Frequency Response
A Powerful Technique for Discerning Gas Phase Diffusional Mechanisms and Rates in Nanoporous Adsorbents

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Today's Objectives

- introduce mass transfer mechanisms in nanoporous adsorbents
- provide impetus behind frequency response (FR) methods: mass transfer *mechanism and rapid PSA*
- discuss methods of measuring mass transfer rates
- describe a unique volumetric FR (VFR) method
- present VFR results from disparate adsorbate-adsorbent pairs from very *slow to very fast diffusing*

results from various techniques will be contrasted against each other

Mechanisms

Mass Transfer Mechanisms in Porous Adsorbent

Goal of Practical Adsorbent

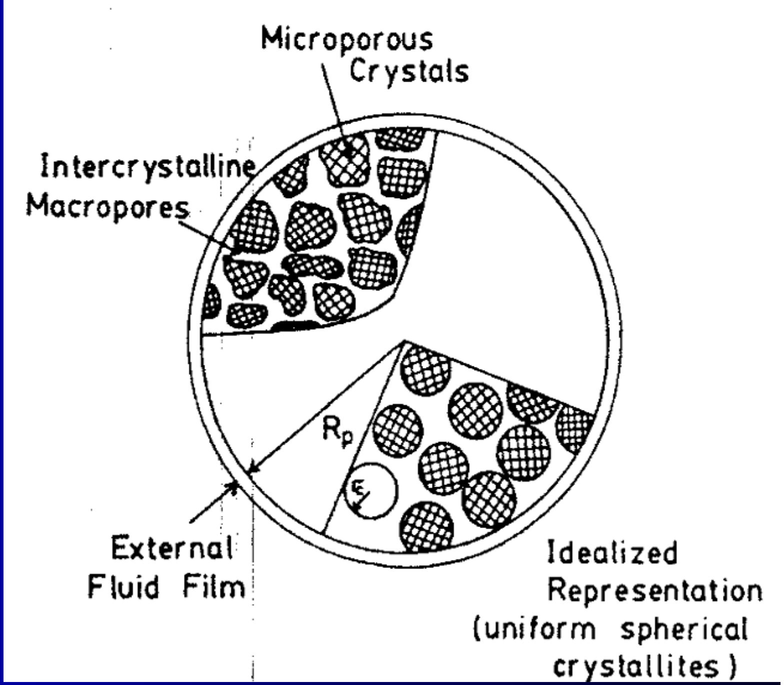
….concentrate a large amount of solid surface area in as small a volume as possible, and process as much gas as possible, while still satisfying process constraints….

powders, beads, pellets, extrudates, granules

Leads to Inherent Resistances

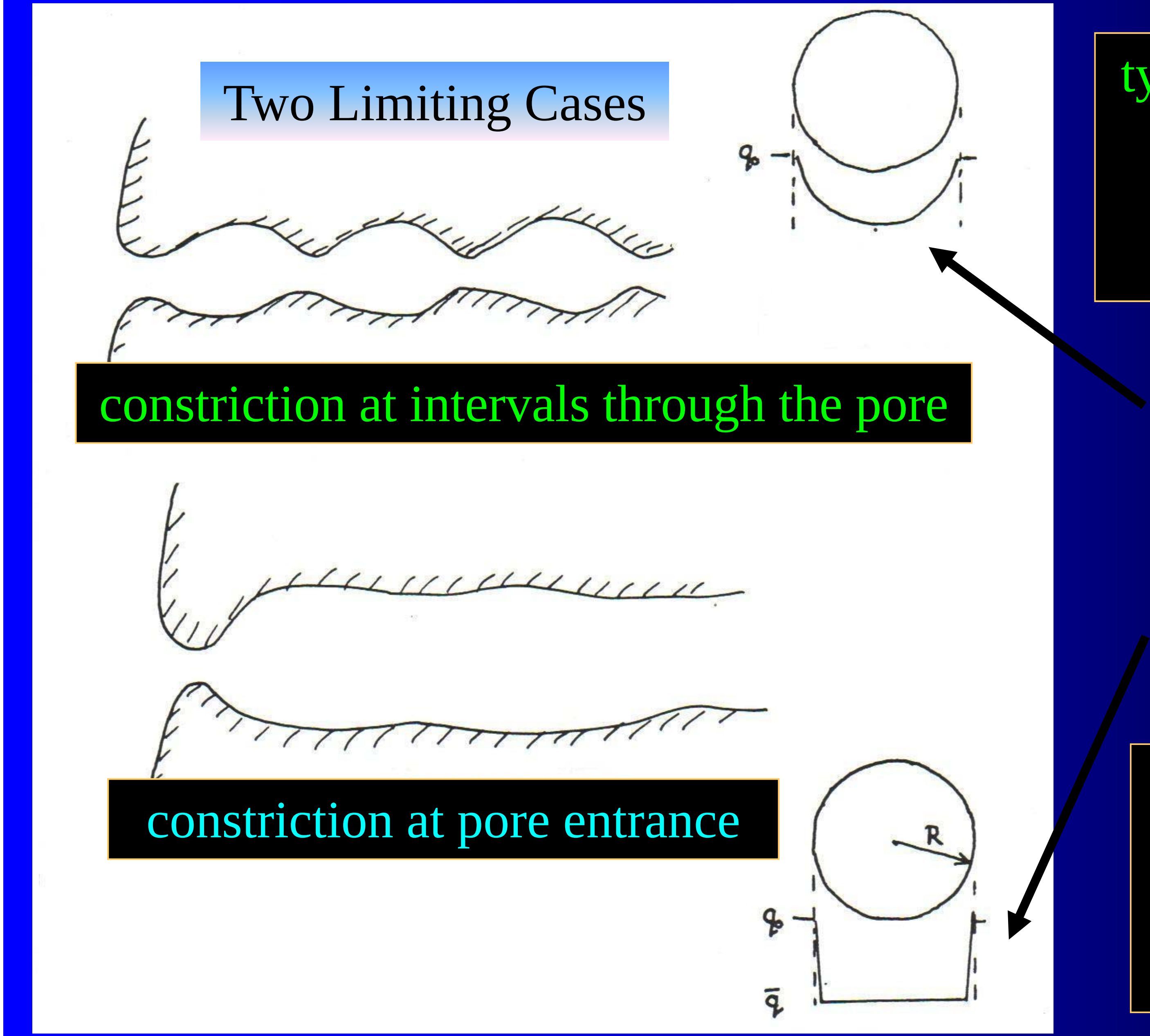
Mass Transfer Mechanisms in Nanoporous Adsorbents

- adsorption-desorption kinetics depend on interplay between various rate processes
- major rate processes
  - film resistance
  - macropore gas diffusion
  - macropore Knudsen diffusion
  - macropore surface diffusion
  - macropore advection
  - micropore pore mouth resistances
  - micropore diffusion
- dominant mass transfer mechanism varies with system



Karger, and Ruthven, 1992.

Intraparticle Micropore Resistance



Two Limiting Cases

constriction at intervals through the pore

constriction at pore entrance

typical of zeolites and other microporous adsorbents

concentration profile in the particle

typical of CMSs and other adsorbents with surface barrier

Impetus

Which of the previous
mass transfer mechanisms
dominate, how do you
find out, and do
significant *T*, *P* and *n*
dependencies exist?

With respect to rapid PSA, what can be discovered from measuring mass transfer rates over a broad range of frequencies, easily up to 10 Hz and possibly up to 100 Hz?

Notion of Rapid PSA

Is it possible to achieve a 1/10th volume reduction?

- increase working capacity 10 fold (herculean)
- operate at 1/10th cycle time (achievable)
- known as rapid PSA

❖ *issues with adsorbent attrition and pressure drop due to high velocities*

although rapid PSA offers potential for a low-cost solution for CO_2 capture, the extent of size reduction achievable is, at the moment, unknown

QuestAir H-6200 RCPSA

Hydrogen Production

~ 12,000 Nm^3/h/module

SeQual's Eclipse

SeQual's Eclipse

- 93% medical grade O$_2$
- 0.5 to 3.0 LPM continuous O$_2$
- 18 lbs with battery

5-bed system

Methods

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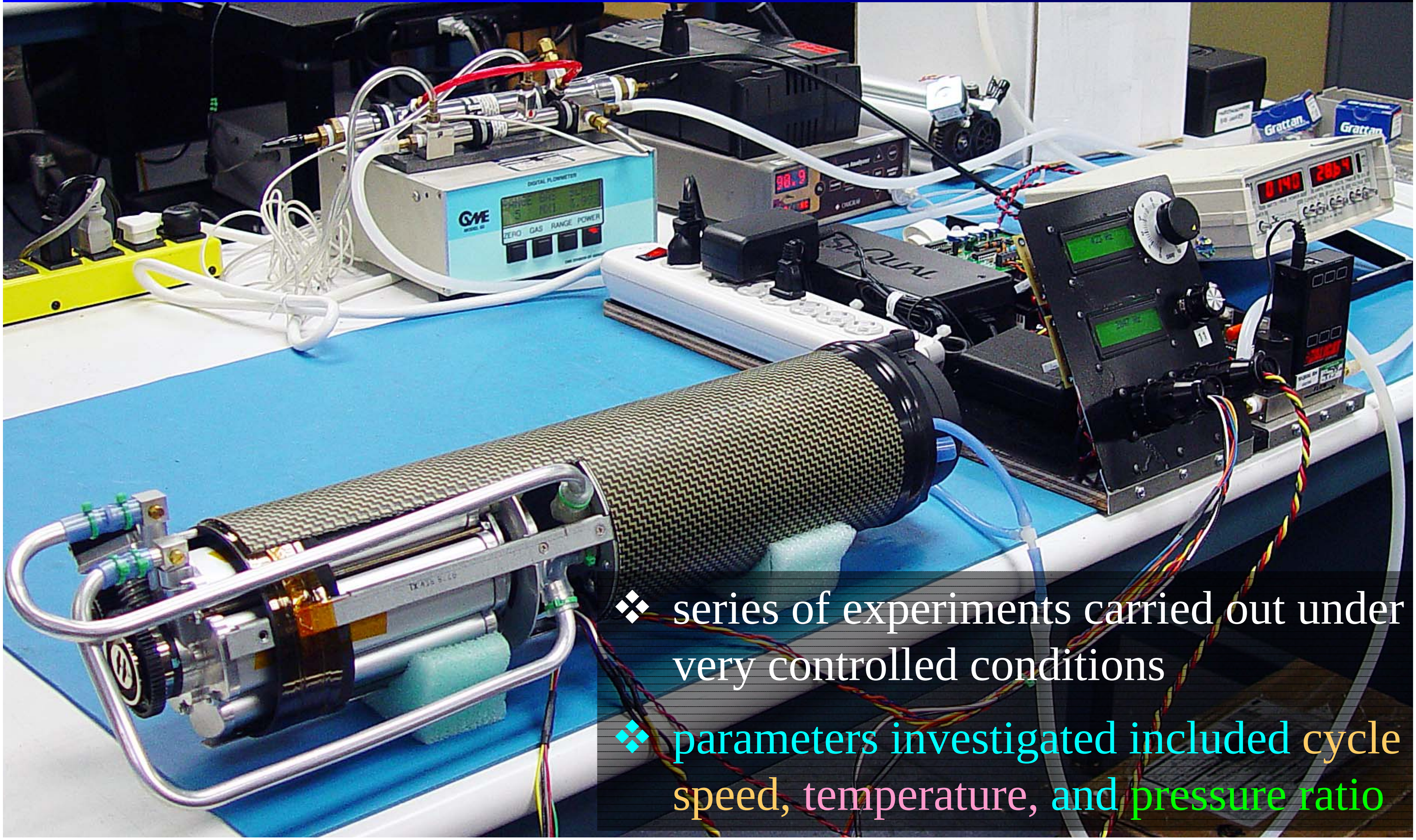
Mathematical Modeling and Process Simulation

Breadboard Test Setup



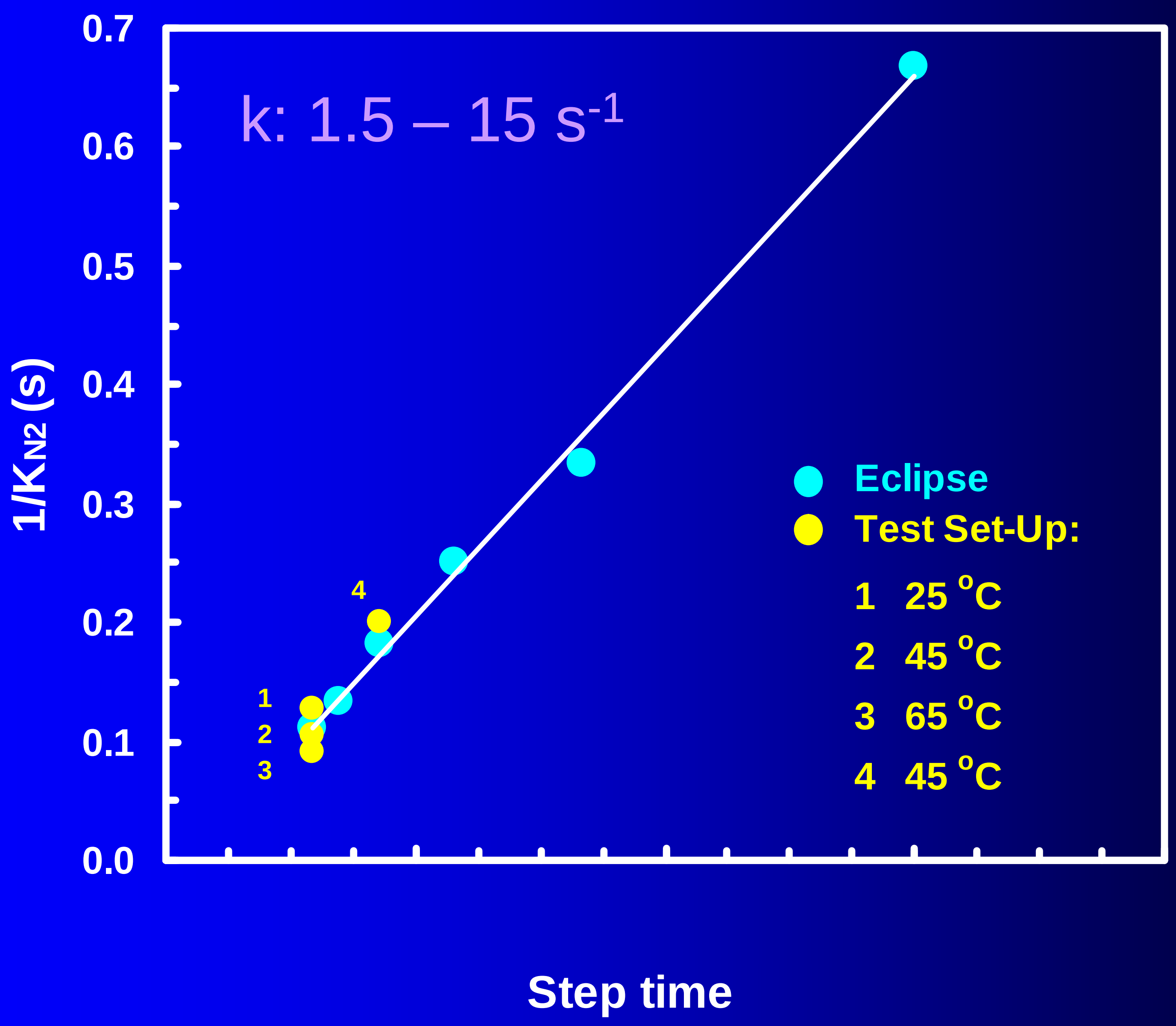
- series of experiments carried out under very controlled conditions
- parameters investigated included cycle speed, temperature, and pressure ratio

Comparison of Experiment with Simulation

Cycle Time A							
Run	T °C		Feed Flow (SLPM)	Tail Gas Flow (SLPM)	Product Flow (SLPM)	Product Purity	MTC s^{-1} k_{N2}/k_{O2} = 0.75
1	25	Experiment	23.1	19.0	3.58	91.3	k_{N2}= 7.8
		Prediction	23.1	19.5	3.58	91.3	
2	25	Experiment	23.0	19.2	3.43	93.1	
		Prediction	23.1	19.7	3.43	92.7	
3	25	Experiment	23.0	19.3	3.17	94.4	
		Prediction	23.1	20.0	3.18	94.4	

