# Tracer ZLC as an Informative Low-cost Technique of Diffusion Measurement

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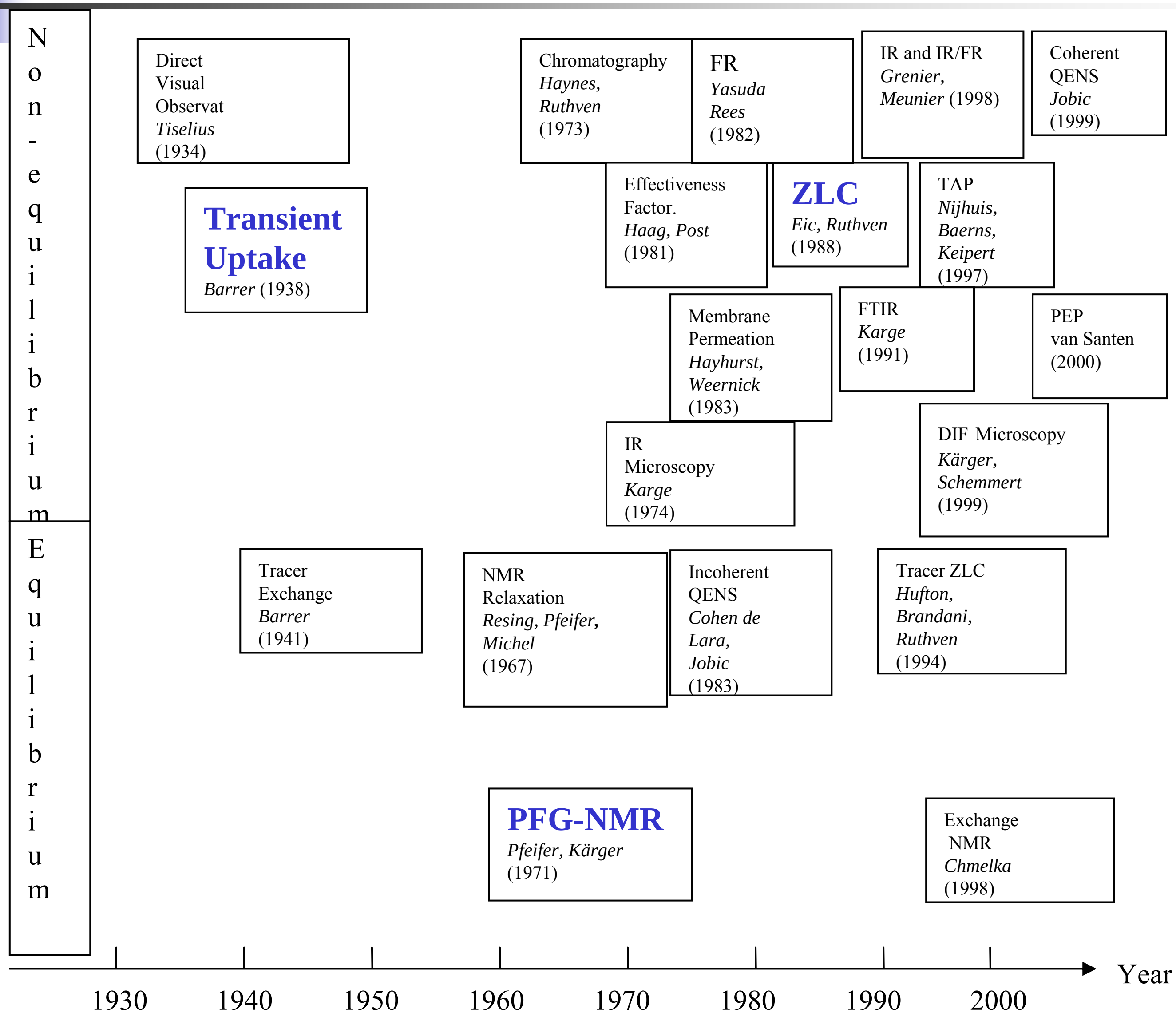
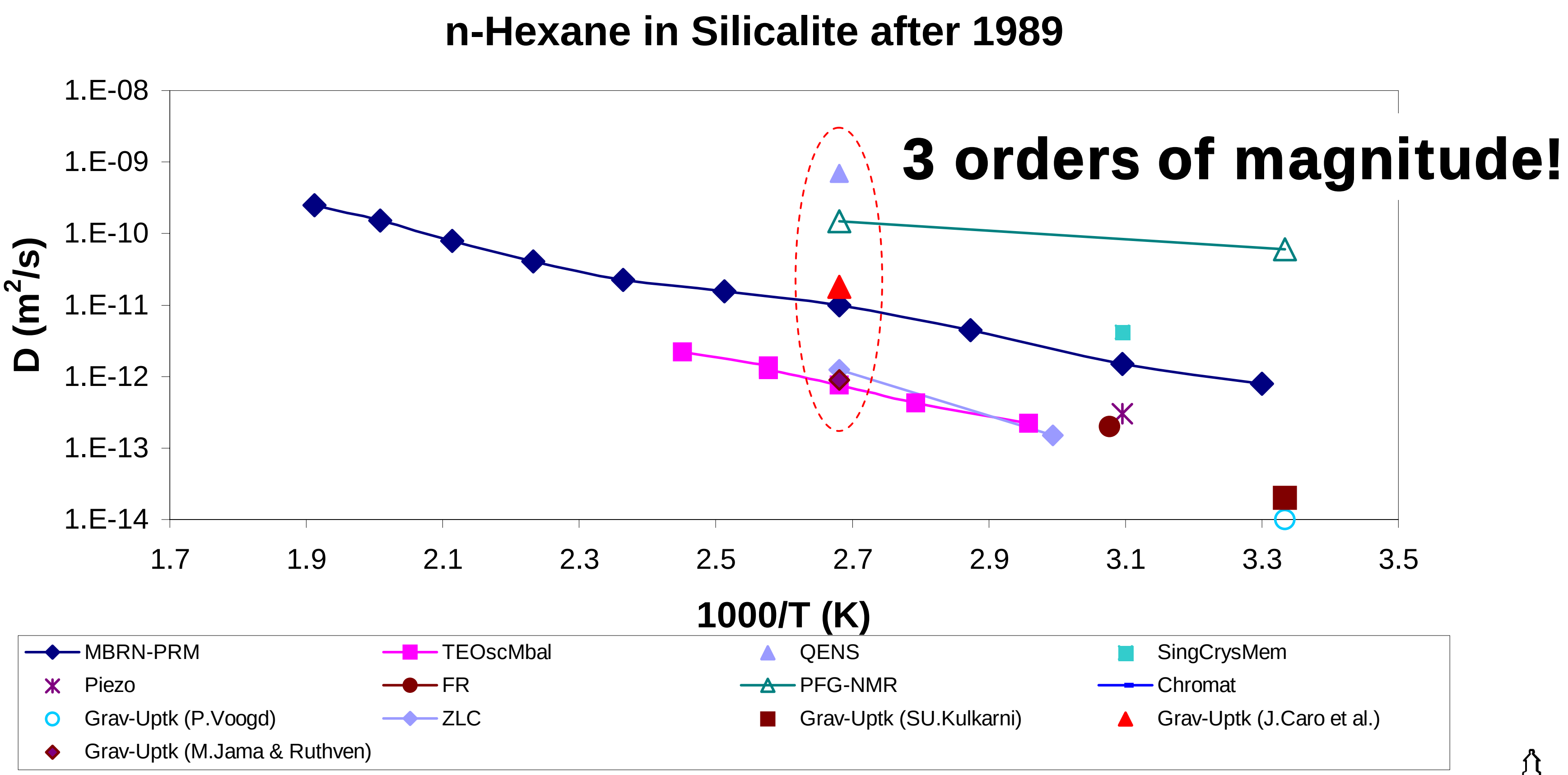
Diffusion in Nanoporous Materials: from Fundamentals to Practical Issues – DECHEMA Kolloquium 15/01/04

