Role of Thermodynamics in Adsorptive Gas Storage

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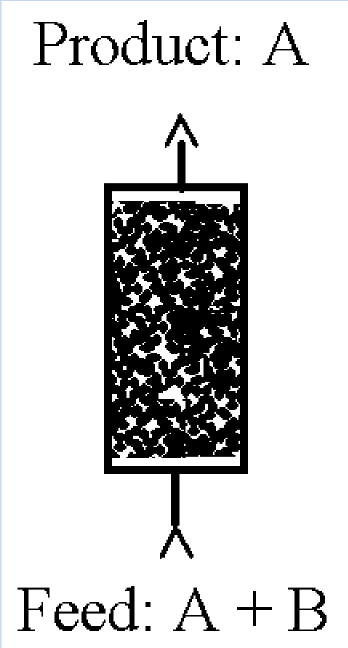
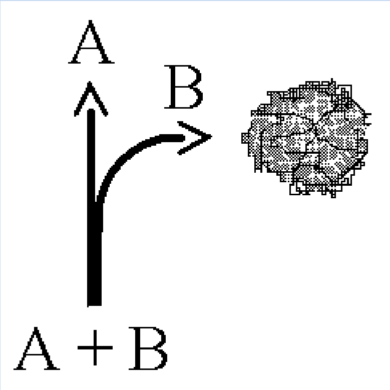
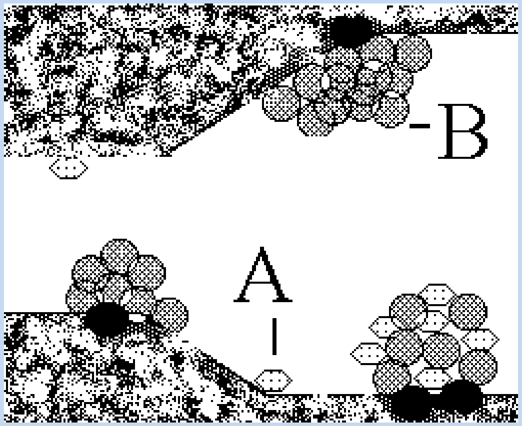
Adsorption is usually associated with separations



Column = 1 m



Particle = 10 μm



Pore = 1 nm

And it inherently involves materials

Separation Examples

Year	Materials, Processes and Patents
1955-1956	synthetic zeolite, A-type
1957	Air Liquide & Skarstom PSA air separation patents
1961	heatless dryer
1962	"Isosiv" for separation of linear hydrocarbons
1966	PSA hydrogen purification
1970	Large scale oxygen PSA process
1972-1973	carbon molecular sieve (CMS)
1976	nitrogen PSA with CMS
1977	large scale PSA hydrogen purification
1983	vacuum swing PSA using X for air separation
1985-1988	second generation synthetic zeolites, X-type
1988	large scale VSA for air separation
1992-1993	high selectivity LiX for air separation
1993	Praxair patents on VSA air separation
2000s	MOFs
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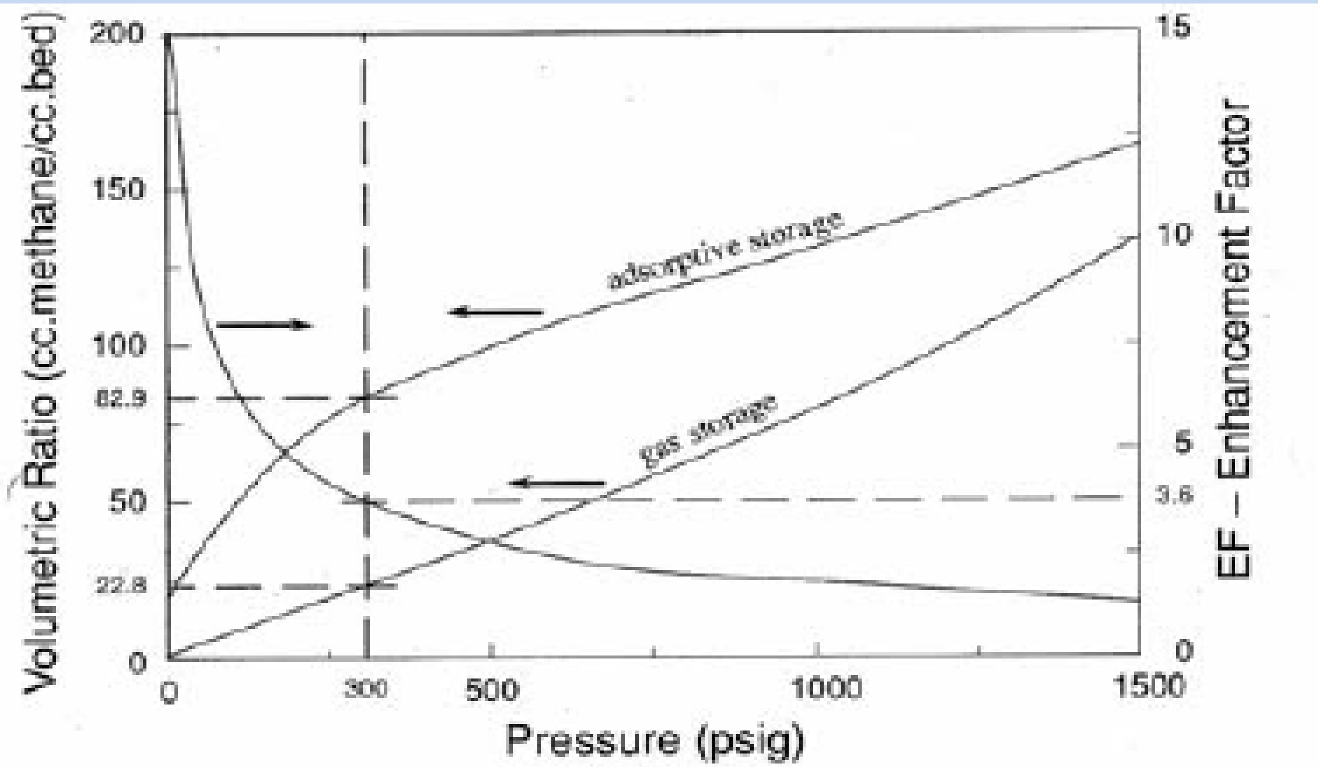
Adsorptive Gas Storage

The purpose is simply to store a compound at a higher <u>overall</u> density than compressed gas at same T and P.



Figuer 1. Storage Capacity of CaX (loose pack)

Talu, Adsorption News, v.1, n.2 (1990)