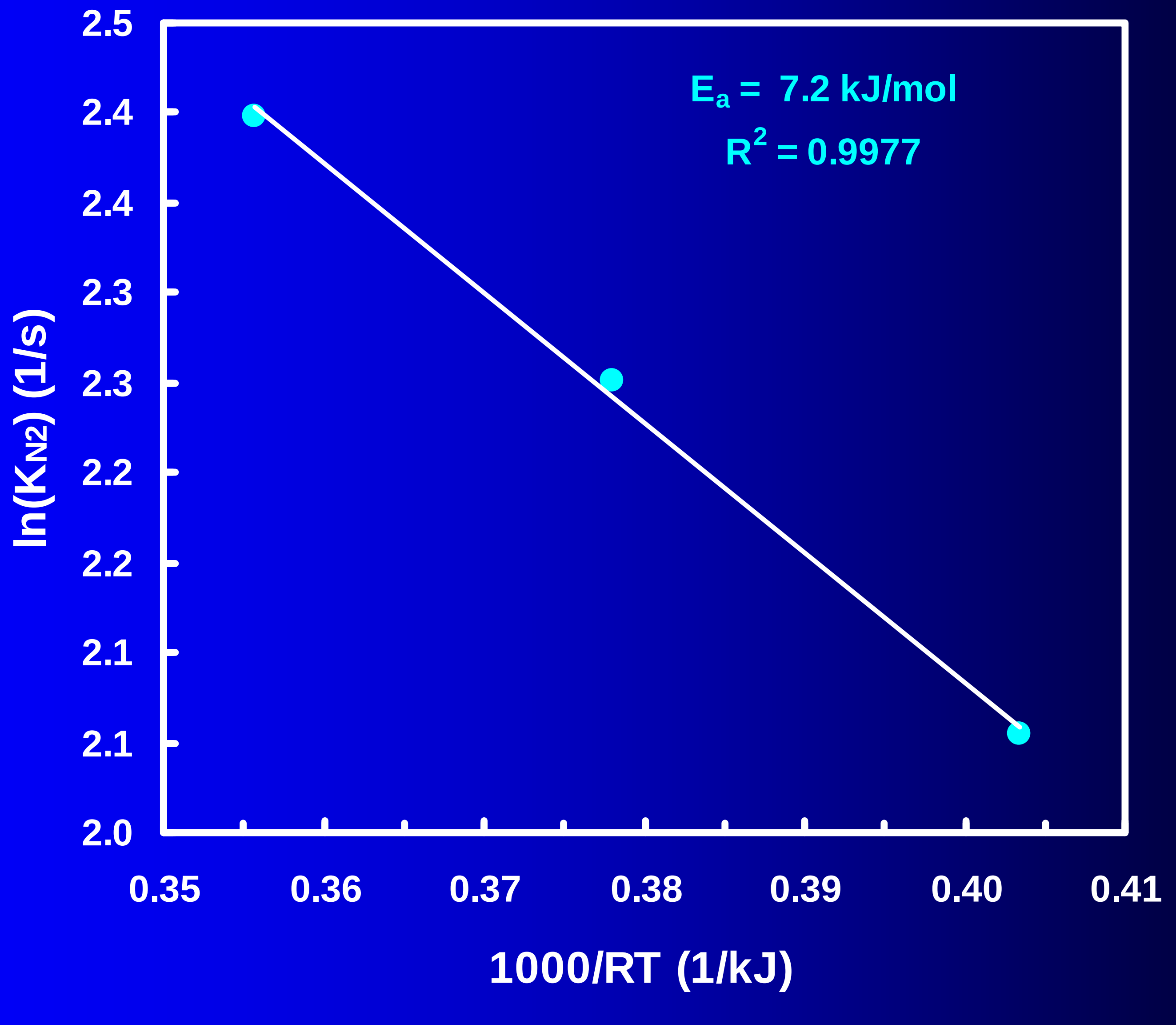
LDF mass transfer coefficient was the only fitting parameter; but, the mechanism was not determinable and the results were confusing!

Mass Transfer Coefficient Correlation



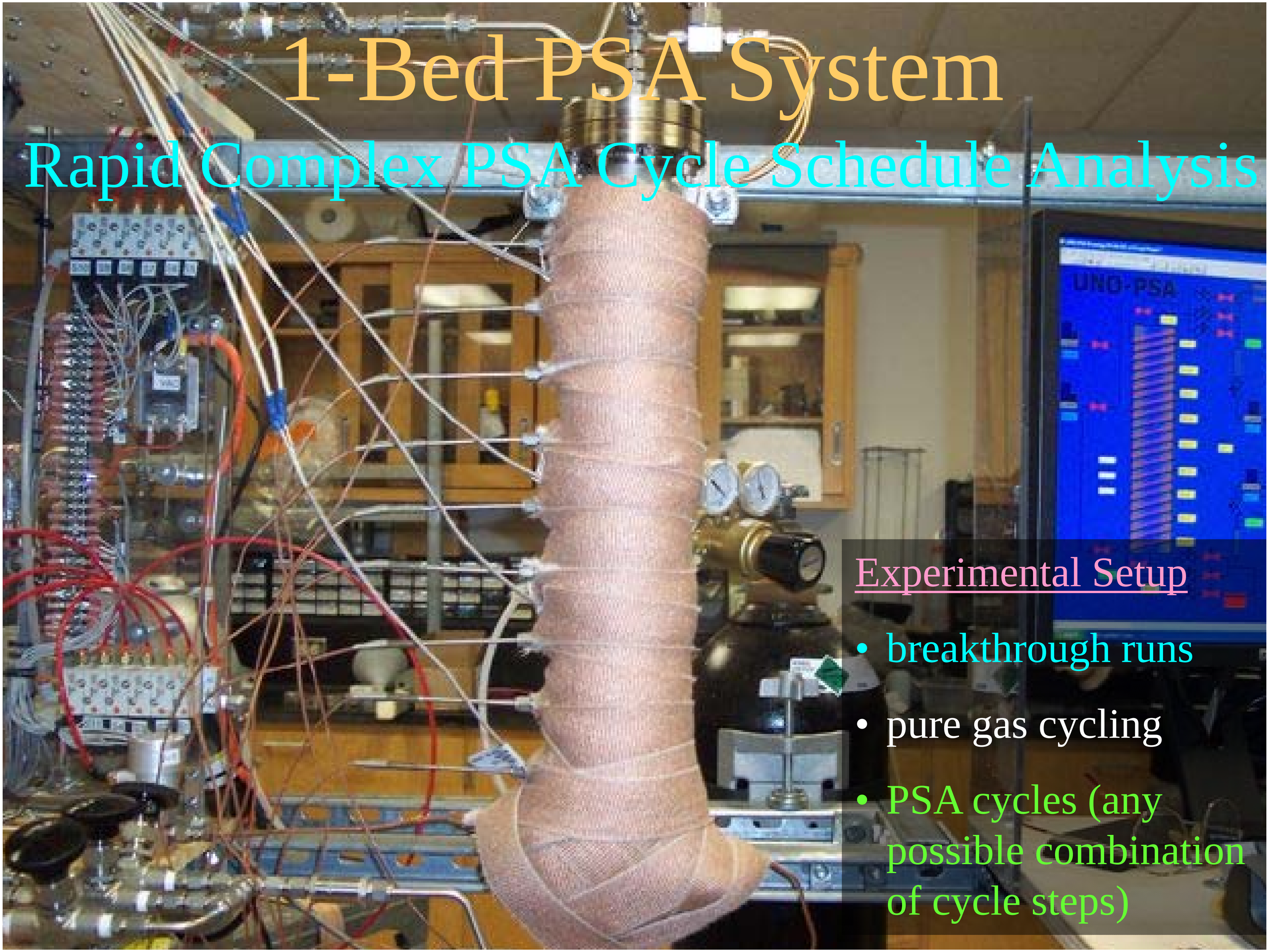
Mass Transfer Coefficient Correlation

Activated Diffusion Process from T-Dependence?



1-Bed PSA System

Rapid Complex PSA Cycle Schedule Analysis

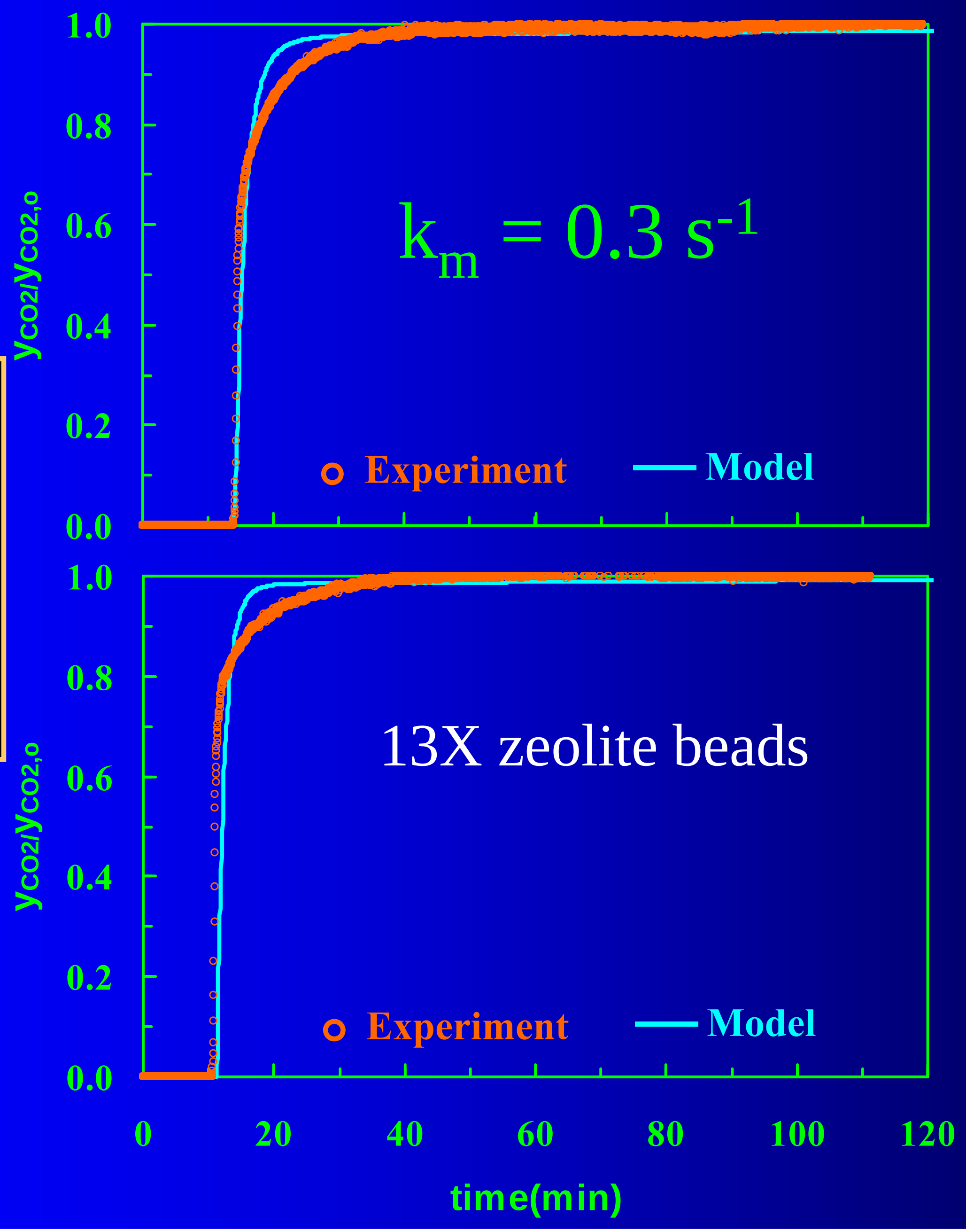


Experimental Setup

- breakthrough runs
- pure gas cycling
- PSA cycles (any possible combination of cycle steps)

CO_2 Breakthrough Experiments

- mass transfer coefficient determination
- isotherm validation
- mechanism?



30% CO_2

70% He

Flow = 10 SLPM

Pressure = 25 psia

Temperature = 25°C

40% CO_2

60% He

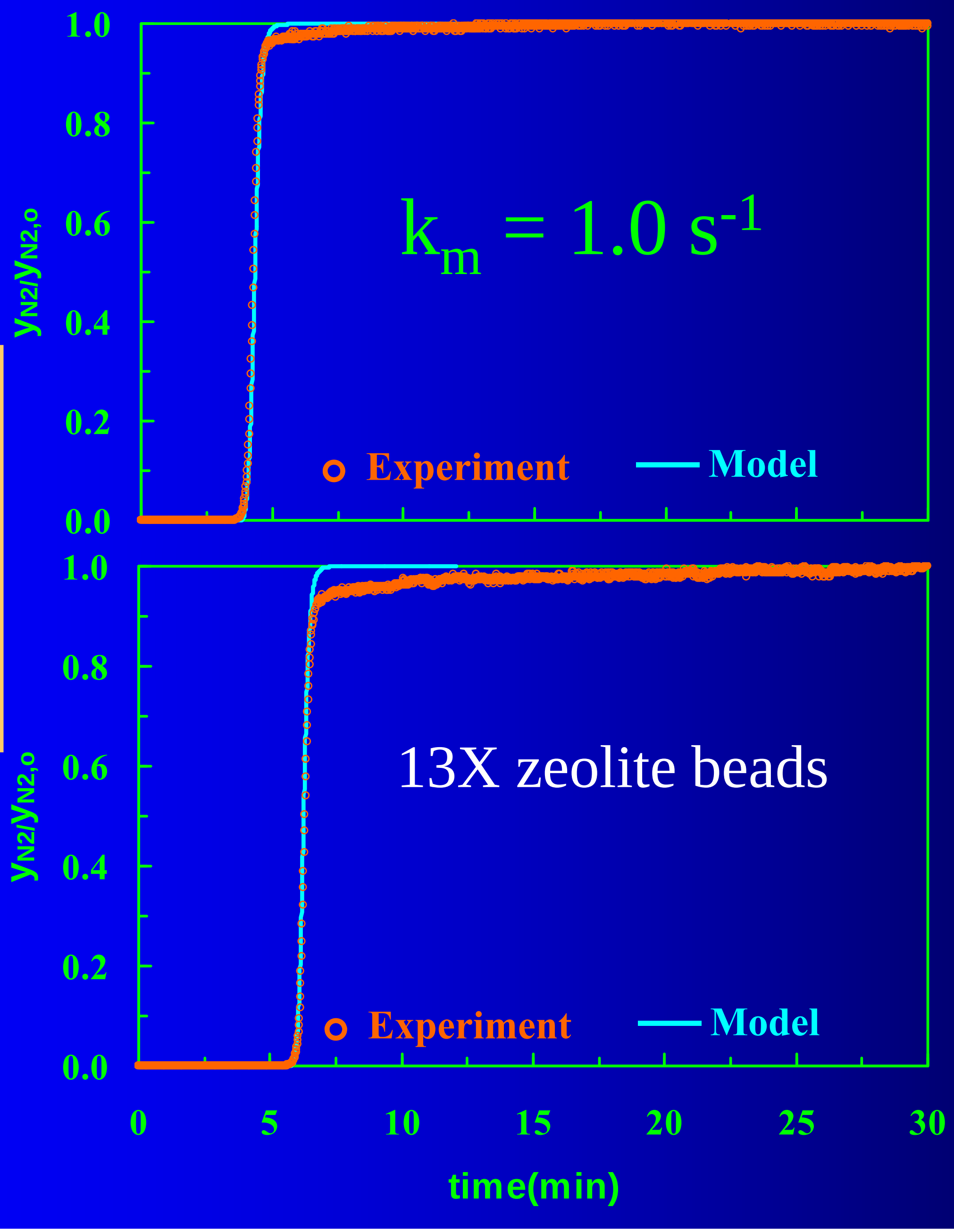
Flow = 10 SLPM

Pressure = 25 psia

Temperature = 25°C

N_2 Breakthrough Experiments

- mass transfer coefficient determination
- isotherm validation
- mechanism?