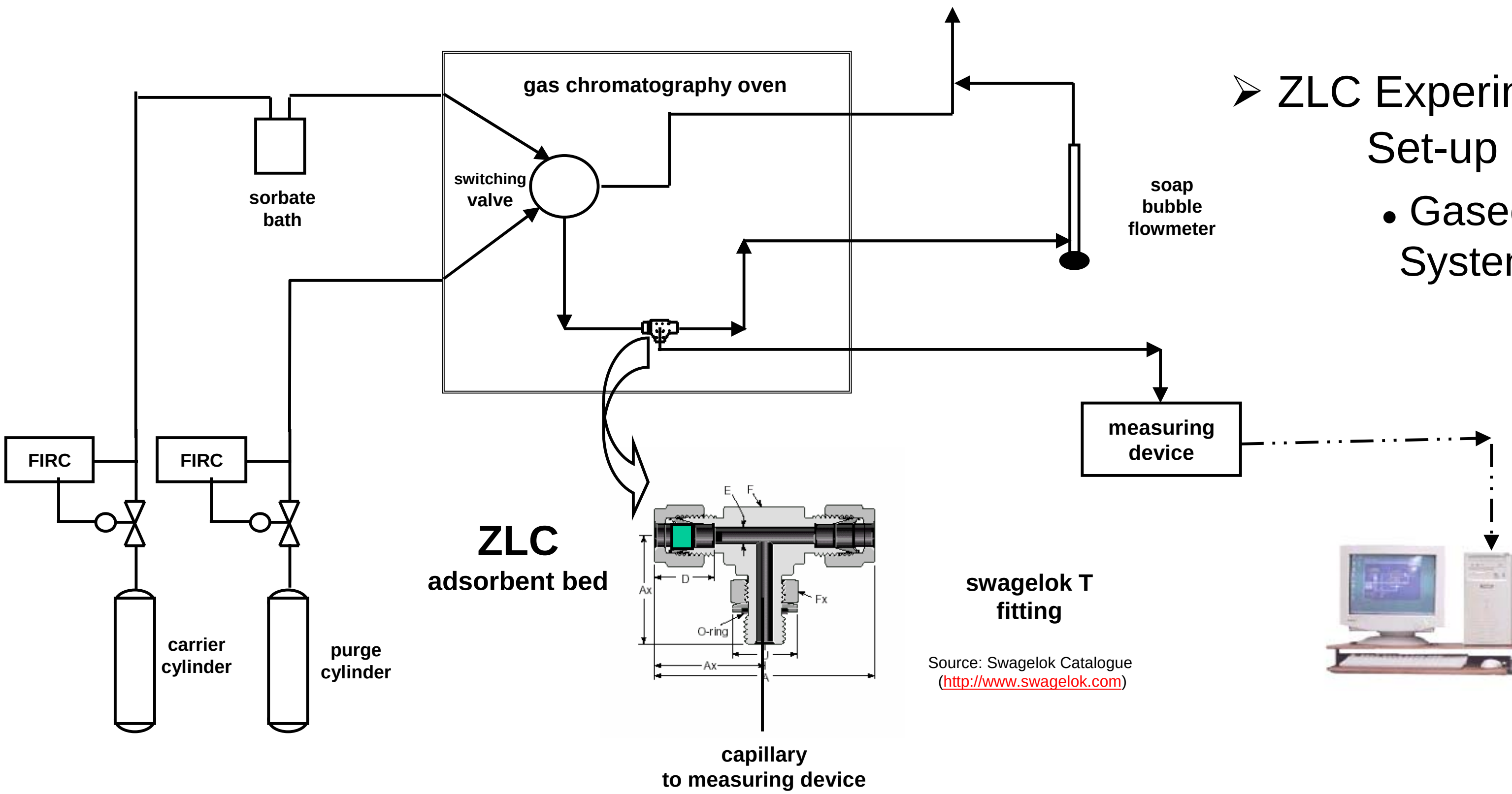
# Historical Development of Diffusion in Zeolites Measurements