Natural Gas (methane) Storage

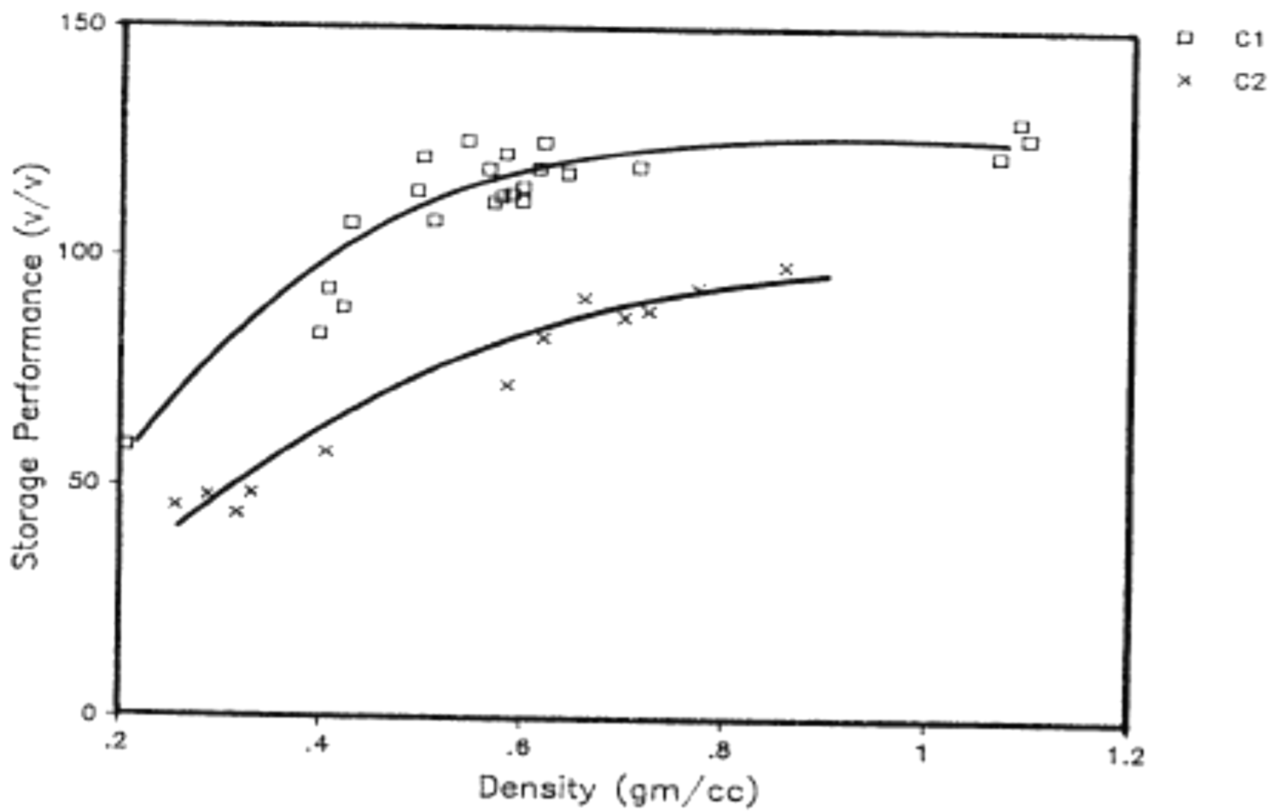
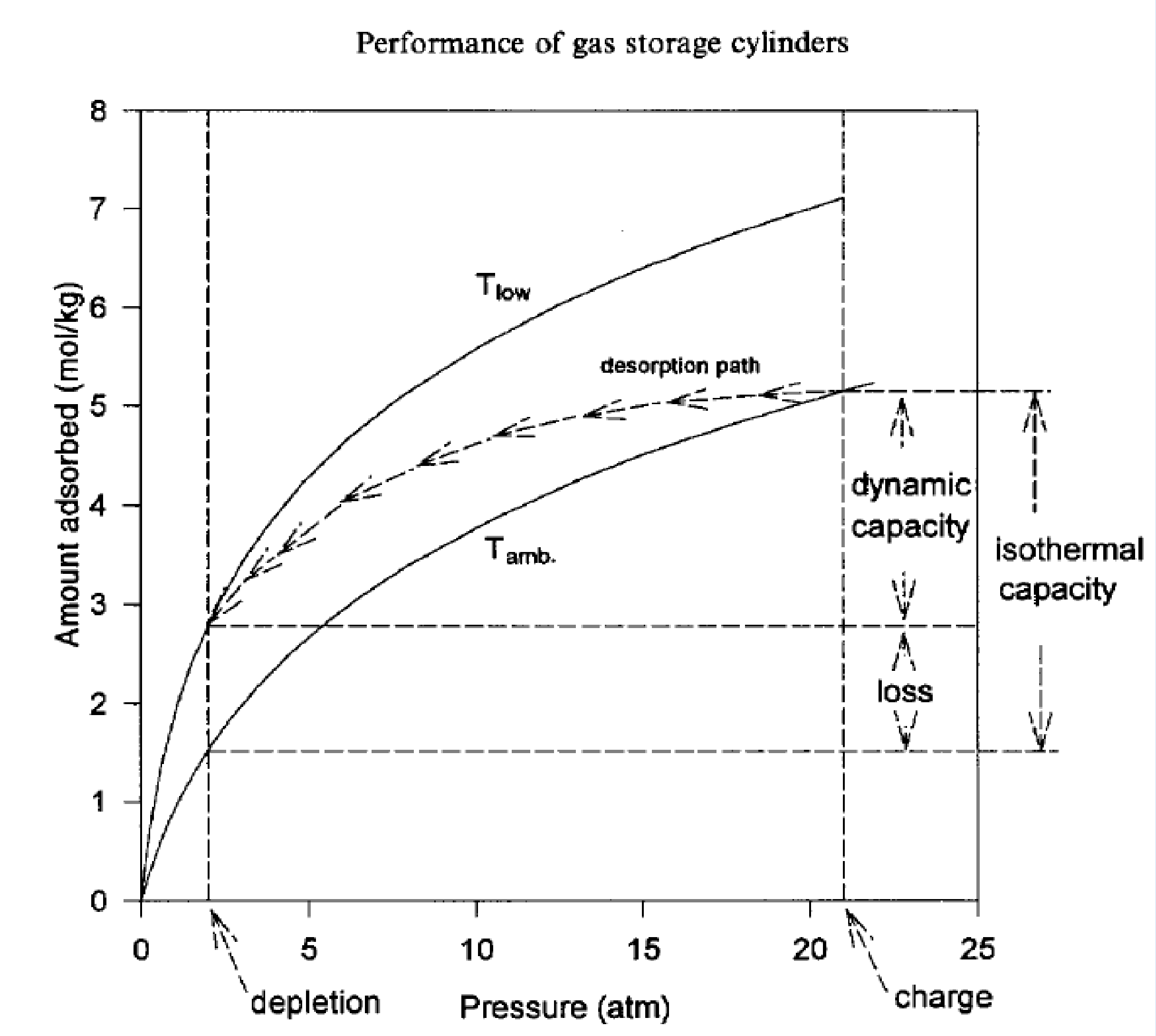


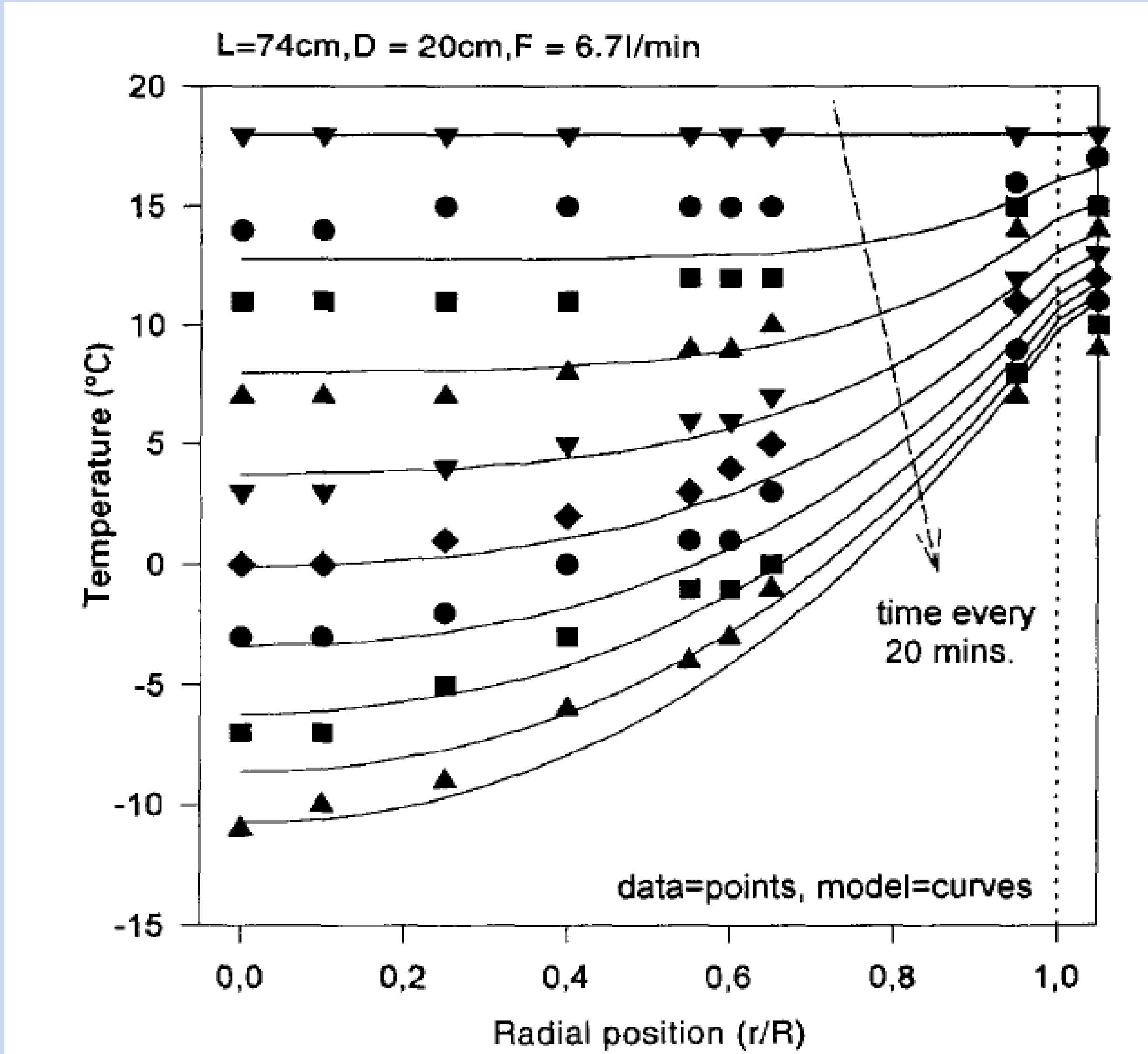
Figure 2. Storage Performance of Compacted Carbons (ambient T)

Talu, Fund. Of Adsorption, p.655 (1992)