20% N_2

80% He

Flow = 2.55 SLPM

Pressure = 25 psia

Temperature = 25°C

30% N_2

70% He

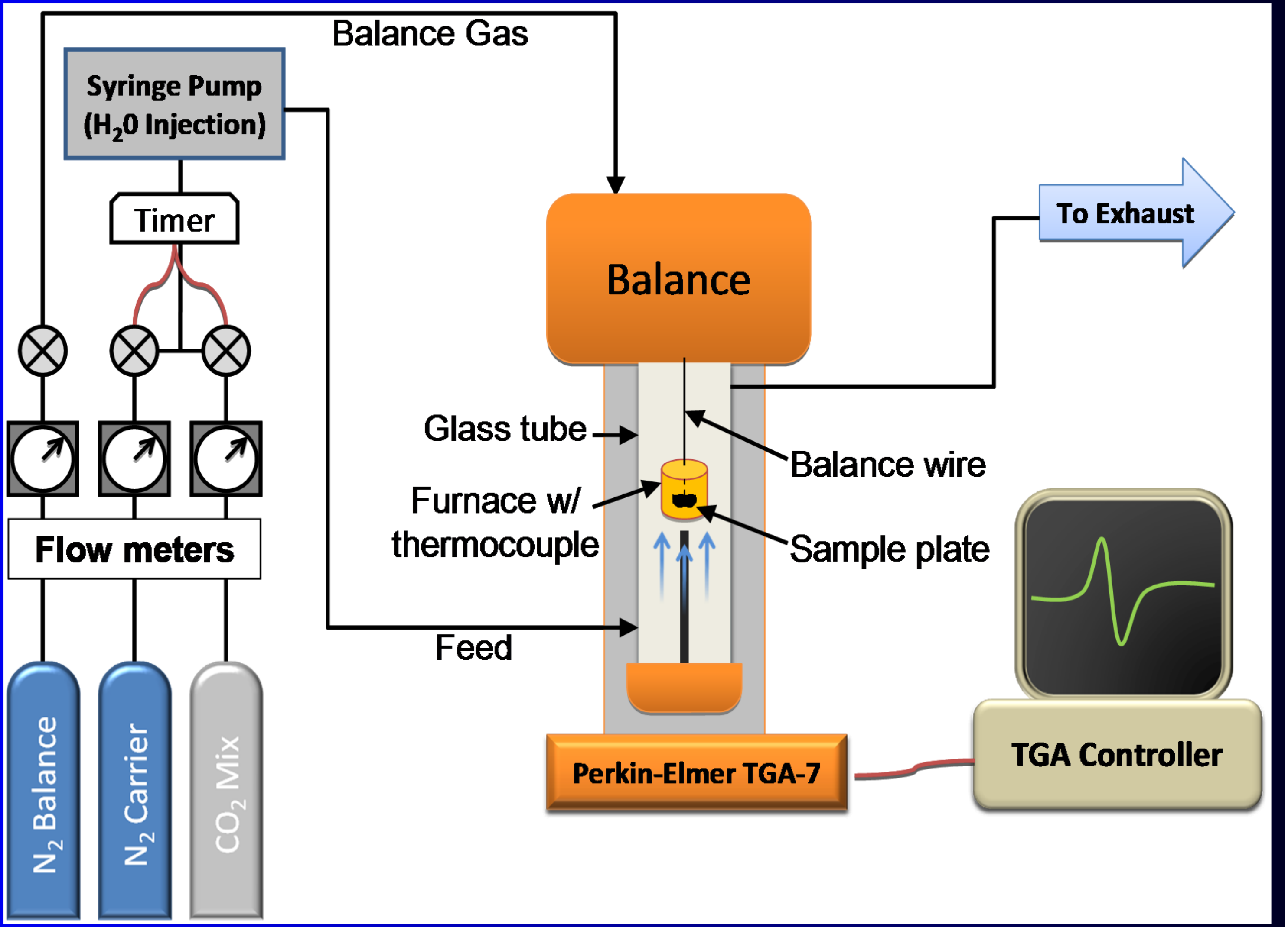
Flow = 1.67 SLPM

Pressure = 25 psia

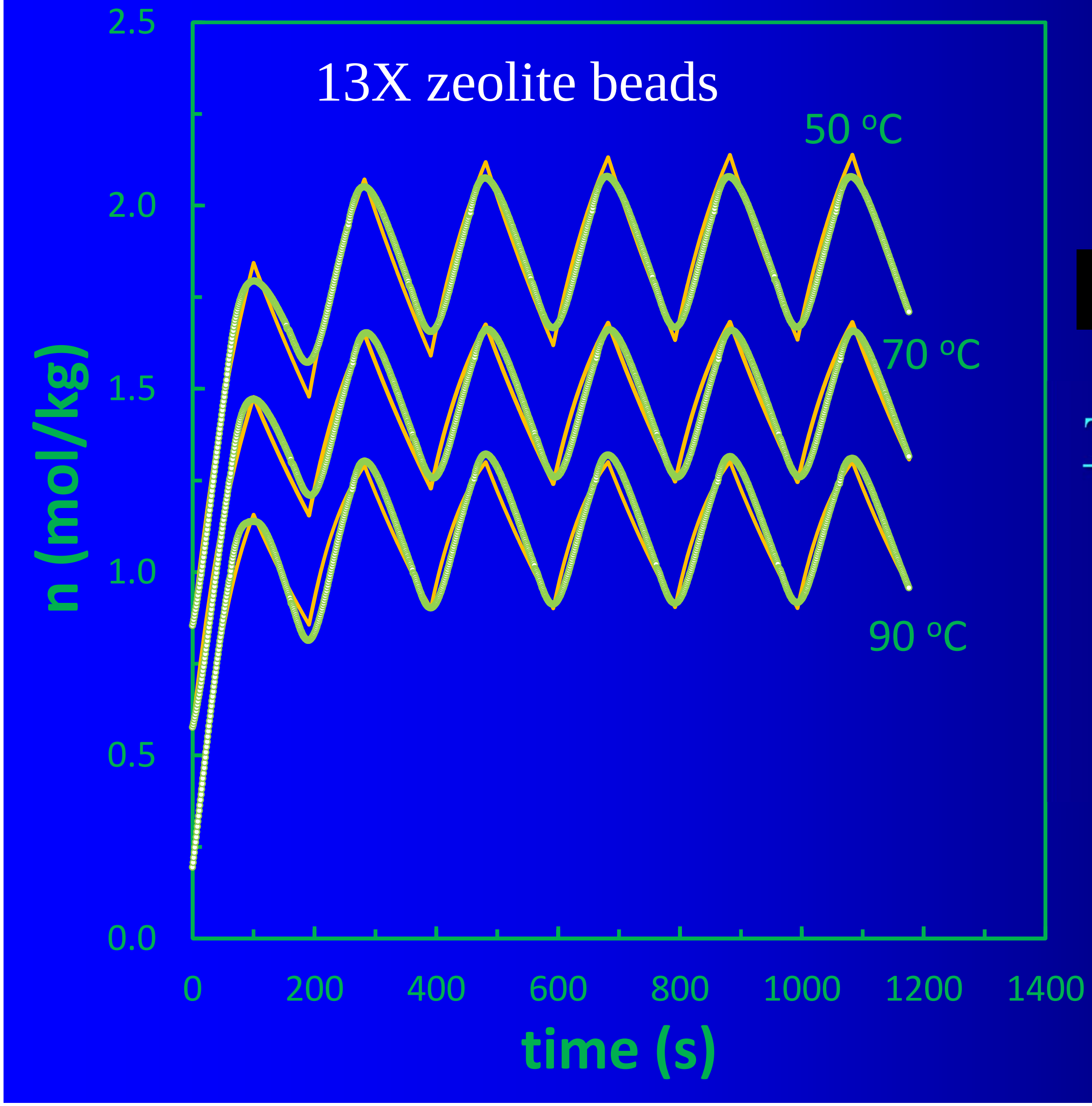
Temperature = 25°C

TGA Uptake and Release Experiments

- **rapid adsorbent characterization**
- **mass transfer coefficient determination?**
- **mechanism?**



TGA Uptake and Release Experiments

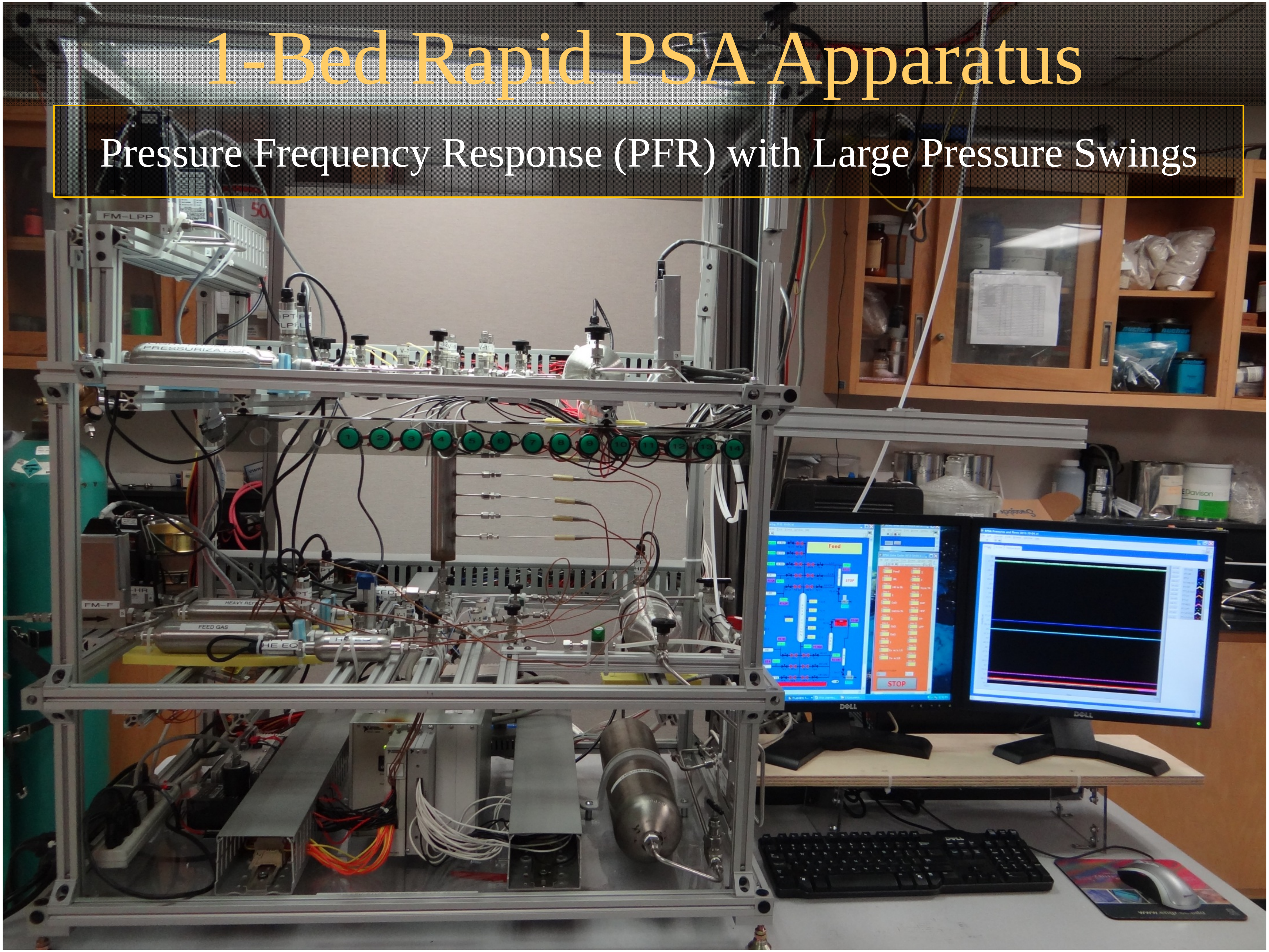


Cycle
100 s Adsorption/100 s Desorption

15% CO_2 in N_2/100 % N_2

T (ºC)	k_m (s^{-1})	
	Ads	Des
50	0.0086	0.0024
70	0.0106	0.0026
90	0.0145	0.0033

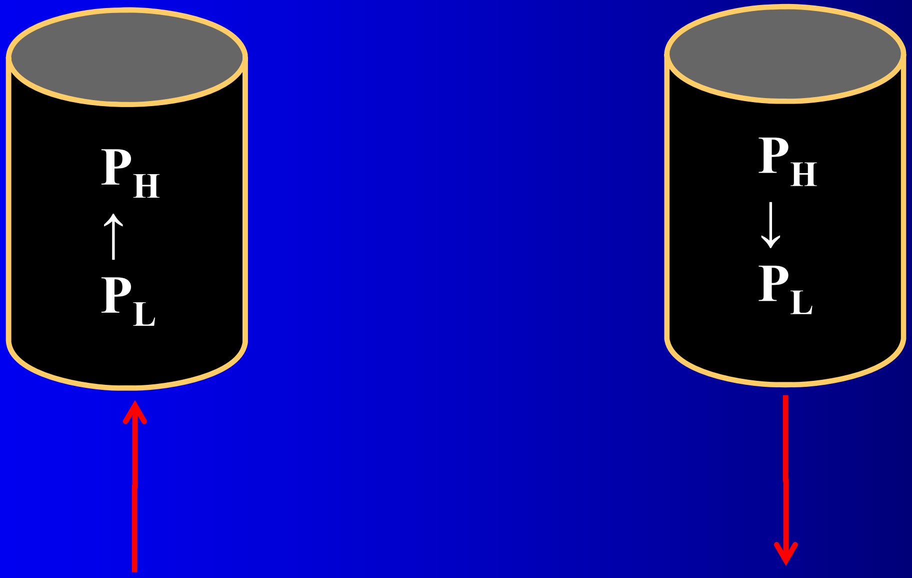
These rates are orders of magnitude slower than BT experiments, due to stagnant film diffusion!



1-Bed Rapid PSA Apparatus

Pressure Frequency Response (PFR) with Large Pressure Swings

Two-Step PFR Cycling Experiments



pure feed gas

effluent

Pressurization

Countercurrent Depressurization

Information Obtained

a) valve C_v

b) excluded volume

c) adsorption/desorption mass transfer coefficients

Experimental Conditions

CO_2

- bed T = 25 °C
  - feed P = 8, 20 psia
- bed T = 50 °C
  - feed P = 8 psia
- bed T = 75 °C
  - feed P = 8 psia

N_2

- bed T = 25 °C
  - feed P = 2.4, 20, 40 psia
- bed T = 50 °C
  - feed P = 20 psia
- bed T = 75 °C
  - feed P = 20 psia

O_2

- bed T = 25 °C
  - feed P = 20 psia
- bed T = 50 °C
  - feed P = 20 psia
- bed T = 75 °C
  - feed P = 20 psia

CH_4

- bed T = 25 °C
  - feed P = 2.4, 20 psia
- bed T = 50 °C
  - feed P = 20 psia
- bed T = 50 °C
  - feed P = 20 psia

Ar

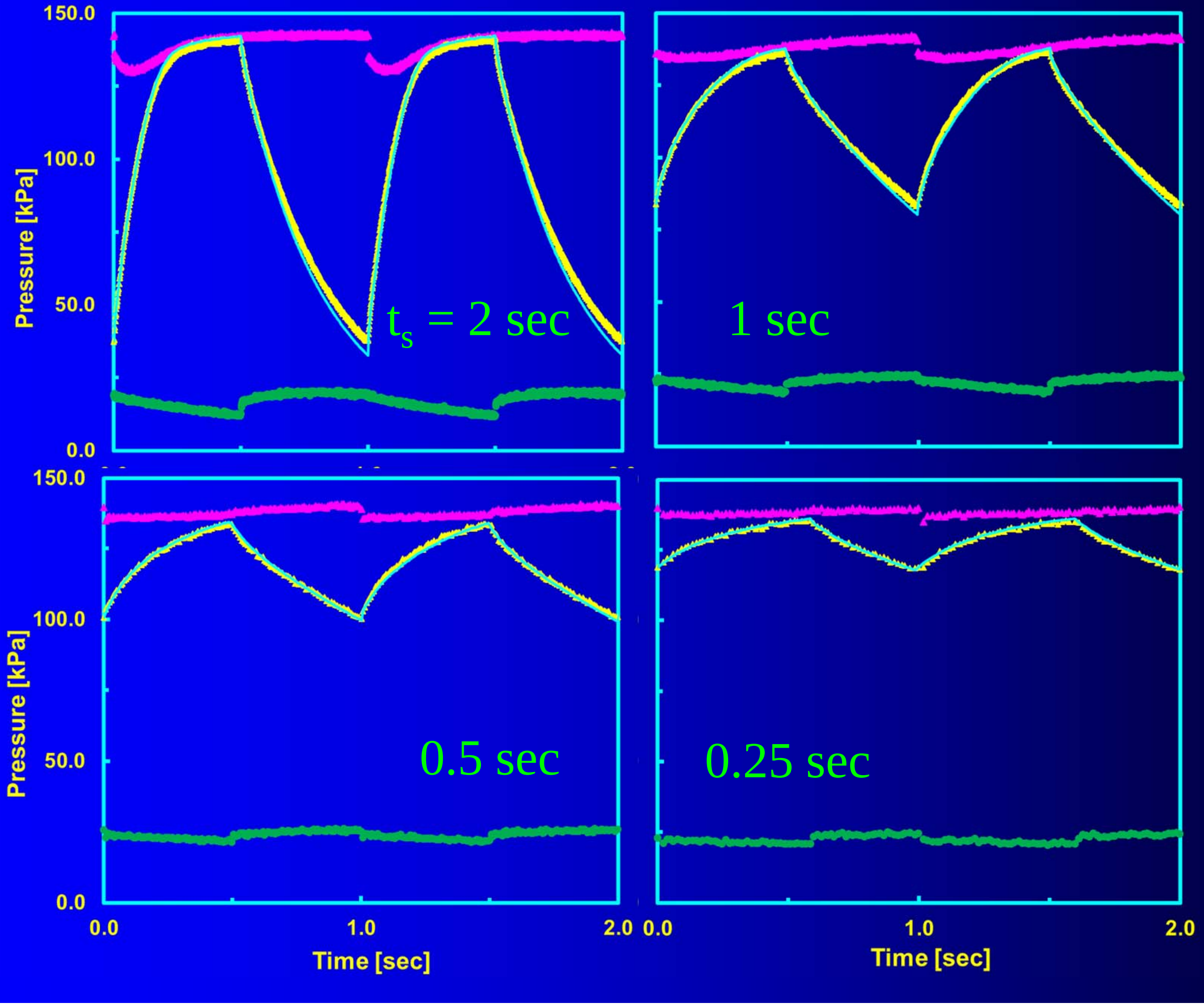
- bed T = 25 °C
  - feed P = 2.4, 20 psia
- bed T = 50 °C
  - feed P = 20 psia
- bed T = 50 °C
  - feed P = 20 psia

runs carried out at half cycle times (i.e., t_s) of
0.25, 0.5, 1.0, 2.0, 3.0 and 10 s