# Some recent measurements...



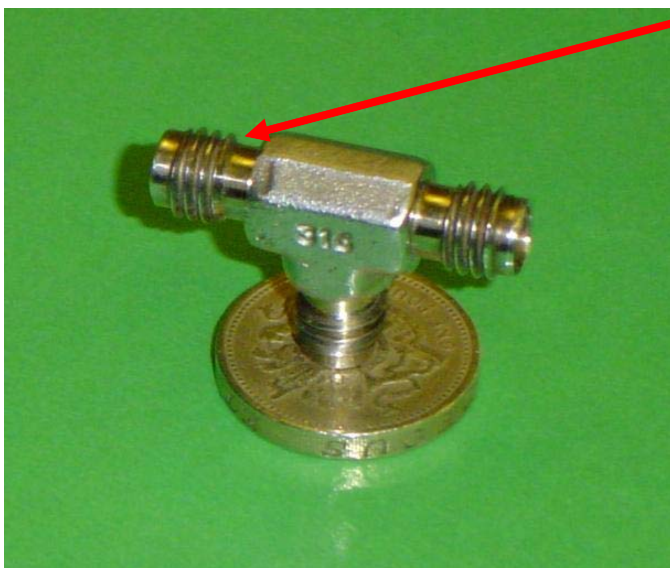
# The ZLC apparatus

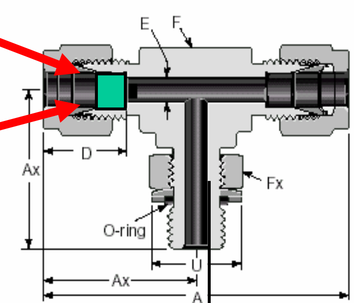



- ZLC Experimental Set-up
  - Gaseous Systems

# The ZLC column

Packing: 0.5 – 2 mg

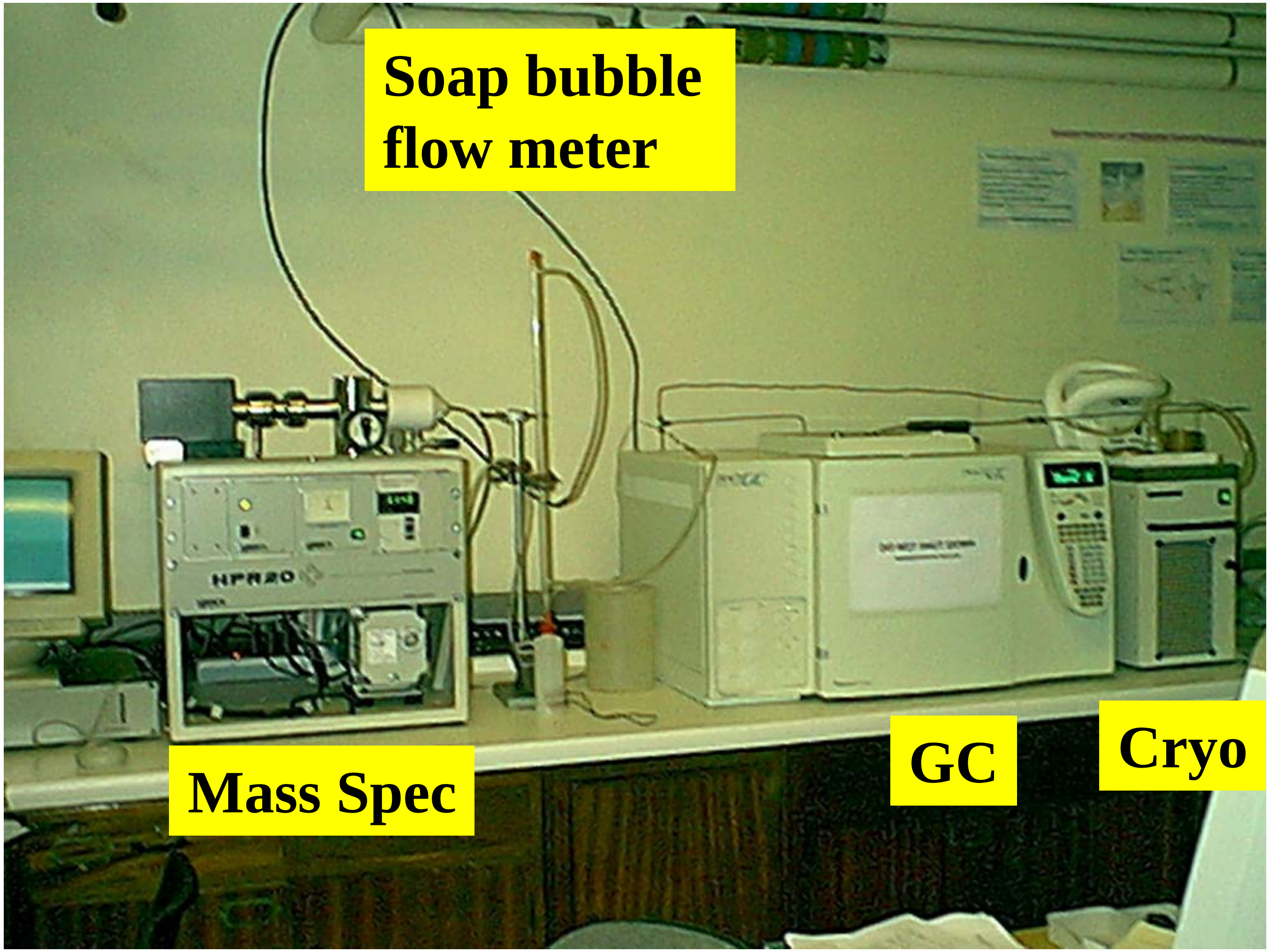





**swagelok T fitting**

**capillary to measuring device**

# The (Tracer) ZLC apparatus



# What can be measured (kinetics)?

- The *transport diffusivity* at zero loading

  Eic M. and Ruthven D.M., *Zeolites*, **1988**, *8*, 40–45.

- *Liquid phase counter diffusion*

  Ruthven D.M. and Stapleton P., *Chem. Engng Sci.*, **1993**, *48*, 89-98.

- The *tracer diffusivity* – Tracer ZLC

  Brandani S., Hufton J.R. and Ruthven D.M., *Zeolites*, **1995**, *15*, 624–631.

- The *transport diffusivity in mixtures*

  Brandani S., Jama M. and Ruthven D.M. , *Ind. & Eng. Chem. Res.*, **2000**, *39*, 821-828.

# What can be measured (equilibrium)?

- Henry law constants

  Brandani F., Brandani S., Coe C.G. and Ruthven D.M., **2002**, *Fundamentals of Adsorption 7*, 21–28.

- Single component isotherms

  Brandani F., Ruthven D.M. and Coe C., *Ind. Eng. Chem. Res.*, **2003**, *42*, 1451-1461.

- Multicomponent isotherms

  Brandani F. and Ruthven D.M., *Ind. Eng. Chem. Res.*, **2003**, *42*, 1462-1469.

- Zero loading heat of adsorption

# ZLC parameters - gases.

- For gases: $$\gamma = \frac{1}{3}\frac{V_F}{KV_S} \approx \frac{1}{3K} \approx 0$$

