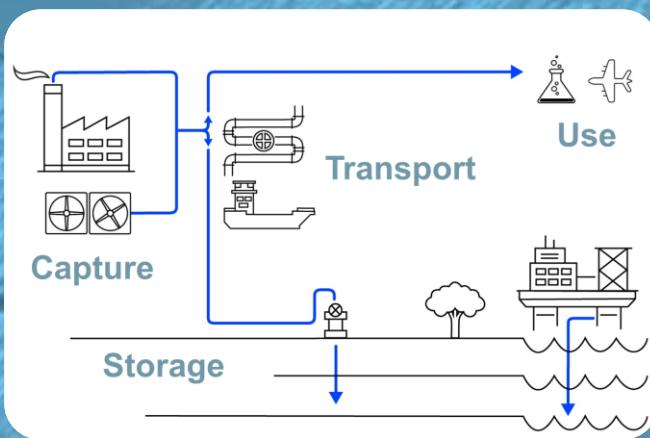
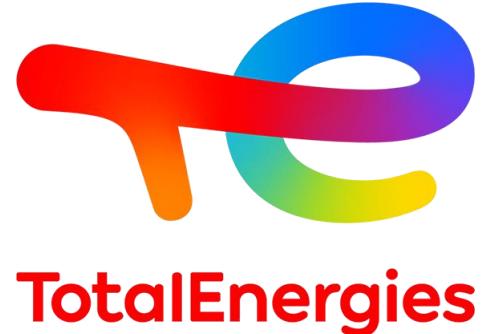


CCUS

Carbon Capture (Utilization) & Storage



0%
CO₂



Modeling adsorption isotherms

Philip Llewellyn

R&D Manager for CCS and CO₂ Utilisation
Sustainability Program

Why adsorption : (1) characterization, (2) use



Characterization by physisorption →



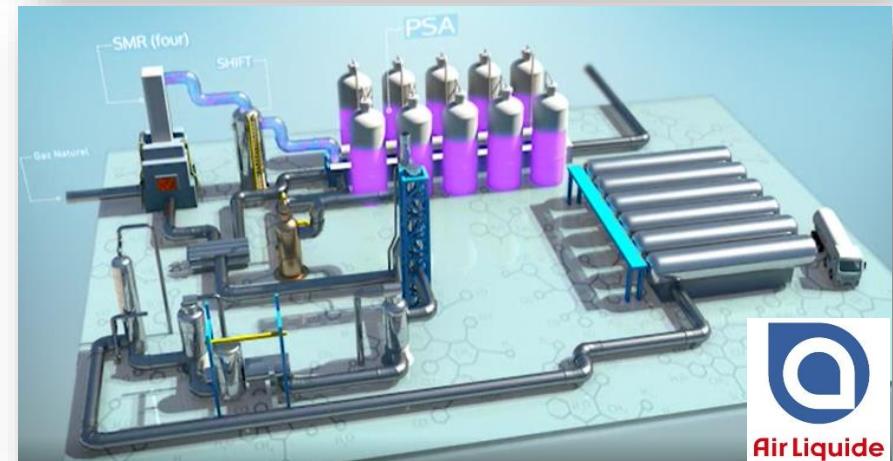
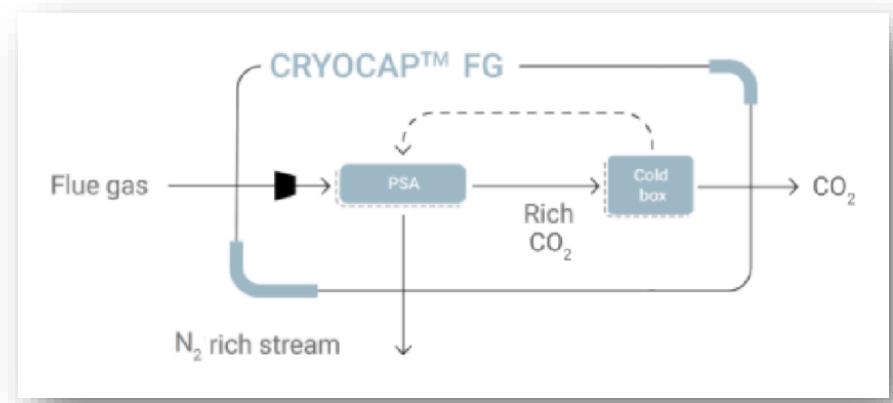
Pilot-scale testing →



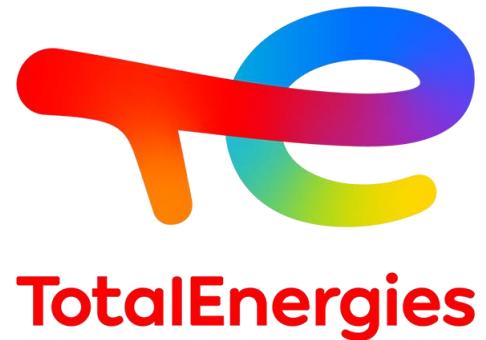
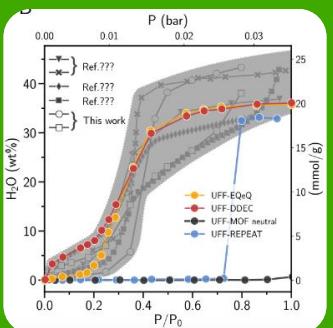
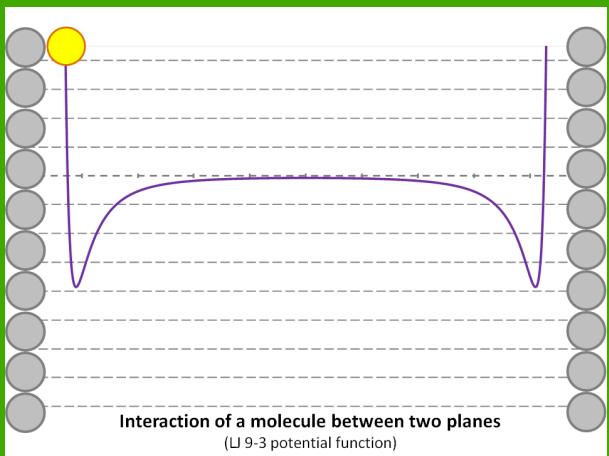
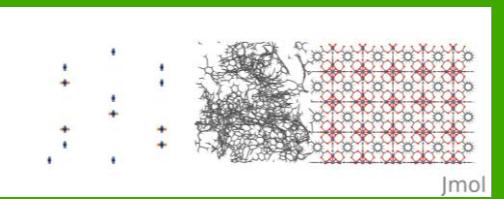
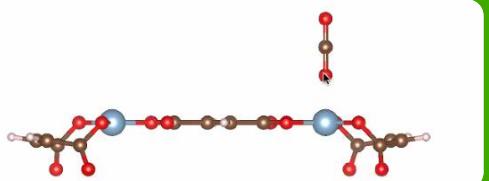
Svante

0,1 t_{CO₂}/day

Industrial use



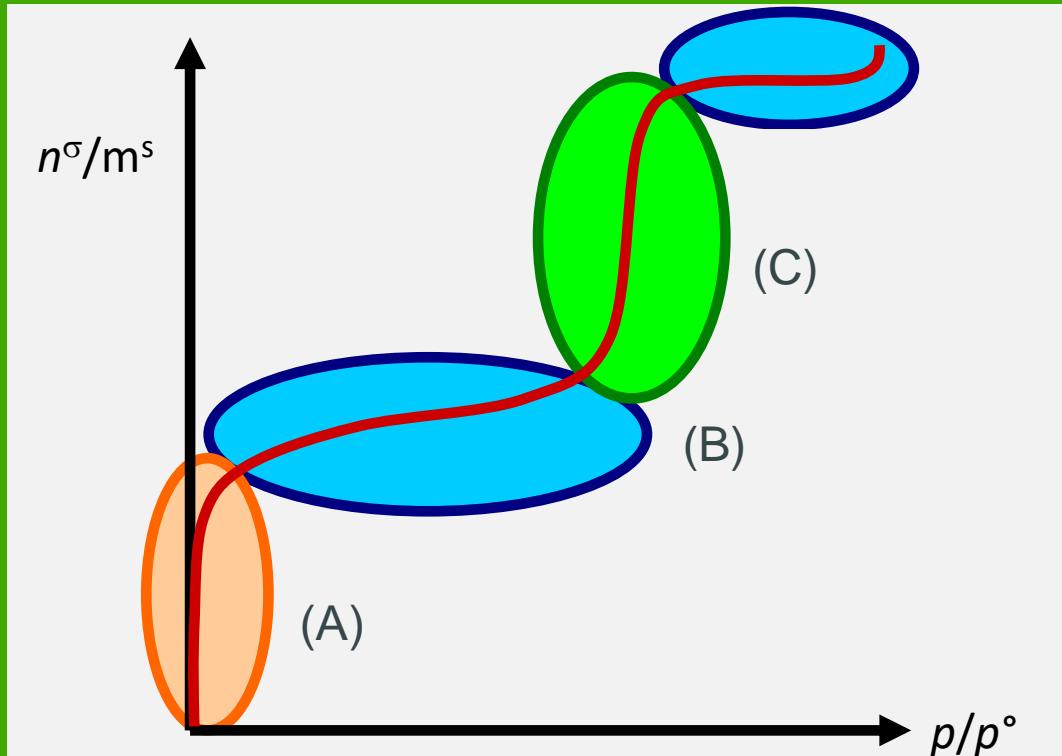
Zeeland : 900 kt/yr



Modeling adsorption isotherms

- (1) Models to aid interpretation of adsorption phenomena
 - often from physisorption isotherms ($T < T_c$)
 - materials characterization → materials KPI
- (2) Models to predict KPI's for initial process evaluation
 - often at room temperature and above
 - sometimes at above atmospheric pressure
- (3) What KPI's can we predict ?
 - Energies
 - Selectivities

Lessons learned



Sub-critical adsorption isotherm
(e.g. N₂@77K or Ar@87K)

→ In the chat, can you give a quick interpretation of the three phenomena (A – B – C) observed

Why model isotherms ?

(1) to aid mechanism interpretation
→ model adsorption phenomena

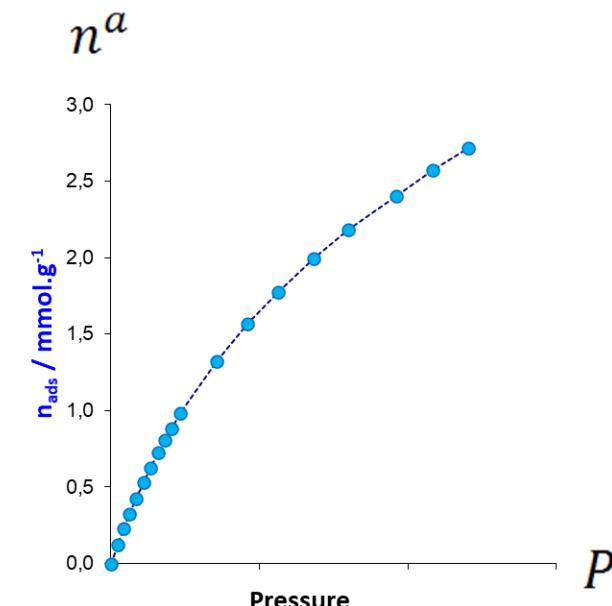
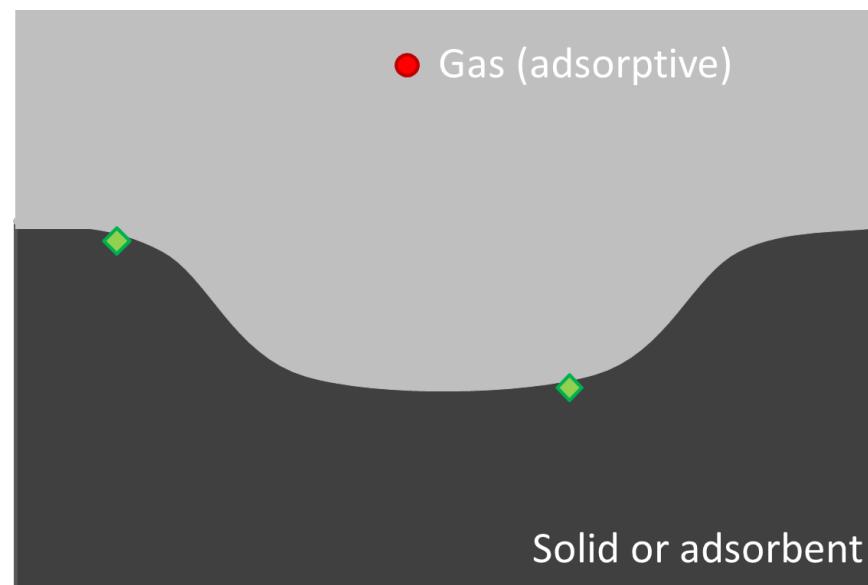
e.g. Materials characterization → KPI

So how do we mathematically model different adsorption phenomena (1) Low coverage



William Henry
(1774-1836)

- Low coverage
 - Infinitely low concentrations → no lateral interactions → equation of state analogous with ideal gas law
 - Initial linear region observed in the isotherm → amount adsorbed proportional to pressure
 - Analogy to Henry's law
 - $n^a = K_H(T) \cdot p$
 - K_H : energetic constant (Henry constant), only depends on temperature

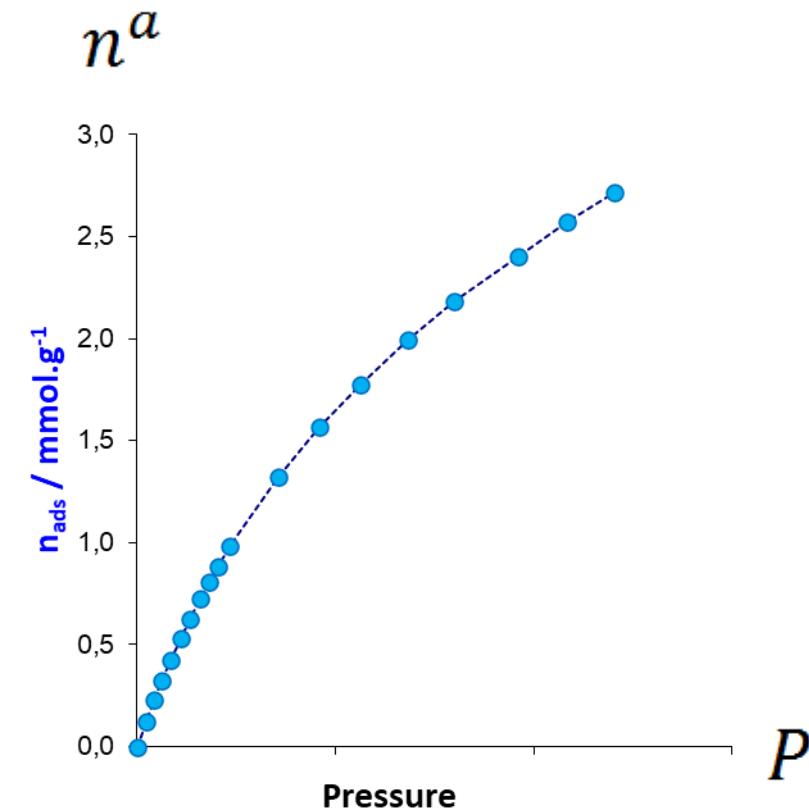


Calculating the Henry constant

- Initial linear region of isotherm:

$$n^a = K_H(T)P$$

$$K_H(T) = \lim_{P \rightarrow 0} (n^a / P)$$



Calculating the Henry constant

- Initial linear region of isotherm:

$$n^a = K_H(T)P$$

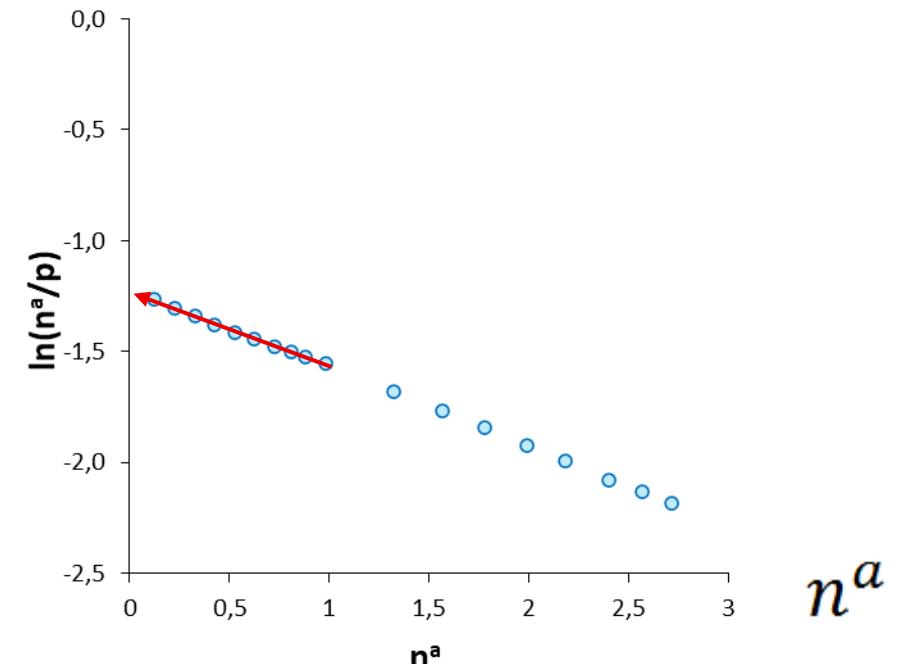
$$K_H(T) = \lim_{P \rightarrow 0} (n^a / P)$$

