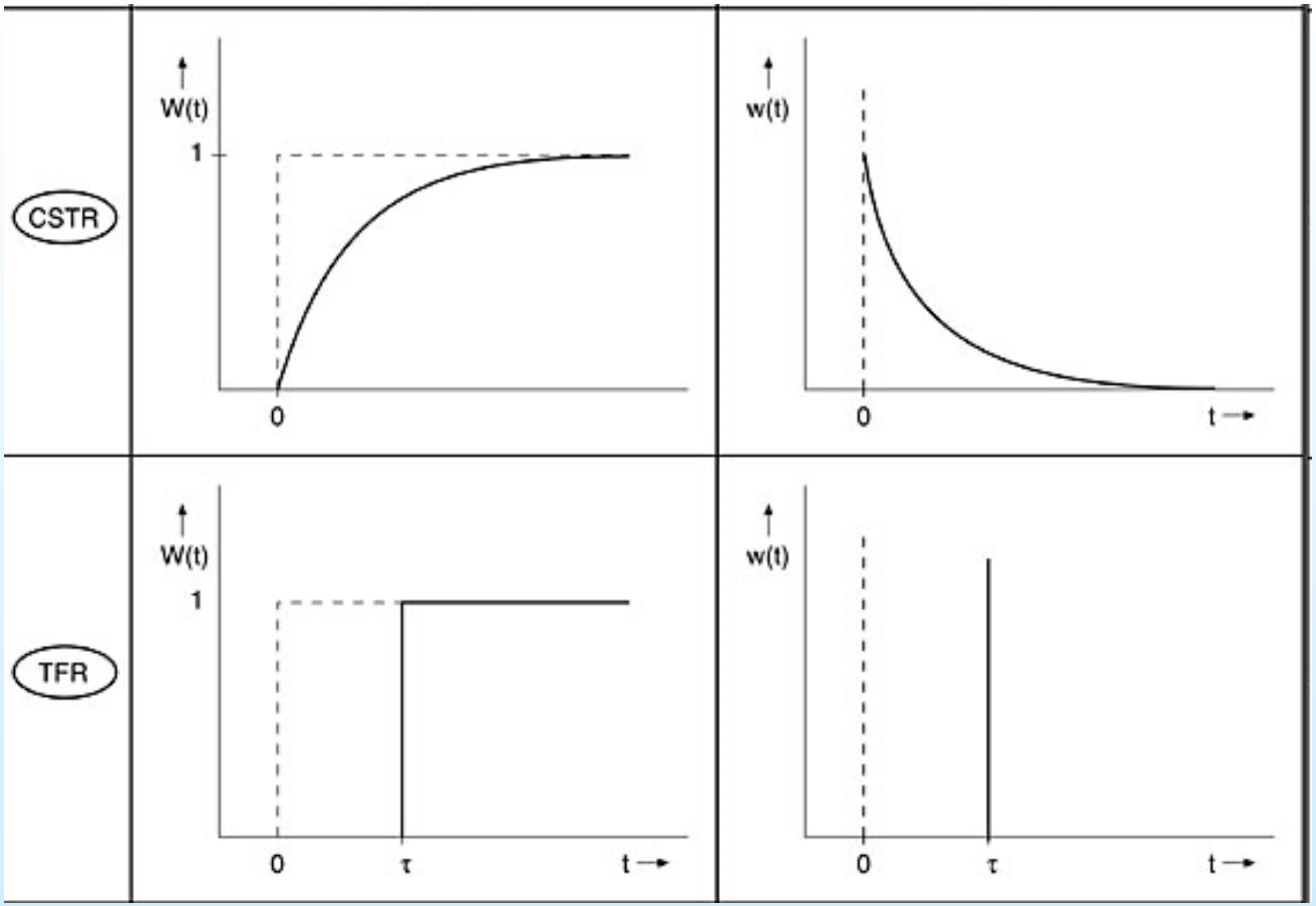
- Re characterizes fluid behavior
- empty tubes: L = tube diameter

