The ZLC Method

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The ZLC apparatus

ZLC Experimental Set-up
- Gaseous Systems

Source: Swagelok Catalogue (http://www.swagelok.com)
The ZLC column

Packing: 0.5 – 2 mg

swagelok T fitting

capillary to measuring device
The (Tracer) ZLC apparatus

Soap bubble flow meter

Mass Spec

GC

Cryo
ZLC column inside GC oven
What can be measured?
Kinetics

• The *transport diffusivity* at zero loading

• *Liquid phase counter diffusion*

• The *tracer diffusivity* – Tracer ZLC

• The *transport diffusivity in mixtures*
Tracer ZLC

- ZLC measurements are carried out using a tracer, such as a $\text{C}_6\text{D}_6$ for $\text{C}_6\text{H}_6$.
- Total concentration constant
- ALWAYS LINEAR + ISOTHERMAL
- DIRECTLY COMPARABLE TO MICROSCOPIC MEASUREMENTS
- Requires a mass spectrometer
Experimental Signals - Silicalite

n-decane $T=125$ C, $P=0.006$ Torr

- $F_p=250$ cc/m
- $t_e=5$ mins
Partial Loading Experiment: surface barriers

\[ \tau_{\text{Sat}} \approx \frac{R^2}{D} \]

\[ L > 10 \]
Determination of $D_0$

$n$-decane, 125°C, P=0.006 Torr

![Graph showing the determination of $D_0$ for $n$-decane at 125°C and 0.006 Torr. The graph plots $c/c_0$ against $t-t_0$ with two lines representing different flow rates ($F_p=200$ ml/m and $F_p=250$ ml/m).]
Check $D_0$ with Partial-Loading Experiment

n-decane, 125 C, P=0.006 Torr
Adsorbed Phase Concentration

n-decane, 125°C, P=0.006 Torr

\[ V_s \frac{d\bar{q}}{dt} + V_f \frac{dc}{dt} + F_c = 0 \]

Confirmation of no surface effects

5-min equilibrated

fully-equilibrated
Results for silicalite – comparison with IRG
Comparison with IRG values – 5A

Variation of Diffusivity with Chain Length (473K)

![Graph showing variation of diffusivity with chain length at 473K. The graph includes data points for NSE, D_{transport}, PFGNMR, D_{self}, Simulation, ZLC (new), and ZLC (old). The x-axis represents carbon number, and the y-axis represents diffusivity in units of 10^{-12} \text{ m}^2/\text{s}.]
What can be measured?
Equilibrium

• Henry law constants

• Single component isotherms

• Multicomponent isotherms

• Zero loading heat of adsorption
Mass flux from chemical potential driving force

\[ J_A = -\frac{D_0}{RT} q \frac{\partial \mu_A}{\partial z} \]

\[ J_A = -D \frac{\partial q}{\partial z} \]

\[ J_A = -D_0 q \frac{\partial \ln P_A}{\partial z} \]

At constant \( T, P \)

\[ D = D_0 \frac{\frac{d \ln P_A}{d \ln q}} \]

The transport diffusivity is a strong function of concentration

Corrected Diffusivity

Darken Correction Factor
Darken Correction

Typically the corrected diffusivity is assumed to be constant, since the thermodynamic correction has a strong composition dependence.

\[
\frac{d \ln P_A}{d \ln q} = \frac{q}{P_A} \frac{d q}{d P_A}
\]

Need VERY ACCURATE equilibrium data to evaluate the derivative.

Langmuir

\[
\frac{d \ln P}{d \ln q} = \frac{1}{1 - q/q_S} = \begin{cases} 
1 & \text{if } P = 0 \\
\infty & \text{if } P = \infty
\end{cases}
\]
Darken Correction cont.

![Graphs showing Darken Correction](image)

- **Graph 1:**
  - **Y-axis:** $q/q_s$
  - **X-axis:** $P$ log scale
  - Curves for Langmuir and Dual Site Langmuir

- **Graph 2:**
  - **Y-axis:** $\frac{d \ln P_A}{d \ln q}$
  - **X-axis:** $q/q_s$
  - Curves for Dual Site Langmuir and Langmuir
Equilibrium ZLC CO$_2$ - Silicalite.

CO$_2$-column4 (T= 30$^\circ$C, $p_0$= 0.0025 atm)

$F = 5.1$ [cc/min]
$F = 7.5$ [cc/min]
$F = 10.7$ [cc/min]
Experimental ZLC curves.

CO₂-column4 (T= 30°C, p₀= 0.0025 atm)

\[ q^*V_S = \left( \int_0^\infty \frac{y}{1-y} \, dFt - \int_0^t \frac{y}{1-y} \, dFt - V_F \cdot y \right) \frac{P}{RT} \]
Adsorption isotherms.

\( \text{CO}_2 \)

\( T = 30 \, ^\circ\text{C} \)
Assuming 20% binder
nC10 on NaCaA

Stach & Fiedler

Abb. 2. Experimentelle (Symbole) und berechnete (---) Adsorptionsisothermen von n-Dekan am Zeolith NaCaA