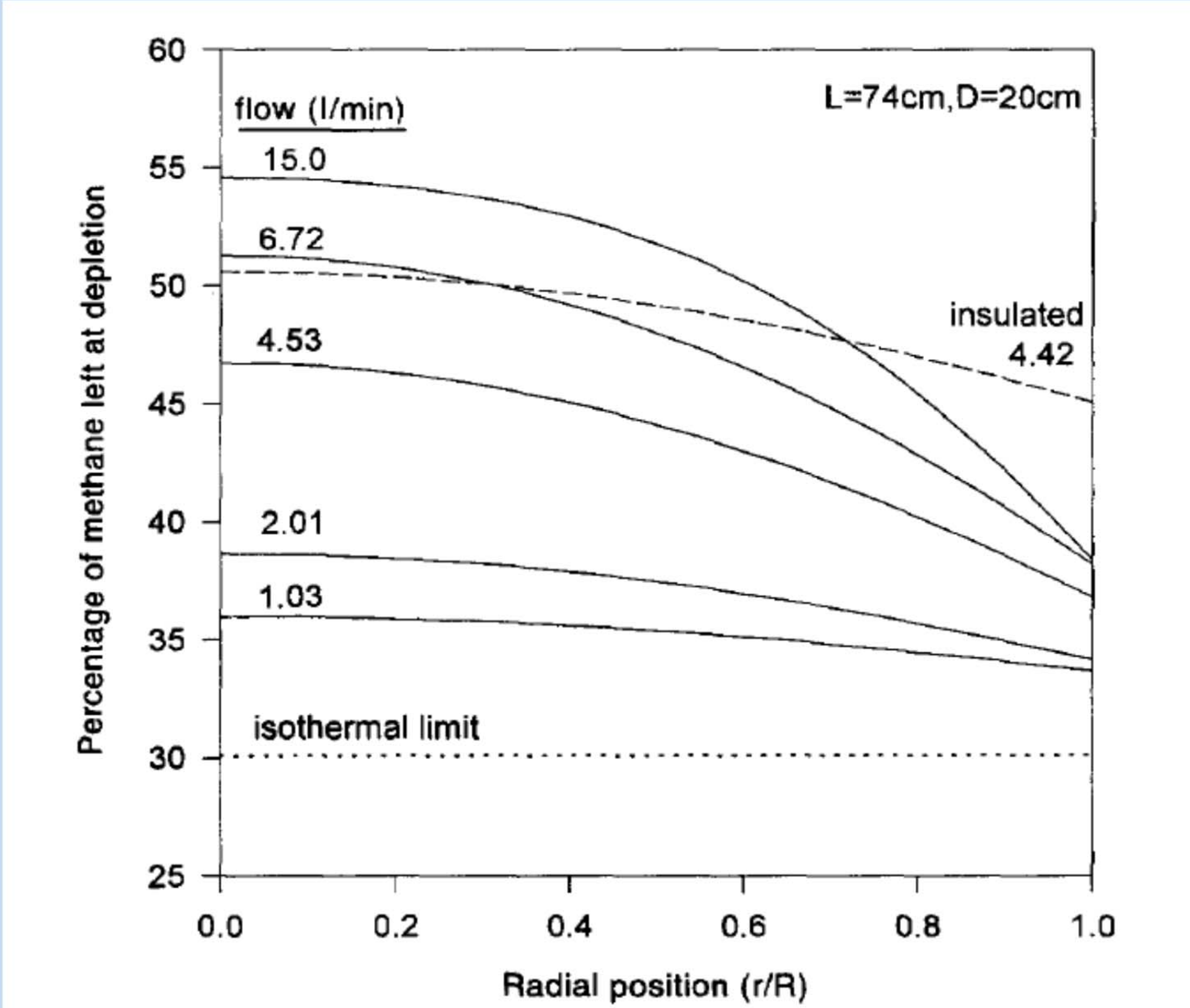
Effect of Heat of Adsorption



Chang and Talu, App. Thermal Eng., v.16, p.356 (1996)



Chang and Talu, App. Thermal Eng., v.16, p.356 (1996)



Chang and Talu, App. Thermal Eng., v.16, p.356 (1996)

Change flow direction with perforated tube !

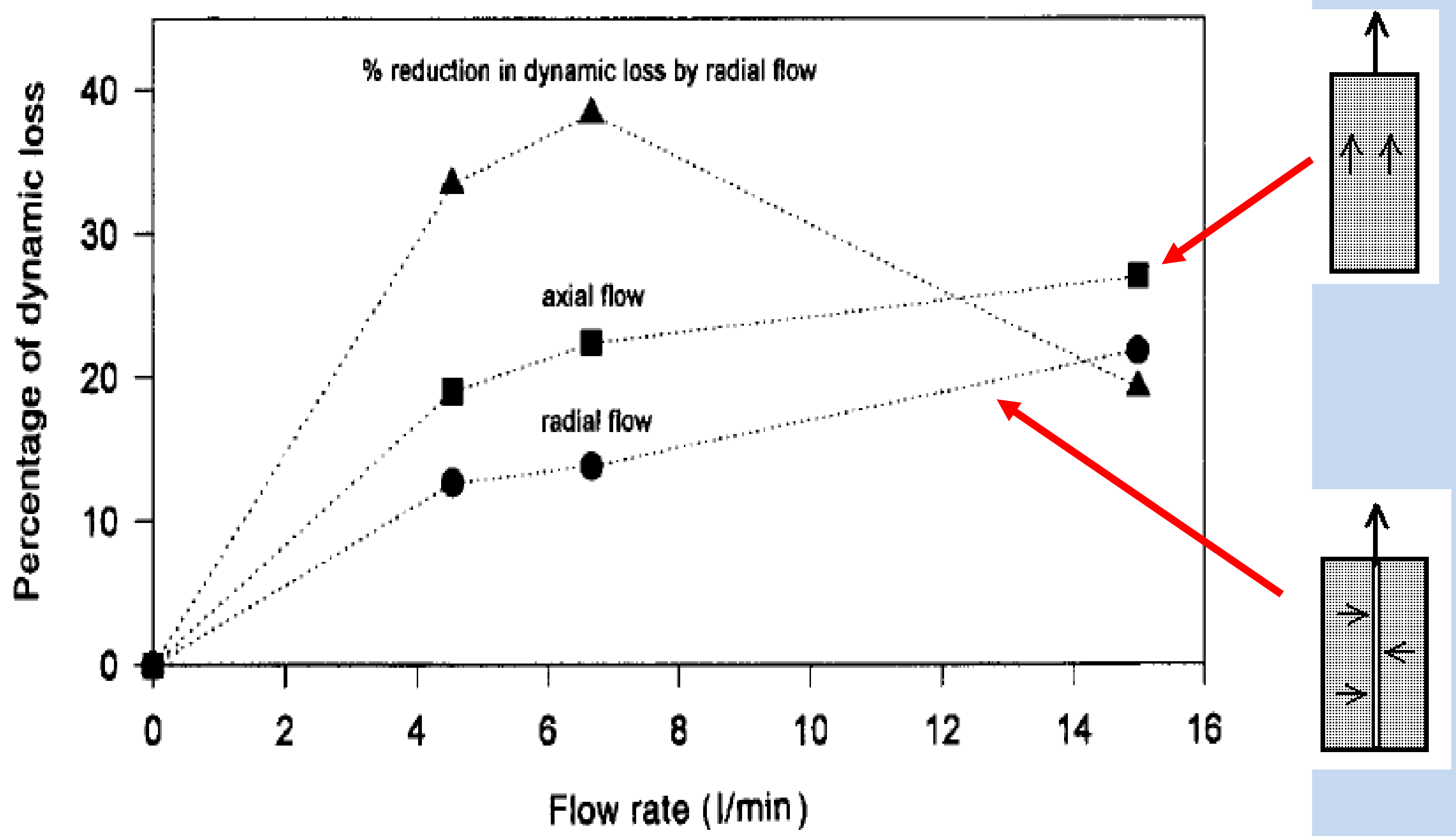


Fig. 12. Experimental data for the effect of flow direction during discharge of ANG cylinders.