  Re<2500 → laminar; Re>4000 →turbulent
- packed beds: L = particle diameter

  Re<10 → laminar; Re>2000 →turbulent
- in lab reactors usually no turbulent flow

  but: tube diameter as low as possible, particle diameter as large as possible, flow as high as possible

reactor: residence time distribution of PFR



CSTR:
- ideal reactor
- total backmixing

changing feed

pulse response

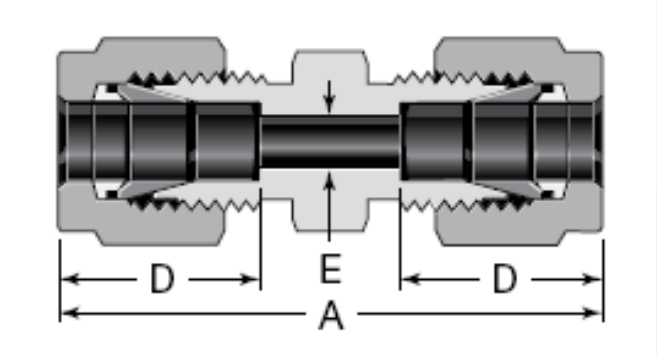
reactor: material

- glass:
  cheap, inert, transparent,
  only low temperature, low pressure
- quartz:
  transparent, inert, high temperature,
  only low pressure
- stainless steel:
  robust, leak-tight, high pressure,
  only low temperature
- GLT (glass-lined tubing):
  like stainless steel, but inert

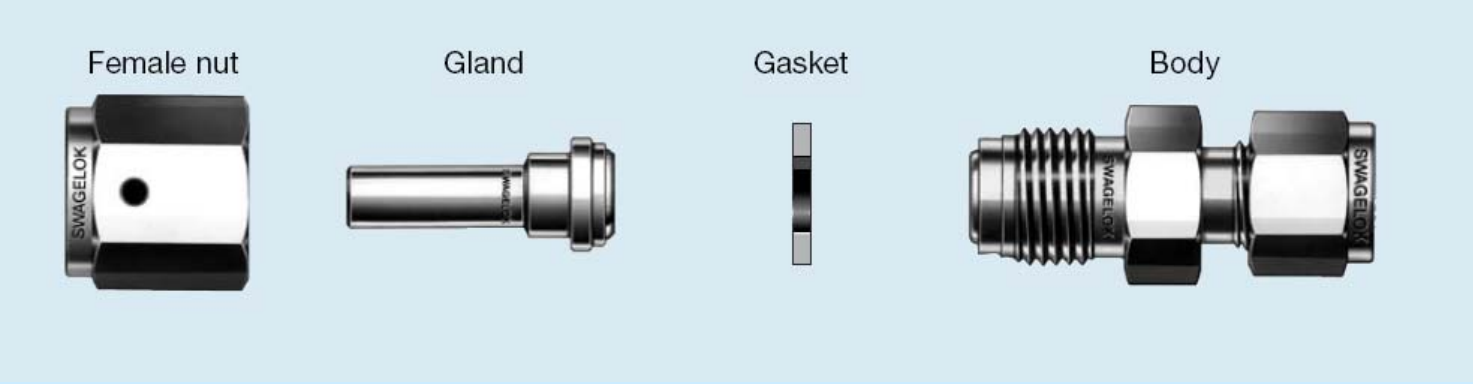
reactor: connection to gas delivery system

for SS/GLT:

- Swagelok connection



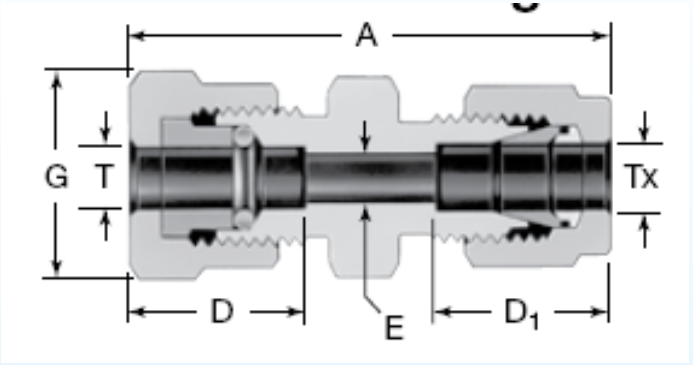
- VCR connection



reactor: connection to gas delivery system

for glass/quartz:

- Cajon UltraTorr
  cheap, easy to use,
  not very leak tight

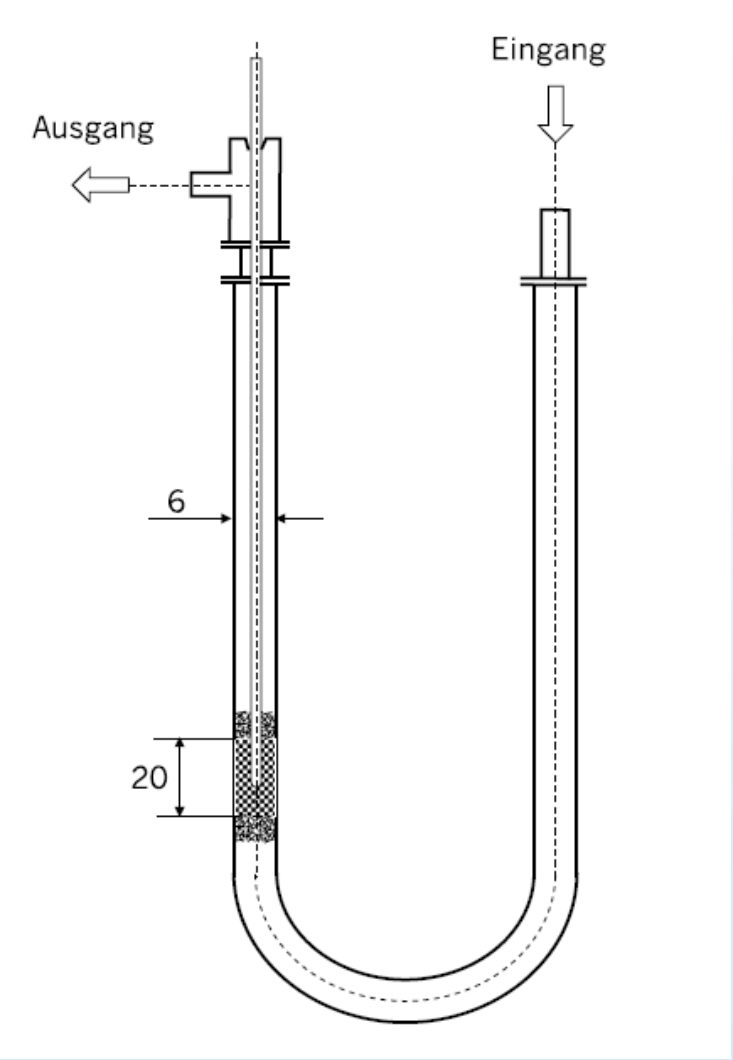


- KF flange
  UHV tight, more reliable,
  expensive
- glass/metal junction
  highly leak tight,
  expensive, not mechanically stable