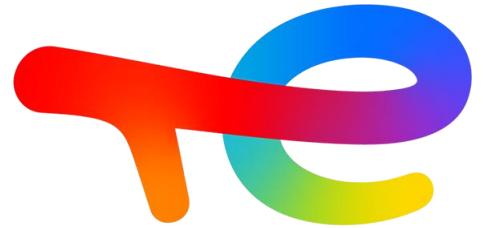
- Often represent $\ln(n^a/P)$ as a function of n^a :

$$\ln(K_H(T)) = \lim_{P \rightarrow 0} (\ln(n^a / P)) = -1,214$$

$$K_H(T) = 0,297$$

$$\ln(n^a / P)$$

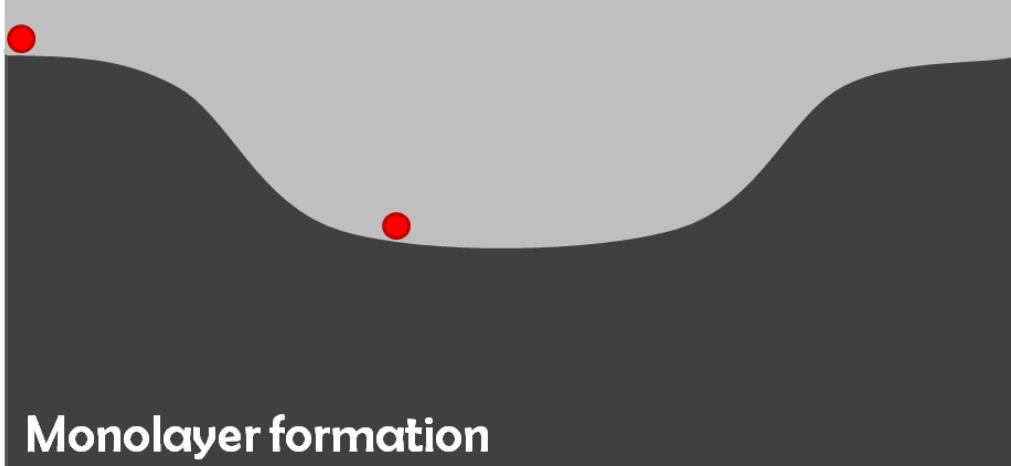




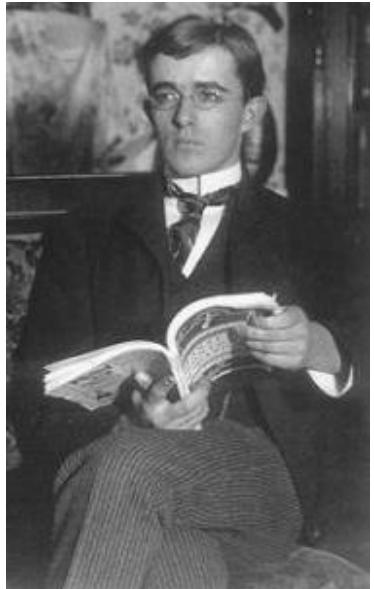
TotalEnergies

How do we mathematically model different adsorption phenomena

(a) Monolayer formation



Irving Langmuir, 1881-1957

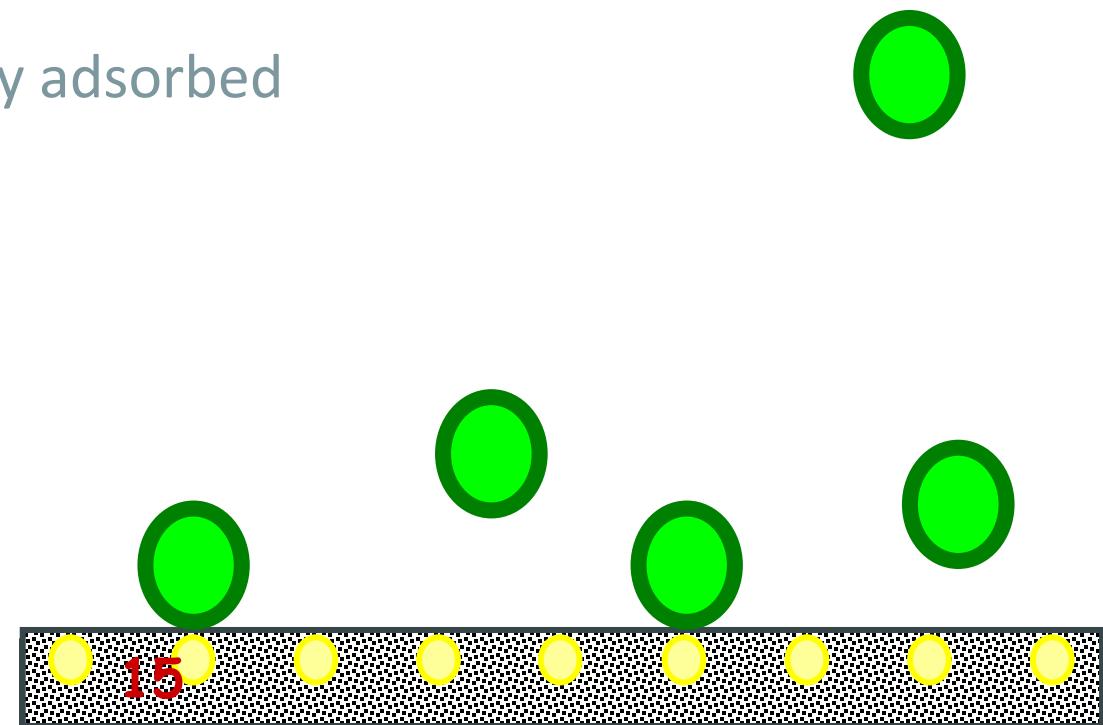


Irving Langmuir
(1881 – 1957)



☒ Condensation / Evaporation Mechanisms

- All sites are energetically identical
- Gas sticks to the surface : 1 layer only possible
- No lateral interactions
- Gas bounces off a species already adsorbed



Langmuir isotherm (1918)

- **Hypotheses:**
 - homogeneous surface: all adsorption sites are energetically identical
 - localized adsorption: one molecule per adsorption site → monolayer of capacity
 - no lateral interactions between adsorbed molecules

- Fraction coverage:
$$\theta = \frac{N^a}{N^s} = \frac{n^a}{n_m^a}$$

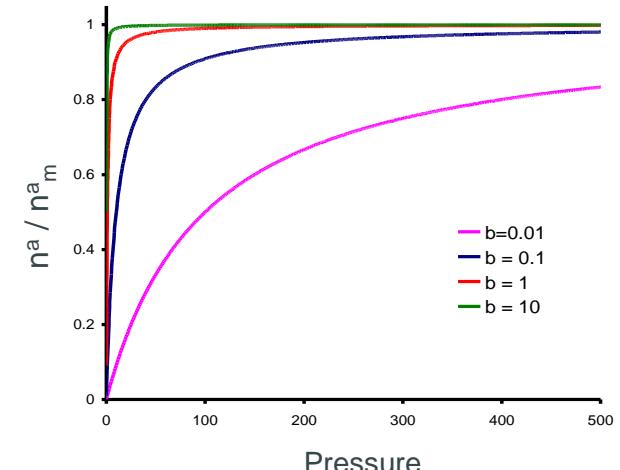
N^a = number of adsorbed molecules
 N^s = number of adsorption sites

$$n^a = n_m^a \frac{bP}{1 + bP}$$

$$b = b_\infty \exp\left(\frac{Q}{R_g T}\right)$$

b is the coefficient of adsorption or affinity constant

n_m^a is the monolayer capacity



Langmuir isotherm & Thermodynamic coherence

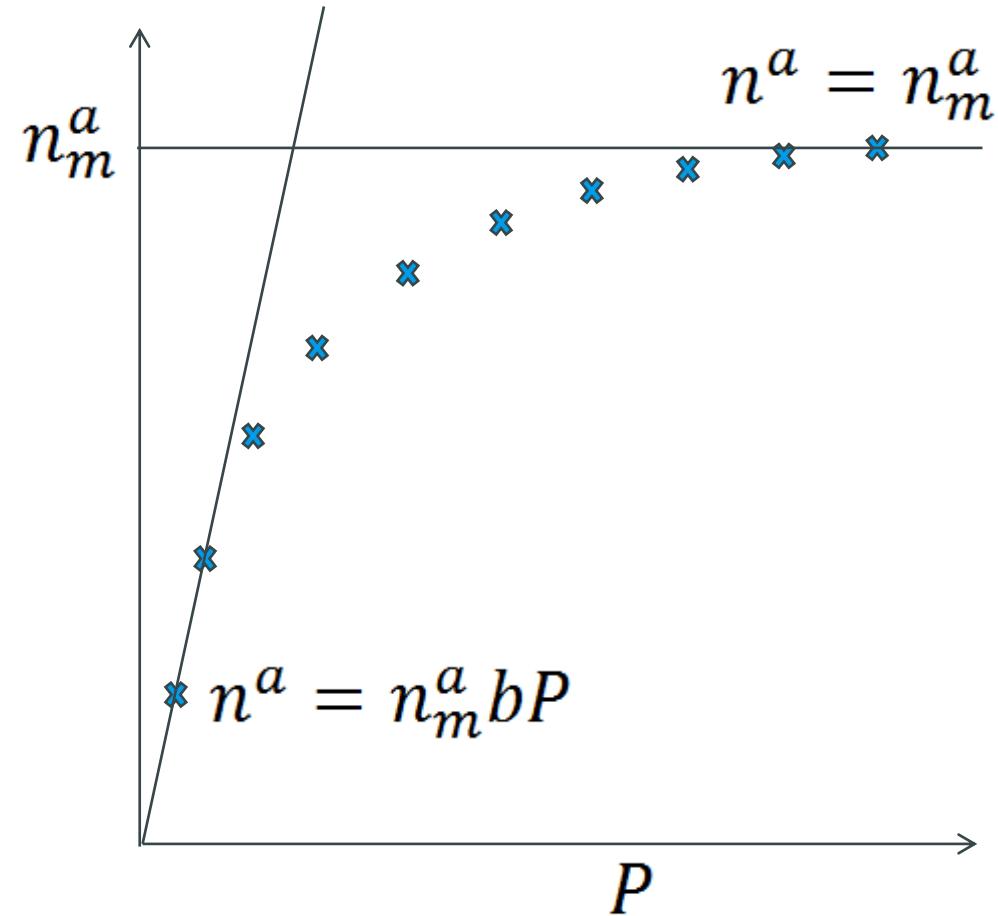
$$n^a = n_m^a \frac{bP}{1 + bP}$$

- At very low pressure: $bP \ll 1$
 - Henry's law: $n^a = n_m^a bP$

- At sufficiently high pressure:
 - Finite limit: $bP \gg 1$

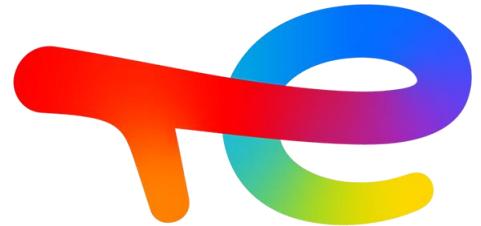
$$n^a = n_m^a$$

- Henry's law at low pressure
- Finite limit at high pressure



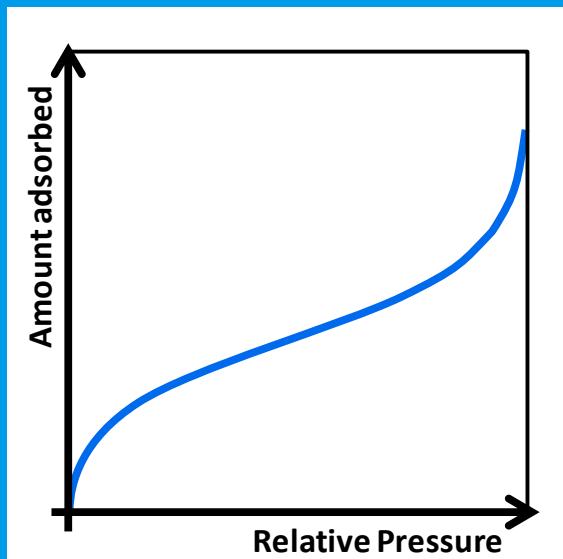
BUT

- Phenomenon models only monolayer adsorption
- Used for Chemisorption or at Room Temperature



TotalEnergies

How do we mathematically model different adsorption phenomena

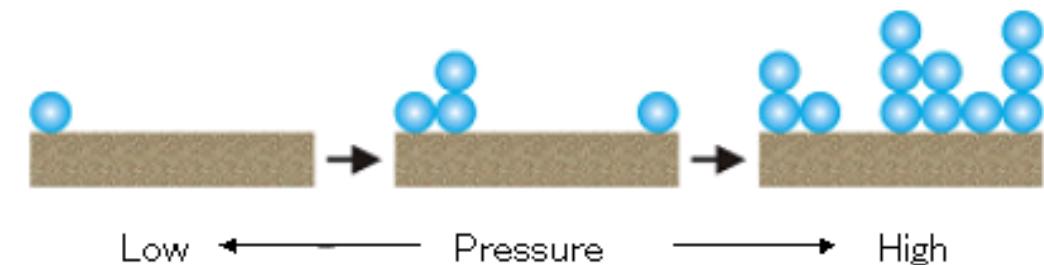


→ In the chat, can you name the Type of isotherm according to the IUPAC ?

(b) Mono/Multilayer formation on a non-porous solid

How do we model (b) Monolayer/Multilayer coverage ?

- Multilayer coverage
 - Brunauer, Emmet, Teller 1938
 - Surface adsorption sites equivalent
 - No lateral interactions
 - Energy of adsorption of second and further layers = $E_{\text{Liquefaction}}$
 - **At any point on the isotherm the solid is in equilibrium with any number of adsorbed layers**

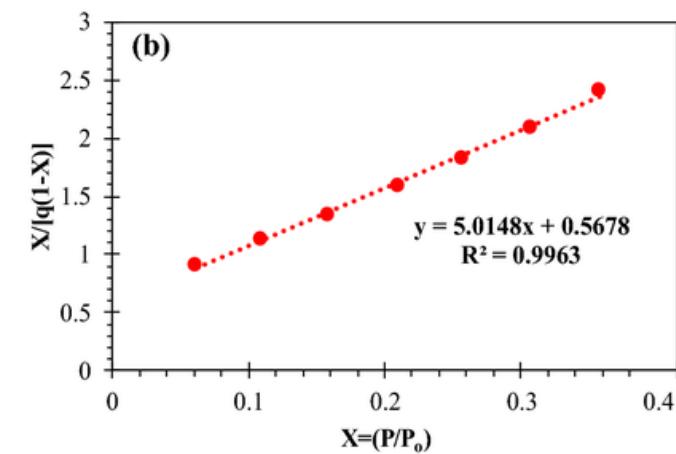
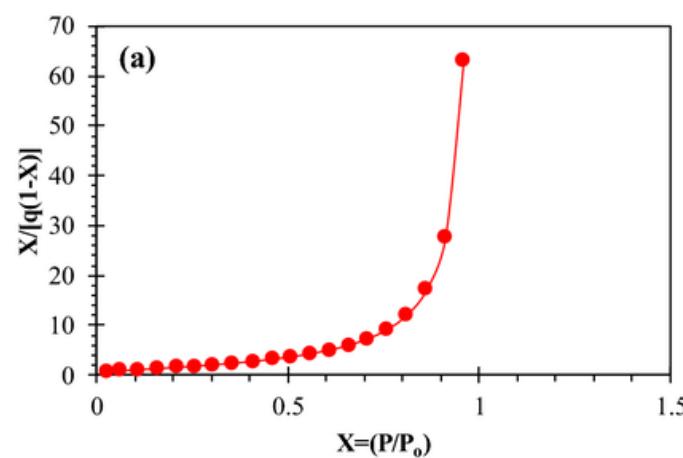


$$\frac{n}{n_m^a} = \frac{Cx}{1-x} \cdot \frac{1-(N+1)x^N + Nx^{N+1}}{1+(C-1)x - Cx^{N+1}}$$

- $x = p/p^\circ$
- C : energetic constant
- N : number of layers formed

$$C \approx \exp\left(\frac{E_1 - E_L}{RT}\right)$$

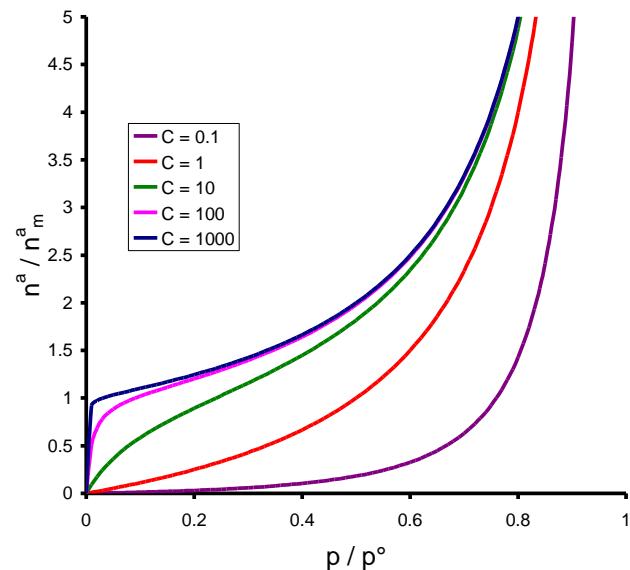
- Henry's law at low pressure



How do we model (b) Monolayer/Multilayer coverage ?

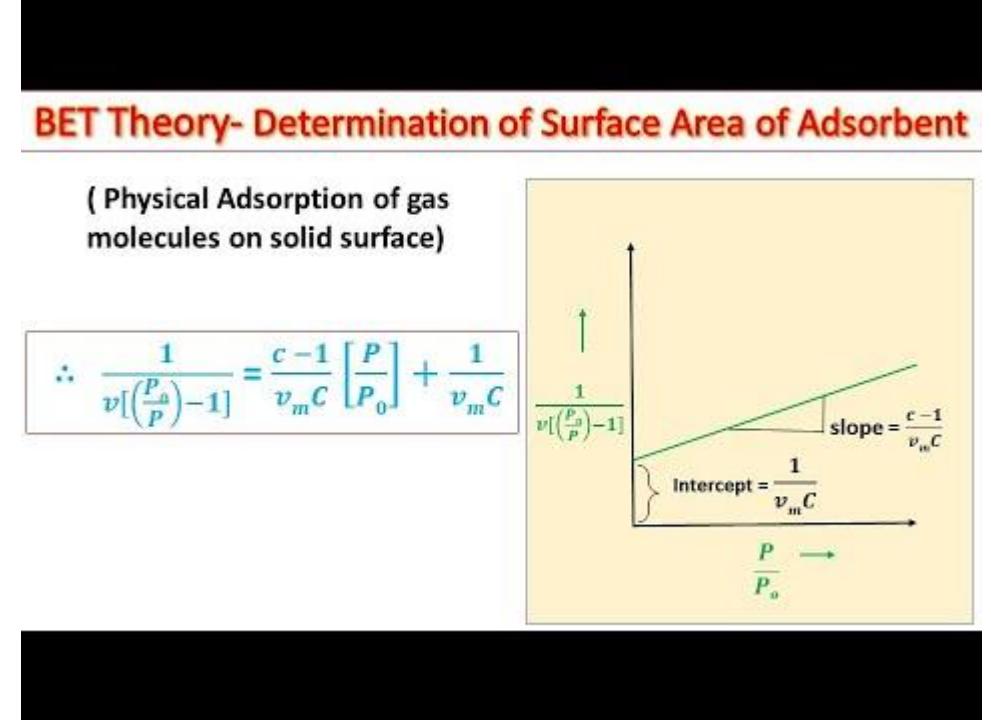
- Brunauer, Emmet, Teller Equation

$$\frac{n}{n_m^a} = \frac{Cx}{1-x} \cdot \frac{1-(N+1)x^N + Nx^{N+1}}{1+(C-1)x - Cx^{N+1}}$$



→ Set N to ∞

$$\frac{n}{n_m^a} = \frac{Cx}{(1-x)[1+x(C-1)]}$$

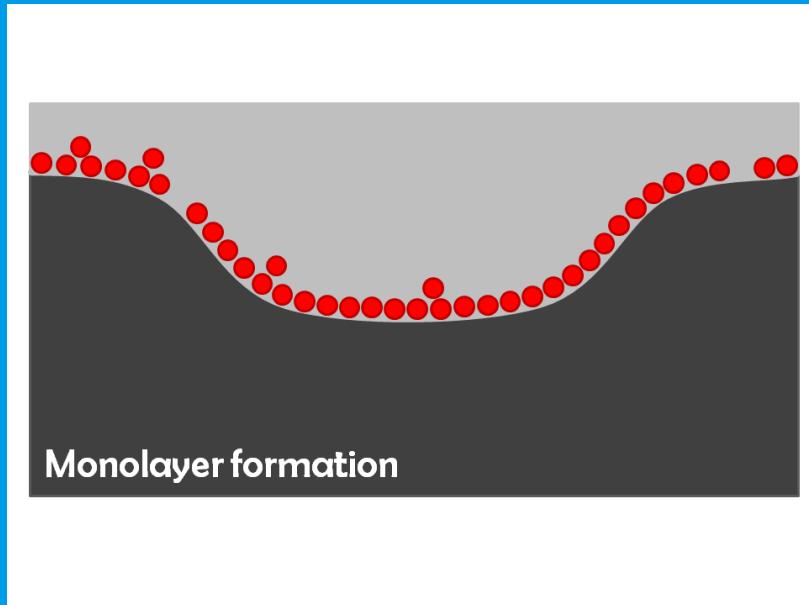


KPI → estimation of the available surface area → BET area

* For further reading
Adsorption by Powders and Porous Solids, Rouquerol et al., Academic Press, 2013