Chang and Talu, App. Thermal Eng., v.16, p.356 (1996)

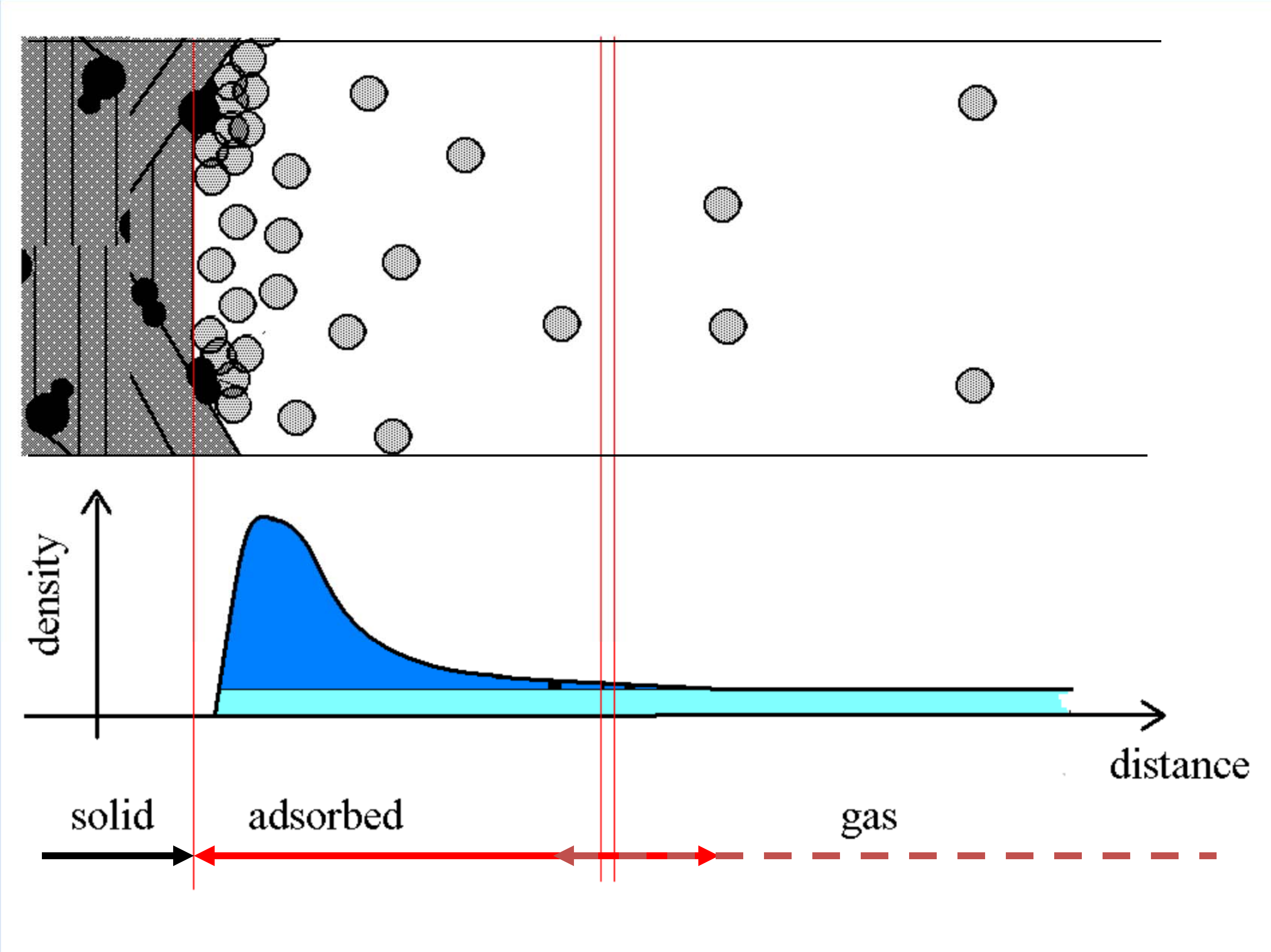
Storage Examples

Year	Materials, Processes and Patents
1985-1995	Adsorbed Natural Gas Storage (ANG)
1990	G-Tech patents for welding applications
2000-	MOFs
2005	hydrogen storage attempts
2008	PCN-14 for methane very promising
????	

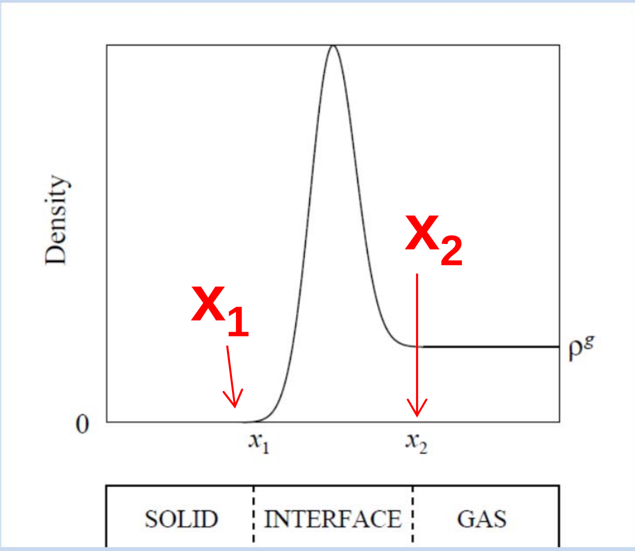
Reality Check

Gas	MW	Critical T (K)	Boiling point (K)	LJ σ (A)	LJ ε/k (K)
Methane	16	191	112	3.73	149
Oxygen	32	152	90	3.11	143
Carbon dioxide	44	304	195	2.98	133
Ozone	48	261	161		
Ammonia	17	406	240		
Hydrogen	2	33	20	2.87	**34**
Helium	4	5.2	4.2	2.28	10.2

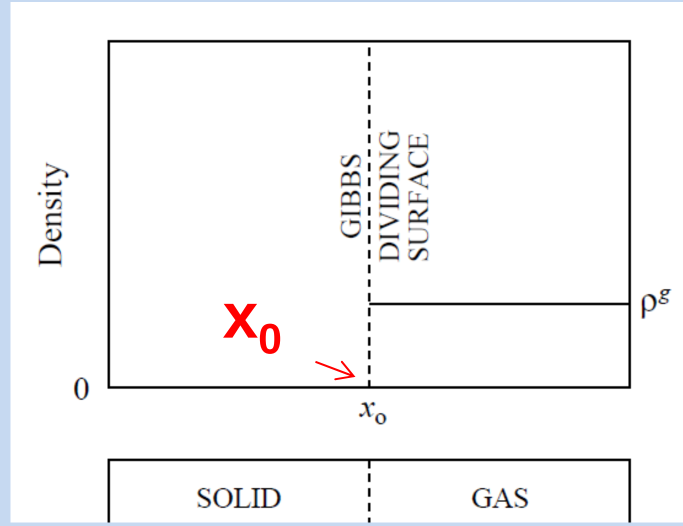
Density near an “open” surface



Gibbs definition of adsorption



Gibbs definition



$$\Gamma^{tot} = \int_{x_1}^{x_2} \rho(x).\,dx$$

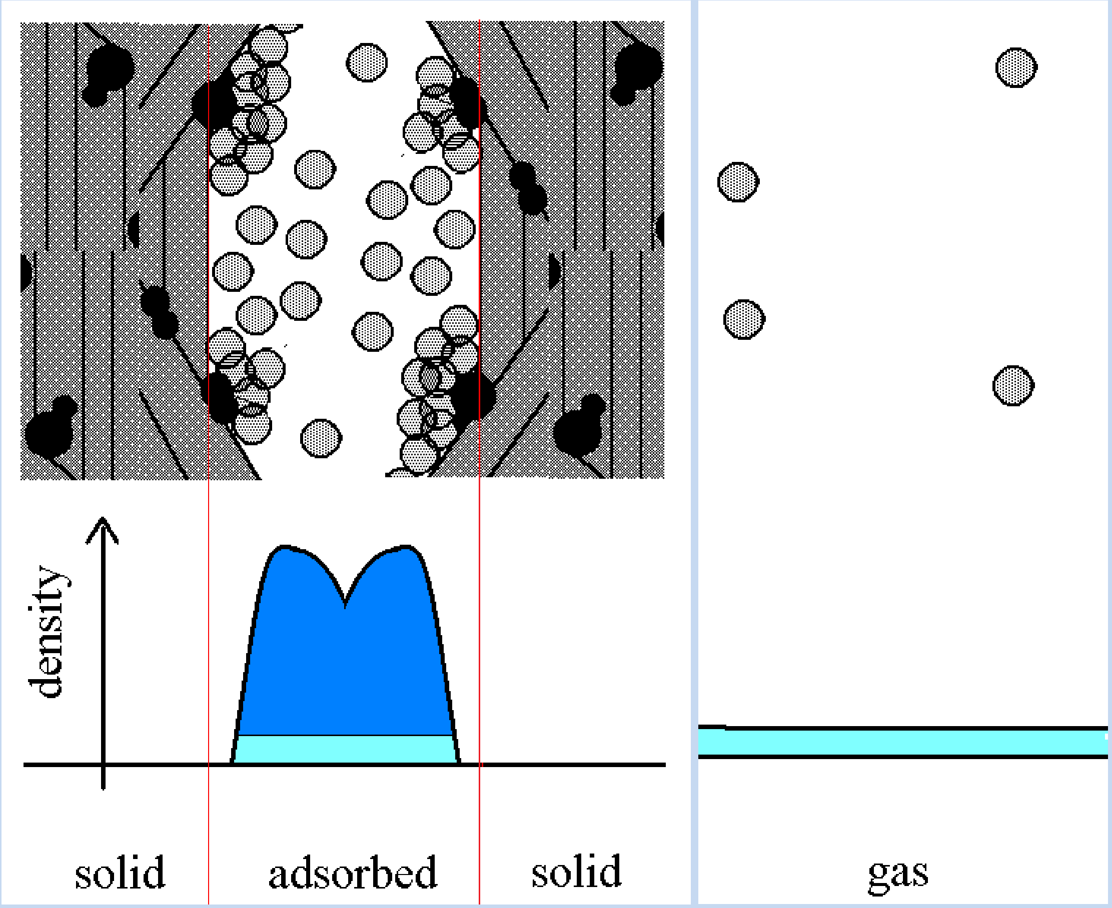
x_1, x_2 = unknown

$$\Gamma^{ex} = \int_{x_0}^{\infty} (\rho(x) - \rho^{g}).\,dx$$

x_0 = unknown, BUT Γ is based on area measured independently without any gases (w/o adsorption)