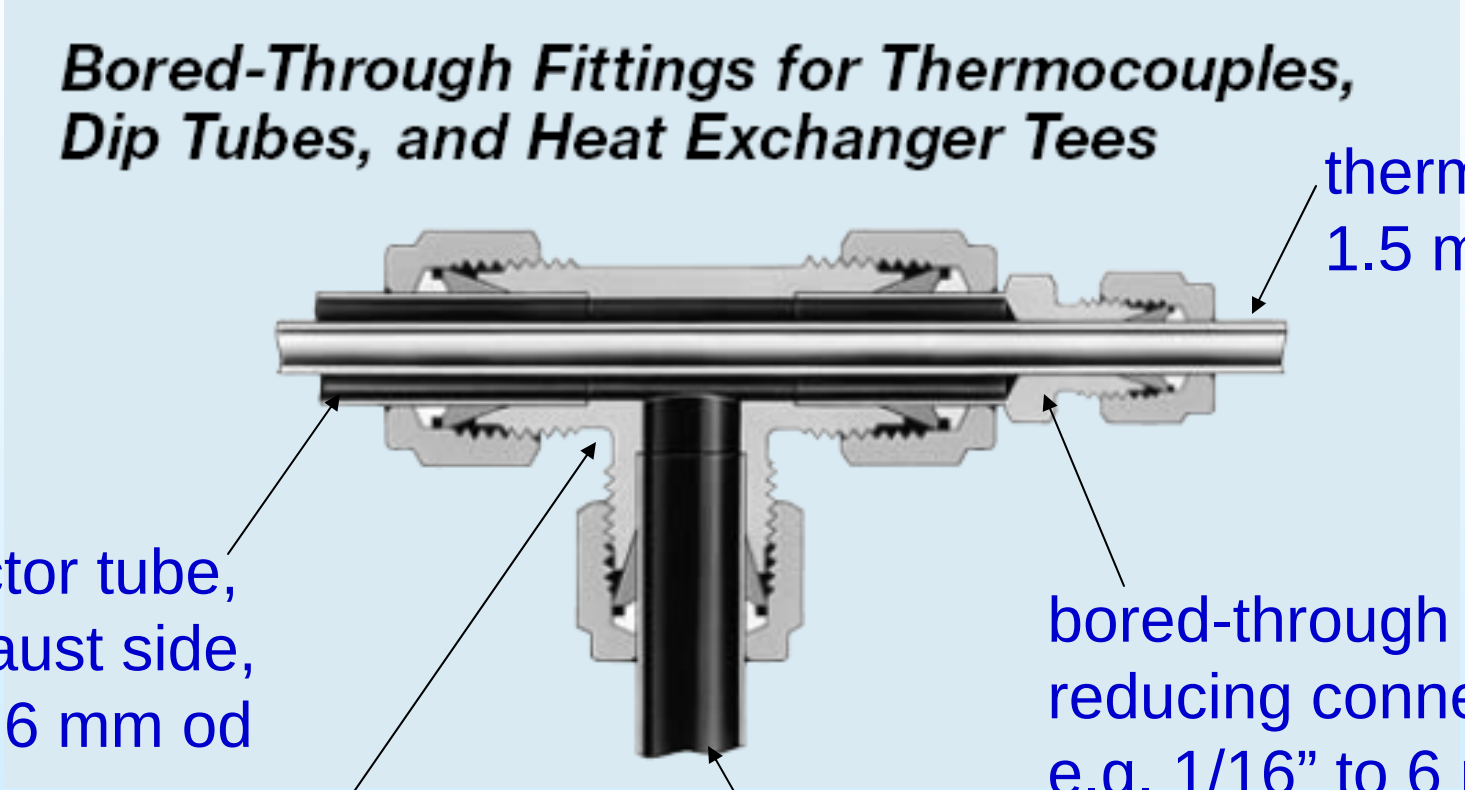
reactor: geometry

mainly two types:

- straight tube
  - cheap
  - easy to use
  - may require a split tube oven
- U-tube
  - preheating of feed
  - compact
  - transfer to glove box



reactor: internal thermocouple



reactor: heating

for high T > 400 °C:

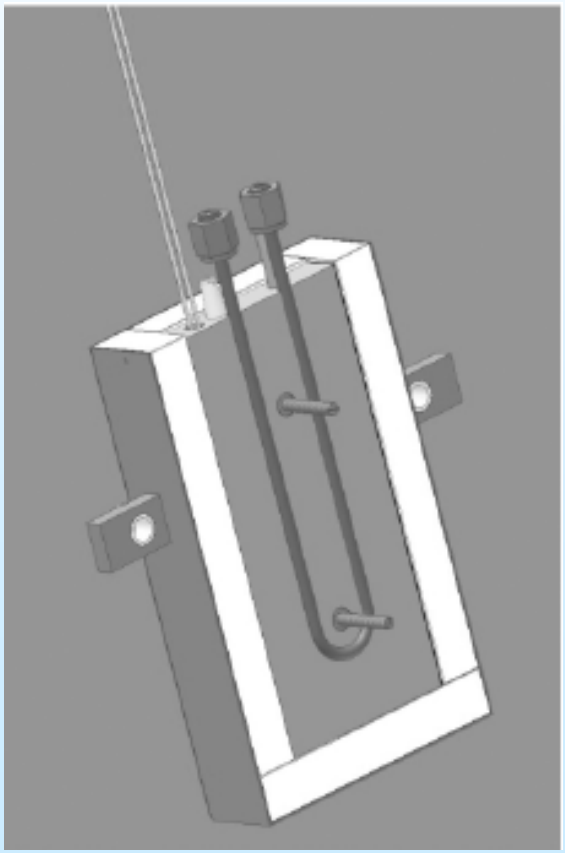
- ceramic or quartz tube with heating tape
  - cheap
  - low isothermicity
- commercial furnace, e.g. Carbolite, Reetz
  - expensive
  - better isothermicity

better:
vertical position
caveat:
chimney effect

reactor: heating

for medium T < 400 °C:

- furnace built by FHI workshop
- metal block (Cu, Al, SS) with heating cartridges
- very good isothermicity
- very good contact to reactor possible



reactor: heating (cooling)

for low T:

- thermostat/cryostat with circulation pump, Julabo, Huber, Lauda
- U-tube in bath
- glass reactor with cooling jacket

reactor: catalyst bed

fluid dynamics and heat transport:

long and thin catalyst bed best

caveat: pressure drop

parameters:

- bed diameter (reactor id)
- bed length
- particle size

parameters interconnected

reactor: catalyst bed

- bed length > 5 times bed diameter
- particle size as large as possible
- particle size < 1/10 of reactor id

typical values:

- reactor id: 4 – 6 mm, bed length > 20 mm
- particle size: 400 – 200 µm
  (pressing, crushing sieving)
- dilution with inert material (SiC, up to 1:10)
  for heat exchange or bed length

reactor: test for excluding transport limitations

- correct rates only measured in kinetic regime
- rates independent of catalyst particle size L or gas velocity u