TotalEnergies

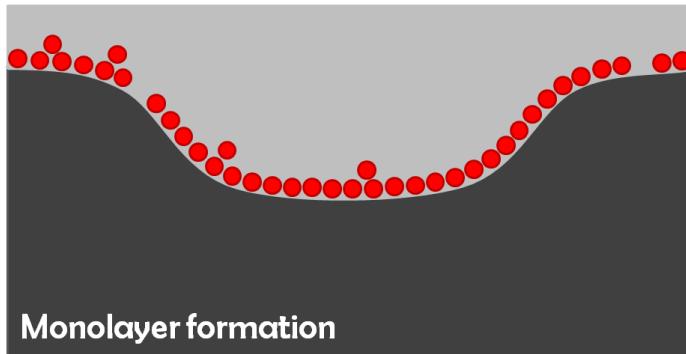


How do we mathematically model different adsorption phenomena

(c) Multilayer formation

How do model (c) Multilayer coverage

- Other relationships to model multilayer coverage
 - Relate thickness of liquid-like adsorbed film to relative pressure of gas phase

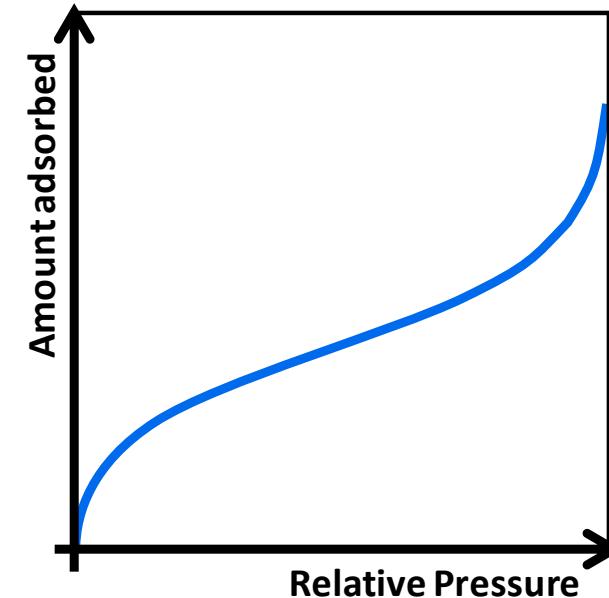


- Harkins & Jura (N_2 @77K)

$$t = \left(\frac{0.1399}{0.034 - \log(p/p^\circ)} \right)^{1/2}$$

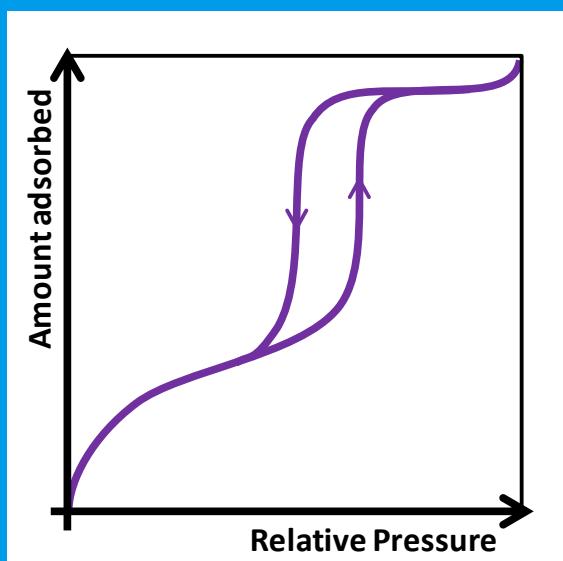
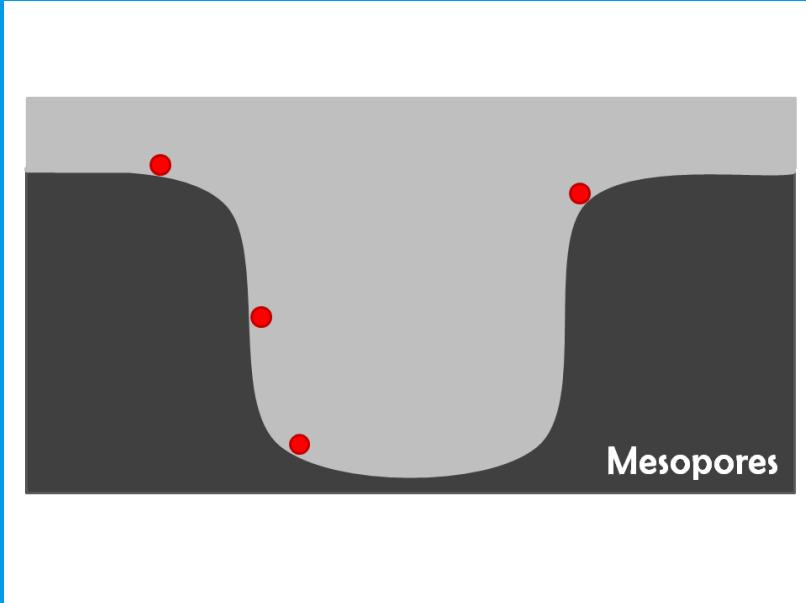
- Frankel, Halsey & Hill (N_2 @77K)

$$t = 0.354 \times \left(\frac{-5}{\ln(p/p^\circ)} \right)^{1/3}$$

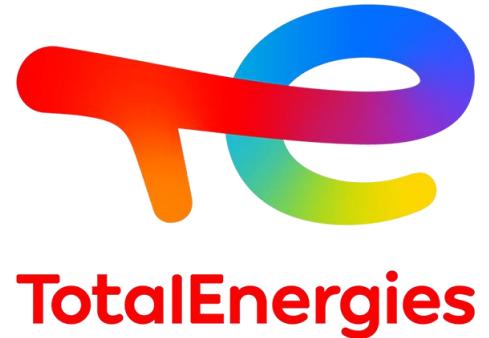


Experimental data from «de Boer»
 ‘Physical and Chemical Aspects of Adsorbents and Catalysts’
 Ed B. G. Linsen, Acad. Press, London (1970) p.33.

KPI (t-method) → estimation of the ‘external’ surface area



→ In the chat, can you name the Type of isotherm according to the IUPAC ?

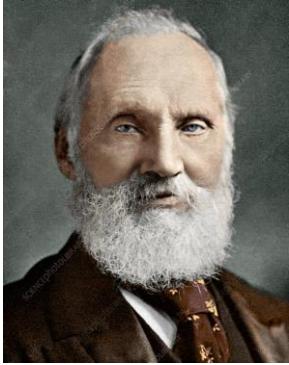


How do we model different adsorption phenomena

(d) Capillary condensation

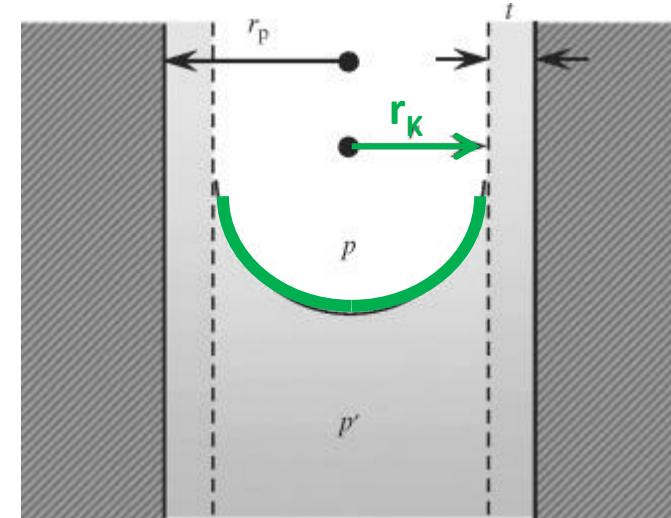
Phenomena modeled (4)

Capillary condensation in Mesoporous solids



William Thomson,
Lord Kelvin (1824-1907)

$$\ln \frac{p}{p^\circ} = -\frac{2\gamma \cdot V_m}{r_k \cdot RT}$$

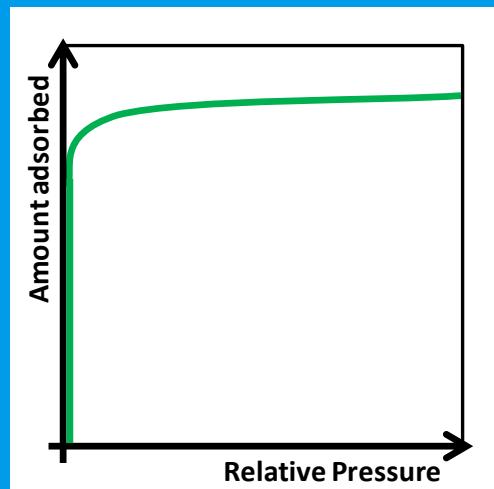
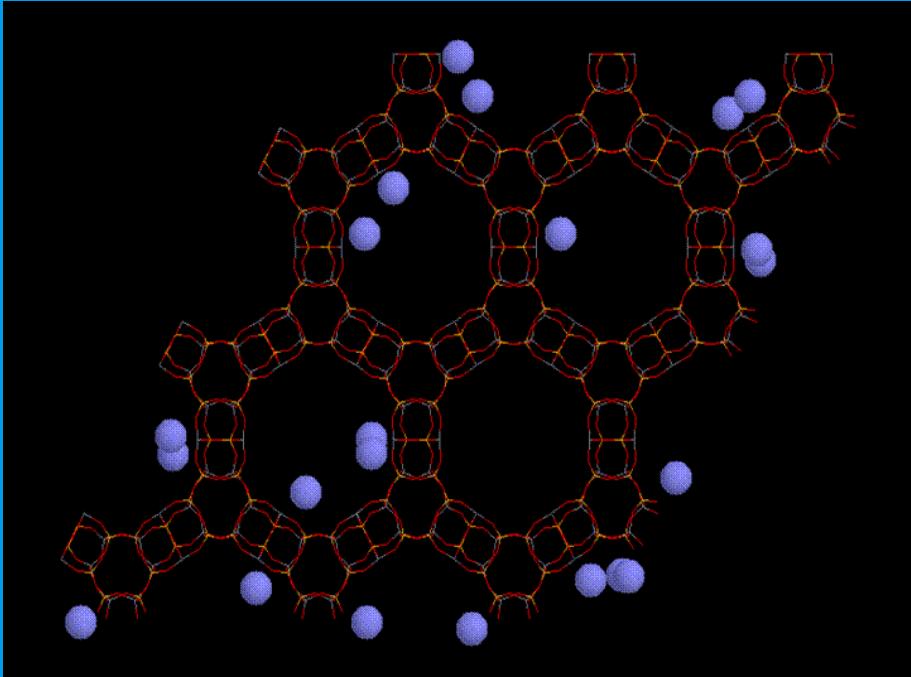


Kelvin equation

- relates p/p° of pore filling to capillary radius
- γ = surface tension; V_m = molar volume

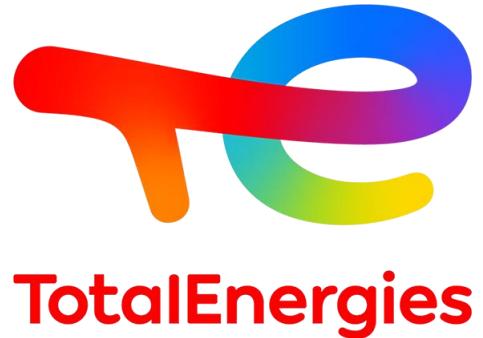
* W. T. Thomson, Phil. Mag. 42, 448 (1871)

KPI (via BJH) → estimation of pore size



→ In the chat, can you name the Type of isotherm according to the IUPAC ?

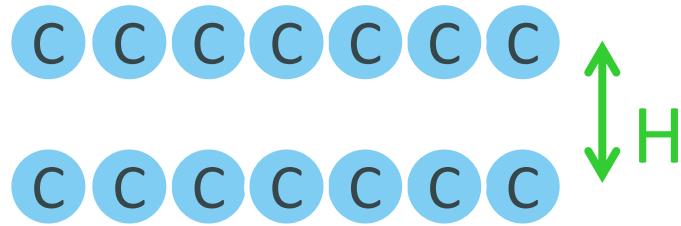
! Not a Langmuir isotherm



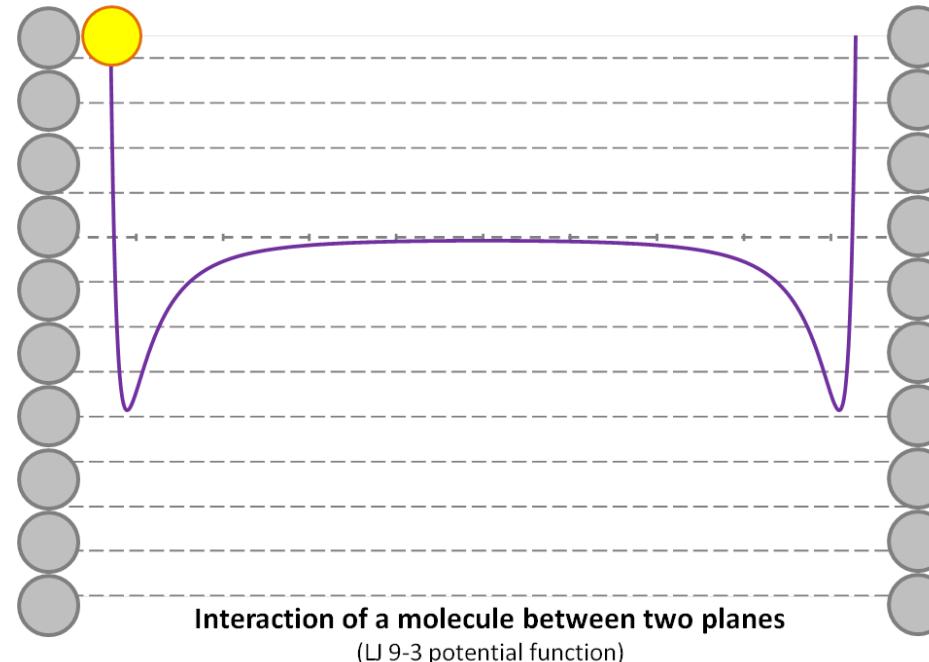
How do we model different adsorption phenomena

(e) Micropore filling

Horwath-Kawazoe model to estimate micropore size/volume

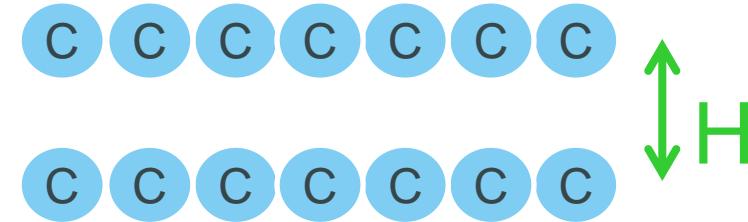


Possible to relate micropore size to relative pressure of pore filling



Méthode de Horwath-Kawazoe : calculs

- Pression remplissage des pores \propto interaction gaz-solide
- Mis au point pour des micropores en fente d'un charbon



$$\Phi(z)_{pore} = \Phi_{g-s}(z) + \Phi_{g-s}(H - z)$$

Méthode de Horvath et Kawazoe (HK)



Hypothèses

- ❖ Pores plats de largeur H
- ❖ Pression de remplissage des micropores liée à l'énergie d'interaction adsorbable-adsorbant

Calculs : N₂, 77 K / tamis moléculaire de C

$$\ln(p / p^\circ) = \frac{61,23}{(H - 0,64)} \left[\frac{1,895 \cdot 10^{-3}}{(H - 0,32)^3} - \frac{2,709 \cdot 10^{-7}}{(H - 0,32)^9} - 0,05014 \right]$$

Méthodes de Horwath-Kawazoe et de Saito-Foley : formules !



- H-K
 - 10-4 fonction de potentiel plus expression des interactions :

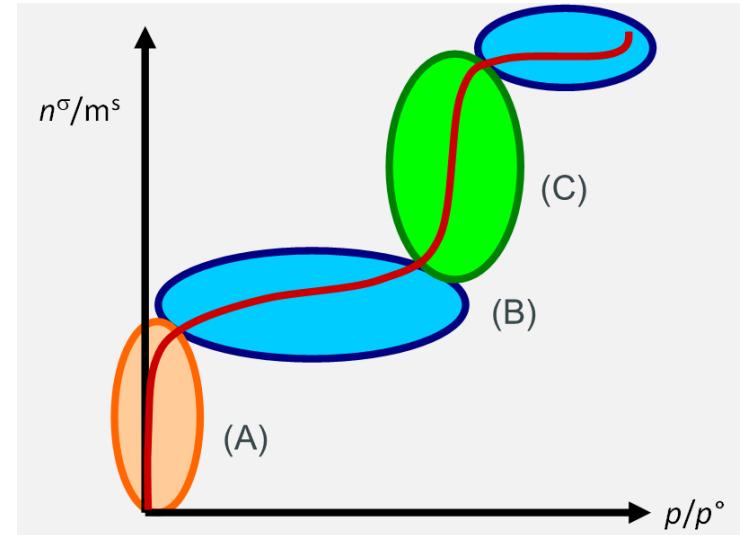
$$\Phi(z)_{pore} = k \int \left[\left(\frac{\sigma}{z} \right)^{10} - \left(\frac{\sigma}{z} \right)^4 + \left(\frac{\sigma}{H-z} \right)^{10} - \left(\frac{\sigma}{H-z} \right)^4 \right]$$

$$\bullet \text{ S-F} \quad \ln\left(\frac{p}{p^0}\right) = \frac{62.38}{H-0.64} \cdot \left[\frac{1.895 \cdot 10^{-3}}{(H-0.32)^3} - \frac{2.7087 \cdot 10^{-7}}{(H-0.32)^9} - 0.05014 \right]$$

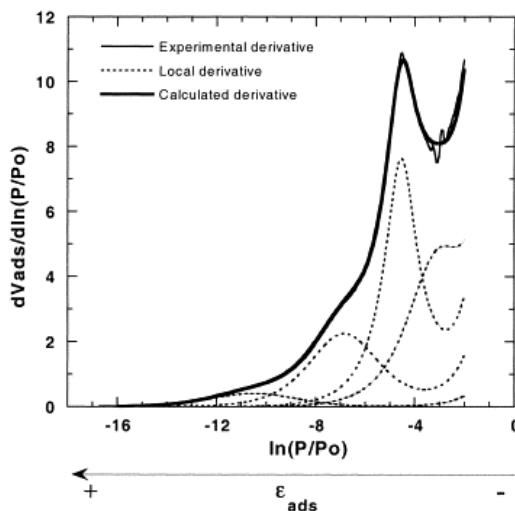
$$\ln\left(\frac{p}{p^0}\right) = \frac{28.57}{H-0.612} \cdot \left[\frac{1.584 \cdot 10^{-3}}{(H-0.306)^3} - \frac{1.729 \cdot 10^{-7}}{(H-0.306)^9} - 4.793 \cdot 10^{-2} \right]$$



Frederic Villiéras
Nancy



Combining various equations to fully model the isotherm



Texture and surface energetic heterogeneity of solids from modeling of low pressure gas adsorption isotherms
 F Villiéras, JM Cases, M François, LJ Michot, F Thomas
Langmuir 8 (7), 1789-1795

Henry



Langmuir



BET



Harkins & Jura / FHH



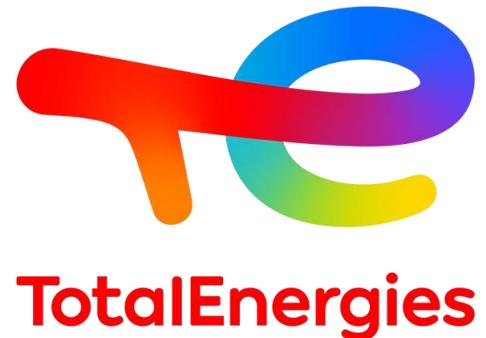
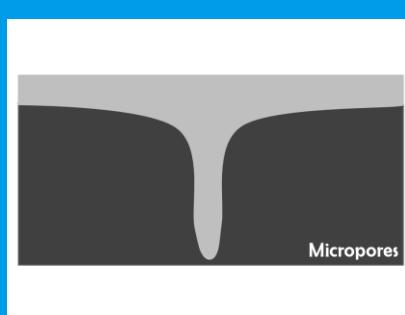
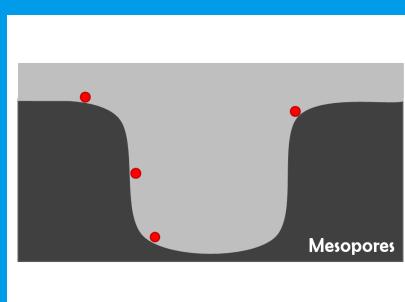
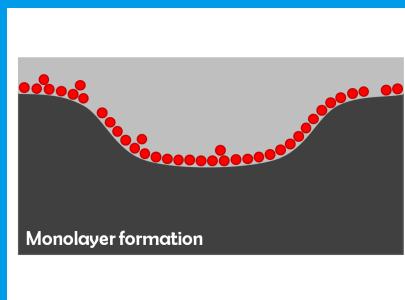
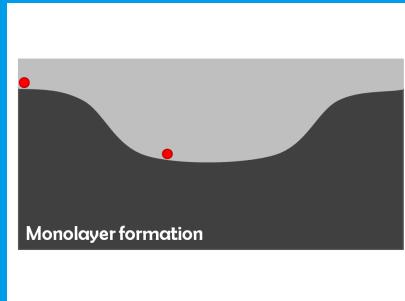
Kelvin



Polyani/Dubinin



Horwath-Kawazoe



Modeling adsorption phenomena for porous materials characterization

→ *sub-critical adsorption*



Why model isotherms ?