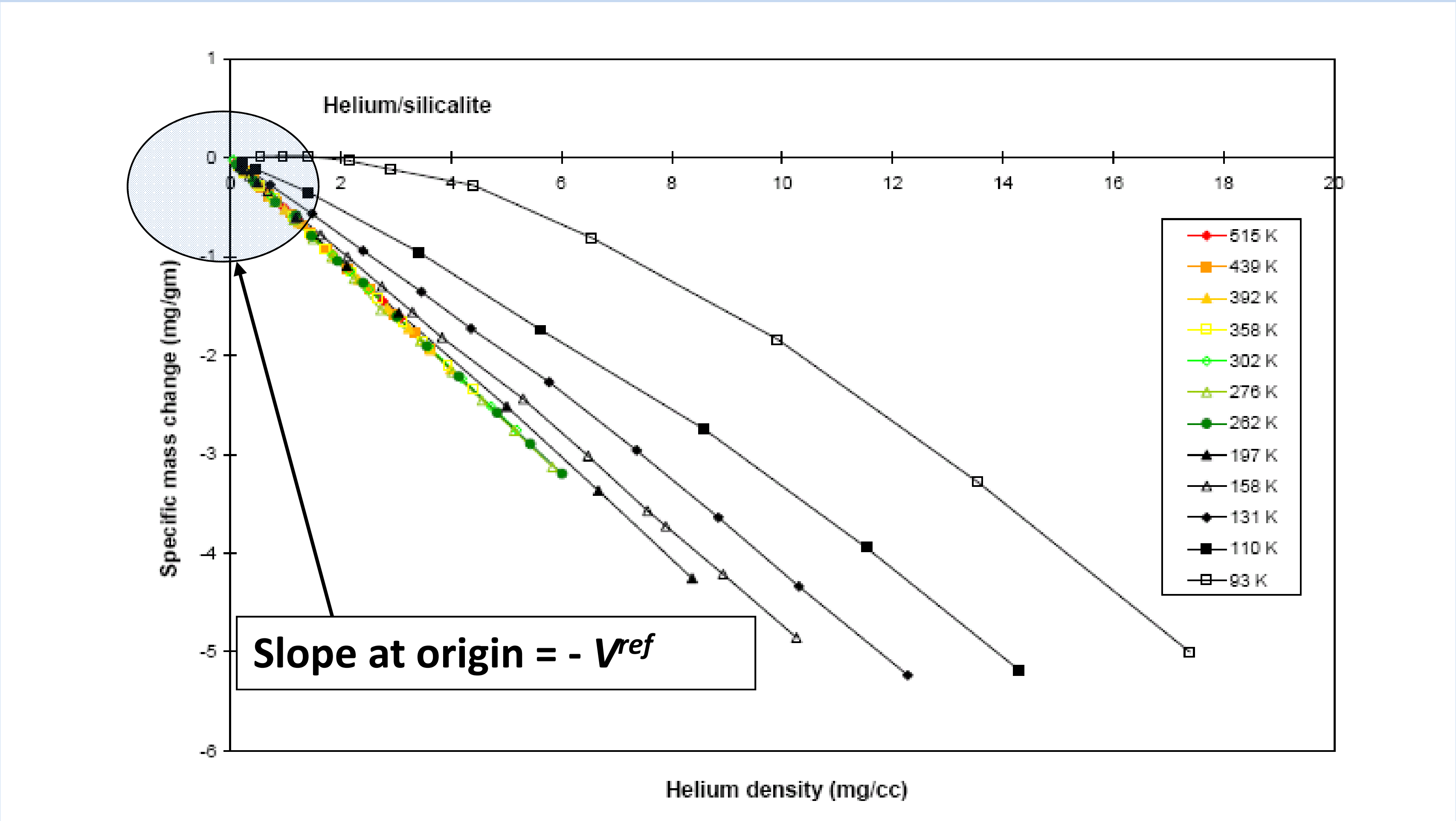
Illustrations from Myers (AIChE J., 2002)

Density in a microporous solid & gas



Only independently measurable quantity is vacuum mass of solid for microporous solids. Any probe molecule is **expected** to have pore density different than gas density.

PROBLEM-1: Even helium adsorbs in a simple non-polar microporous solid !



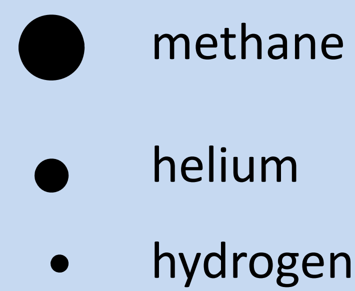
Gumma and Talu, **9**, 17-23, *Adsorption* (2003)

PROBLEM-2

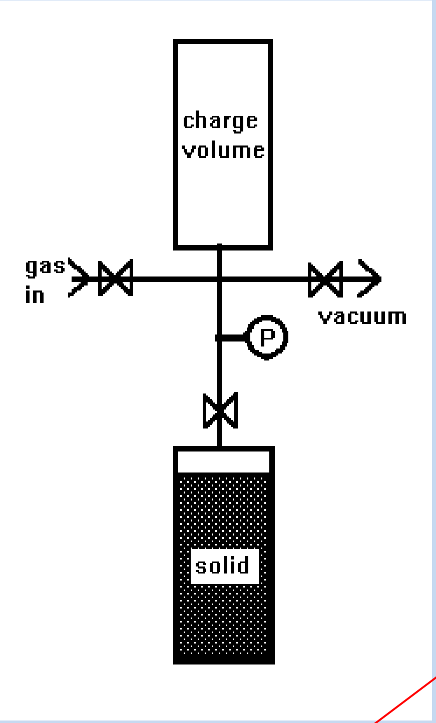
$V^{reference}$ also depends on probe molecule size

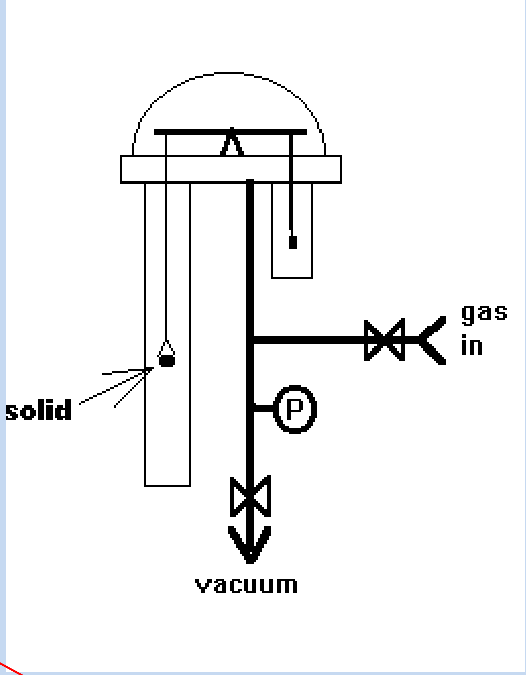
Porous solid

Molecular size



Isotherm experiments





actual data

$$n^{ads} = \frac{\Delta N^{charge} - V^{g}\rho_g}{m_s}$$

$$n^{ads} = \frac{\Delta m + V^{s}\rho_g MW_g}{m_s MW_g}$$

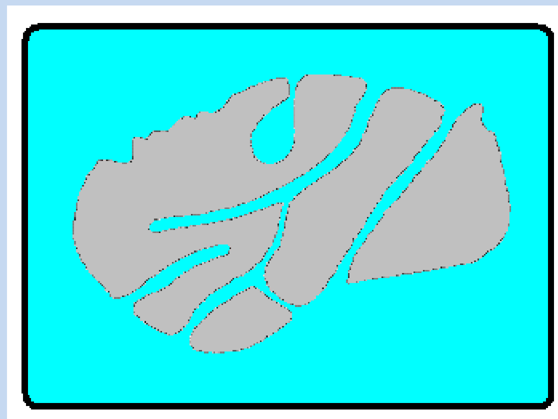
$V^{reference}$ = V^g = "void" volume available to gas