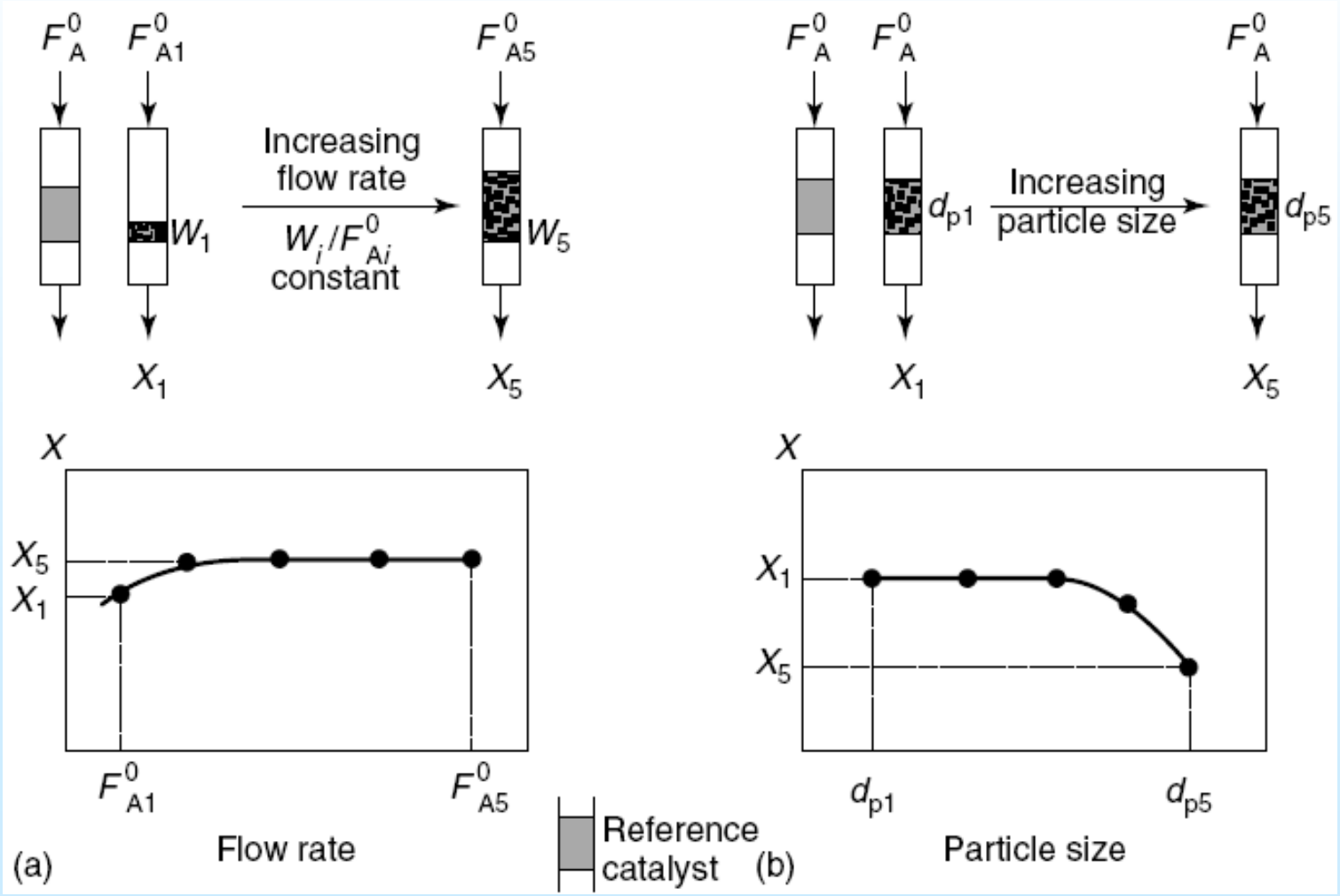
Tab. 4 Apparent catalyst rate behavior depending on rate-controlling regime (isothermal case)

Controlling process	*Apparent order*	*Apparent activation energy*	*Dependency L*	*Dependency u*
Kinetics	n	E_a (true)	–	–
Internal diffusion	$(n+1)/2$	$\frac{1}{2}E_a$ (true)	$1/L$	–
External mass transfer	1	~0	L^{m-2}[a]	u^m[a]

[a] m represents the power of the Reynolds number in the Sherwood correlation in Table 2.