Comparison of Experiment and Model Pressure Profiles

Ar @ 20 psia & 25 °C

$k_M = 43.24\ s^{-1}$



Comparison of Mass Transfer Coefficients

CO_2, N_2, O_2, CH_4 and Ar on 13X Zeolite Beads

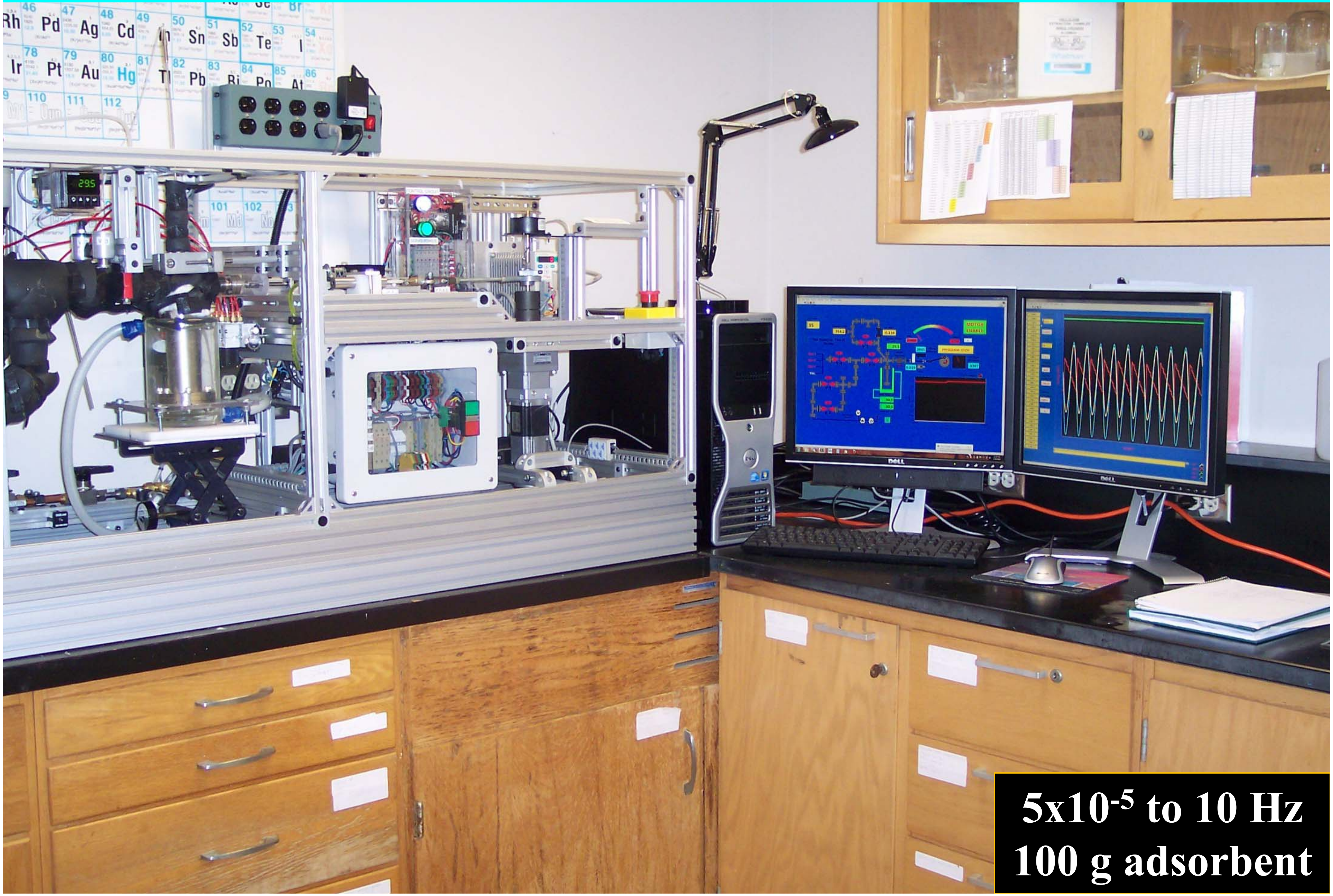
25 °C

Adsorbate	**D_p/R_p^2 s^{-1}**
CO_2	**7.45**
CH_4	**5.63**
N_2	**4.62**
O_2	**2.78**
Ar	**2.41**

Determined macropore diffusion controlling, with the anticipated order and results making sense when considering a large contribution to the flux from surface diffusion.

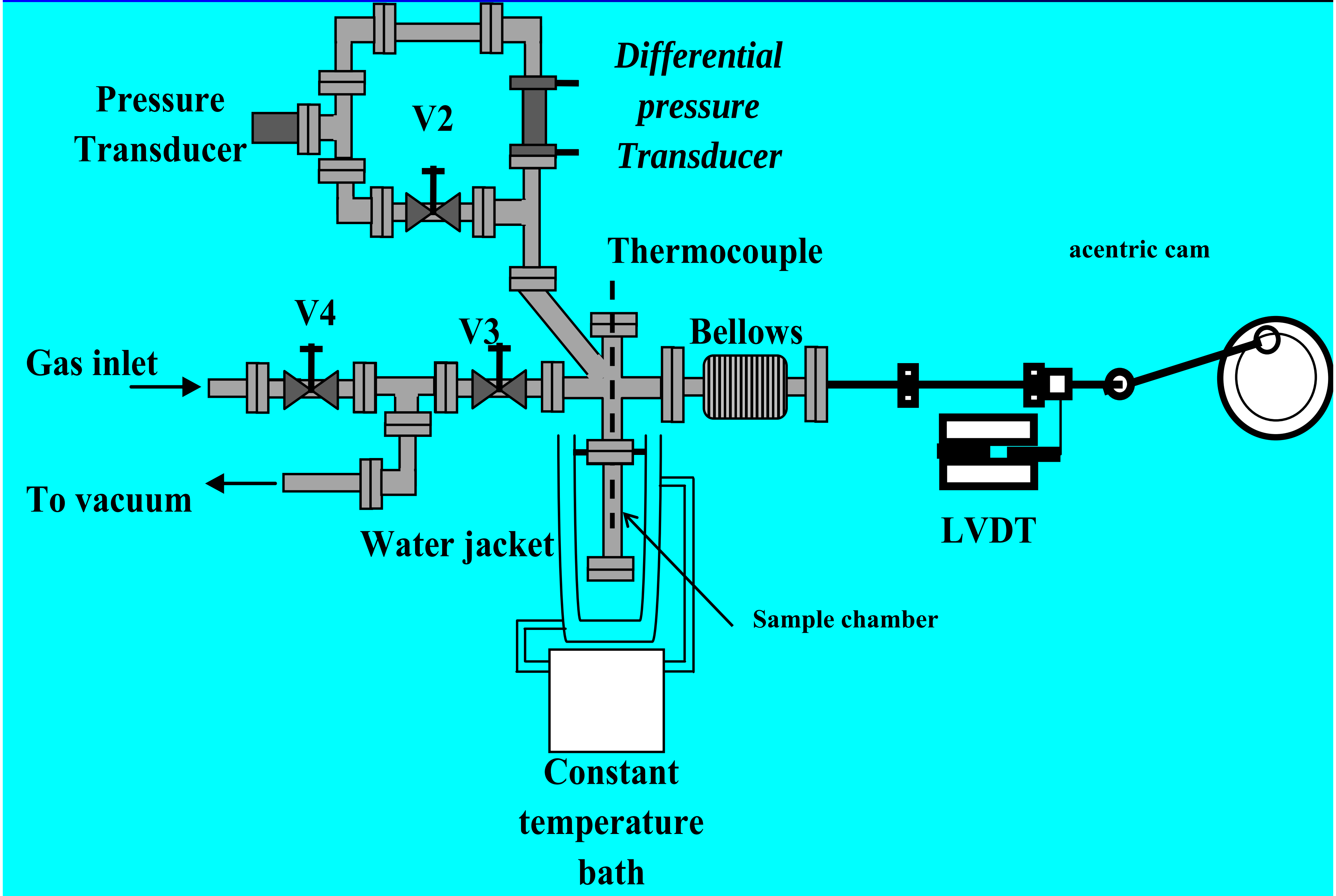
Anticipated Order: $CO_2 > CH_4 > N_2 > O_2 \sim Ar$

Volumetric Frequency Response Apparatus (VFRA)