$V^{reference}$ = V^s = "solid" volume not available to gas

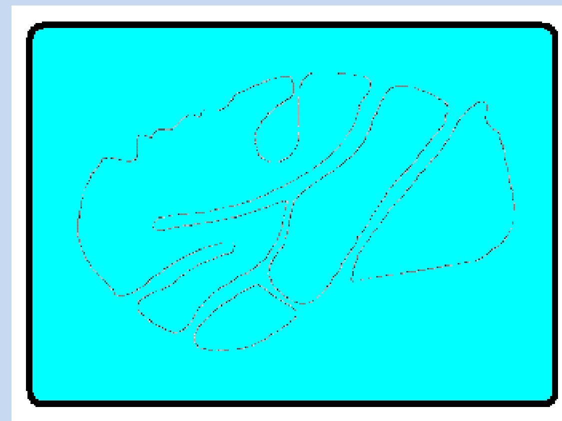
REFERENCE STATES FOR MICROPORE ADSORPTION

Coolidge classification A, B and C (1934)

Absolute



Excess

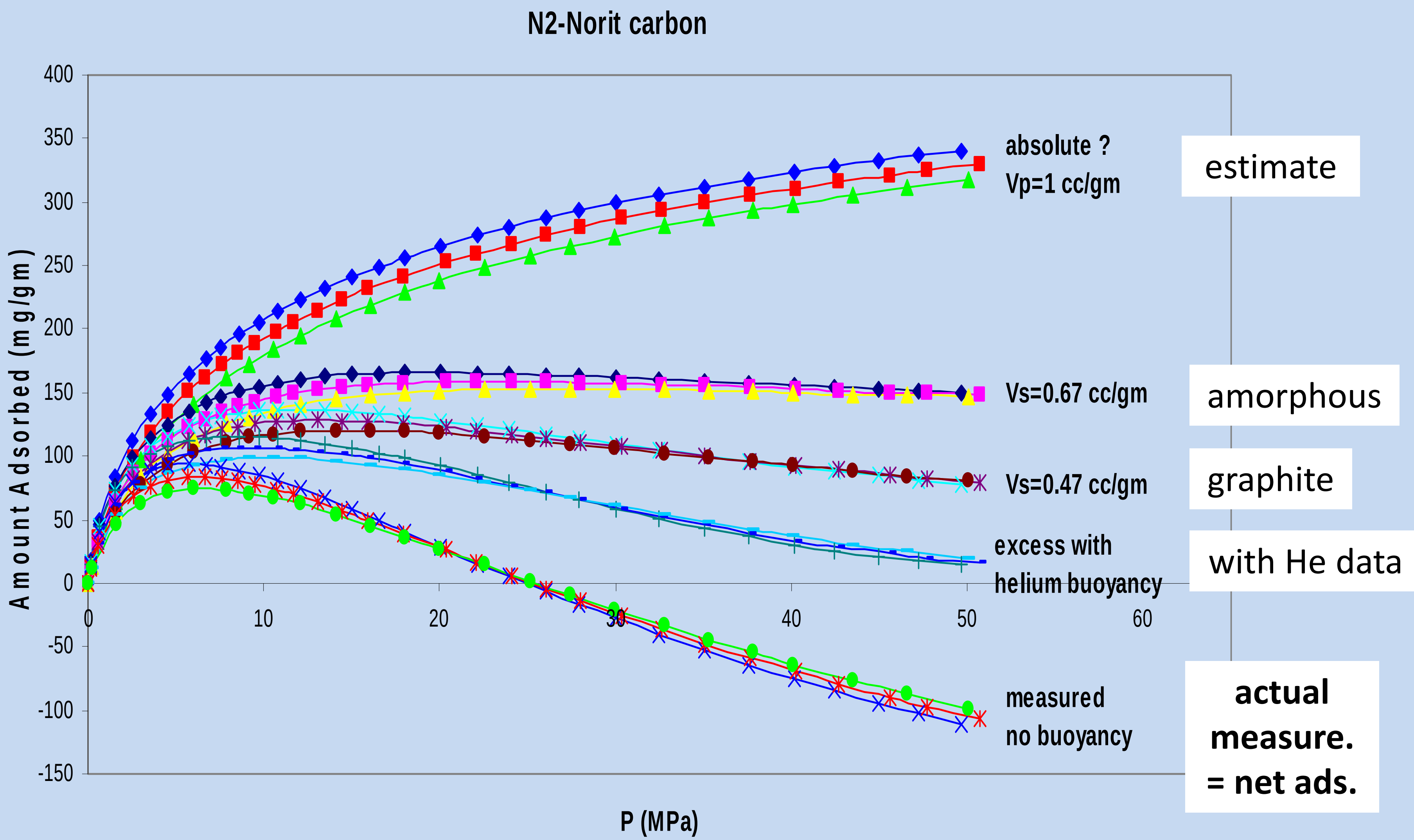


Net

<u>Gibbs dividing "hyper-surface" :</u>

- Solid side

- Gas side



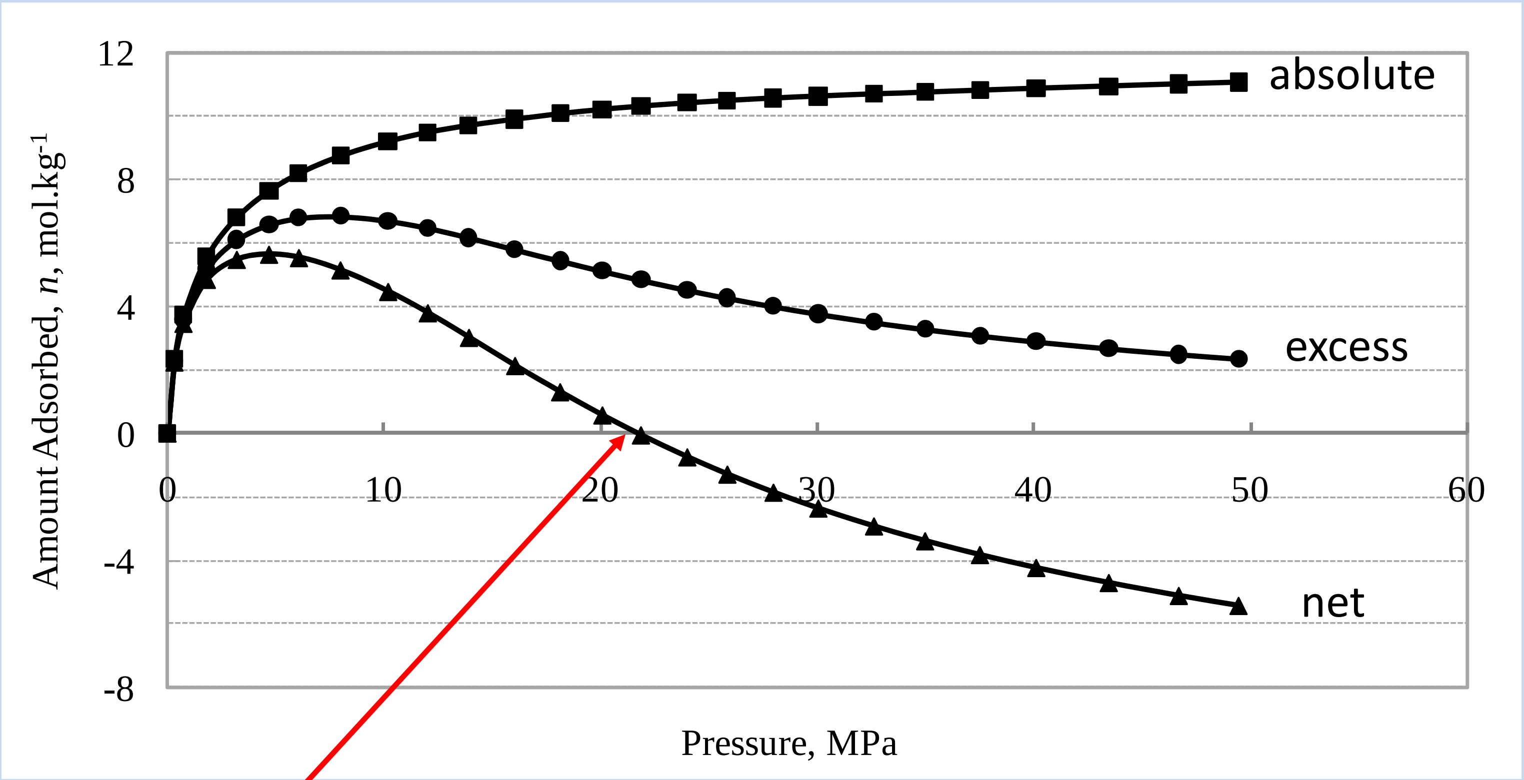
Data from Herbst, and Hartig (*Adsorption J., 2003)*