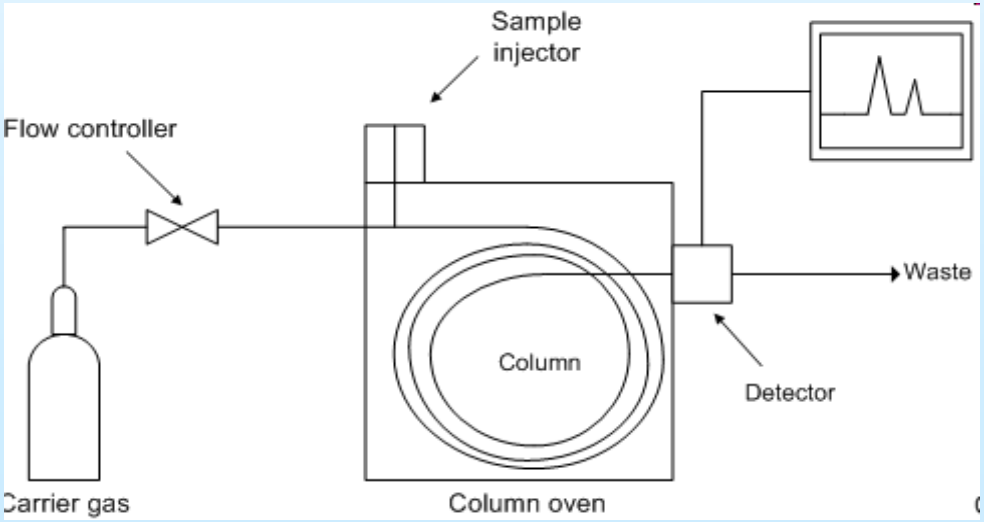
reactor: test for excluding transport limitations

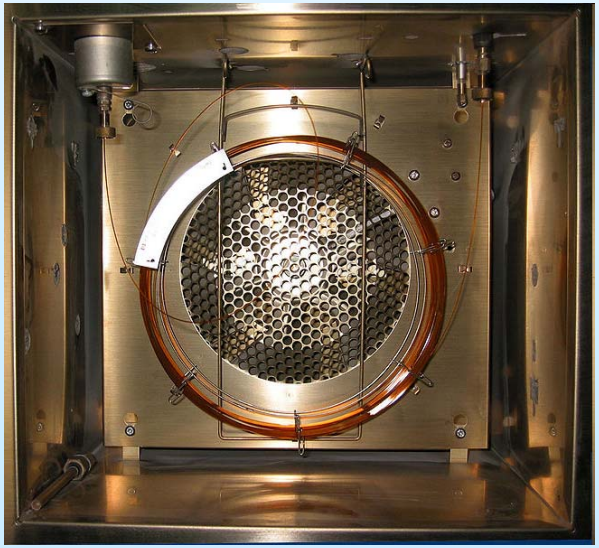
Diagnostic tests for (a) extraparticle limitations and (b) intraparticle limitations.