- The parameter **L** controls the ZLC response

$$L = \frac{1}{3}\frac{FR^2}{KV_S D}$$

$\mathrm{L} < 1$ Equilibrium

$\mathrm{L} > 5$ Kinetics

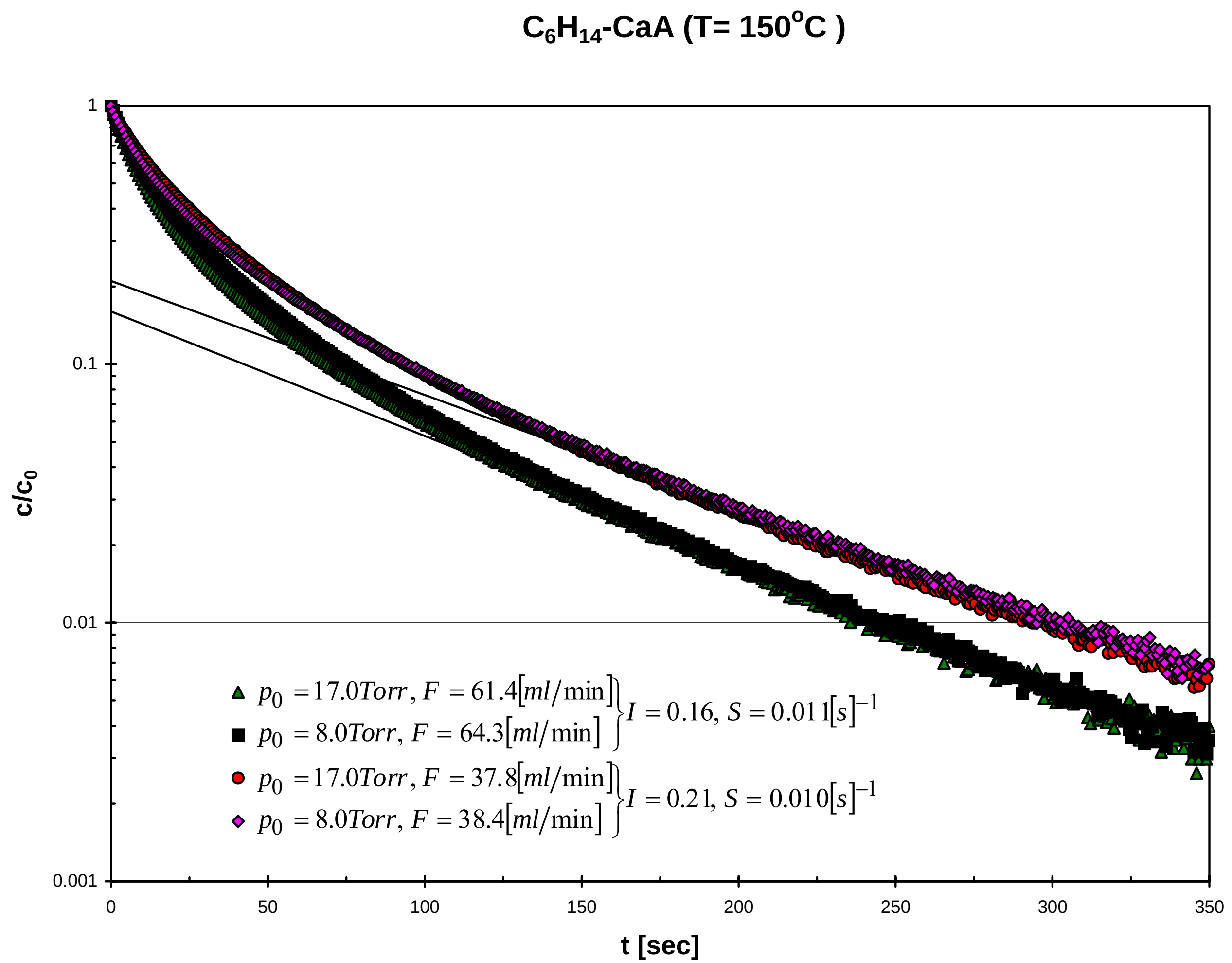
# Long time asymptote - gases.

- Assumptions
  - Linear equilibrium
  - Isothermal
  - Negligible hold-up in fluid phase: $\gamma < 0.1$
  - Cell is perfectly mixed

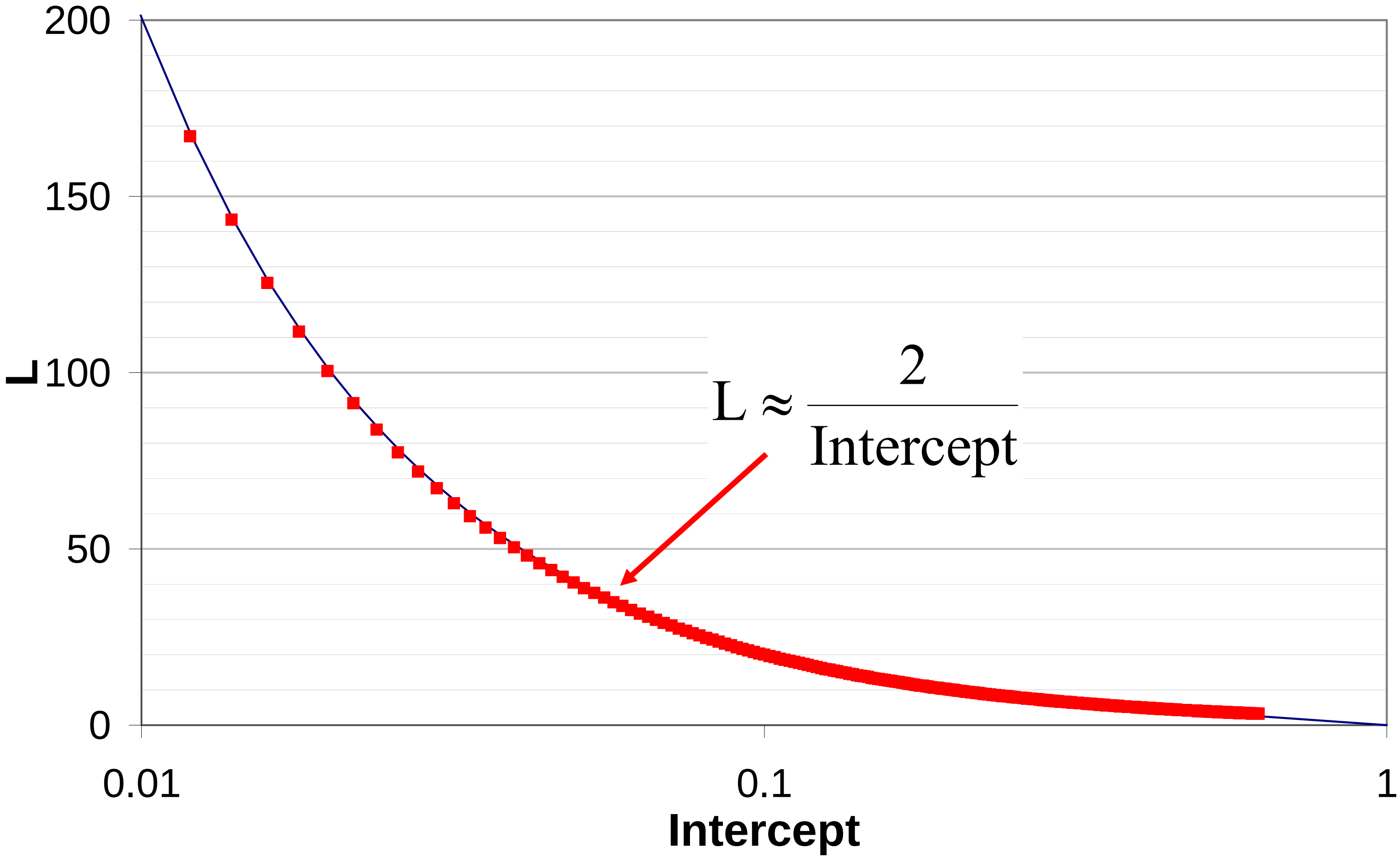
$$\ln\left(\frac{c}{c_o}\right) \approx \ln\left[\frac{2L}{\beta_1^2 + L(L-1)}\right] - \beta_1^2 \frac{D\,t}{R^2} \qquad \beta_1 \cot\beta_1 + L - 1 = 0$$