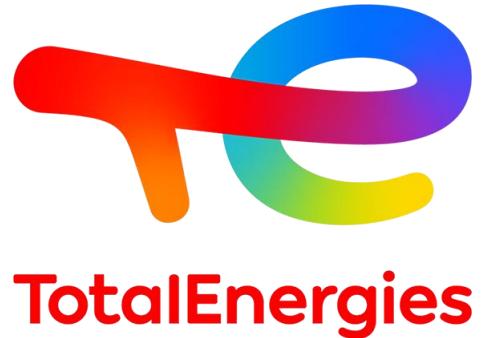
(2) to predict KPI's

e.g. Initial process evaluation

- often at room temperature and above
Anthropogenic CO₂ capture @ 40-50°C → TSA
- sometimes at above atmospheric pressure
Natural gas treatment / H₂ production → PSA



→ In the chat, can you write down which of the above equations are most often be used for RT isotherm treatment



Why model isotherms ?

(2) to predict KPI's

e.g. Initial process evaluation

- often at room temperature and above
Anthropogenic CO₂ capture @ 40-50°C → TSA
- sometimes at above atmospheric pressure
Natural gas treatment / H₂ production → PSA

Henry



Langmuir

Empirical models

Langmuir-based
extensions

Virial model



Why model isotherms ?

(2) to predict KPI's for initial process evaluation

The empirical approach

Single component equations: Freundlich equation

- Initial linear region of isotherm:

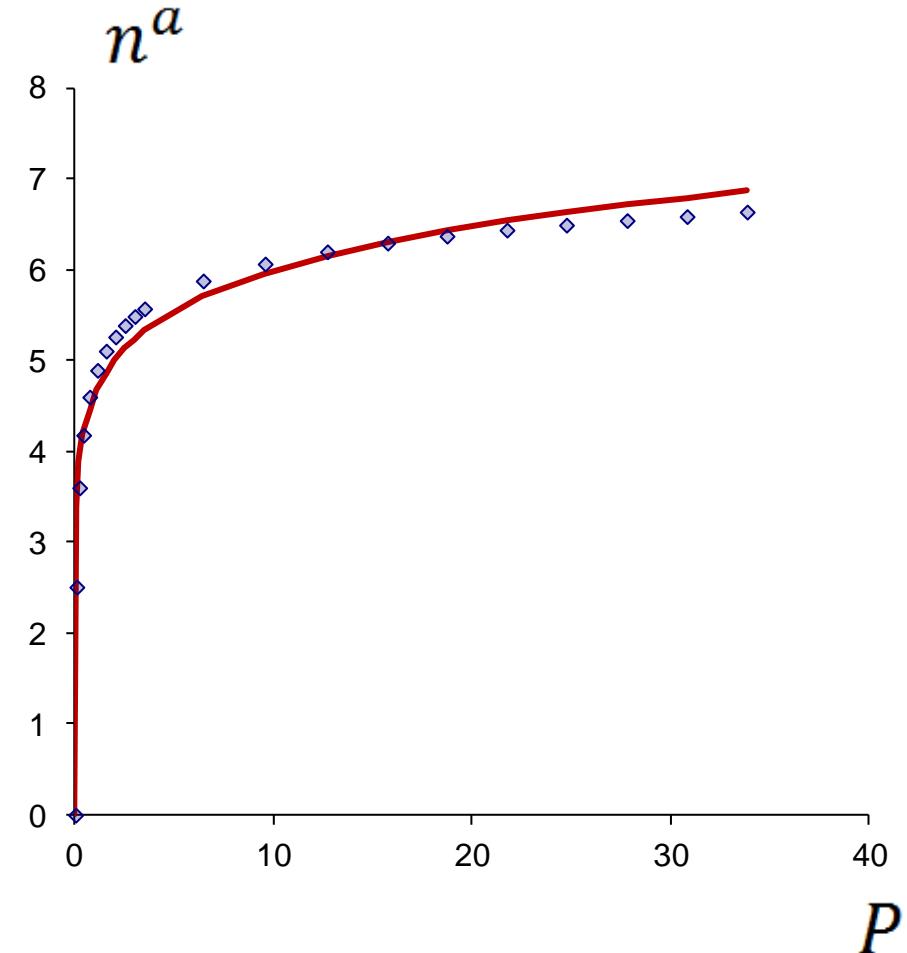
$$n^a = K_H(T)P$$

$$K_H(T) = \lim_{P \rightarrow 0} (n^a / P)$$

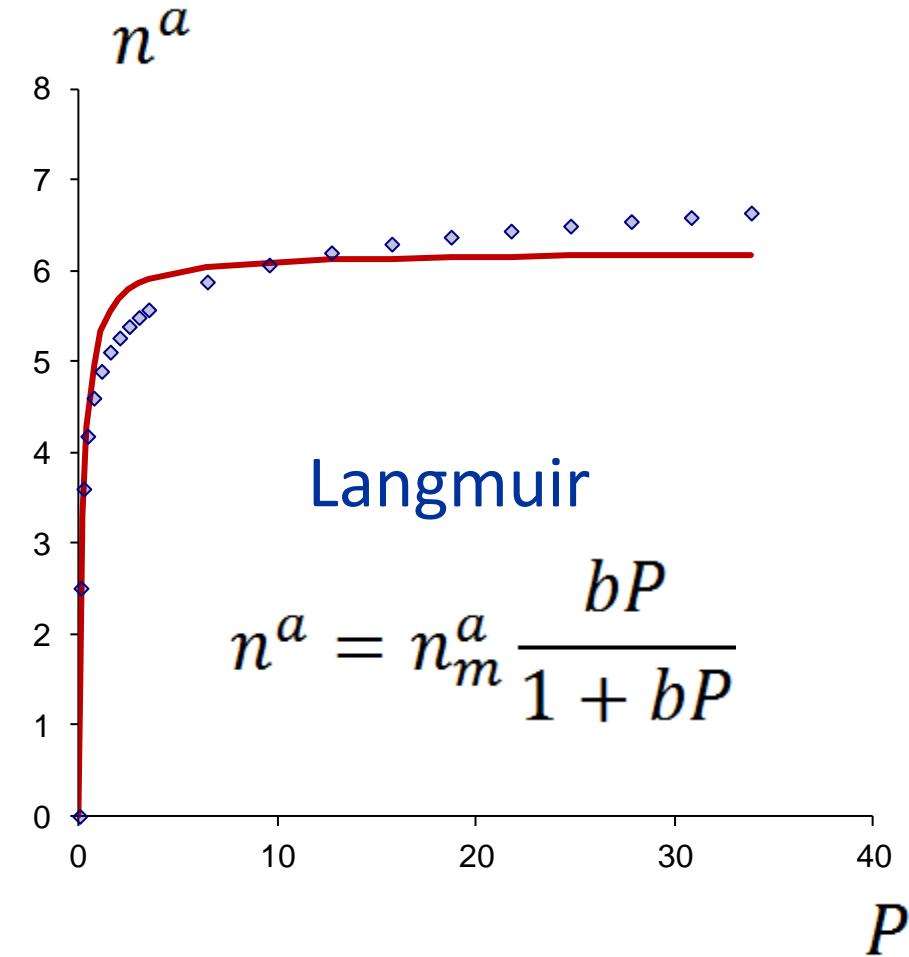
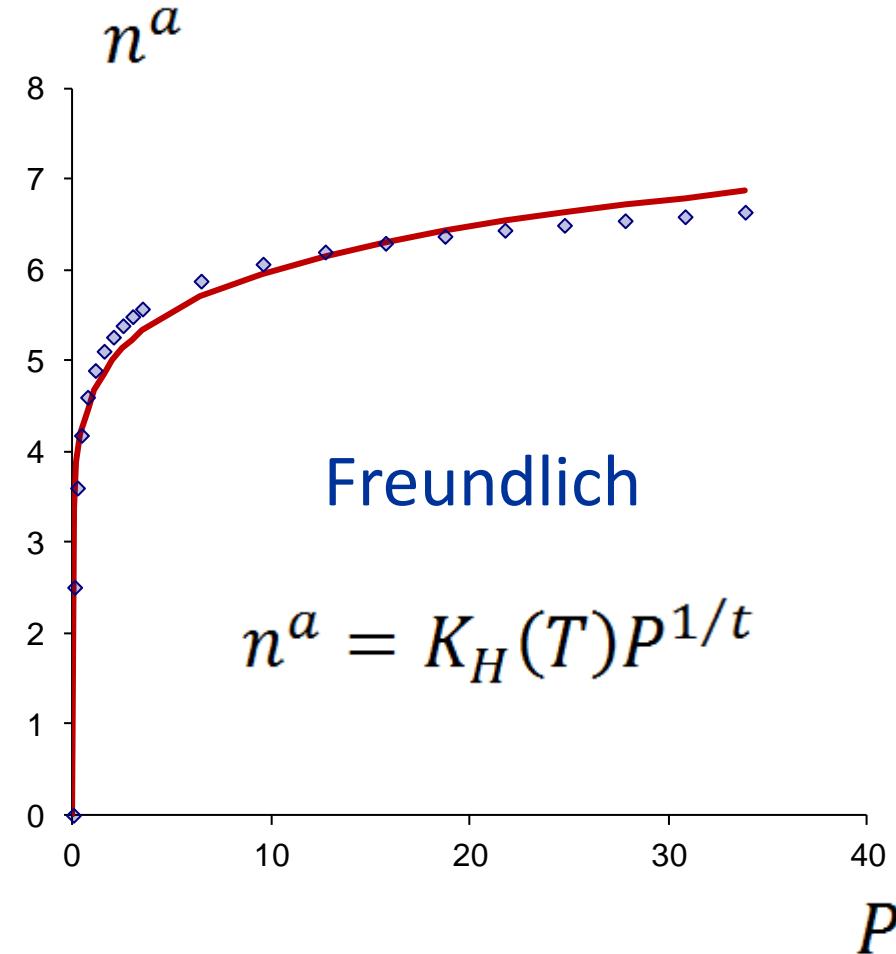
- Extension to describe the plateau:

$$n^a = K_H(T)P^{1/t}$$

- No finite limit at high pressure
- No thermodynamic founding



Single component equations: Comparison



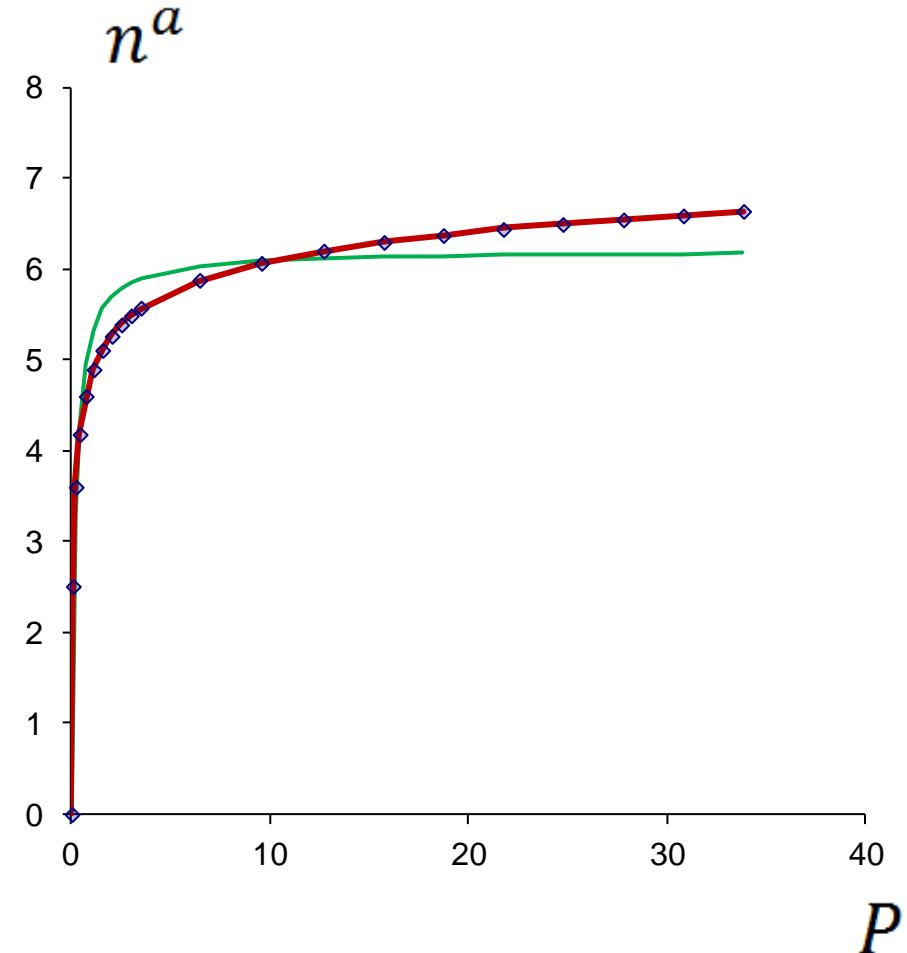
Equations derived from Langmuir

Pure component equations: Multi-site Langmuir equation

- Hypothesis: heterogeneous surface with several distinct types of homogeneous adsorption sites
- One Langmuir equation per type of site:

$$n^a = \sum_i n_{m,i}^a \frac{b_i P}{1 + b_i P}$$

- Often used for crystalline materials such as zeolites and MOFs
- Generally not more than 3 types of sites



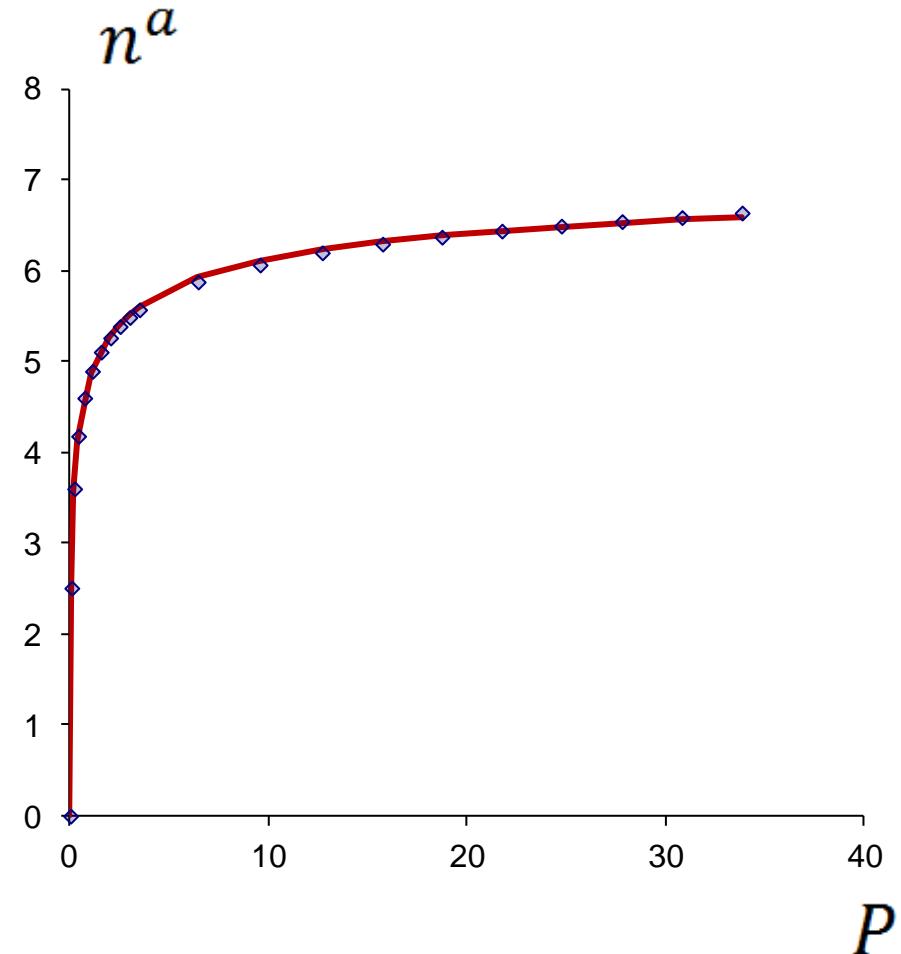
Pure component equations: Toth equation

- Empirical equation:

$$n^a = n_m^a \frac{bP}{(1 + (bP)^t)^{1/t}}$$

- t is a measure of the heterogeneity of the adsorbent surface
- $t \rightarrow 1$ for homogeneous surface
- $t \rightarrow 0$ for heterogeneous surface
- $t = 1 \rightarrow$ Langmuir equation