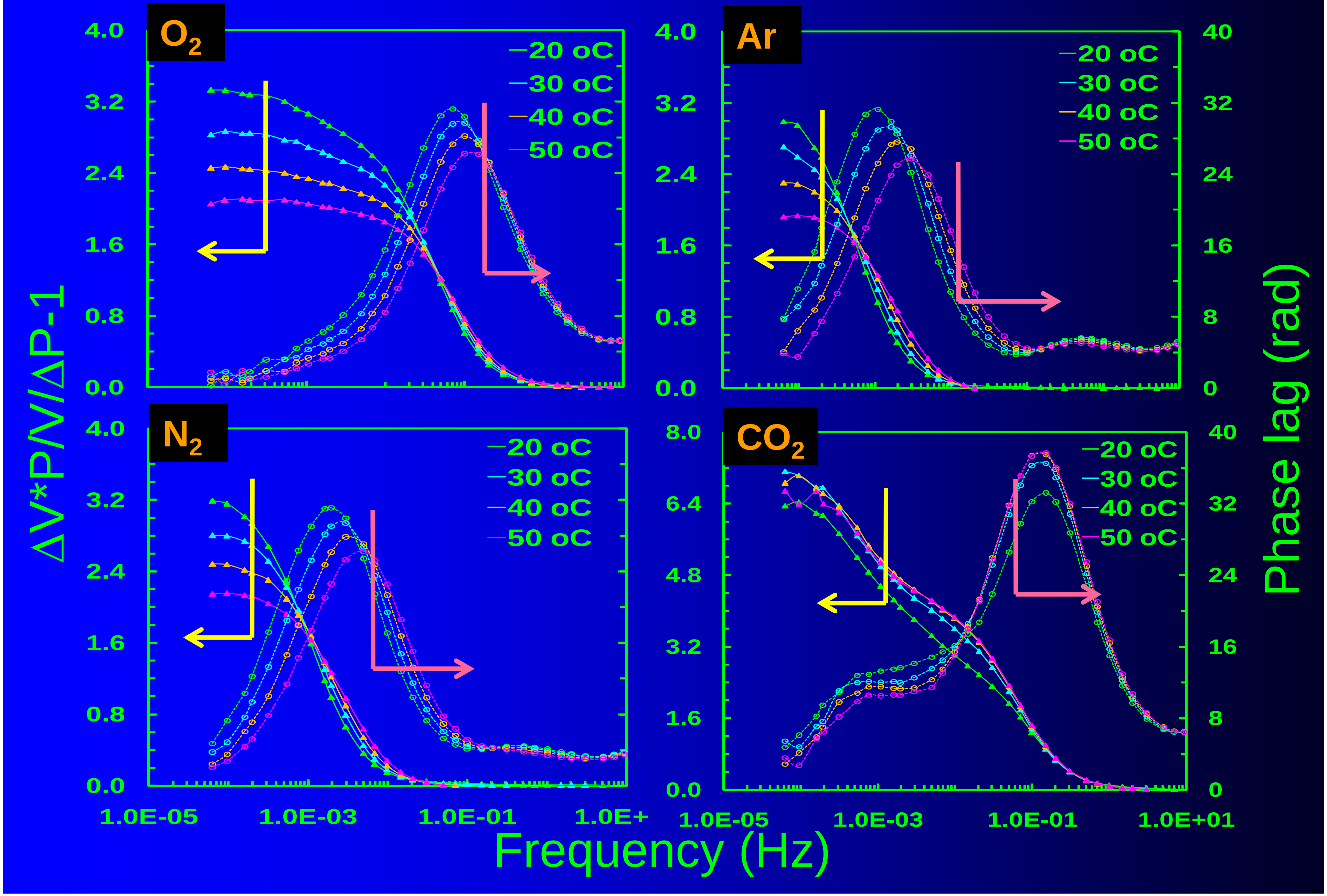


$5\text{x}10^{-5}$ to 10 Hz
100 g adsorbent

VFR Schematic

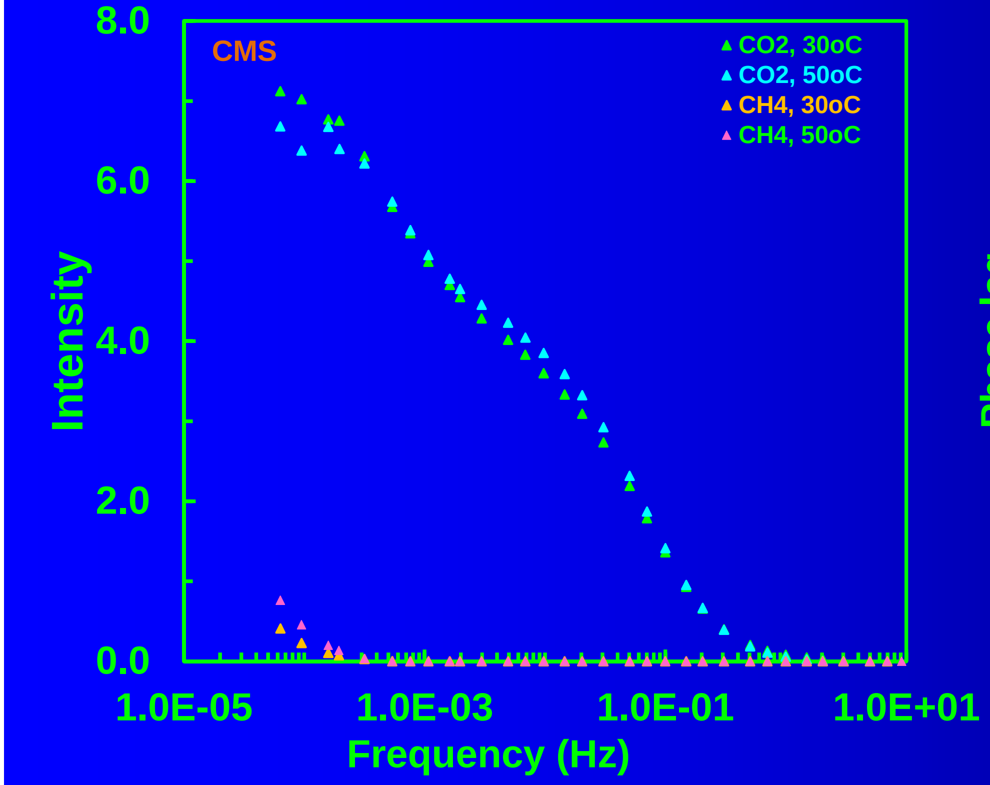


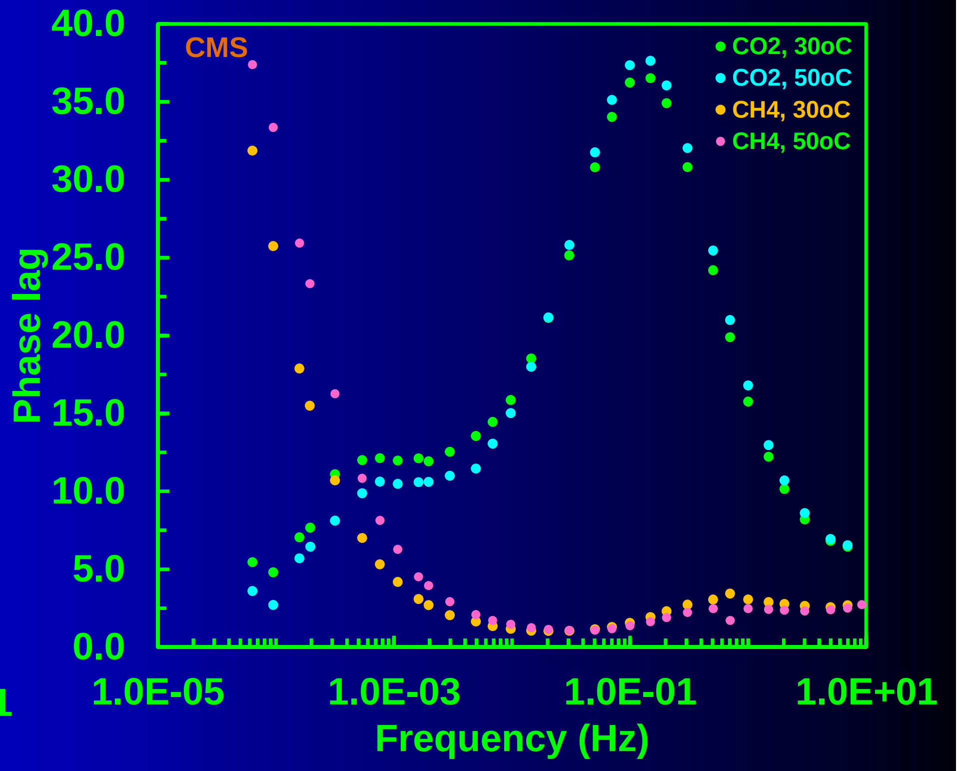
FR Experimental Results



FR Experimental Results

CO_2 and CH_4 in CMS Pellets



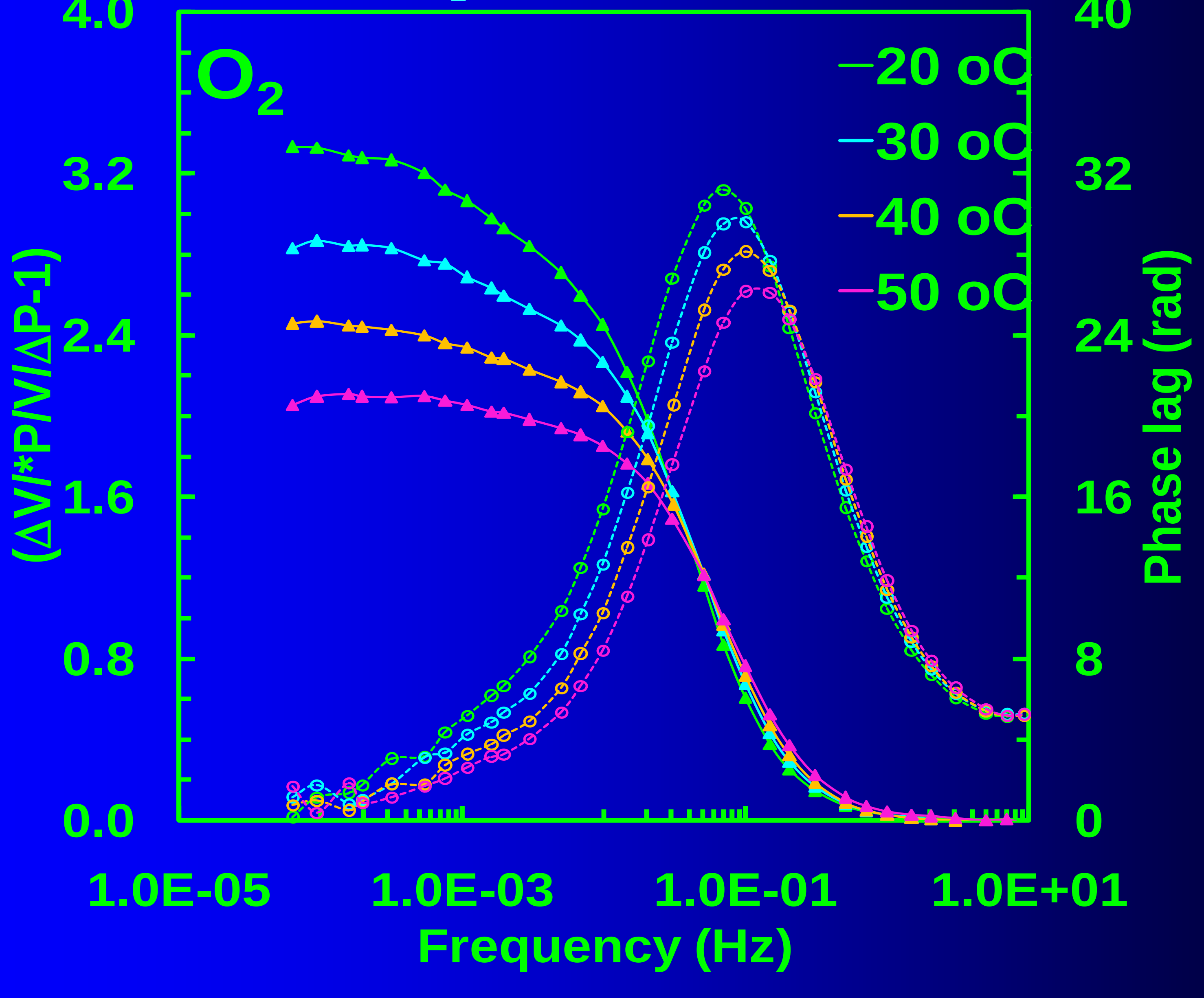


Comparison of very slow (CH_4) to moderate fast (CO_2) kinetics.

Mass Transfer Mechanism of O_2 in CMS

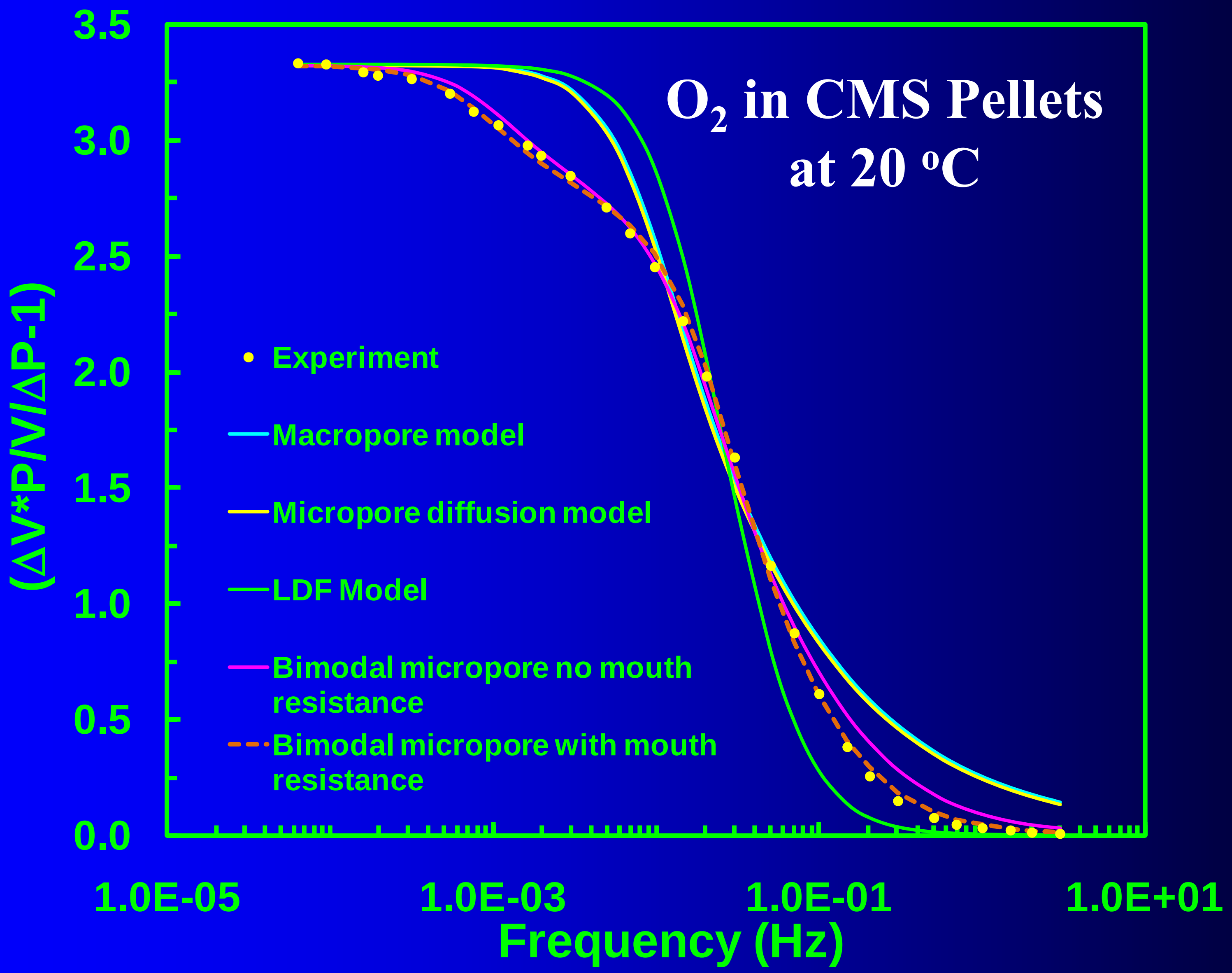
FR Experimental Results

O_2 in CMS Pellets



Fit of Experimental Data with Various Models

Quantify and Identify Mass Transfer Mechanism



Fit of Experimental Data with Various Models

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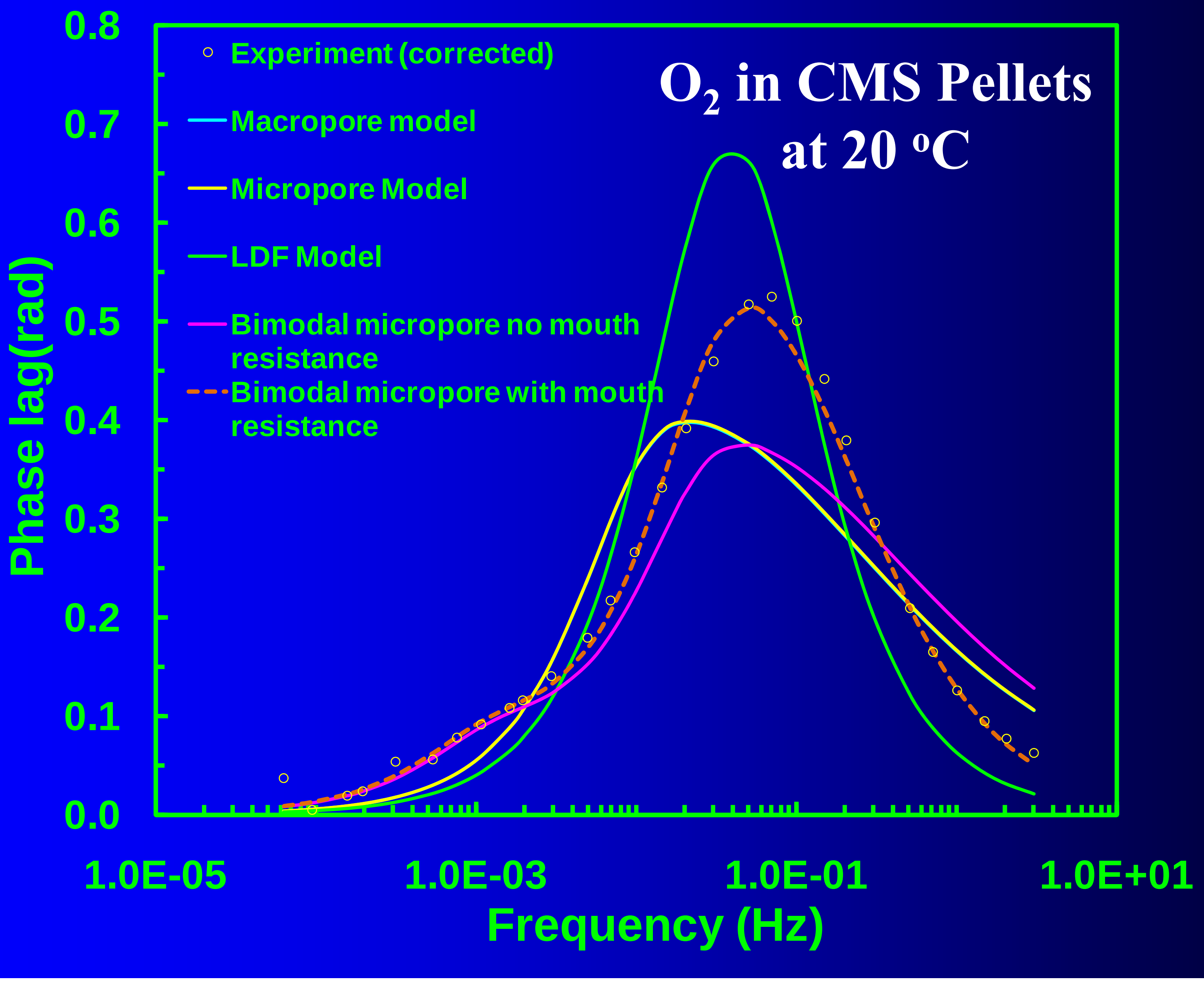
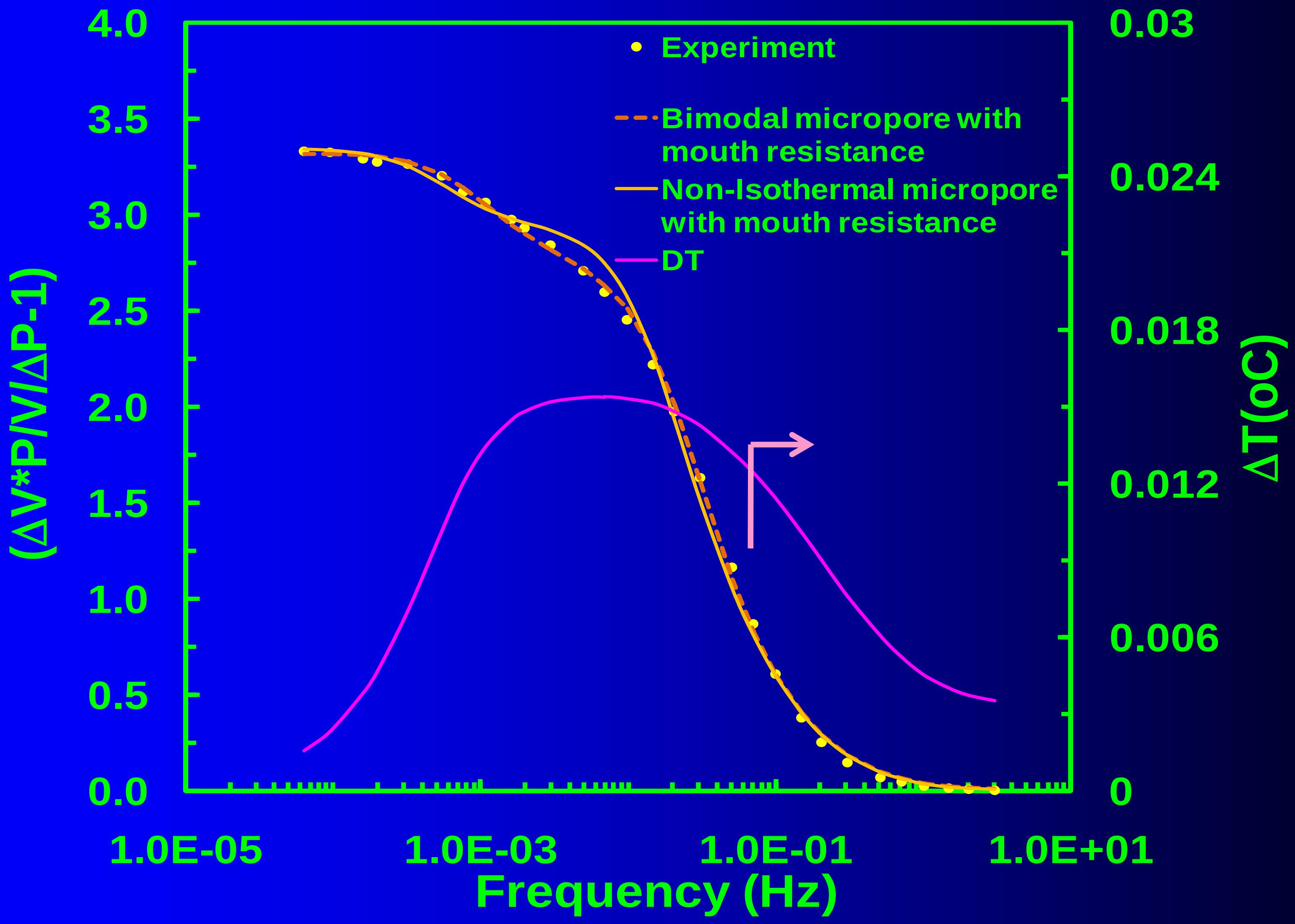