From the **slope and intercept** of the desorption plot L and $D/R^2$ can be obtained

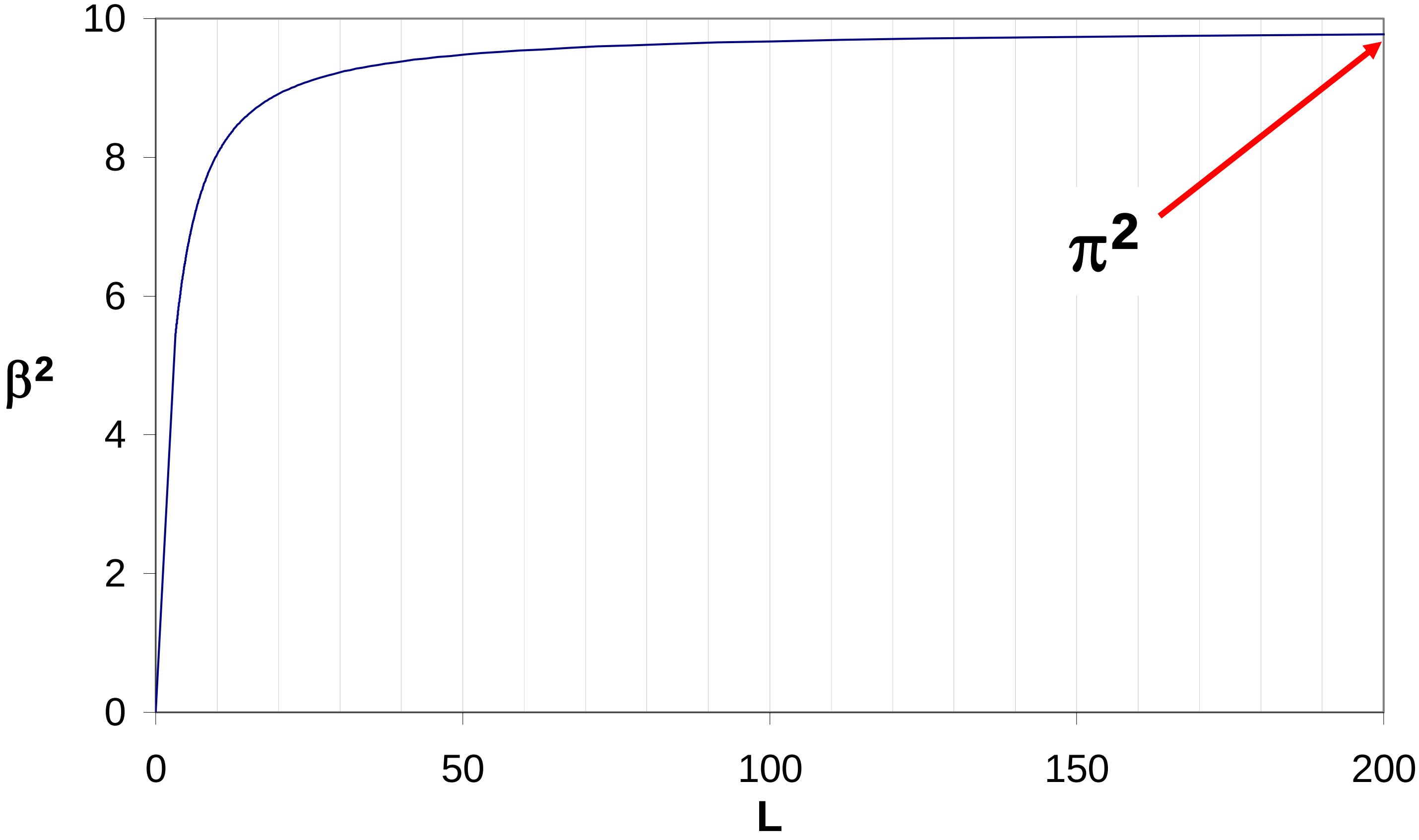
# Long time asymptote - gases.



# Long time asymptote - gases.



# Long time asymptote - gases.



# What can go wrong?

- The sorbate is too strongly adsorbed or is too fast diffusing so the regime L > 5 cannot be reached. Only equilibrium measurements.
- The sorbate is too weakly adsorbed or is too slow: the desorption curve is almost the same as the system's blank.
- Limits in the assumptions

# Isotherm non-linearity.

- Theory
  - Brandani S. *Chem. Engng Sci.*, **1998**, *53*, 2791-2798.

- Experiment
  - Brandani S., Jama M. and Ruthven D.M., , *Chem. Engng Sci.*, **2000**, *55*, 1205-1212.
  - Vary gas concentration to verify linearity
  - Vary gas flow to confirm kinetic control
  - Run TZLC experiment (always linear)