- Henry's law at low pressure
- Finite limit at high pressure



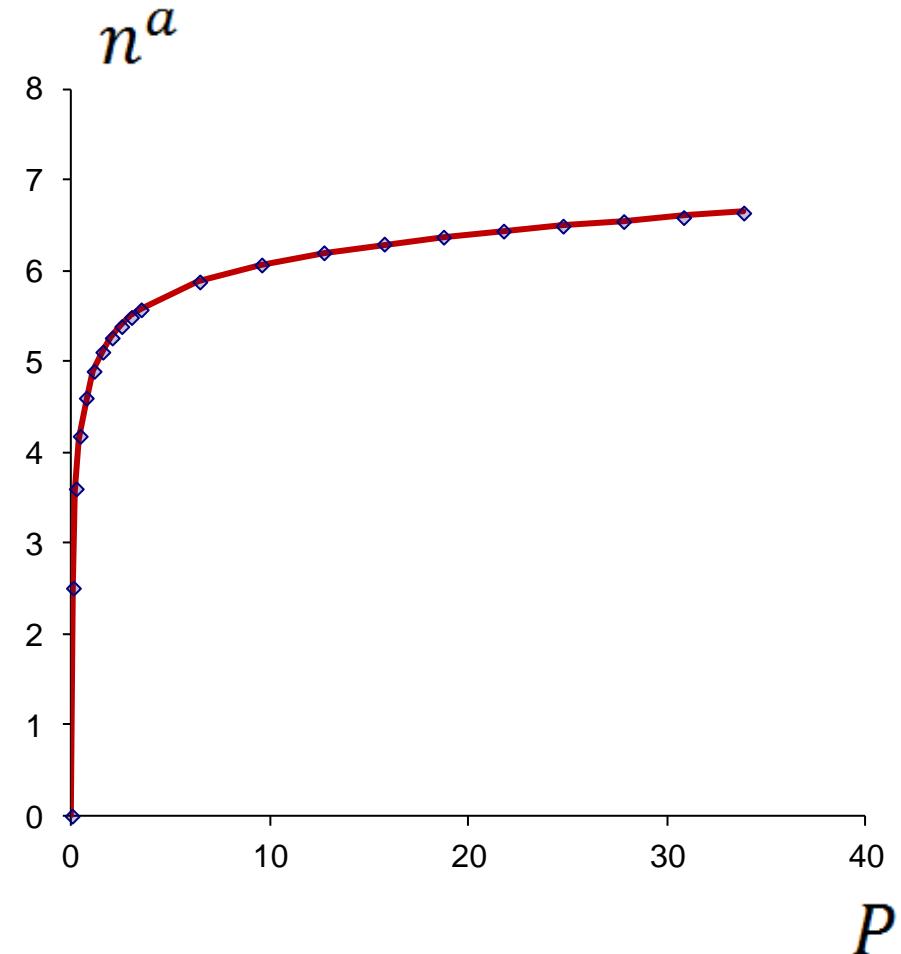
Pure component equations: Jensen – Seaton equation

- Empirical equation:

$$n^a = K_H P \left[1 + \left(\frac{K_H P}{a(1 + \kappa P)} \right)^c \right]^{-1/c}$$

- K_H = Henry's constant
- κ = compressibility of gas phase
- a = saturation capacity
- c = positive empirical constant
- $\kappa = 0 \rightarrow$ Toth equation

- Henry's law at low pressure
 - Not always finite limit at high P



Single component equations: UniLan equation

- Resulting equation:

$$n^a = \frac{n_m^a}{2s} \ln \left(\frac{1 + \bar{b}e^{sP}}{1 + \bar{b}e^{-sP}} \right)$$

with

$$\bar{b} = b_\infty \exp\left(\frac{\bar{E}}{R_g T}\right)$$

$$\bar{E} = \frac{E_{max} + E_{min}}{2}$$

$$s = \frac{E_{max} - E_{min}}{2R_g T}$$

- s is a measure of the heterogeneity of the adsorbent surface
- High values of s characterize a highly heterogeneous system
- $s = 0 \rightarrow$ Langmuir equation

Mixing Langmuir and simple empirical equations

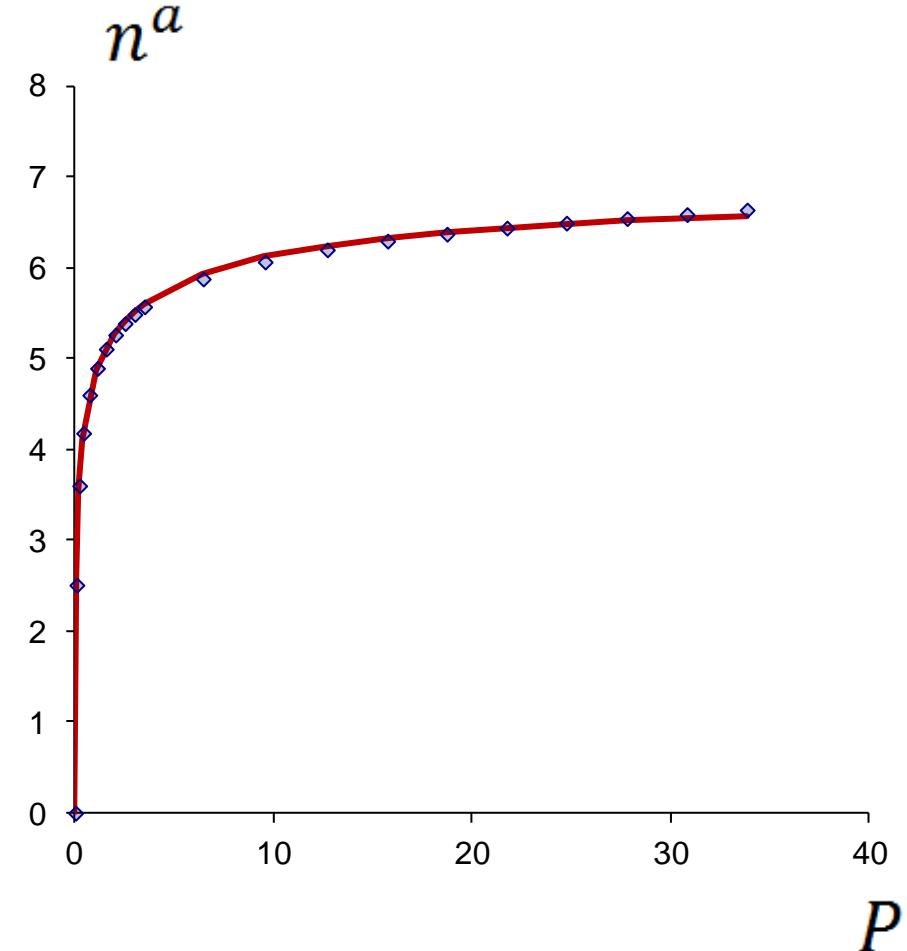
Pure component equations: Langmuir – Freundlich equation (Sips, 1948)

- Empirical equation:

$$n^a = n_m^a \frac{(bP)^{1/n}}{1 + (bP)^{1/n}}$$

- n is a measure of the heterogeneity of the adsorbent surface
- $n = 1 \rightarrow$ Langmuir equation
- Also exists in multi-site form

- No Henry's law at low pressure
- Finite limit at high pressure



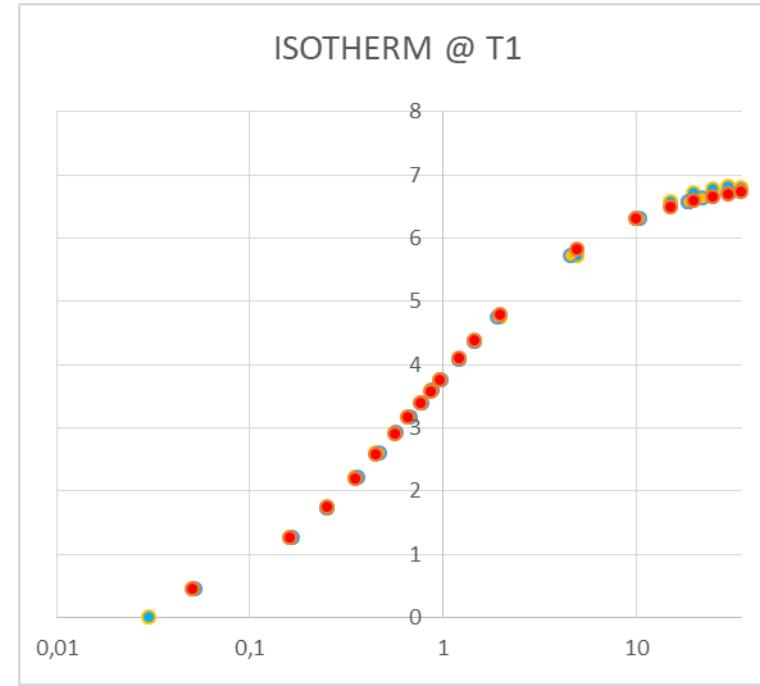
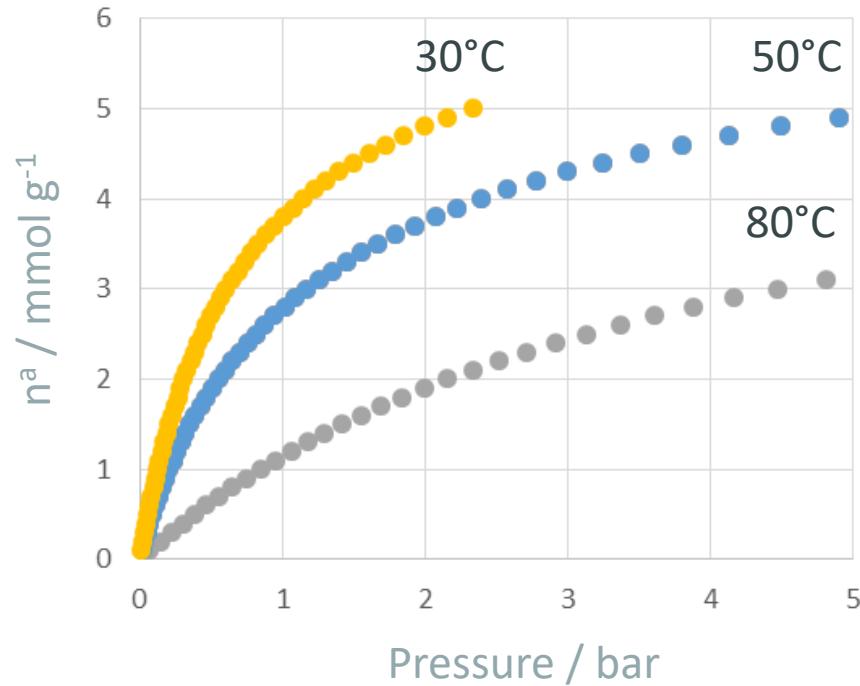
Single component equations: Summary

Model	Equation	Thermodynamically consistent		Henry's constant
		Low pressure	High pressure	
Henry's law	$n^a = K_H(T)P$	✓	✗	K_H
Freundlich	$n^a = K_H(T)P^{1/t}$	✗	✗	-
Langmuir	$n^a = n_m^a \frac{bP}{1 + bP}$	✓	✓	$n_m^a b$
UniLan	$n^a = \frac{n_m^a}{2s} \ln \left(\frac{1 + \bar{b}e^s P}{1 + \bar{b}e^{-s} P} \right)$	✓	✓	
Langmuir – Freundlich (Sips)	$n^a = n_m^a \frac{(bP)^{1/n}}{1 + (bP)^{1/n}}$	✗	✓	-
Toth	$n^a = n_m^a \frac{bP}{(1 + (bP)^t)^{1/t}}$	✓	✓	$n_m^a b$
Jensen – Seaton	$n^a = K_H P \left[1 + \left(\frac{K_H P}{a(1 + \kappa P)} \right)^c \right]^{-1/c}$	✓	✓	K_H

The Virial equation

The Virial approach

$$P(n) = \frac{n}{K_H} \left(\frac{n_m^a}{n_m^a - n} \right) \exp[C_1 n + C_2 n^2 + C_3 n^3 + \dots]$$

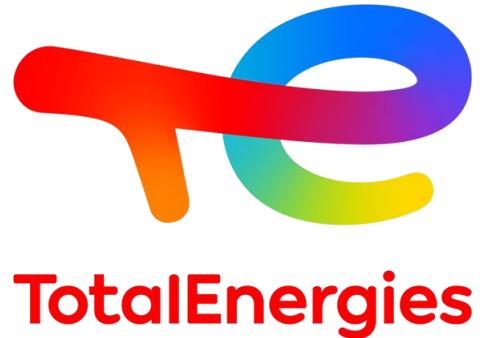


Getting good low-pressure data is important
 The fitting of the experimental data is crucial → and not always trivial

* Alain Myers



→ In the chat, can you write down which of the above equations are most often be used for RT isotherm treatment



What KPI's can we predict ?

- Energies
- Selectivities

Henry



Langmuir

Empirical models

Langmuir-based
extensions

Virial model



What KPI's can we predict ?

Calculations of energies

Adsorption is an exothermic phenomenon

- Adsorption (physisorption) is spontaneous at all temperatures:
 $\Delta G < 0$, $\Delta S > 0$ and $\Delta H < 0$

The **Van't Hoff relationship** is derived, via :

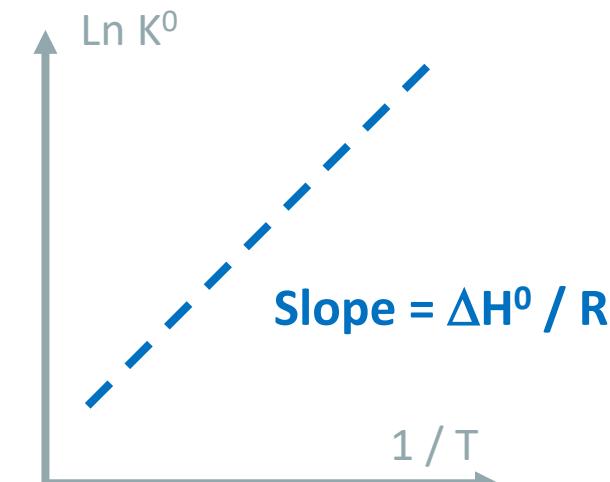
- $\Delta G^0 = \Delta H^0 - T\Delta S^0$
- $\Delta G^0 = -RT \ln K^0$

To give :

- $\ln K^0 = -\frac{\Delta H^0}{RT} + \frac{\Delta S^0}{R}$

Thus, $\Delta_{vap}H^0 = -R \frac{d \ln K^0}{d(1/T)}$

Assume K^0 is approximately equal to p/p°



NB. For the exact relationship $\rightarrow K^0$ is equal to $a_g/a_l = (f/p^\circ)/\Gamma_l$, only approximately equal to p/p°

Van't Hoff plots used in sorption

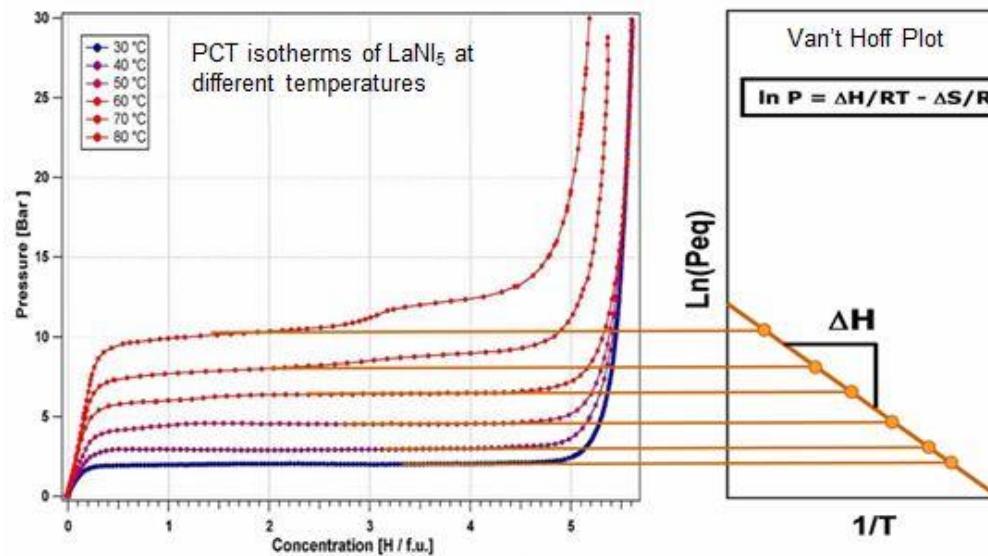
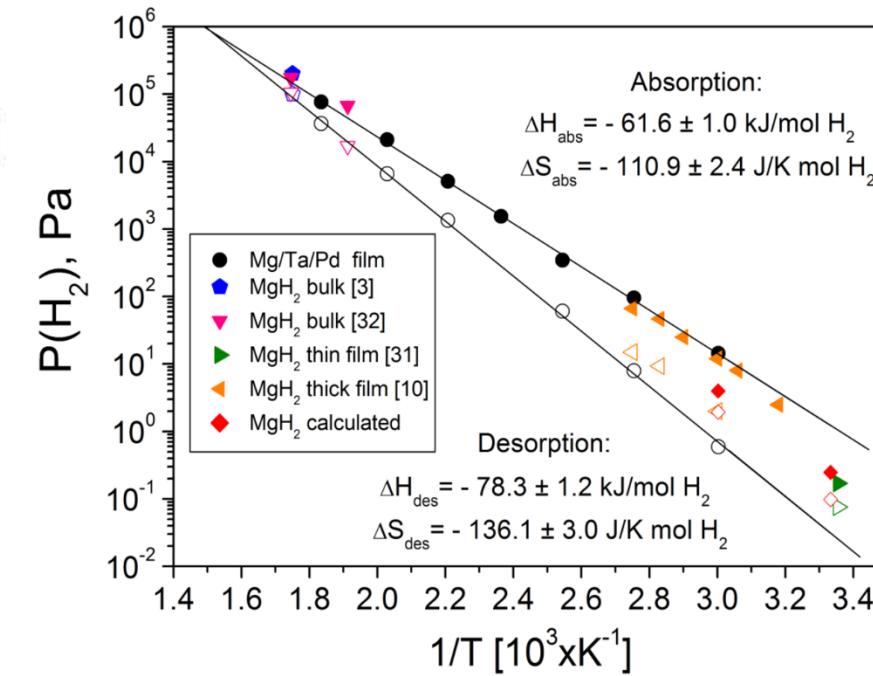


Fig. 1: Classic van't Hoff measurement



Thermodynamic Properties, Hysteresis Behavior and Stress-Strain Analysis of MgH_2 Thin Films,
 Studied over a Wide Temperature Range, Y. Pivak, H. Schreuders, B. Dam, *Crystals*, 2012, 2(2), 710-729