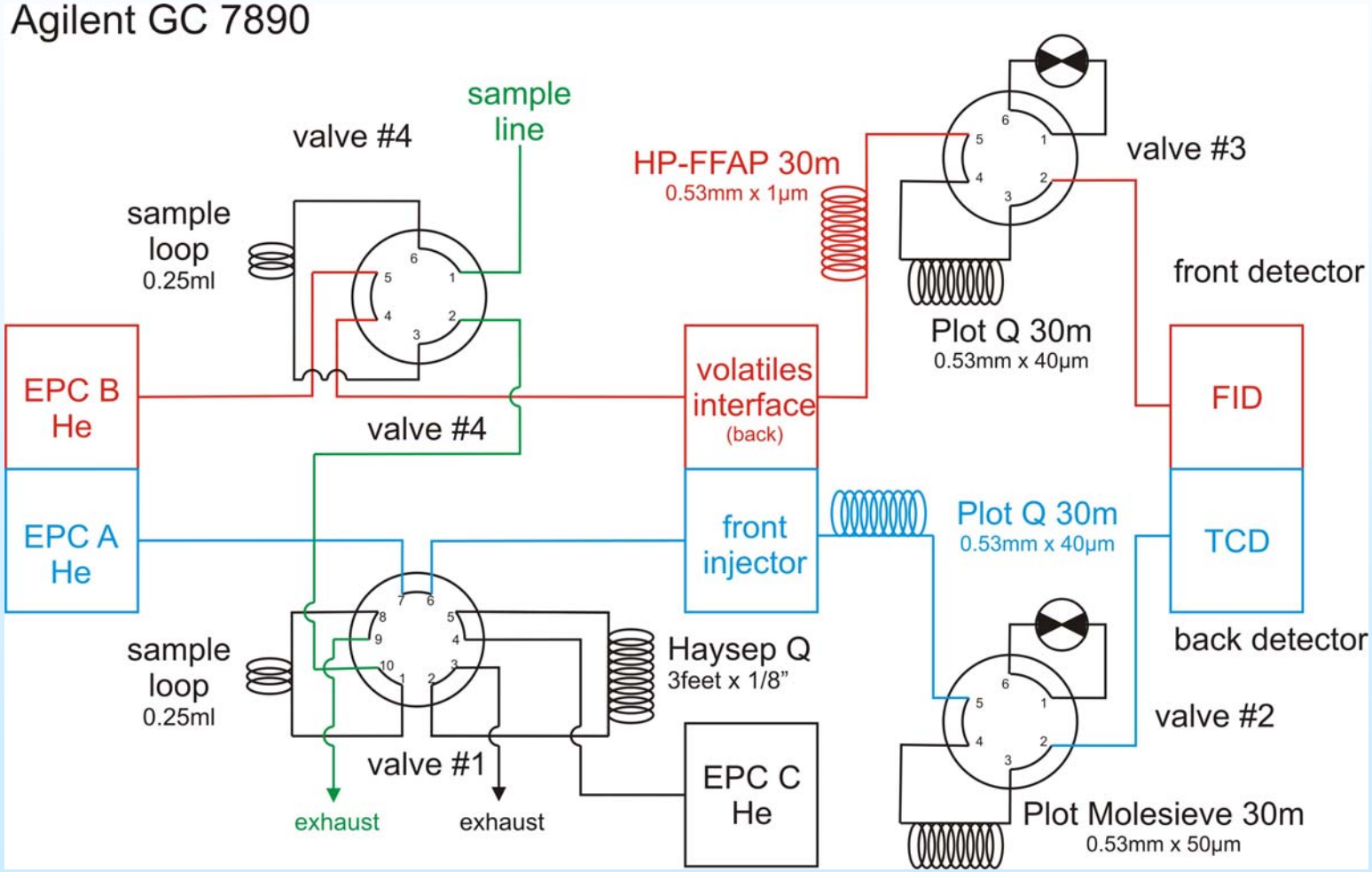
analytics: gas chromatography

- sample injected into a stream of carrier gas (e.g. via sample loop)
- analytes interact with a column and are separated according to size or polarity





analytics: gas chromatography



analytics: gas chromatography

advantages:

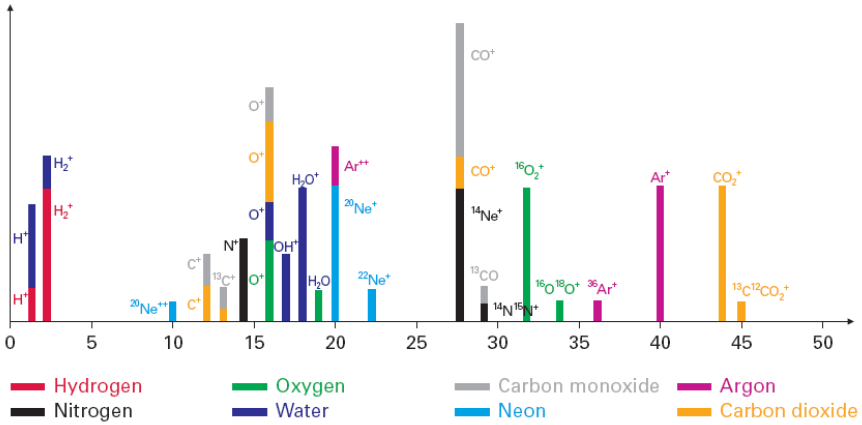
- high sensitivity
- stable sensitivity
- high reproducibility
- easy data processing