# Isotherm non-linearity.



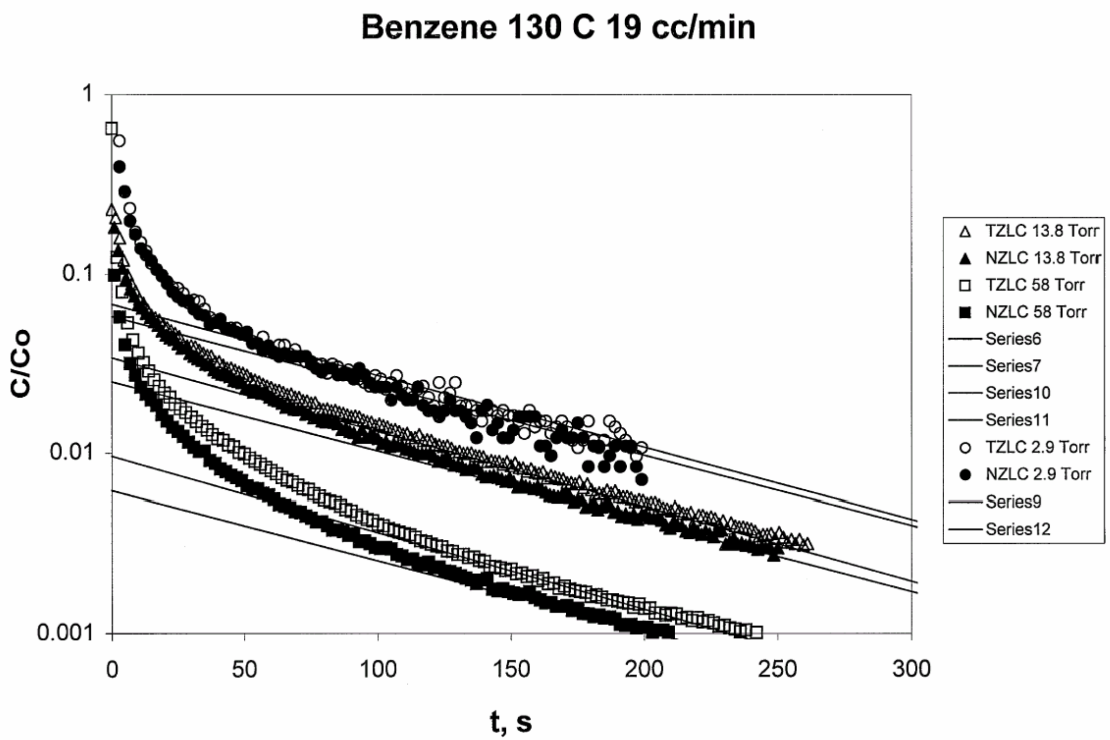
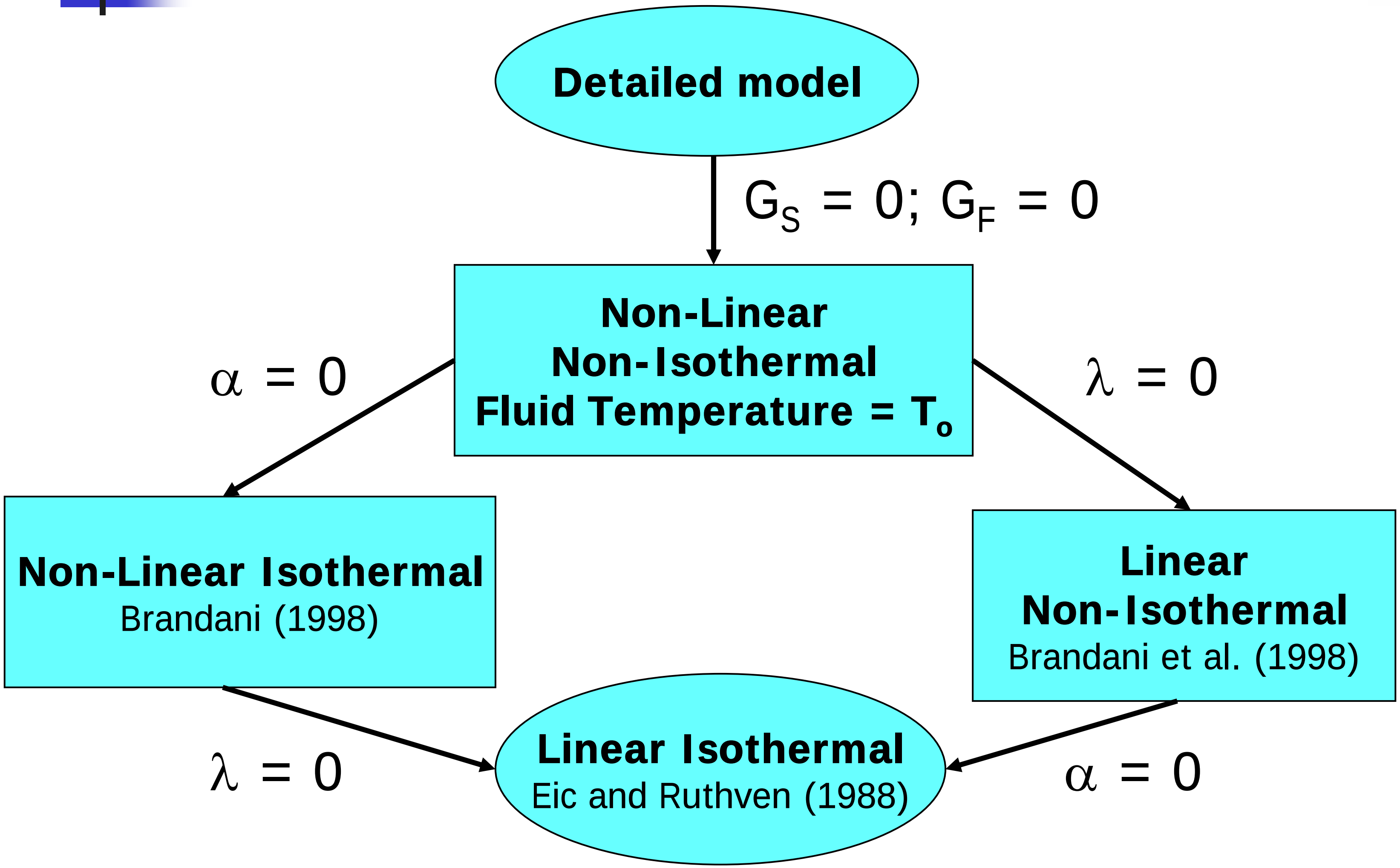



Fig. 4. ZLC desorption curves for benzene at 19 cm/min, 130°C at various partial pressures. Normal (NZLC) curves are shown as filled symbols and tracer (TZLC) curves are shown as open symbols. $P = 13.8$ Torr △ (▲); $p = 58$ Torr □ (■); $p = 2.9$ Torr ○ (●). The linear asymptotes for the NZLC curves are predicted from the tracer data.

# Non-Isothermal ZLC



# Key Grouping - Isothermal criterion

Brandani S., Cavalcante C.L., Guimaraes A.M. and Ruthven D.M., *Adsorption*, **1998**, *4*, 275-285.