Similar to Van't Hoff → Claussius Calpeyron

- $$\Delta_{vap}H \approx -R \frac{d \ln (p/p^\circ)}{d(1/T)}$$

Derivation assumes $V_m(g) \gg V_m(l)$

Ideal-gas behavior

Reversible sorption behavior

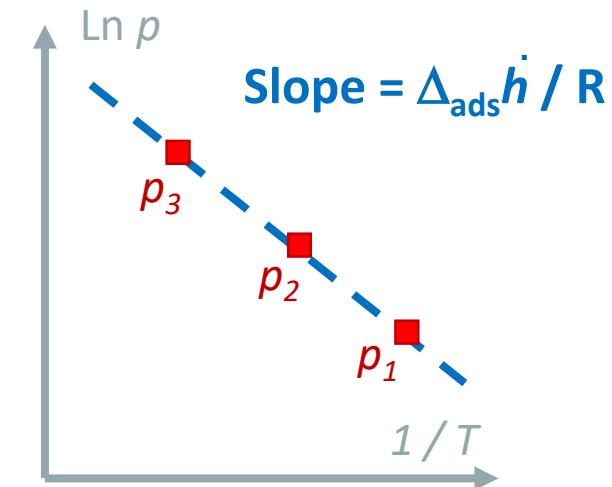
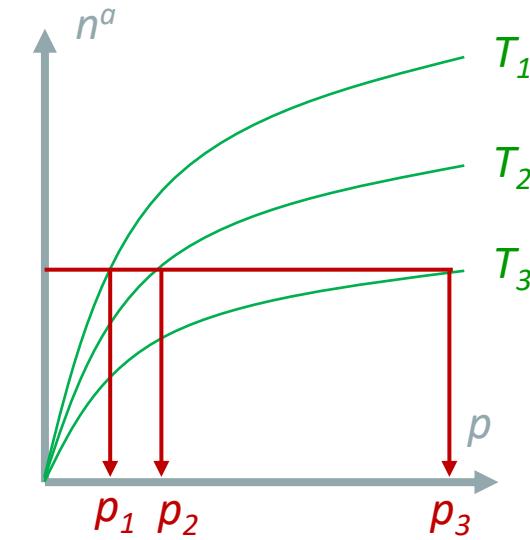
'Valid' for 'small' temperature differences

$\Delta_{vap}H$ is the difference of the molar enthalpies of the real gas and the liquid at the saturation vapour pressure of the liquid

We use:

- $$\ln \frac{p_1}{p_2} = -\frac{\Delta_{ads}\dot{h}}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]_n$$

$$\Delta_{ads}\dot{h} = -R \cdot \frac{T_1 \cdot T_2}{T_2 - T_1} \cdot \ln \left[\frac{p_2}{p_1} \right]_{n^\sigma / m^s}$$



The Virial Method

- $q_{st}(n_{exp}) = R(-\ln p_{exp}) + g(n_{exp}) + \ln n_{exp}$

At first, the adsorption data are fitted using the virial-type equation:

$$\ln p = \ln N + \left(\frac{1}{T}\right) \sum_{i=0}^m a_i N^i + \sum_j b_j N^j \quad (E3)$$

Here p is the pressure expressed in Torr, N is the amount adsorbed in mmol/g, T is the temperature in K, a_i and b_i are virial coefficients, and m , n represent the number of coefficients required to adequately describe the isotherms. Then the Clausius–Clapeyron equation (E1) was employed to calculate the enthalpies of CO₂ adsorption. Combining equations (E1) and (E3), the isosteric heat of adsorption can be calculated using the following equation:

$$Q_{st} = -R \sum_{i=0}^m a_i N^i \quad (E4)$$

* Mietek Jaroniek



Frederic Villieras
Nancy

Combining various equations to fully model the isotherm



Christelle Miqueu



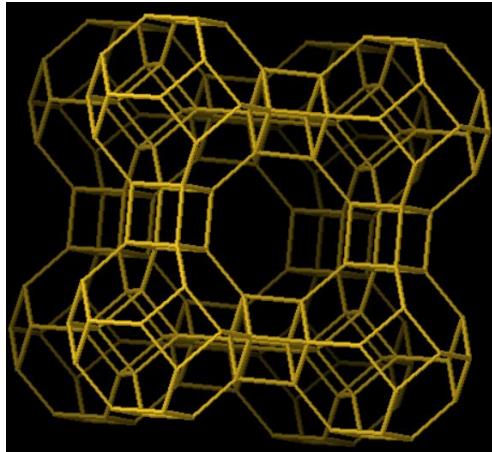
Frédéric Plantier



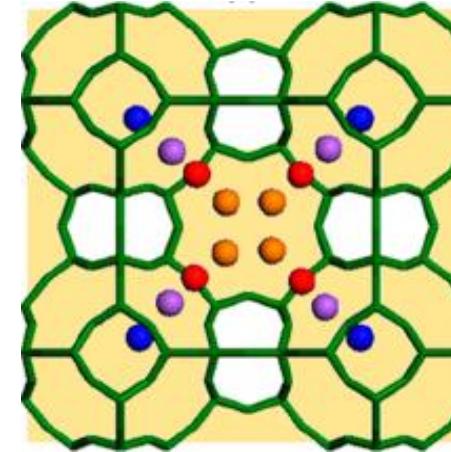
Alejandro Orsikowsky

Mécanismes d'adsorption

➤ Exemple sur la zéolithe 5A



Source : IZA database



Source : Martin-Calvo et al., 2014

Mécanisme d'adsorption du CO₂

Adsorption sur sites I

Adsorption sur sites II

Adsorption sur sites III

Remplissage des pores

Basse pression

Haute pression

Mécanisme d'adsorption de l'azote et du CH₄

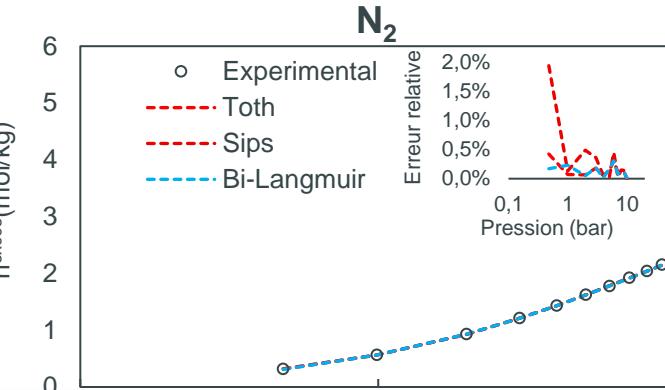
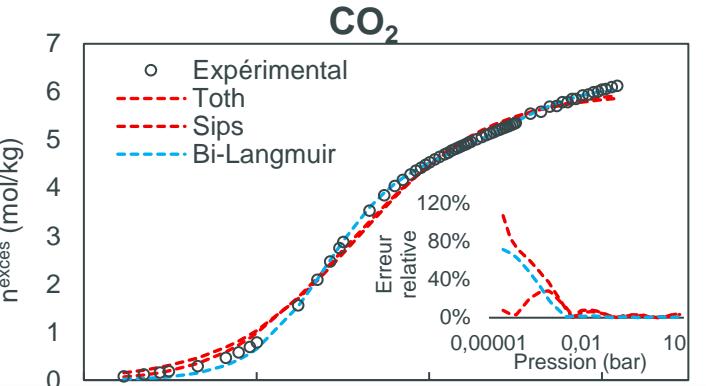
Basse pression

Remplissage des pores

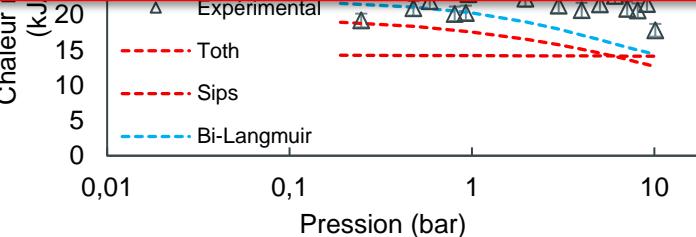
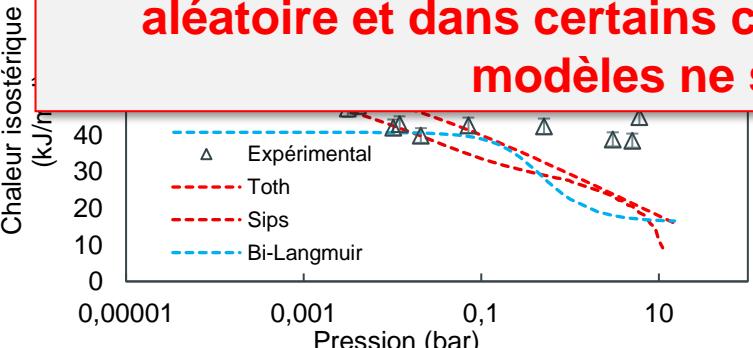
Haute pression

Evaluation des modèles macroscopiques classiques – Toth, Sips et bi-Langmuir

Modèle	Equation	Chaleur isostérique	Type d'approche
BI-LANGMUIR	$q_{ads} = \frac{q_{m1}b_1P}{1+b_1P} + \frac{q_{m2}b_2P}{1+b_2P}$	$(-\Delta H)_1 = Q_1; (-\Delta H)_2 = Q_2$	Cinétique thermodynamique
TOTH	$q_{ads} = \frac{q_m b P}{[1 + (b P)^t]^{1/t}}$	$(-\Delta H) = Q - \frac{1}{t}(\alpha R_g T_0) \left\{ \ln(bP) - [1 + (bP)^t] \ln \left[\frac{bP}{(1 + (bP)^t)^{1/t}} \right] \right\}$	Semi - empirique
SIPS	$q_{ads} = \frac{q_m (bP)^{1/n}}{1 + (bP)^{1/n}}$	$(-\Delta H) = Q - (\alpha R_g T_0) n \ln(bP)$	Semi - empirique



L'évolution des différents paramètres avec la température est très aléatoire et dans certains cas les expressions théoriques des modèles ne sont pas respectées



➤ Adsorption sur site : approche thermodynamique

Equation de Gibbs

$$\left(\frac{d\pi}{d\ln P} \right) = \frac{n}{A} RT$$

π : pression d'étalement

Equation d'état type van der Waals

$$\pi\sigma = RT \frac{\sigma}{\sigma_0} \ln\left(\frac{\sigma}{\sigma - \sigma_0}\right) - \frac{c w}{2} \frac{\sigma_0}{\sigma}$$

$$bP = \frac{\theta}{1-\theta} e^{(-c\theta)}$$

Paramètres

$b \rightarrow$ constante d'affinité

$$b = b_0 e^{\left(\frac{Q}{RT}\right)}$$

$c \rightarrow$ Interactions entre les molécules

$$c = \frac{zw\left(\frac{1}{T}\right)}{RT}$$

< 0 : répulsion
> 0 : attraction

Combinaison de ces deux modèles pour décrire les mécanismes d'adsorption identifiés au niveau microscopique

➤ Remplissage de pores : théorie du *pore filling*

$$\theta = f\left(\frac{A}{E}, n\right)$$

A : potentiel d'adsorption

Forme de distribution de Weibull

$$f\left(\frac{A}{E}, n\right) = e^{-\left[\left(\frac{A}{E}\right)^n\right]}$$

$$\frac{q_e}{q_m} = e^{-\left[\left(\frac{A}{E}\right)^2\right]}$$

Equation de Dubinin – Raduskevich (DR)

Paramètres

$P_0 \rightarrow$ Pression de saturation de l'adsorbat

$$P_0 = 10^{A - \frac{B}{C+T}}$$

Equation d'Antoine

$E \rightarrow$ Energie caractéristique

$q_m \rightarrow$ Capacité à saturation

$$q_m = q_0 \exp(-\gamma(T - T_0))$$

Expansion thermique de la phase adsorbée

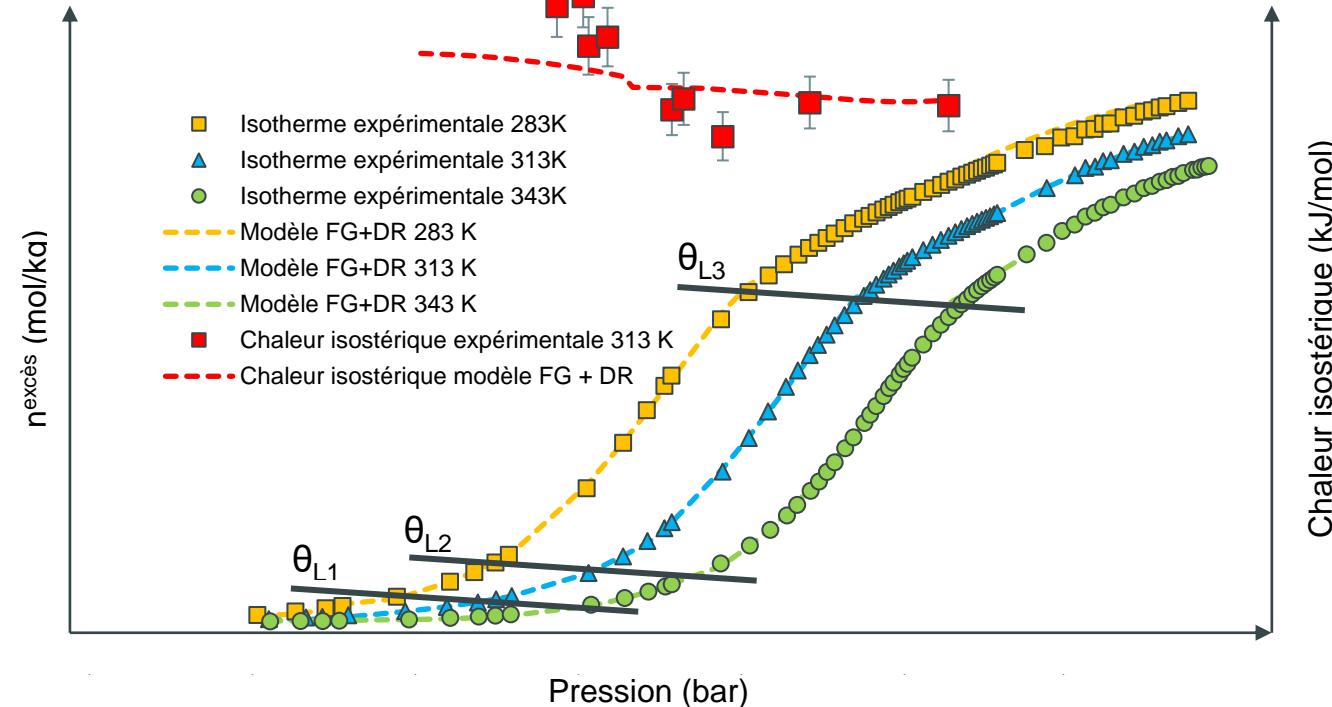
Nouvelle méthodologie – exemple de l'adsorption du CO₂ sur la zéolithe 5A

Sites I $\theta < \theta_{L_1}$ $b_1 P = \frac{\theta}{1-\theta} e^{(-c_1 \theta)}$ FG1

Sites III $\theta_{L_2} < \theta < \theta_{L_3}$ $b_3 P = \frac{\theta}{1-\theta} e^{(-c_3 \theta)}$ FG3

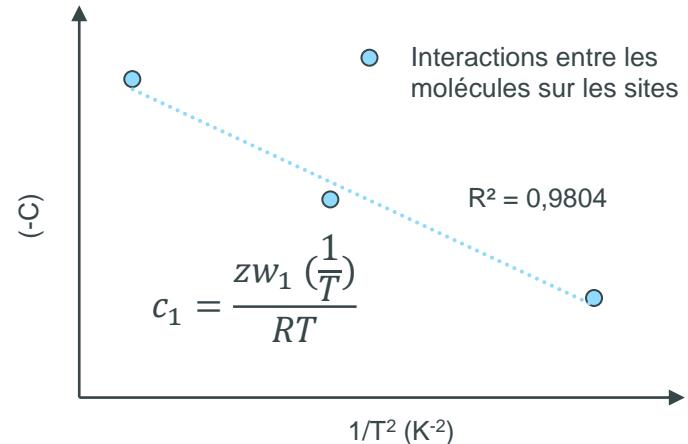
Sites II $\theta_{L_1} < \theta < \theta_{L_2}$ $b_2 P = \frac{\theta}{1-\theta} e^{(-c_2 \theta)}$ FG2

Remplissage de pores $\theta_{L_3} > \theta$ $\frac{qe}{qm} = e^{-\left(\frac{(A)}{E}\right)^2}$ DR

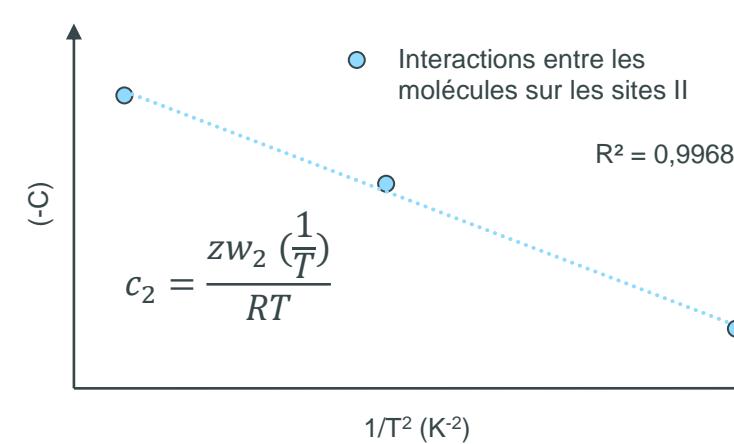


Nouvelle méthodologie – exemple de l'adsorption du CO₂ sur la zéolithe 5A

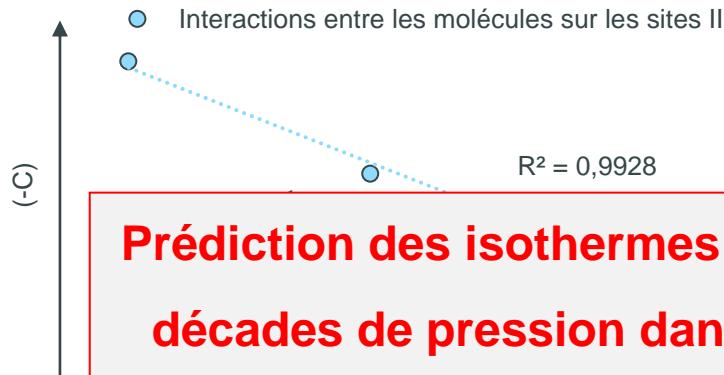
Si $\theta < \theta_{L_1}$ → interactions avec les sites I



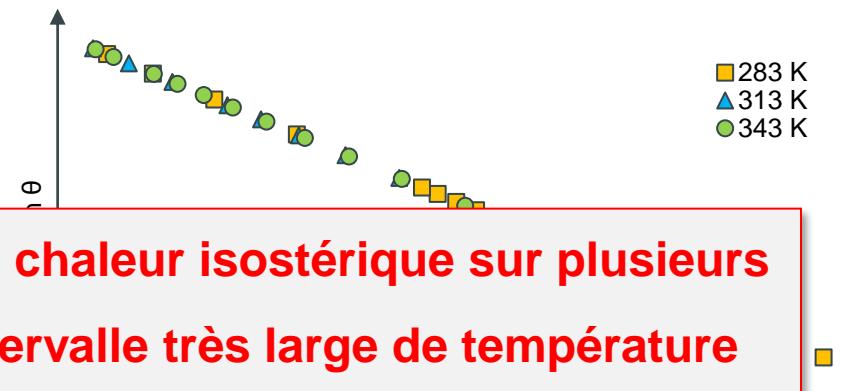
Si $\theta_{L_1} < \theta < \theta_{L_2}$ → interactions avec les sites II



Si $\theta_{L_2} < \theta < \theta_{L_3}$ → interactions avec les sites III



Si $\theta > \theta_{L_3}$ → Remplissage de pores



Prédiction des isothermes et de la chaleur isostérique sur plusieurs décades de pression dans un intervalle très large de température ($\Delta T = 70^\circ\text{C}$) à partir de la mesure de seulement deux isothermes

Calculations of selectivities

Extended Langmuir and related models to predict coadsorption behaviour

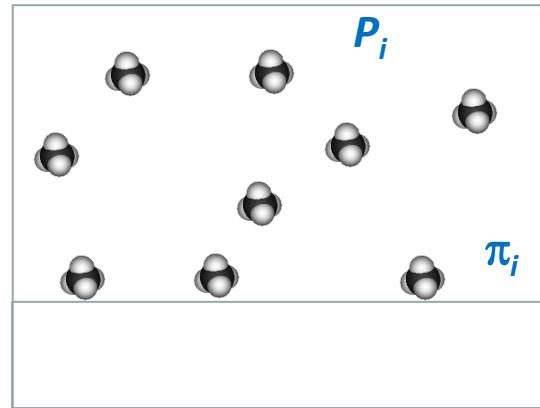


- Heterogeneous Extended Langmuir (Kapoor et al, 1990)
 - takes into account heterogeneity in adsorption sites through energy distribution (UniLan parameters)
- Multi-Region Extended Langmuir (Bai and Yang, 2001)
 - takes into account differences in saturation capacities
- Multi-Region Heterogeneous Extended Langmuir (Bai and Yang, 2002) ...