COMPARISON OF REF. STATES

	Absolute	**Excess**	**Net**
Volumetric: V_{ref}	$V_{column} - V_{solid} - V_{pore}$	$V_{column} - V_{solid}$	V_{column}
Gravimetric: V_{ref}	$V_{bucket} + V_{solid} + V_{pore}$	$V_{bucket} + V_{solid}$	V_{bucket}
Simulation: V_{ref}	0	$V_{box} - \int_{V_{box}} e^{-\frac{\Gamma}{kT}} .dV$	V_{box}
Extra effort	Helium isotherm + ??? for V_{pore}	Helium isotherm	---
Ref. State property of:	Sample + apparatus	Sample + apparatus	Apparatus

EXPERIMENT EXAMPLE

Methane on Norit R1 at 298 K

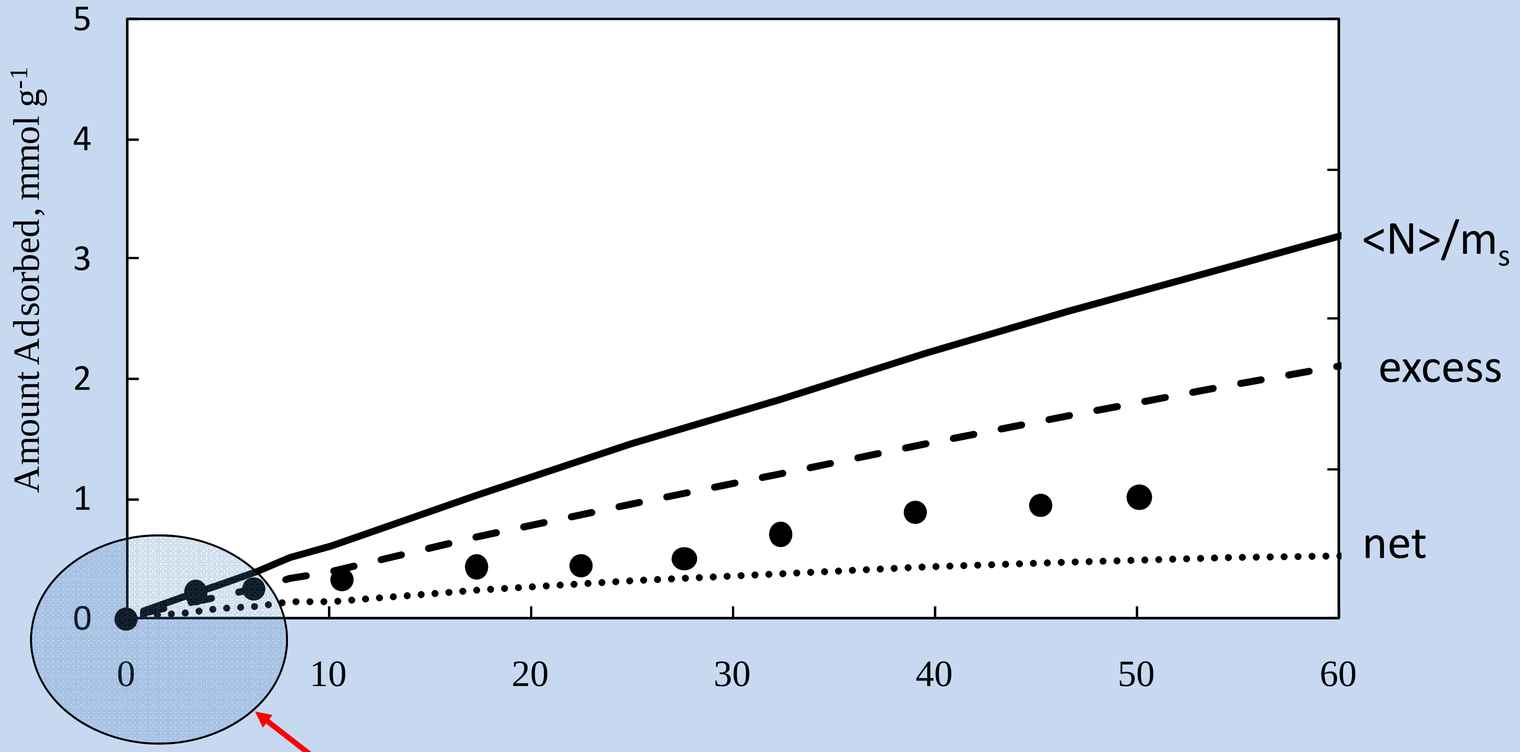


Column **without adsorbent** contains more methane when P>21 MPa

Data from Herbst and Harting (Adsorption, 2002)

SIMULATION EXAMPLE

Hydrogen on HKUST-1, MOF at 298 K

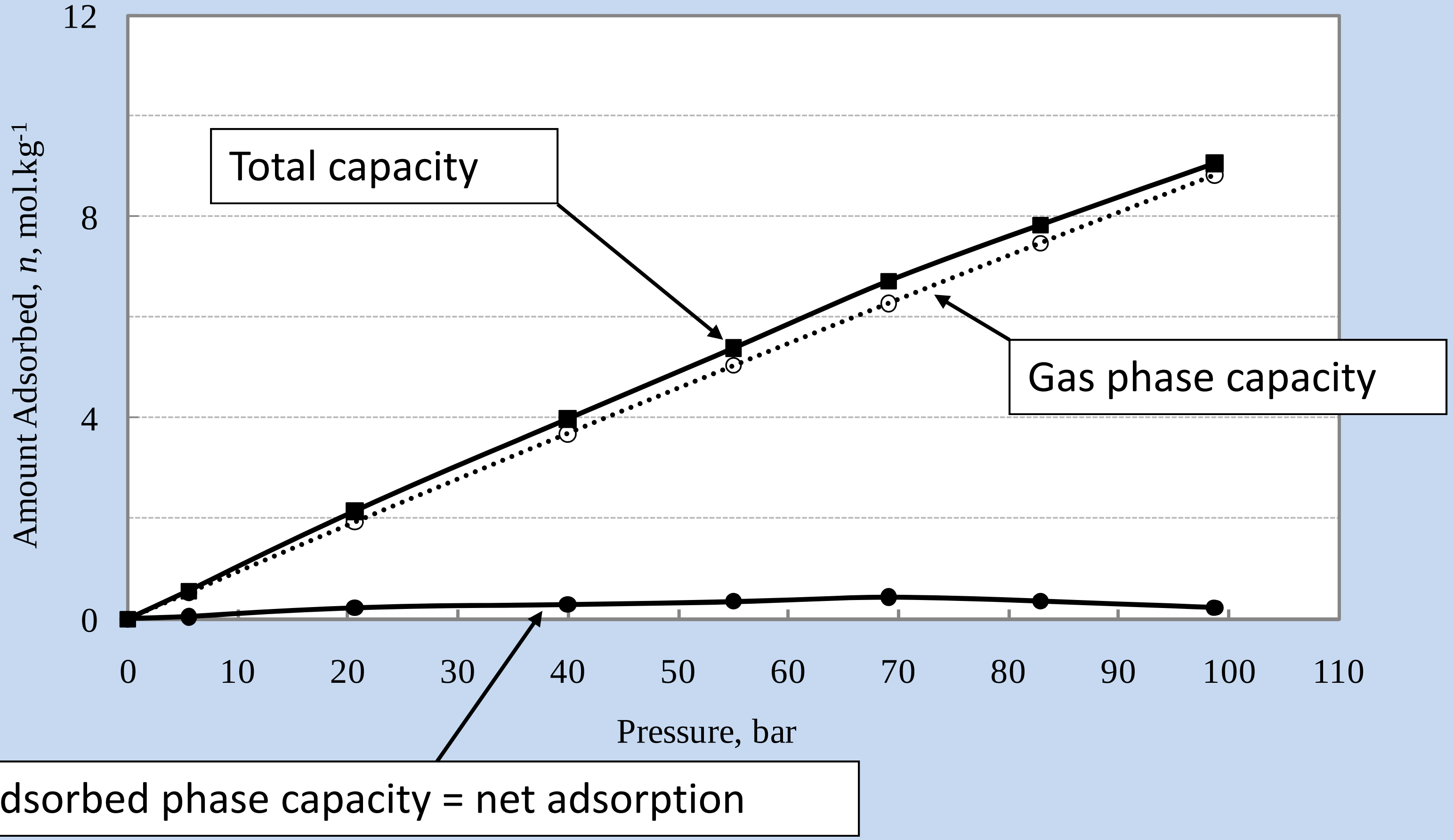


Note differences in Henry constants

Data from Liu. et.al. (J. Phys. Chem. C 2007)

APPLICATION EXAMPLE

Hydrogen storage by MOF-177 at 298 K



Data from Li and Yang (Langmuir, 2007)

Contents of an adsorptive storage tank

Net adsorption

$$N^{stored} = mass * n^{net} + \rho^{gas} * \ V^{tank}$$

Helium excess adsorption

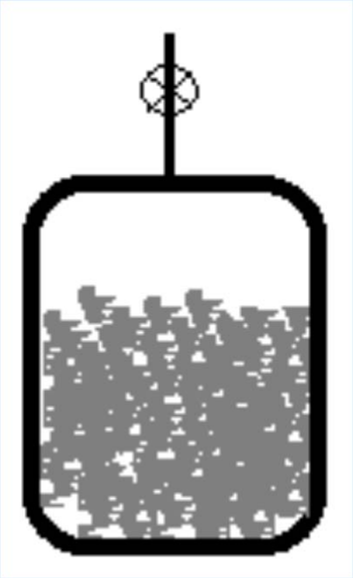
$$N^{stored} = mass * n^{ex} + \rho^{gas} * \ (V^{tank} - V^{s.He})$$

Absolute adsorption w/helium and ? for pore volume

$$N^{stored} = mass * n^{abs} + \rho^{gas} * \ (V^{tank} - V^{s.He} - V^{p.?})$$

Thermodynamic Relations

System: heterogeneous system containing: 1)microporous solid, 2) gas mixture, and 3) an "adsorbed phase"



Any total extensive property is given by

$$Z^t = Z^s + Z^a + Z^g$$

- Only total value, Z^t, can be measured in experiments.
- The values of Z^s, Z^a and Z^g depend on Gibbs dividing hyper-surface definition/location.