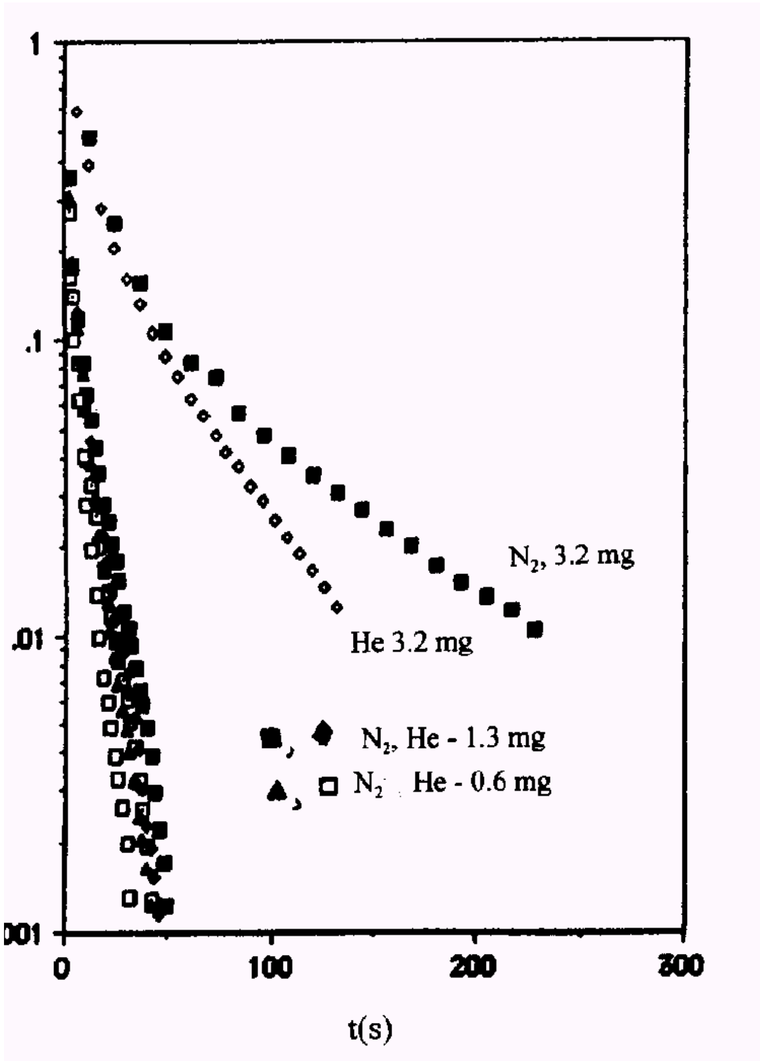
$$\alpha = \frac{L\delta\sigma}{Bi\,Le} = \left(\frac{\Delta H}{\Re T_o}\right)^2 \frac{q_o \Re F}{K_o h a V_s}$$

$$\alpha \approx \left(\frac{\Delta H}{\Re T_o}\right)^2 \frac{q_o \Re F}{3 k_F K_o V_s} R^2 \qquad \text{for} \qquad Nu = 2$$

$$\alpha < 1$$

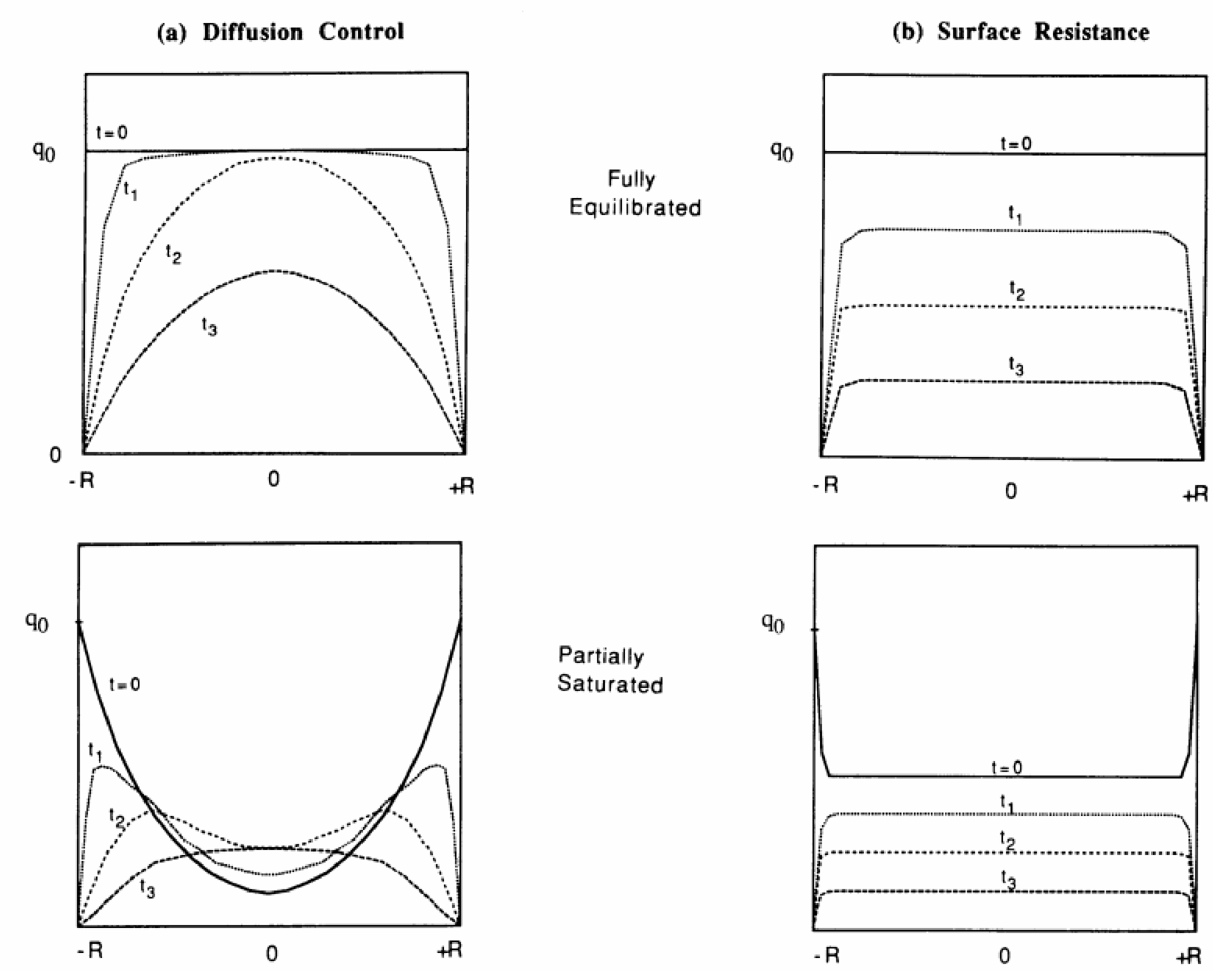
For crystals this is generally valid.

# Surface resistances: fluid film + bed resistance




- Change the carrier gas, i.e. He, Ar or $N_2$
- Example: Benzene - NaX 50 μm crystals 250°C.