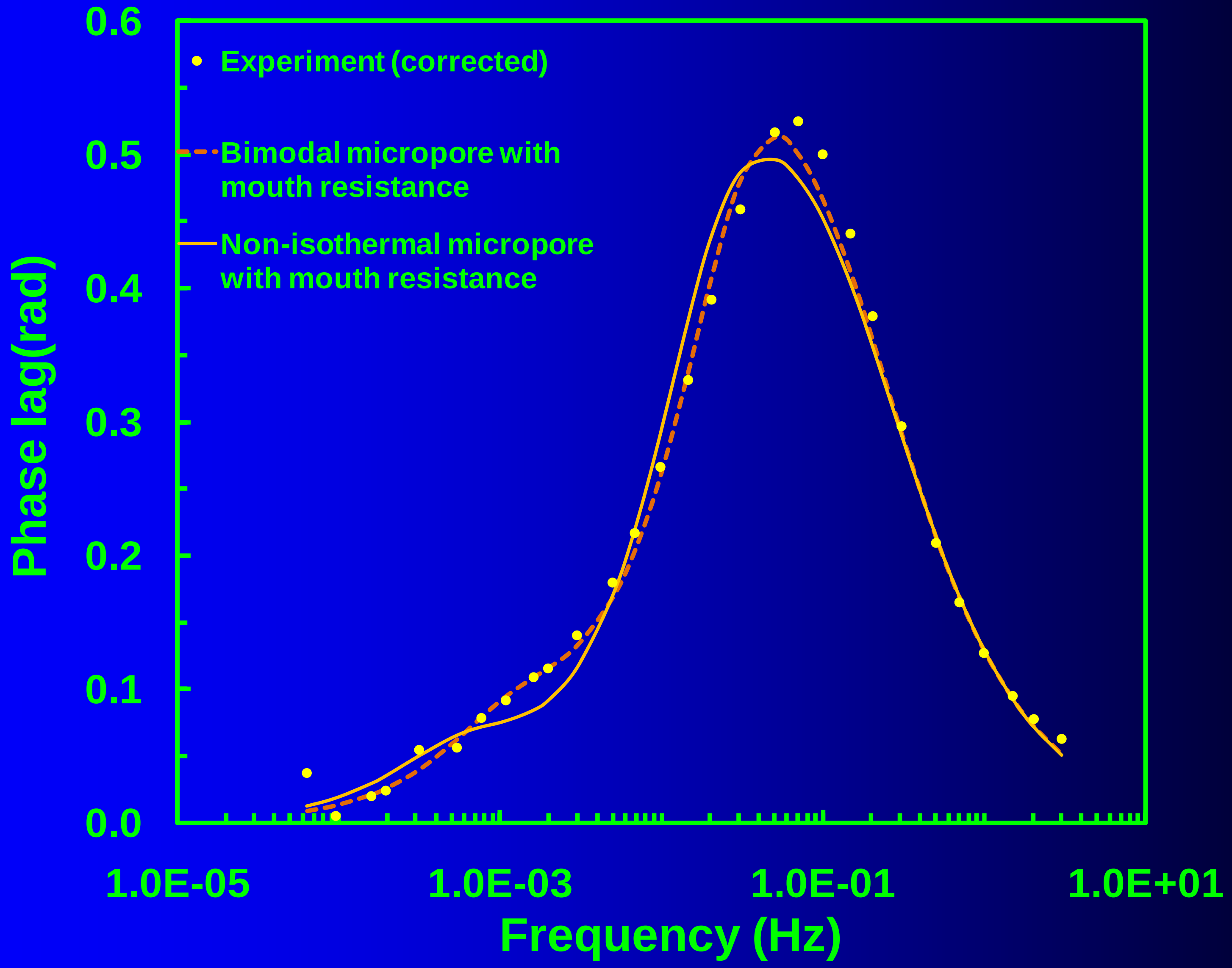
Non-Isothermal Model

O_2 in CMS Pellets at 20 °C



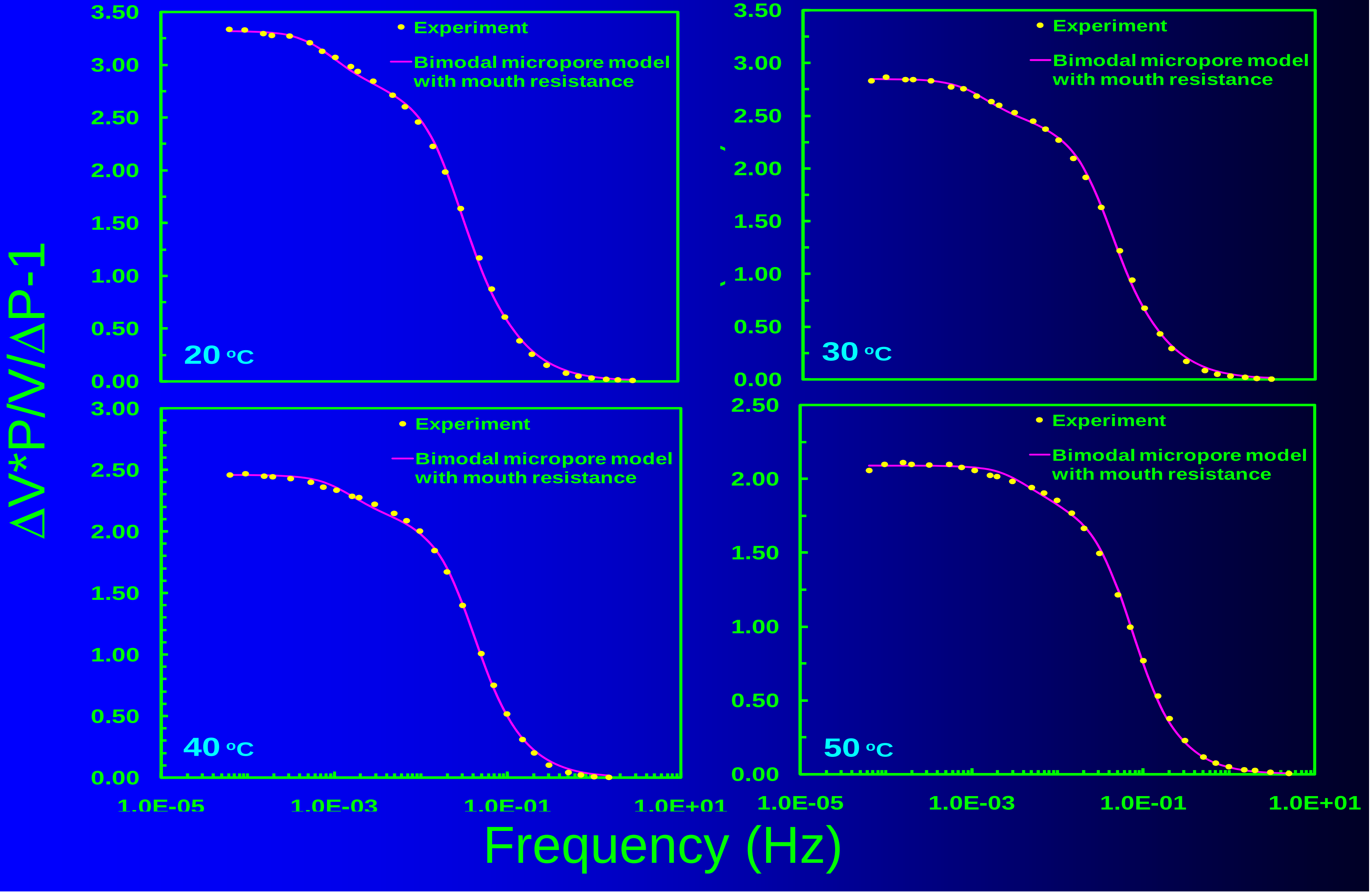
Non-Isothermal Model

O_2 in CMS Pellets at 20 °C



Experiment vs Model

O_2 in CMS Pellets at Different Temperatures



T-Dependence of Mass Transfer Coefficients

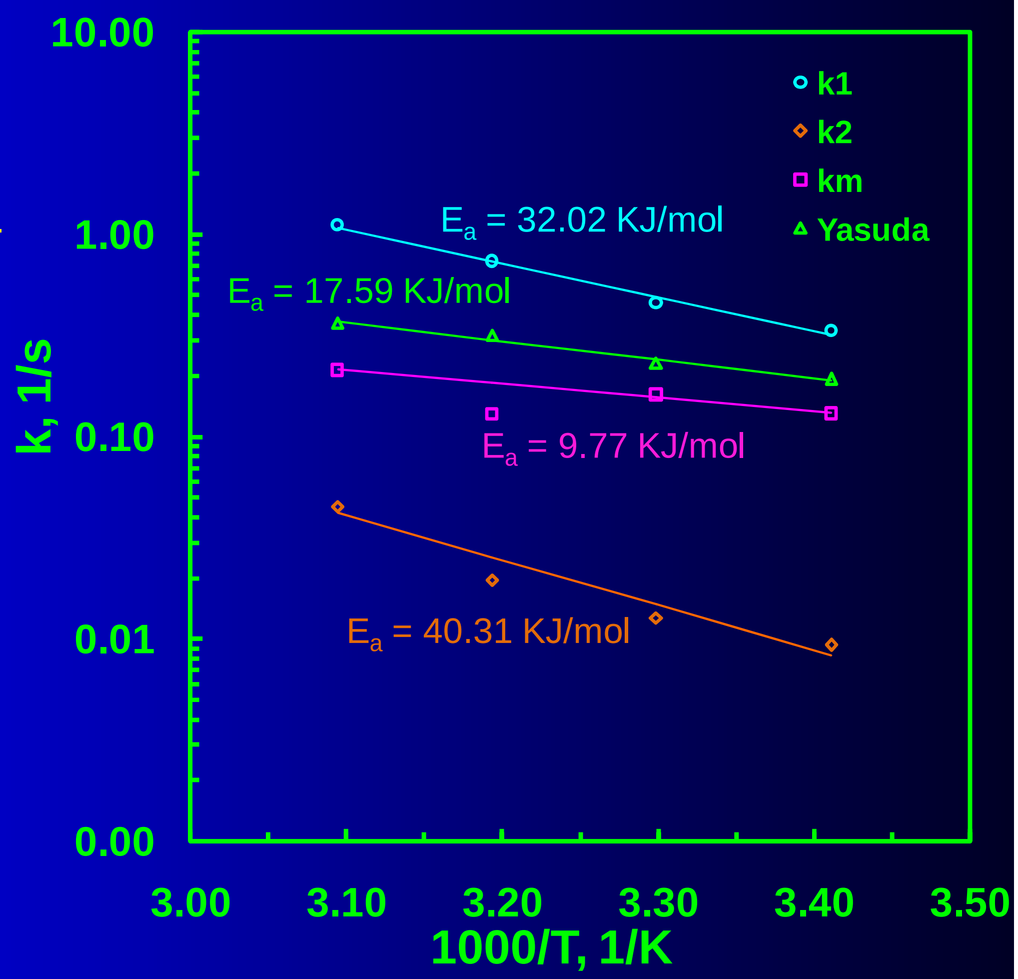
O_2 in CMS Pellets

T (°C)	$k_1 = 15^* D_{c1}/R_{c1}^2$ (1/s)	$k_2 = 15^* D_{c2}/R_{c2}^2$ (1/s)	k_m (1/s)	Mass fraction of crystal 1
20	0.335	0.009	0.130	0.751
30	0.458	0.013	0.161	0.782
40	0.737	0.019	0.129	0.751
50	1.110	0.045	0.213	0.783

k_1= mass transfer coefficient
of crystal 1

k_2= mass transfer coefficient
of crystal 2

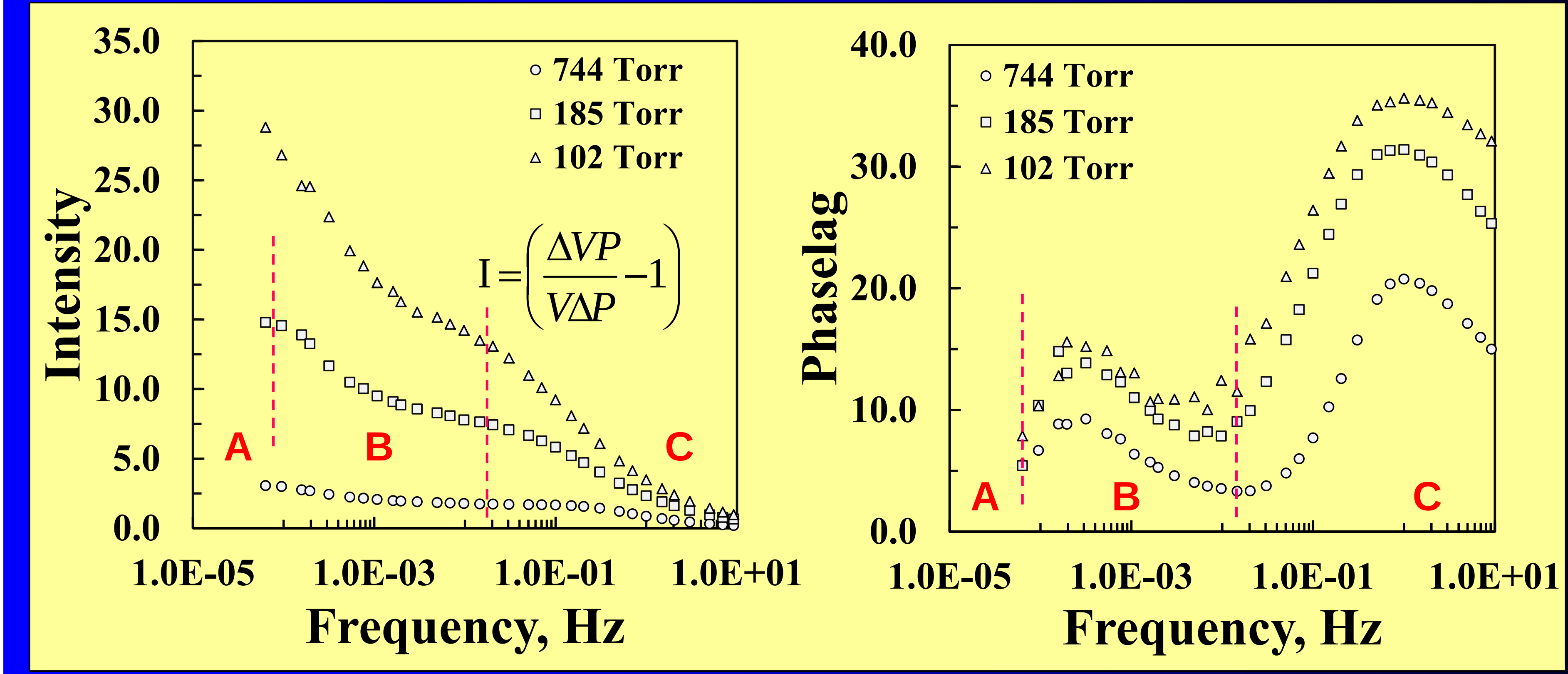
k_m= mass transfer coefficient
of mouth resistance