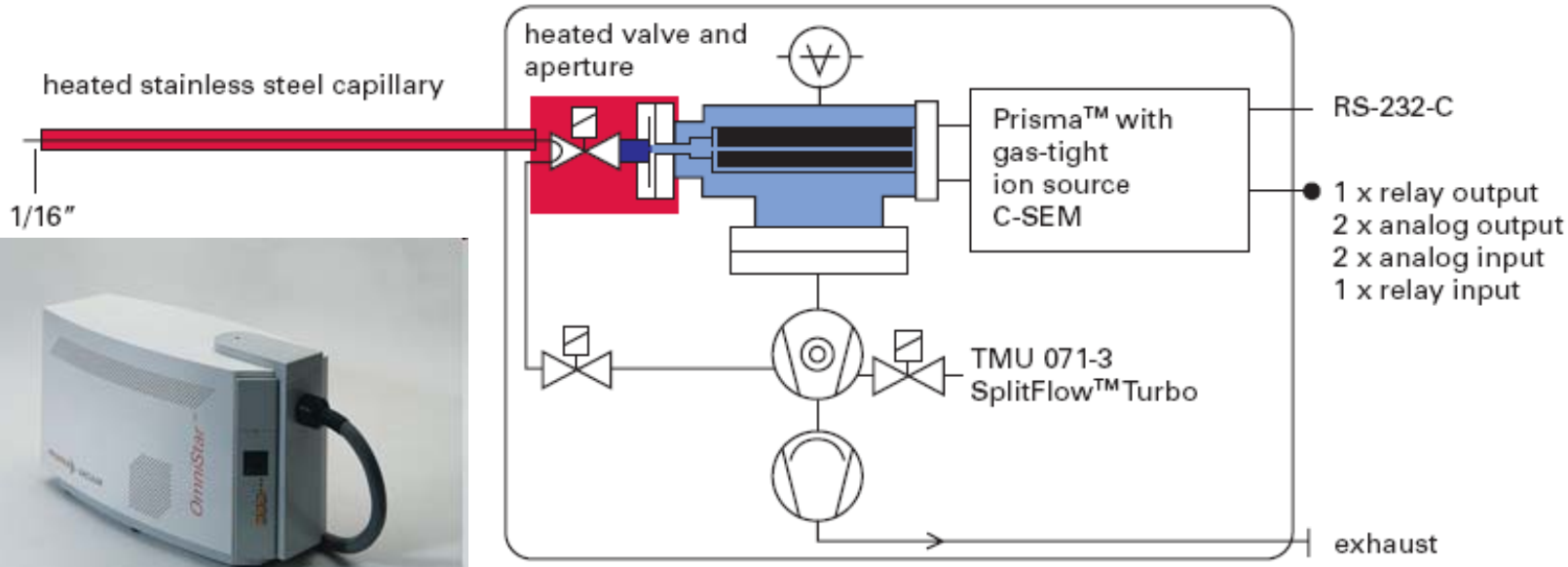
disadvantages:

- method development
- species identified by retention time only
- demands maintenance
- isotopes not separated
- slow (steady states)

analytics: mass spectrometry

- ionization of gas molecules
- separation by ion mass
- detection by SEM
- fragmentation pattern





analytics: mass spectrometry

- concentrations calculated from fragmentation patterns
- patterns often overlap

Components	Fragments									
	Fr[28]	Fr[39]	Fr[41]	Fr[43]	Fr[44]	Fr[45]	Fr[56]	Fr[58]	Fr[60]	Fr[72]
CO	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
Propylene	0.04	0.83	1.00	0.02	0.00	0.00	0.00	0.00	0.00	0.00
Propane	3.37	1.00	0.70	1.07	1.19	0.04	0.00	0.00	0.00	0.00
CO2	0.18	0.00	0.00	0.00	1.00	0.00	0.00	0.00	0.00	0.00
Acrolein	1.91	0.08	0.02	0.04	0.08	0.00	1.00	0.00	0.00	0.00
Acetone	0.40	0.20	0.08	4.00	0.08	0.00	0.00	1.00	0.00	0.00
Acetic acid	0.78	0.02	0.13	2.22	0.22	2.02	0.00	0.00	1.00	0.00
Acrylic acid	1.26	0.02	0.06	0.17	0.74	0.67	0.05	0.00	0.00	1.00

$$I_{28} = I_{CO} \times 1.00 + I_{propylene} \times 0.04 + I_{propane} \times 3.37 + I_{CO2} \times 0.18 + I_{Acrolein} \times 1.91 + I_{Acetone} \times 0.40 + I_{AceticAcid} \times 0.78 + I_{AcrylicAcid} \times 1.26$$

analytics: mass spectrometry

advantages:

- species identified by fragmentation pattern
- fast (time resolved)
- isotopes separated
- sampling easy

disadvantages:

- complex data processing
- lower sensitivity
- less stable sensitivities
- background not stable

starting point for literature research:

Kapteijn, F. and Moulijn, J. A. 2008. Laboratory Catalytic Reactors: Aspects of Catalyst Testing. Handbook of Heterogeneous Catalysis. 2019–2045.
Weitkamp, J. and Gläser, R. 2008. Ancillary Techniques in Laboratory Units for Testing Solid Catalysts. Handbook of Heterogeneous Catalysis. 2045–2053.

This is the end.

Thanks for your attention…