- **Regardless of where dividing hyper-surface is located!**

Total fundamental property relation for the heterogeneous system is:

$$d(U^t) = Td(S^t) - Pd(V^t) + \sum_i^C \mu_i d\left(N_i^t\right) + \mu^s d(M)$$

Legendre transform for Gibbs-Duhem relation is:

$$S^t d(T) - V^t d(P) + \sum_i^C N_i^t d(\mu_i) + Md(\mu^s) = 0$$

(REFERENCE: O.Talu, *J.Phys.Chem.C* 2013, 117, 13059-13071)

Solid sub-system is closed to gas molecules:

$$N_i^t = N_i^s + N_i^a + N_i^g$$

($N_i^s \rightarrow 0$)

Define solid mass-specific values as:

$$n_i^a = \frac{N_i^a}{M} \quad \text{and} \quad v^s = \frac{V^s}{M}$$

Change in chemical potential of solid by adsorption at constant *T* is:
(using ideal gas for simplicity)

$$d\mu^s = -RT\sum_i^C \left(n_i^a - \frac{v^s P_i}{RT}\right) d(LnP_i)$$

GENERAL SOLUTION THERMODYNAMICS FOR MIXTURE ADSORPTION

<u>Phase equilibrium relations</u>

$$Py_i = P_i^o x_i \gamma_i \qquad (ideal\colon \gamma_i = 1)$$

<u>Standard States</u>

$$P_i^o = f\{T, \varphi\}$$

$$\varphi = \varphi_i^o = \varphi_j^o$$

<u>Amount Adsorbed (for ideal solution)</u>

$$\frac{1}{\eta_T} = \sum_i^C \frac{x_i}{\eta_i^o\{T, \varphi\}}$$

Where

$$\eta_T = \sum_i^C \eta_i \quad \text{and} \quad x_i = \frac{\eta_i}{\eta_T}$$

Integration from **pure solid** reference state (at zero pressure) gives the change in solid chemical potential (i.e. Gibbs Adsorption Isotherm Equation):

$$\varphi = (\mu^s - \mu^{s*}) = -RT \int_0^{P_i} \sum_i^C \eta_i \, d(LnP_i)$$

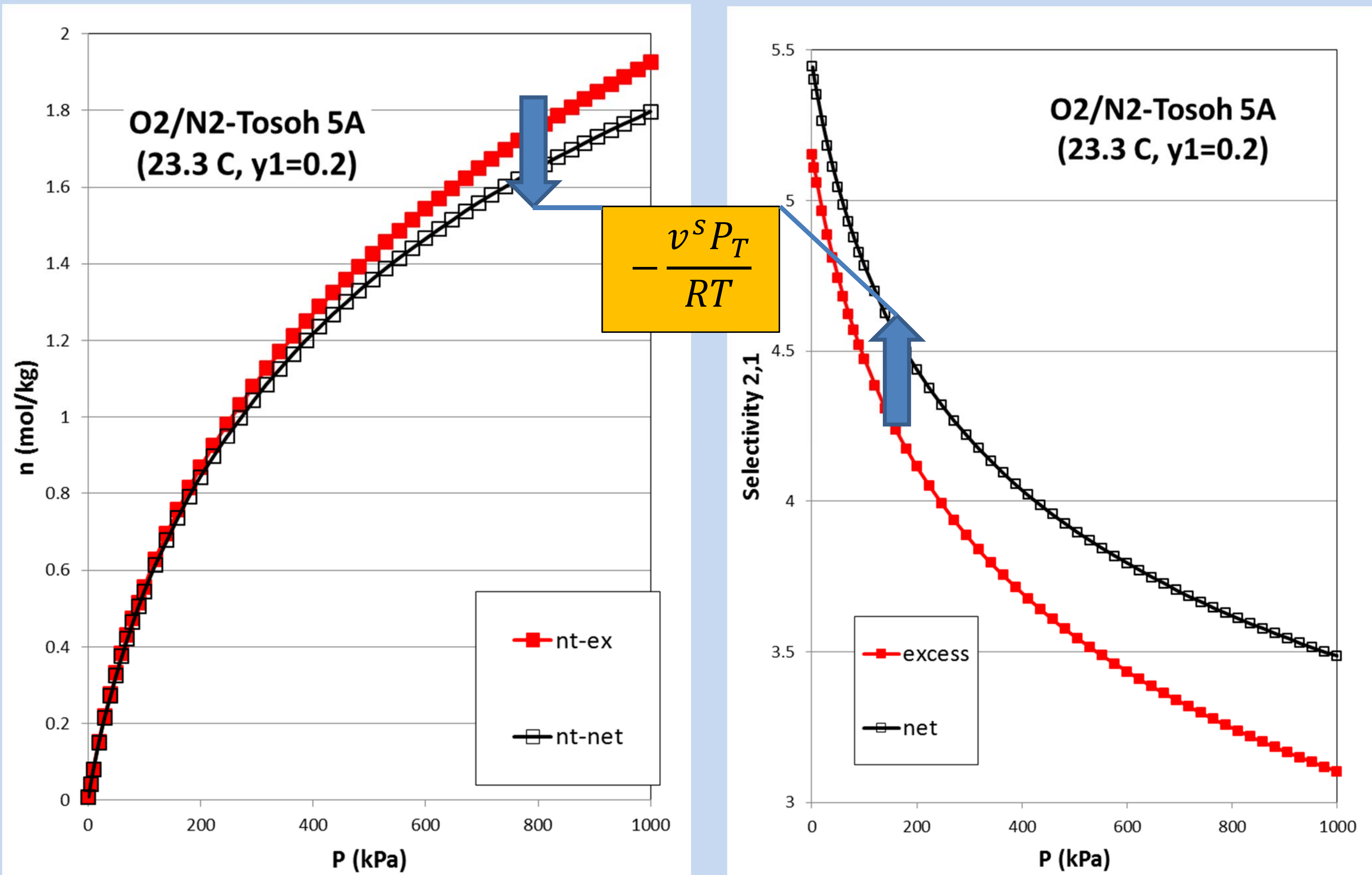
Where

$$\eta_i = n_i^a - \frac{v^s P_i}{RT}$$

- Values of n_i^a and v^s depend on location of dividing hyper-surface.
- But, η_i should not depend on hyper-surface location since φ is a state property.

$\boldsymbol{\eta_i}$ is the *net* amount adsorbed.

Binary Adsorption: pressure



- The impact on mixture phase diagram is **significant** even for simple systems such as O_2/N_2 in 5A-zeolite at moderate conditions
- "Thermodynamic" amount adsorbed is

$$\eta_i = n^{net} = n_i^{ex} - \frac{v^s P_i}{RT} = n_i^{abs} - \frac{(v^s + v^p) P_i}{RT}$$

- $\boldsymbol{v^s}$ ***(and*** $\boldsymbol{v^p}$) needs to be determined/measured to calculate solid chemical potential if net adsorption is not used !
- Net adsorption measures η_i directly by definition, and it is unequivocal, and simpler to use in applications

CONCLUSIONS

1) Actual measurements directly give ***net*** adsorption
2) Excess and ***absolute*** are calculated results by some assumptions and conversions
3) In storage application (as with most applications), ***excess*** and ***absolute*** is converted back to ***net***
4) Conversion factors (i.e. solid and total pore volume) must be included with ***excess*** and ***absolute*** data to be useful for storage application (or any other thermodynamic calculation).
5) "Solid" properties (i.e. volumes, pore size distributions, etc.) are <u>binary</u> properties for solid-guest pair. They are useful for physical understanding but <u>not essential</u> for thermodynamics

<u>References</u>

- *Gumma and Talu, Langmuir 2010, 26(22), 17013-17023*
- *Talu, J.Phys.Chem. C, 2013, 117, 13059-13071*