Mass Transfer Mechanism of CO_2 in 13X Zeolite

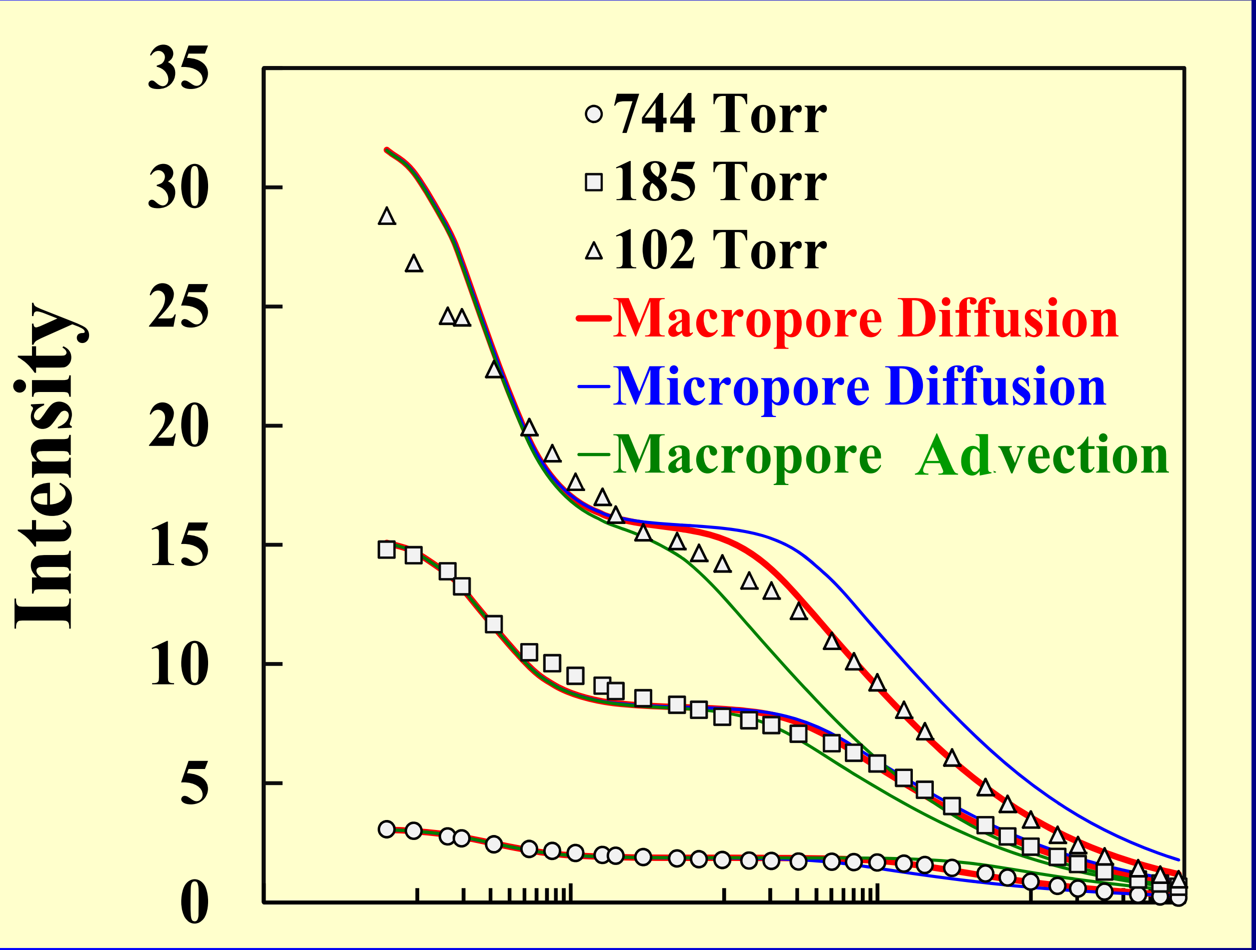
FR Experimental Results

CO_2 in 13X Zeolite Beads at 25 °C



Model vs Experiment

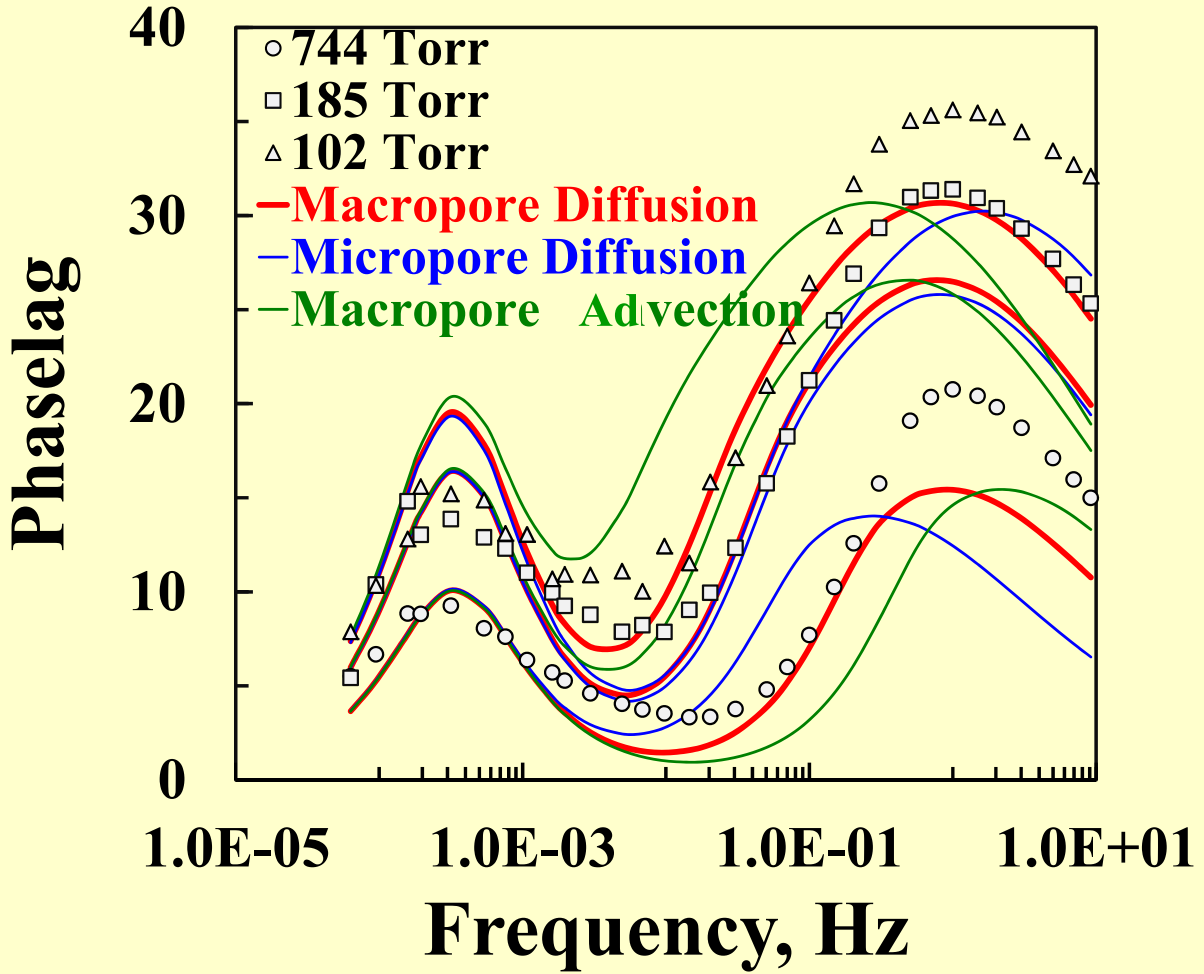
one parameter optimized in each model to fit all three curves



CO_2 on 13X
Zeolite Beads at
25 °C

The macropore diffusion model ($D_p/R_p^2 = 3.32$ 1/s)
describes the results the best.

Model vs Experiment



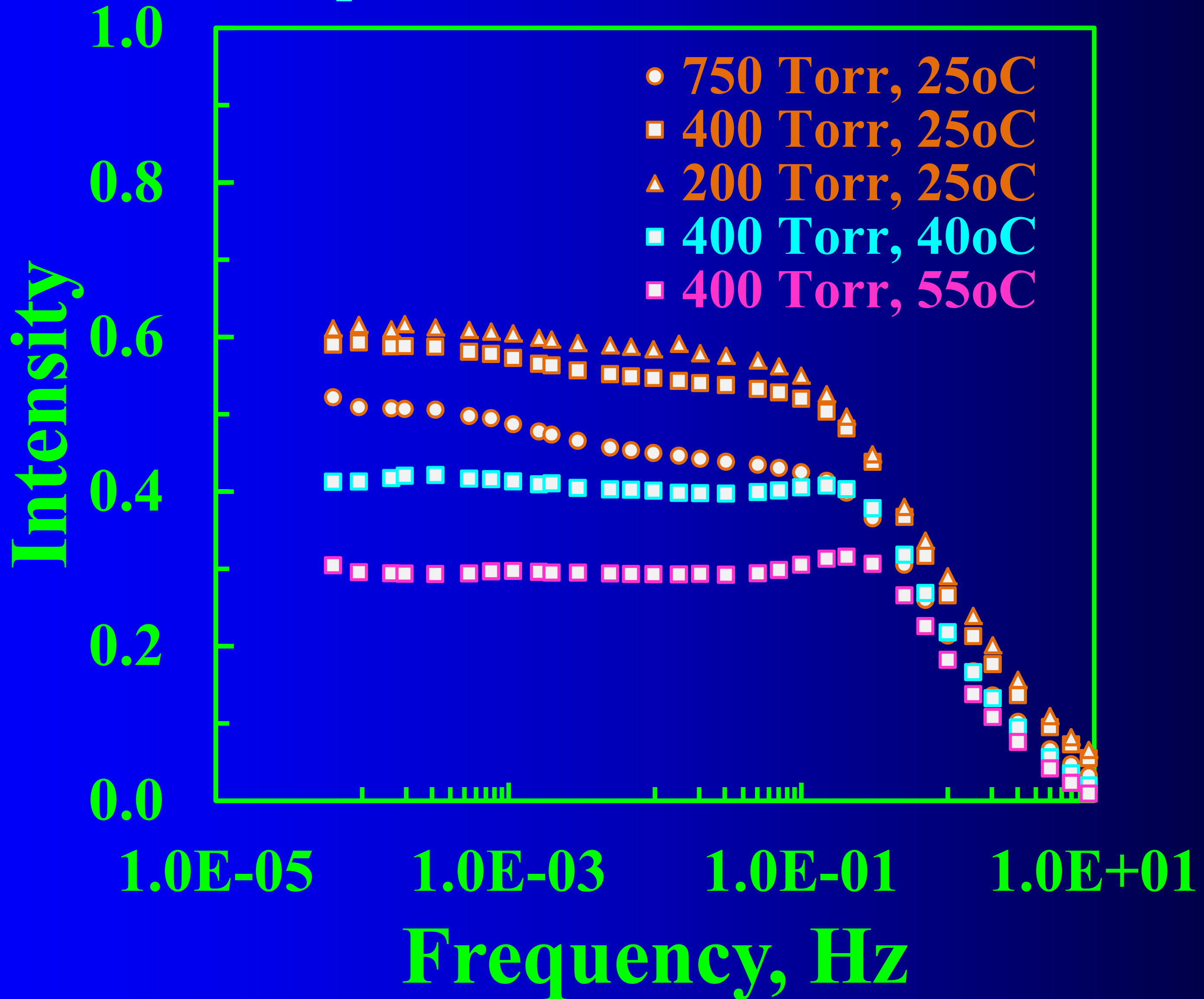
CO$_2$ on 13X
Zeolite Beads at
25 ^{o}C

Research group	Technique	D_p/R_p^2 (s^{-1})
LeVan & coworkers	Pressure & Volume Swing FR	2.3
USC	Volume Swing FR	3.32