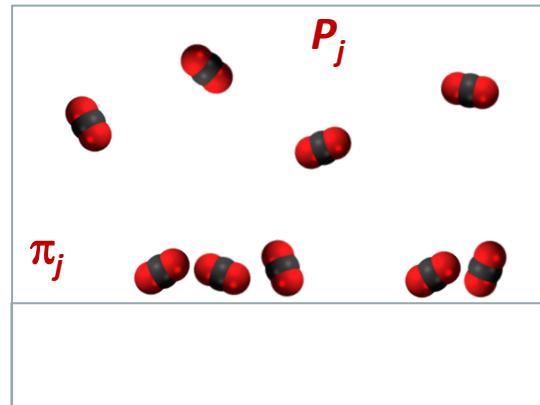
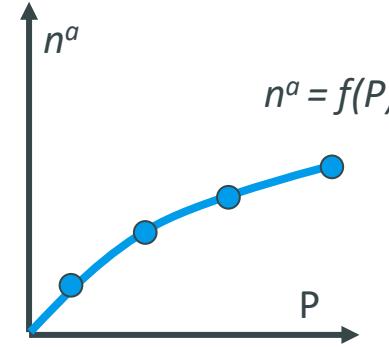
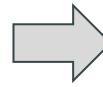
Models for predicting co-adsorption behaviour

Ideal Adsorbed Solution Theory

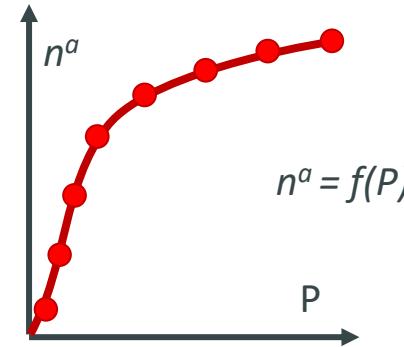
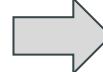
IAST avec les mains (i) chaque gaz est en équilibre avec la surface



Equilibrium gas i

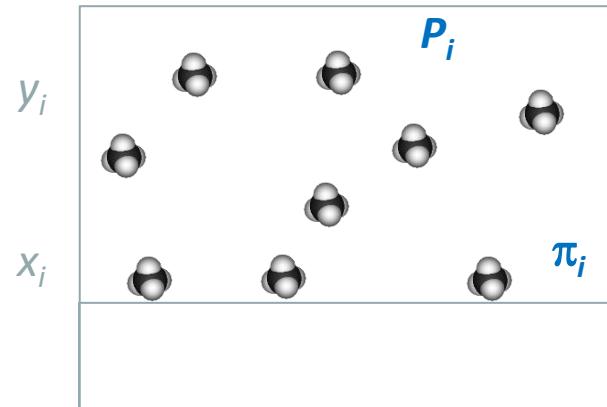


Equilibrium gas j

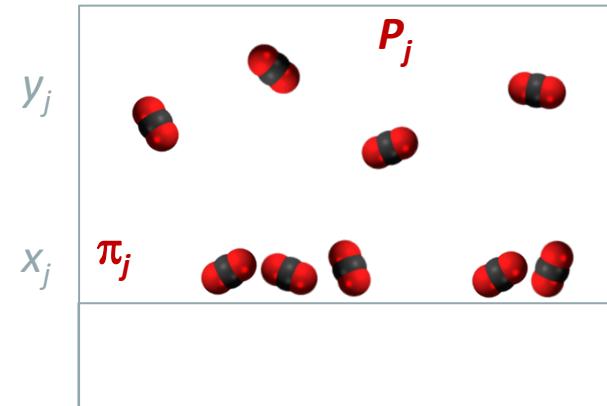


We can fit the single gas isotherms easily

IAST avec les mains (ii) les deux gaz s'adsorbent sans interactions g-g



Equilibrium gas i



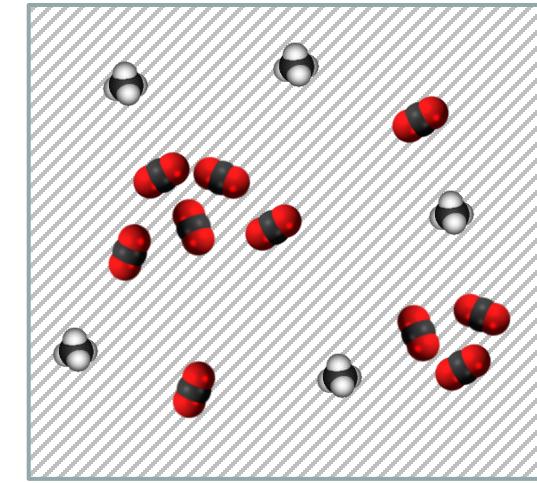
Equilibrium gas j

y : molecules in gas phase
 x : molecules in adsorbed phase

$$P_i \propto y_i P_T$$

Partial pressure of species “ i ”
is related to the total
pressure in the mixture

$$P_j \propto y_j P_T$$

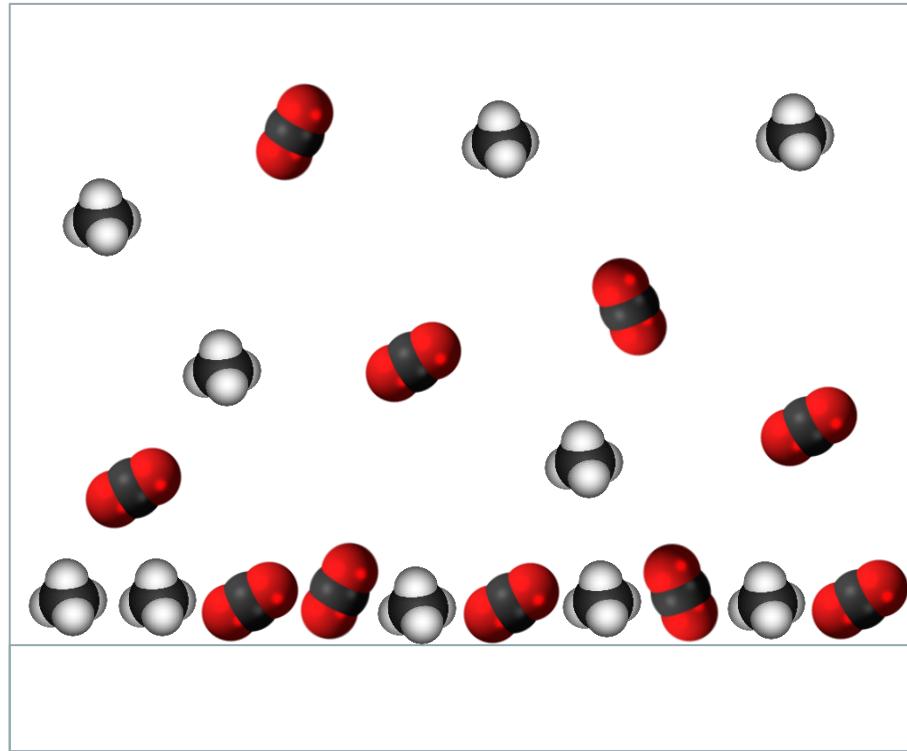


Liquid film

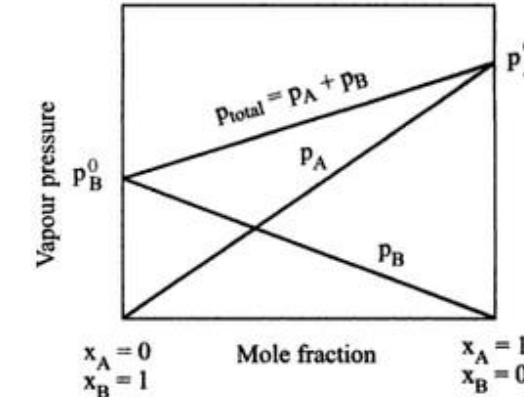
No mixing interactions
(i.e. an ideal mixture)

$$\pi_{\text{tot}} = \pi_i = \pi_j \dots$$

IAST avec les mains (iii) on assume la 'loi de Raoult' → idéalité

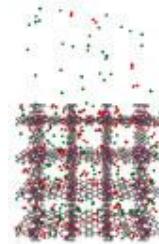


Raoult's law for vapour-liquid equilibria **TotalEnergies**



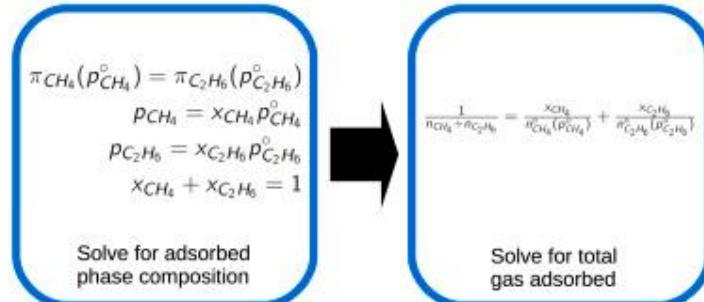
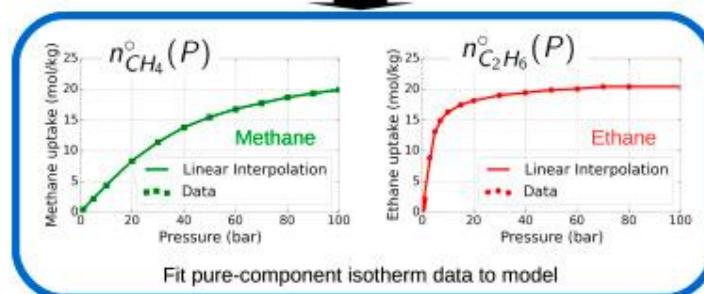
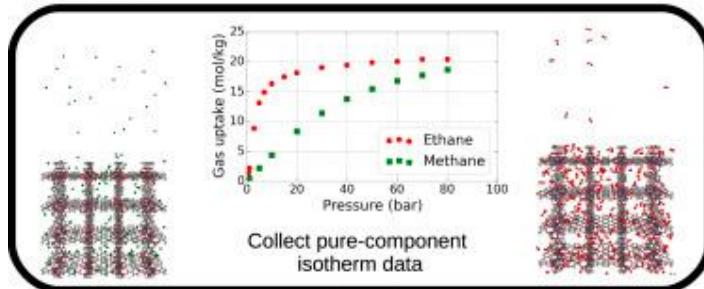
Ideal solution

- Liquid film on surface → no lateral interactions
 - Vapour equilibrium follows Raoult's law
 - $\pi_{tot} = \pi_i = \pi_j \dots$
 - Relation $\pi A = nRT$
 - Relation p°_i & π_i (spreading pressure)
 - n^a , from single component isotherm
- ➡ **Solution non-trivial → iteration required**

$p_{CH_4}, p_{C_2H_6}$


Goal: predict a mixed gas adsorption isotherm

Example: methane/ethane in IRMOF-1



IAST, les calculs

**pyIAST: Ideal adsorbed solution theory (IAST)
Python package**

Cory M. Simon, Berend Smit, Maciej Haranczyk
Computer Physics Communications
Volume 200, March 2016, Pages 364–380

Predicting co-adsorption behaviour: IAST pros and cons



- Advantages
 - It can be used in conjunction with any single component isotherm (Langmuir, Toth, Langmuir – Freundlich, Jensen – Seaton, multi-site Langmuir ...)
 - Is purely predictive: no mixture data required
- Disadvantages
 - Assumes ideal solution → cannot predict azeotropic behaviour
 - Can be computationally heavy depending on single component equation used

Predicting co-adsorption behaviour: Summary



Model	Pure gas equation	Adsorbent	Adsorbed phase	Solution	Specific data required
EL	Langmuir	homogeneous	ideal	explicit	
MR-EL	Langmuir	homogeneous	ideal	explicit	
HEL	UniLan	heterogeneous	ideal	explicit	Pure isotherms at 2 temperatures
MR-HEL	UniLan	heterogeneous	ideal	explicit	Pure isotherms at 2 temperatures
IAST	Any*	homogeneous	ideal	iteration	
HIAST	UniLan	heterogeneous	ideal	iteration	Pure isotherms at 2 temperatures
RAST	Any*	homogeneous	real	iteration	Binary mixture data
VST	VST	heterogeneous	real	iteration	Binary mixture data

* Must be thermodynamically consistent

Practical considerations when fitting isotherms

Practical considerations:

Importance of single component data

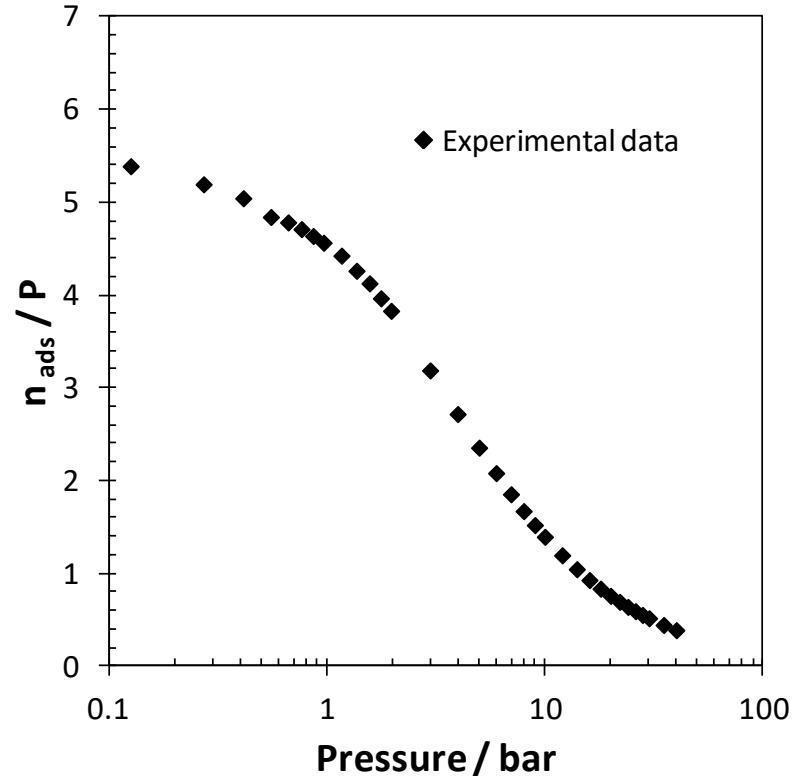
- Detailed low pressure data:

$$\frac{A\pi}{R_g T} = \int_0^{P_i^0} \frac{n_i^a}{P_i} dP_i$$

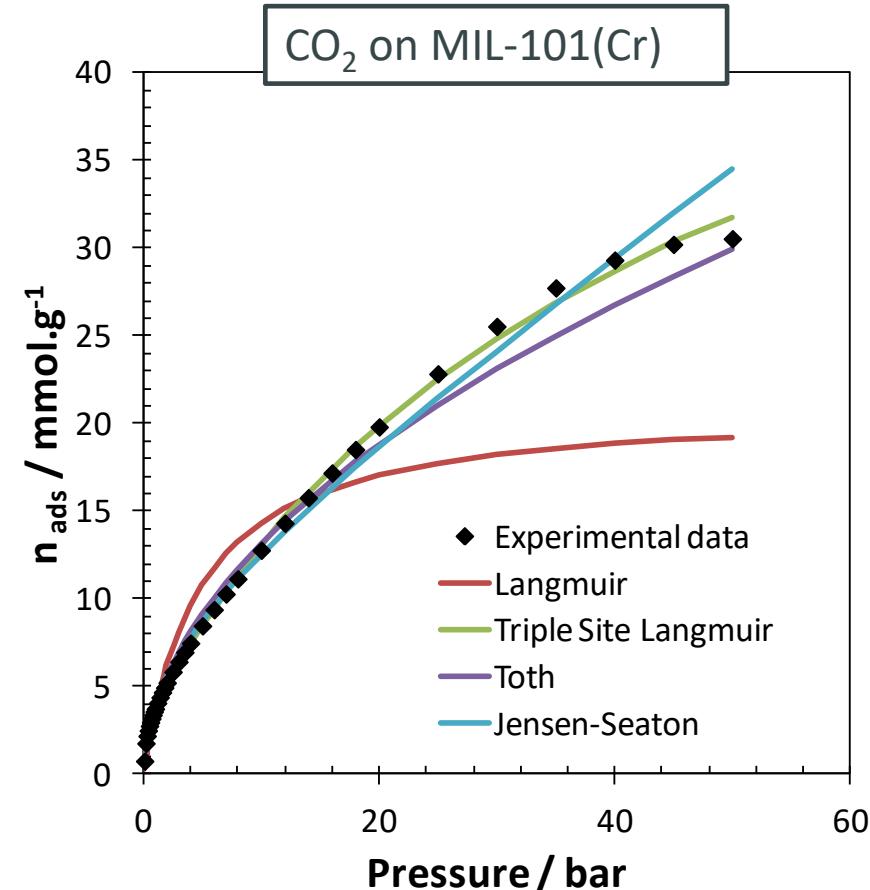
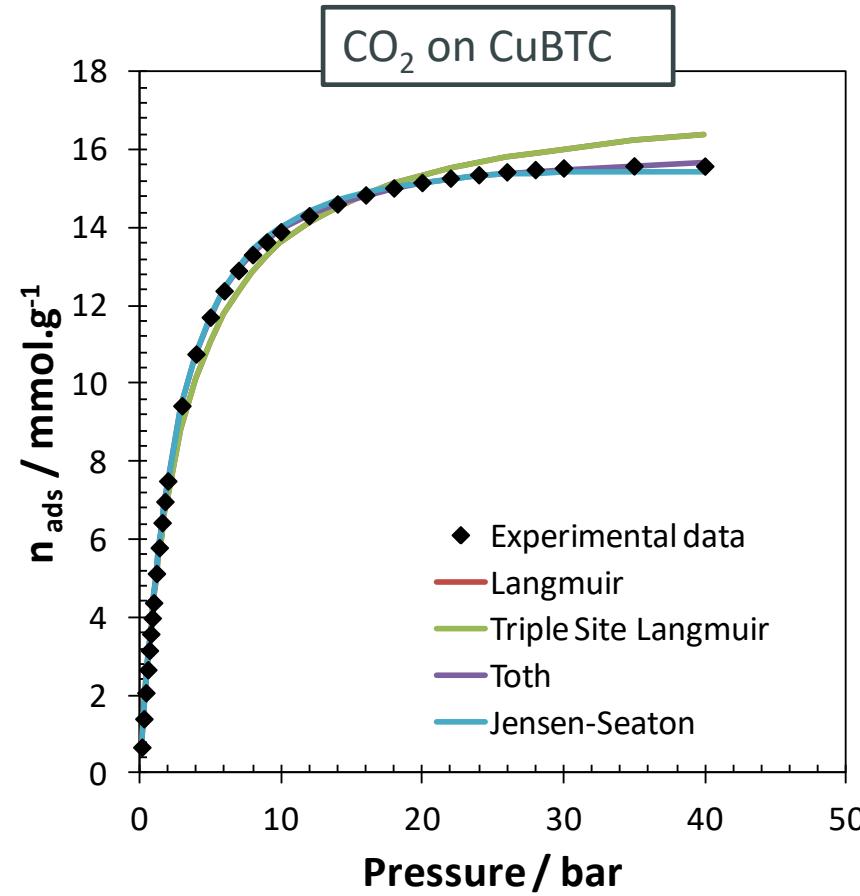
- Experimental data to high pressure

$$n_i^{a,0} = f(P_i^0)$$

- $P_i^0 < P_{system}$ for most adsorbed component
- $P_i^0 > P_{system}$ for least adsorbed component