# Surface resistances: coke deposition




$$\tau_{Sat} \approx \frac{R^2}{D}$$

$$L > 10$$

# Surface resistances: Partial loading experiment

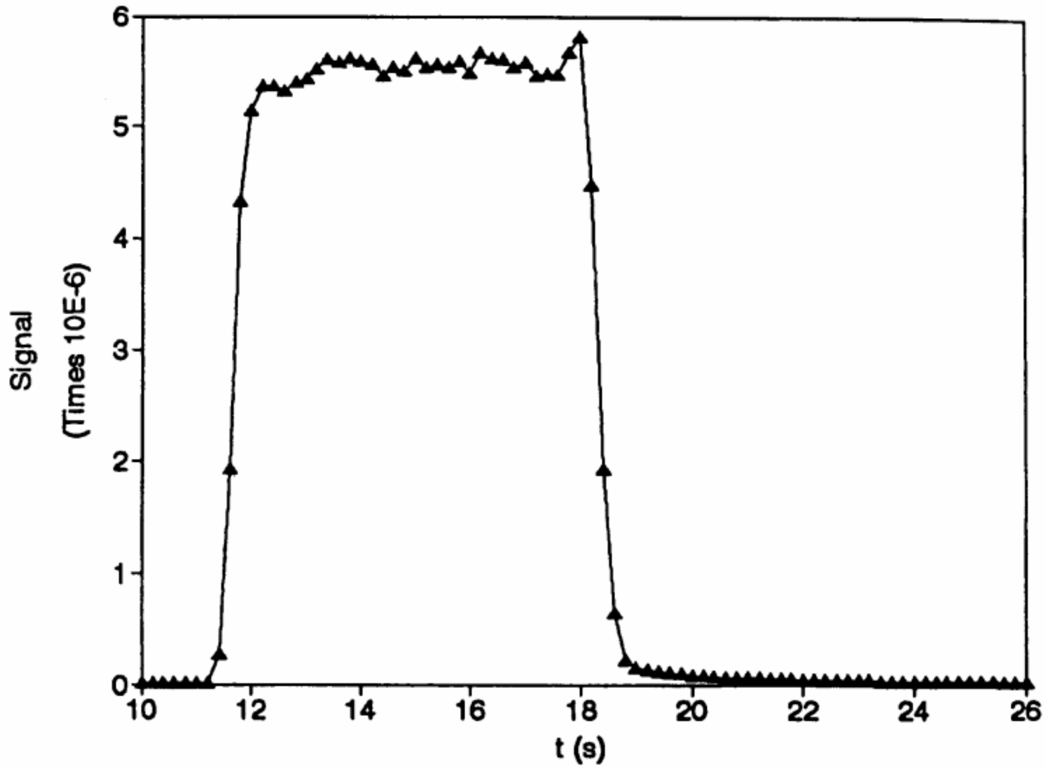
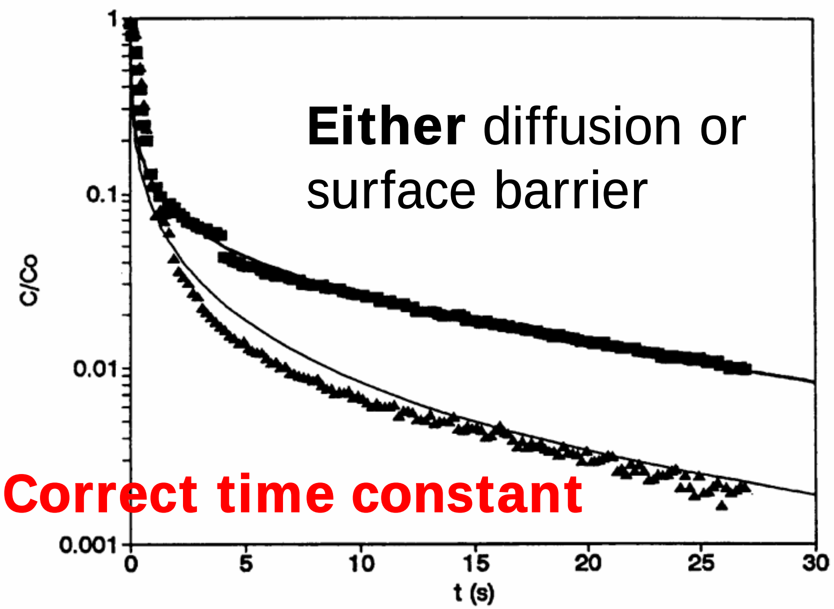



*Figure 10.* Effluent concentration history during partial saturation and desorption of NaX zeolite with propane at 85°C.

# Surface resistances: Partial loading experiment




(b)

*Figure 11.* Experimental ZLC desorption curves for propane—NaX at 85°C for a fully equilibrated sample (■) and a partially equilibrated sample (▲). Theoretical curves for the partially saturated cases are calculated according to Eq. (33) with the parameters ($D/R^2$ and $L$). For details see Table 1.

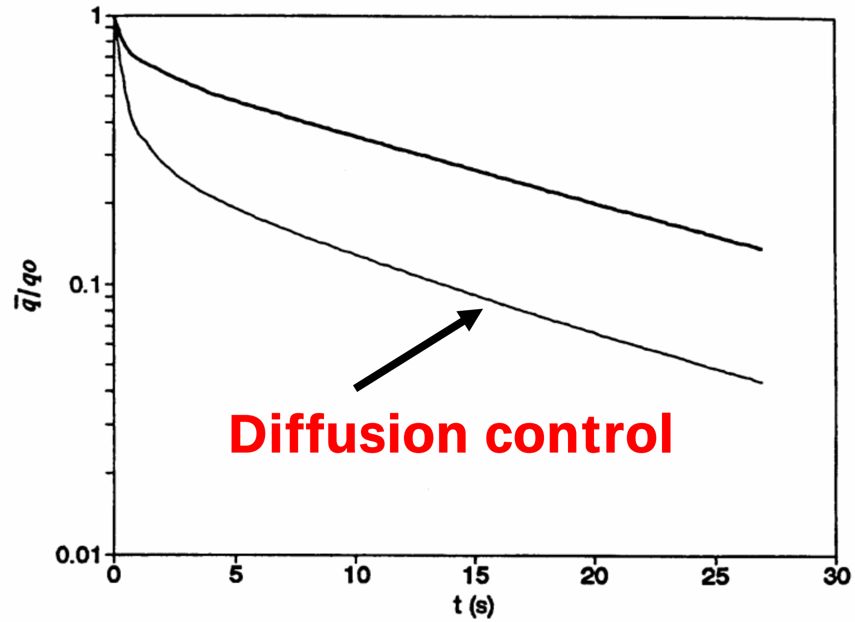



*Figure 12.* Time dependence of average adsorbed phase concentration calculated by integration of the desorption curves of figure 11(b).

# ZLC Experiment - Flexible

- Vary system flow rate

- Vary charging time – partial loading

- Obtain the diffusional time constant from **a number of response curves**

# Tracer ZLC

- ZLC measurements are carried out using a tracer, such as a $C_6D_6$ for $C_6H_6$.
- Total concentration constant
- **ALWAYS LINEAR + ISOTHERMAL**
- **DIRECTLY COMPARABLE TO MICROSCOPIC MEASUREMENTS**
- Requires a mass spectrometer

# Systems reported in literature

- ZLC measurements are carried out in several academic and industrial laboratories
- **More than 70** sorbate-sorbent systems have been studied using the ZLC and reported in the literature
- More than 15 systems with commercial pellets, membrane or monolith fragments.
- **8 liquid** sorbate-sorbent systems
- 10 sorbate-sorbent systems - TZLC
- 3 Multicomponent systems