Mass Transfer Mechanism of N_2 in 13X Zeolite

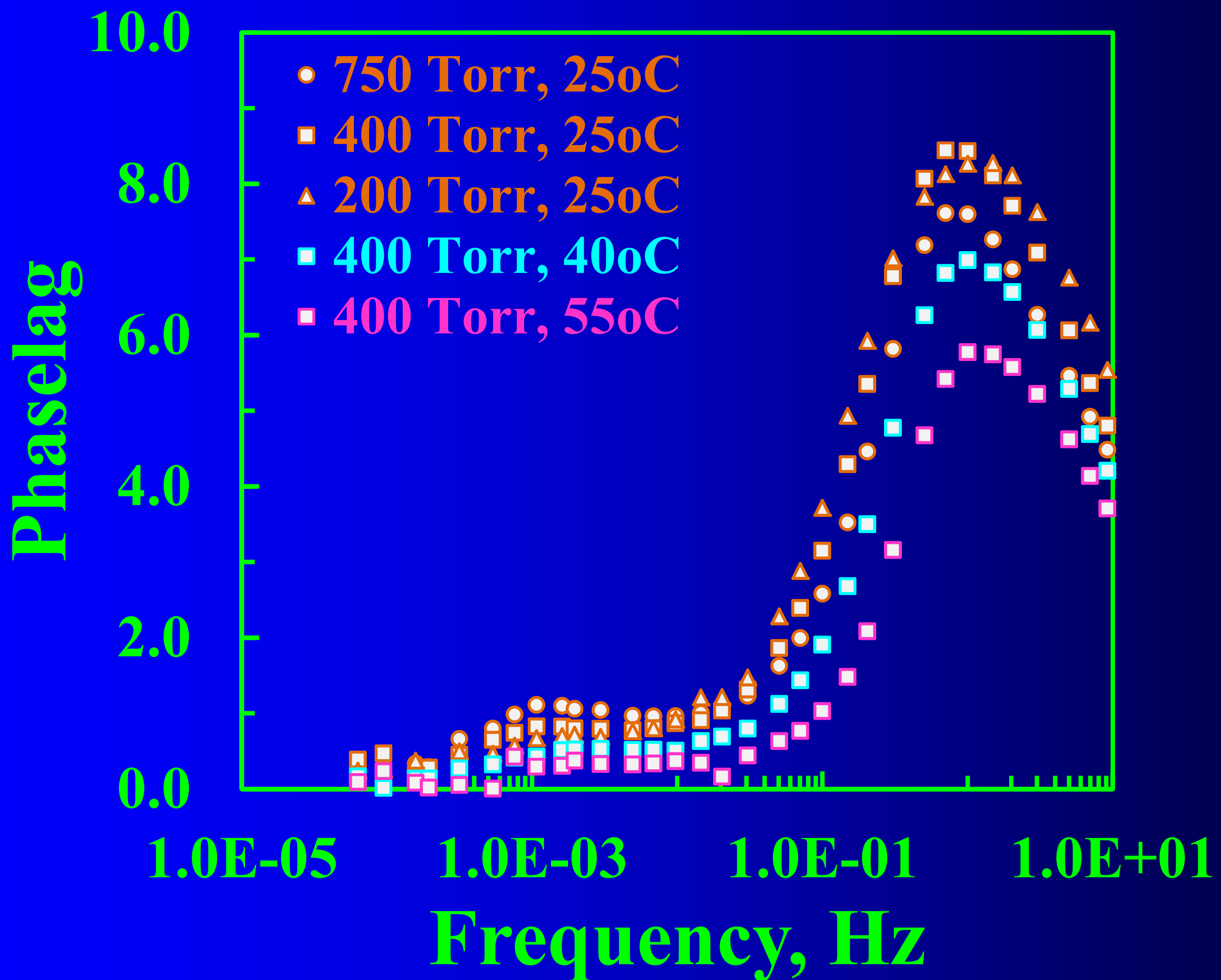
FR Experimental Results

N_2 in 13X Zeolite Beads

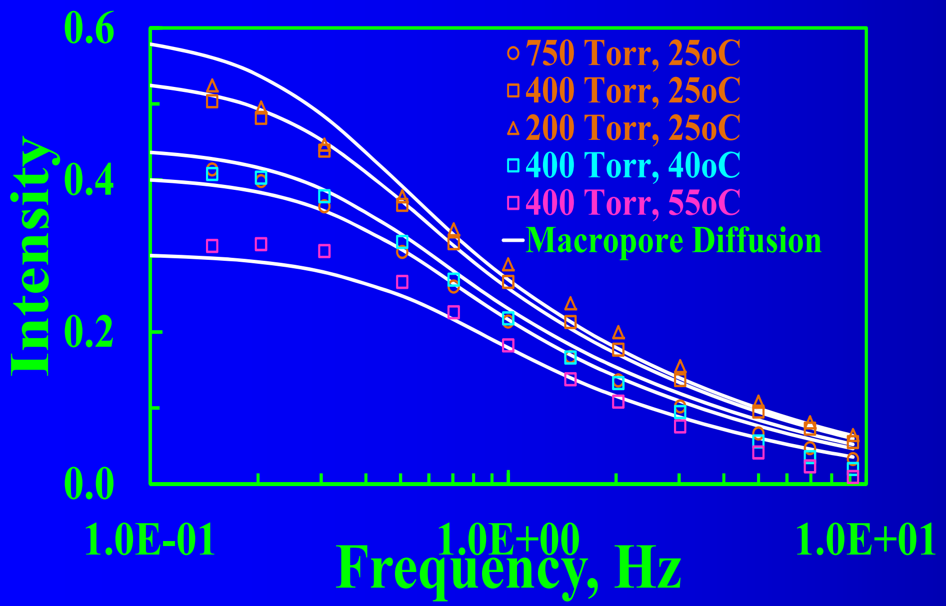


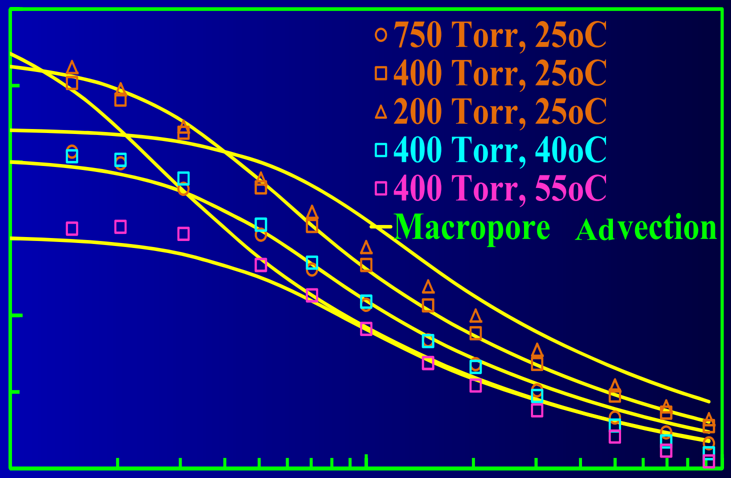
FR Experimental Results

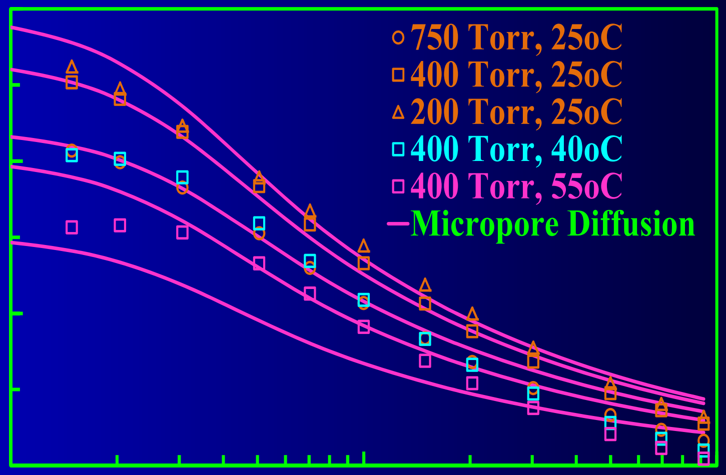
N_2 in 13X Zeolite Beads



Model vs Experiment





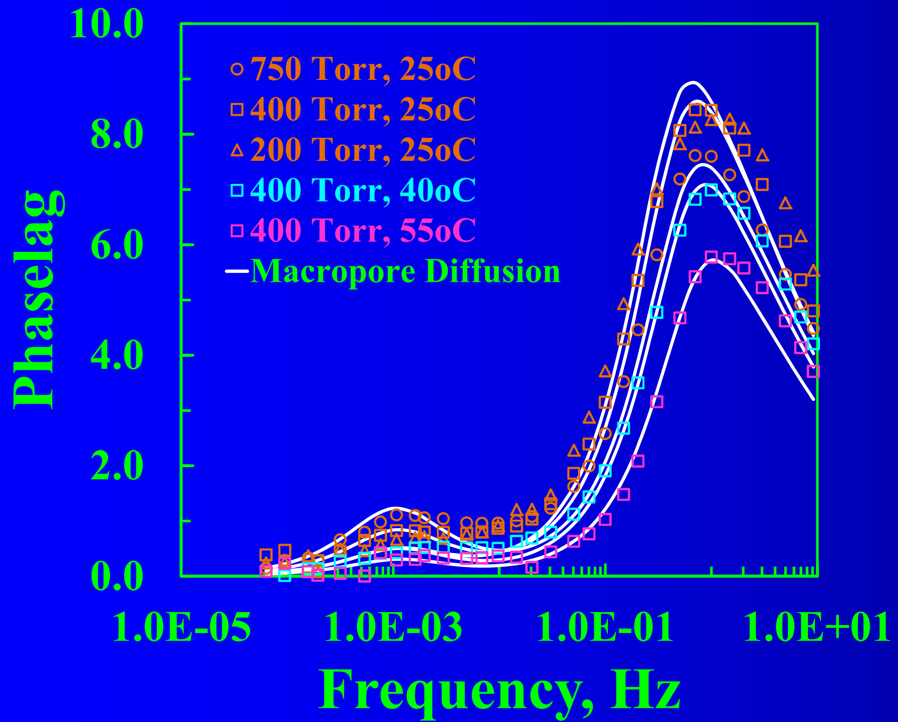


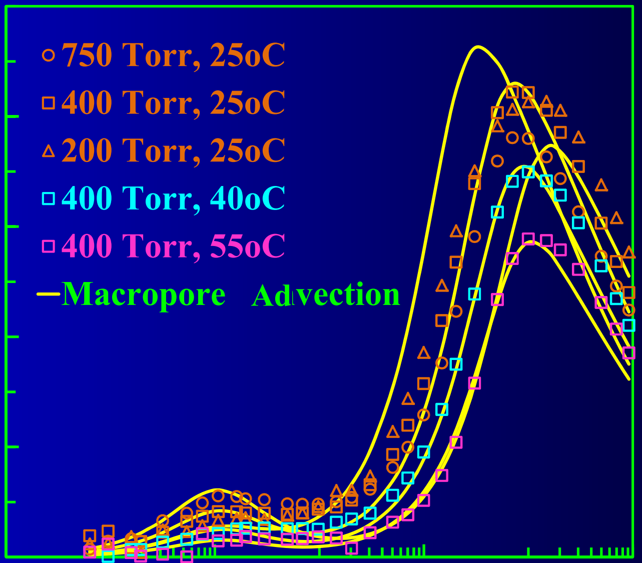
Macropore Diffusion

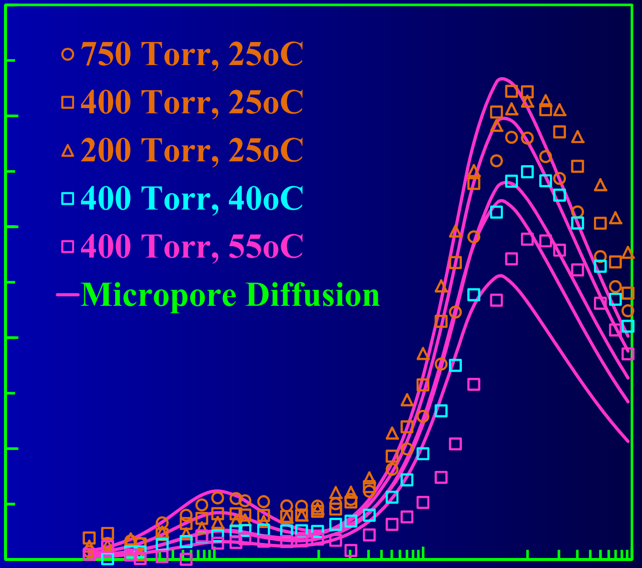
$$D_p/R_p^2 = 3.32\ 1/s$$

N_2 on 13X Zeolite Beads at 25 ^oC

Model vs Experiment







Macropore Diffusion

$D_p/R_p^2 = 3.32$ 1/s

N_2 on 13X Zeolite Beads at 25 °C

Comparison of Mass Transfer Coefficients

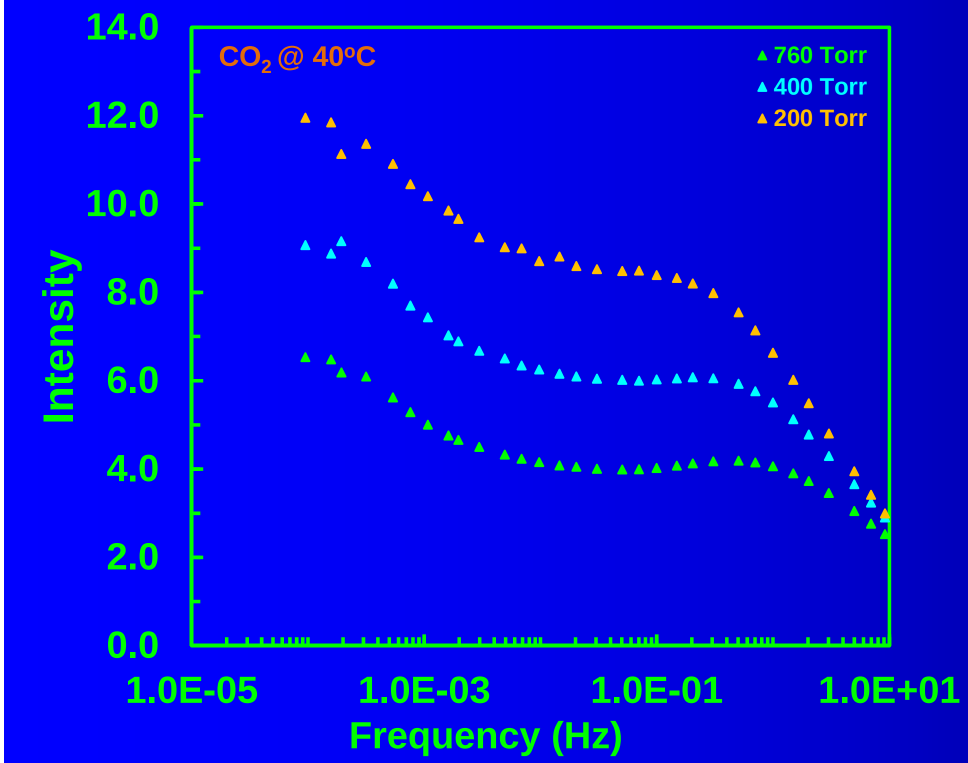
N_2 and CO_2 on 13X Zeolite Beads at 25 ^{o}C

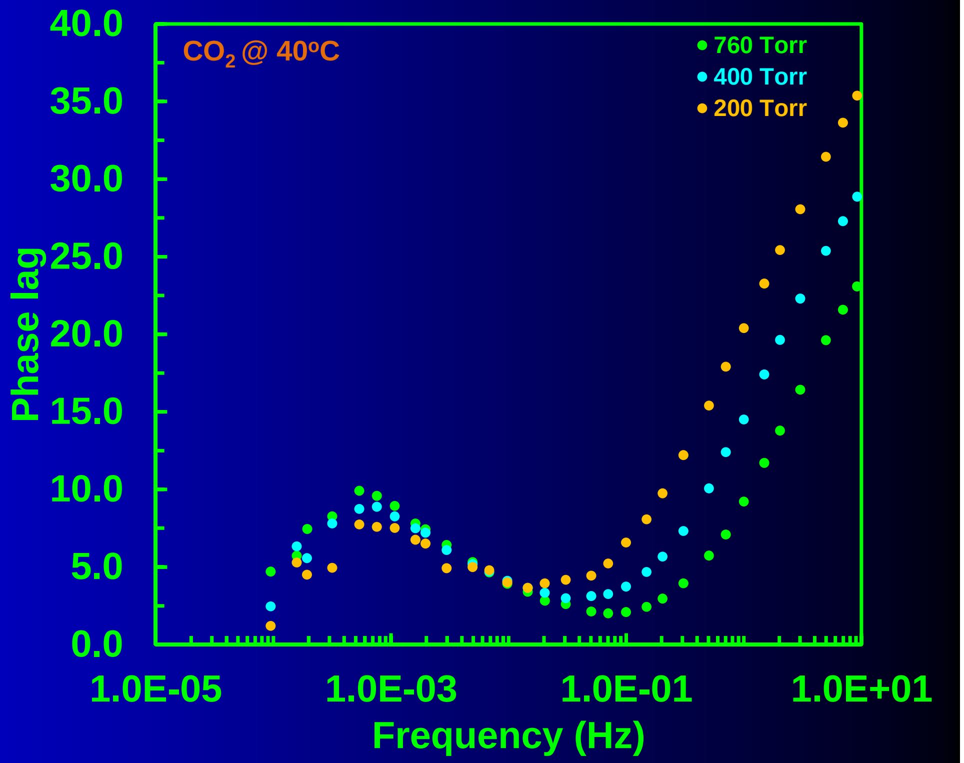
	k s^{-1}			
	VFR	**1-Bed RPSA**	**1-Bed BT**	**TGA**
CO_2	**3.3**	**7.5**	**0.3**	**~ 0.01**
N_2	**5.1**	**4.6**	**1.0**	**---**

These seemingly small differences, in some cases, can make a significant difference in the process performance predicted from a PSA process simulator.

FR Experimental Results

CO_2 in BPL Activated Carbon Pellets

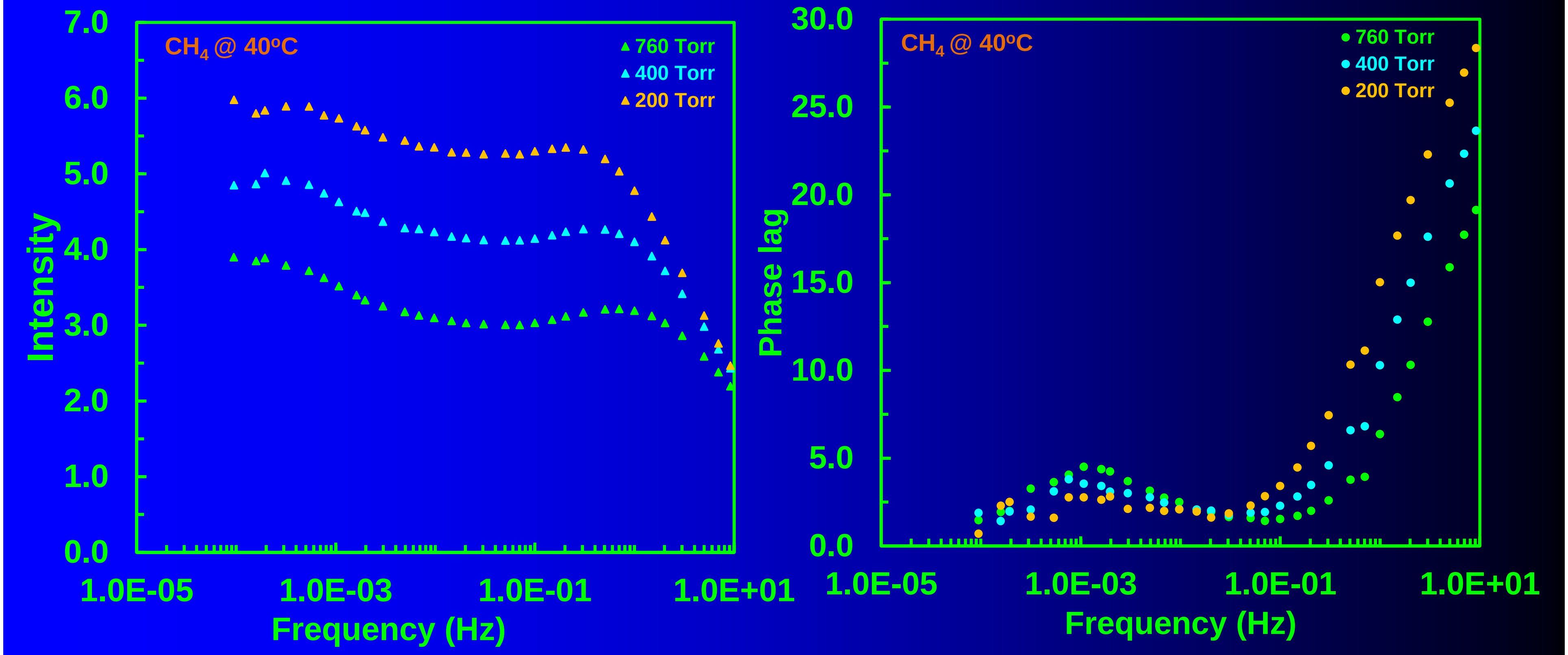




Extremely fast diffusion with phase lag peak >> 10 Hz!

FR Experimental Results

CH_4 in BPL Activated Carbon Pellets



Extremely fast diffusion with phase lag peak >> 10 Hz!

Conclusions

- variety of techniques available for measuring mass transfer rates in nanoporous adsorbents; *some simple, some not*
- mass transfer rates may very widely from different techniques; *accurate values critical to PSA process modeling*
- two FR techniques exhibited fastest mass transfer rates compared to other methods
- two FR techniques with relatively large and very small pressure swings resulted in similar mass transfer rates
- one FR technique also unambiguously identified the mass transfer mechanism, but required results at different Ts and Ps
- some adsorbate-adsorbent pairs surprisingly exhibited mass transfer rates far exceeding 10 Hz; *how to measure and what does it infer?*

Acknowledgements

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Thank You!

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