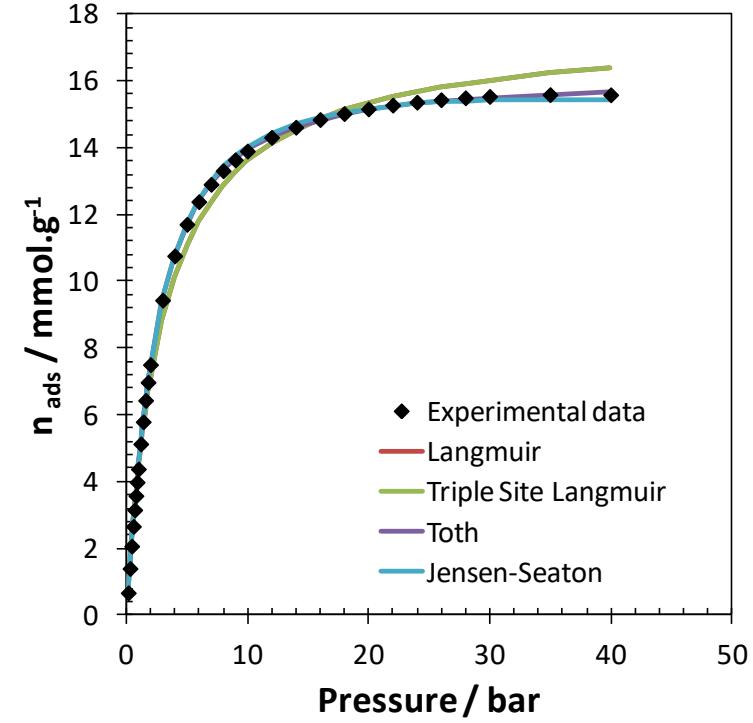
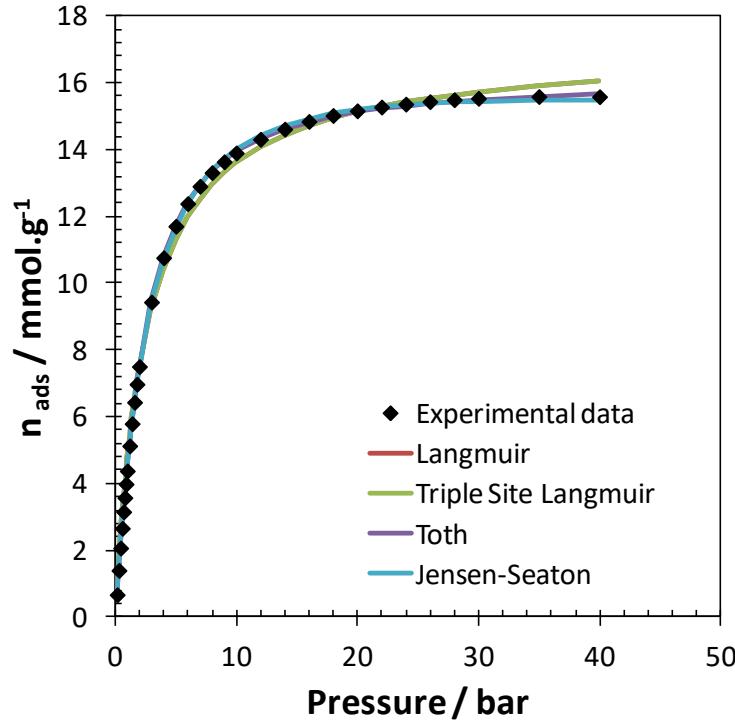
Practical considerations: Choice of single component model



- Choice of model depends on shape of isotherm

Practical considerations:

Method for fitting single component data

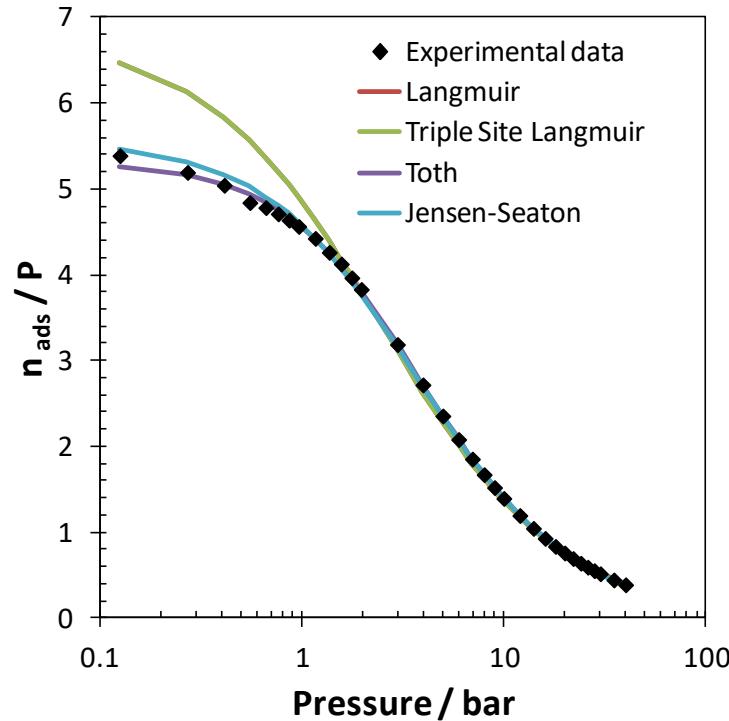


$$f = \sum_i (n_{ads,i}^{exp} - n_{ads,i}^{calc})^2$$

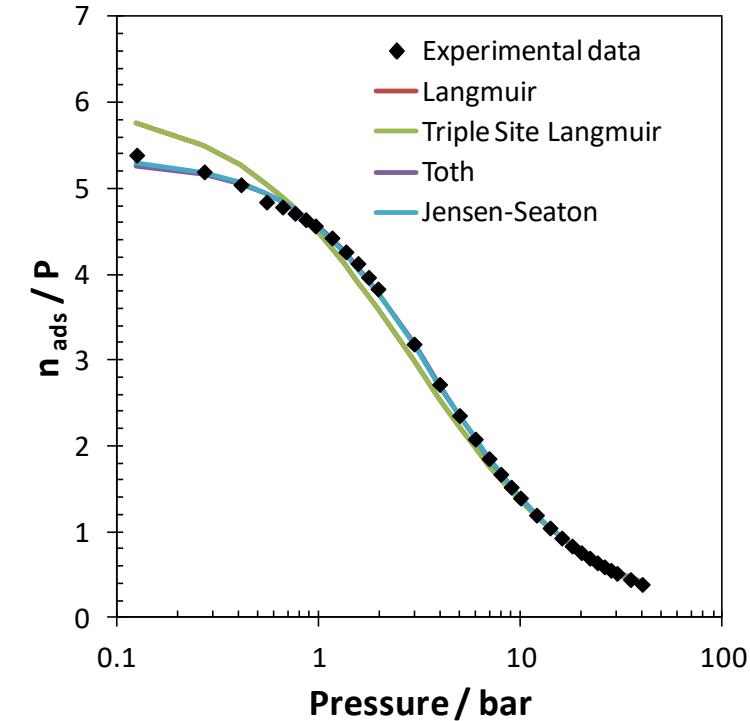
$$f = \sum_i \left(\frac{n_{ads,i}^{exp} - n_{ads,i}^{calc}}{n_{ads,i}^{exp}} \right)^2$$

Practical considerations:

Method for fitting single component data

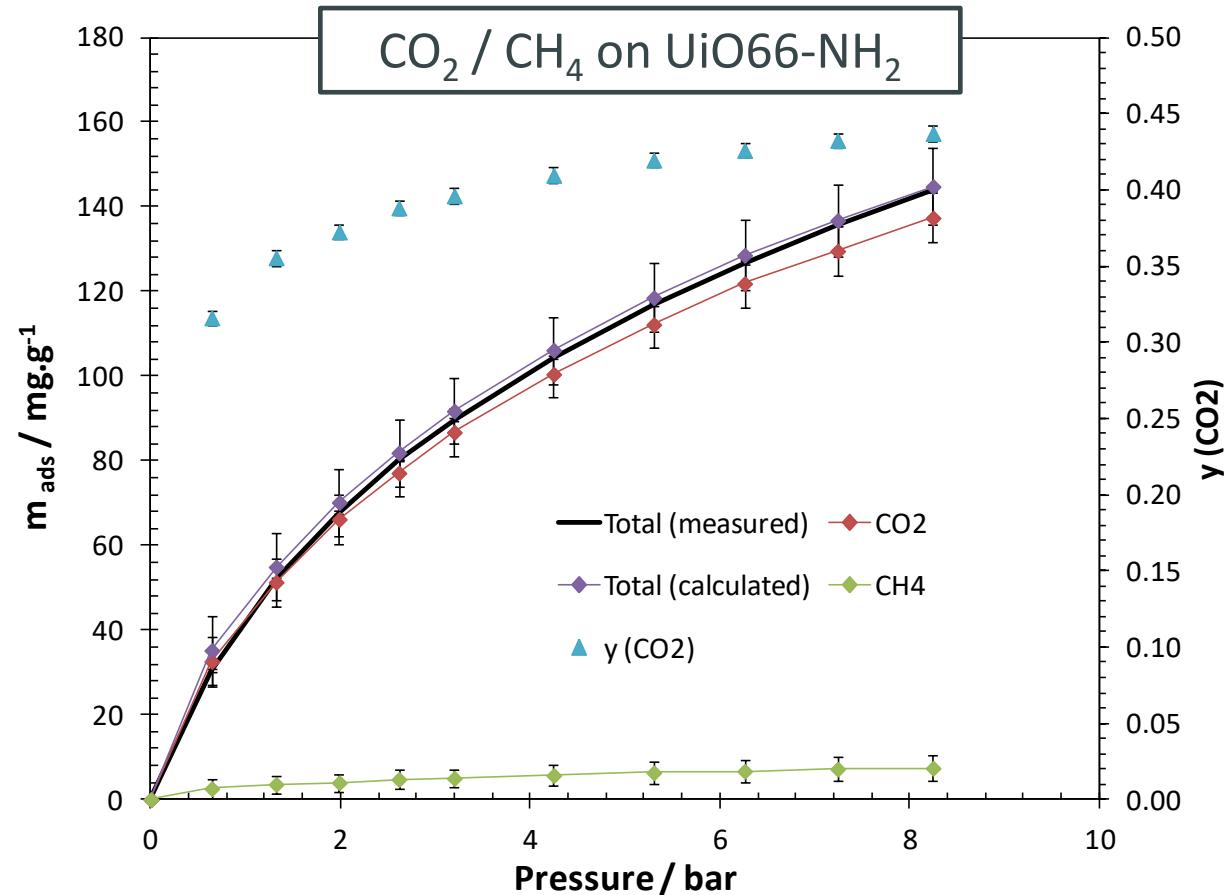


$$f = \sum_i (n_{ads,i}^{exp} - n_{ads,i}^{calc})^2$$



$$f = \sum_i \left(\frac{n_{ads,i}^{exp} - n_{ads,i}^{calc}}{n_{ads,i}^{exp}} \right)^2$$

Practical considerations: Verification with experimental data



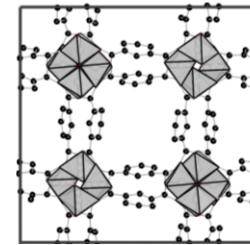
- Mixture adsorption data used for verification must be reliable!!

Screening of Isostructural MOFs

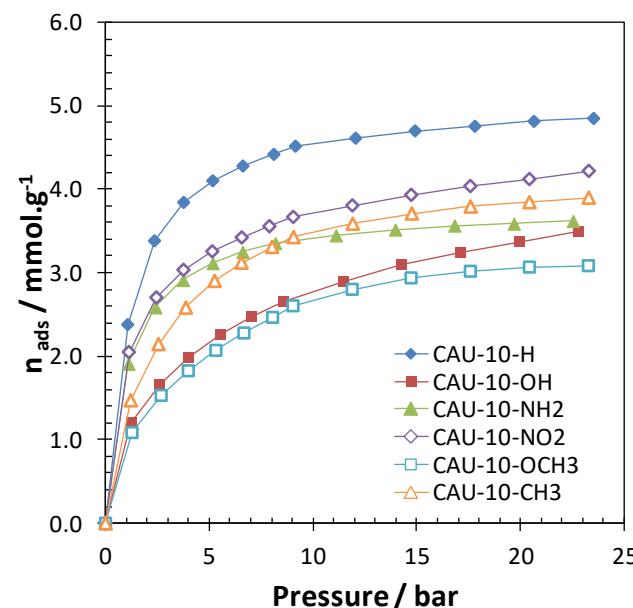


Effect of functionalization:

CAU-10-X



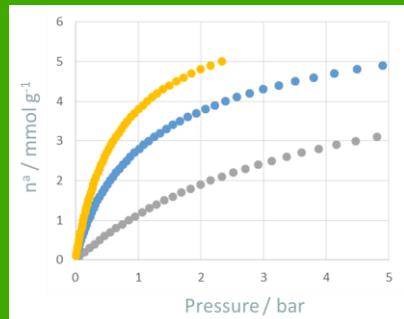
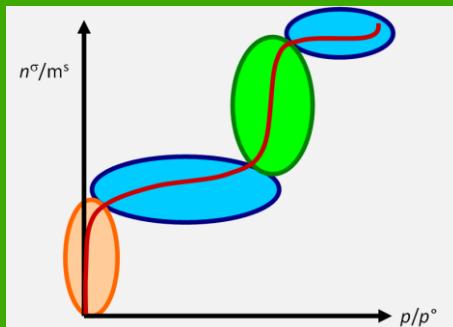
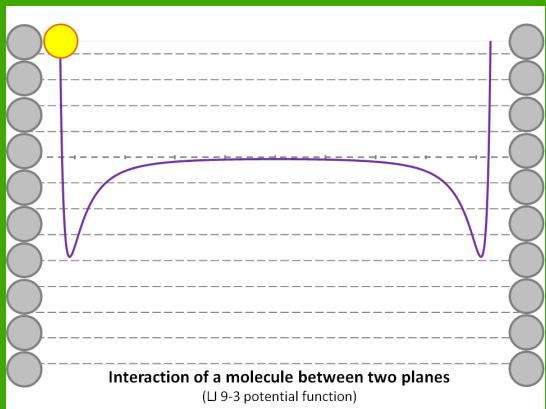
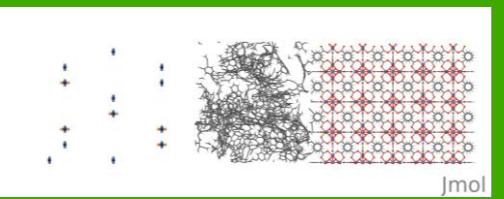
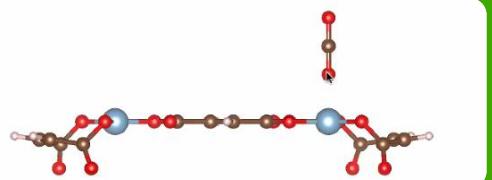
Channels: ~7 Å
Openings: < 4 Å
X = H, OH, NH₂,
NO₂, OCH₃, CH₃



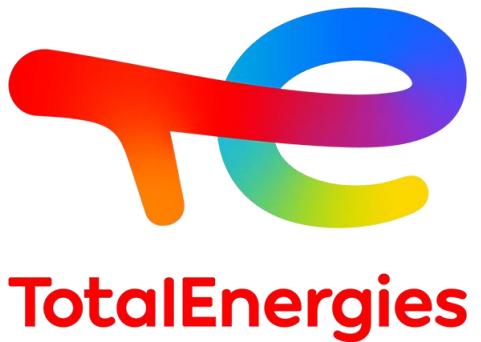
Material	CAU-10-H	CAU-10-NO ₂	CAU-10-OH	CAU-10-NH ₂	CAU-10-OCH ₃	CAU-10-CH ₃
CO ₂ / CH ₄ (50/50) Selectivity (IAST (1 & 5 bar))	5 - 6	10 - 14	5 - 7	3,5	2 - 4	3 – 3.5

→ -NO₂ increases the selectivity towards CO₂

A. D. Wiersum, et al., ACS Comb. Sci., 15(2), 2013, 111-119.

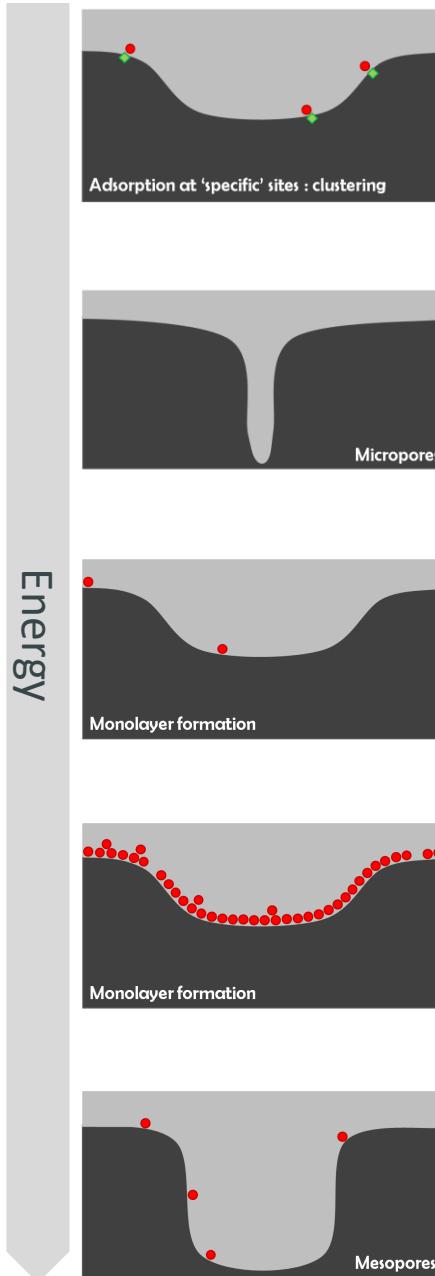


Lessons learned



Adsorbent characterization KPI : surface area, pore size

Henry
↓
Langmuir
↓
BET
↓
Harkins & Jura / FHH
↓
Kelvin
↓
Polyani/Dubinin
↓
Horwath-Kawazoe



“Process” evaluation KPI : enthalpies, selectivities

Langmuir-derived
expressions

Virial

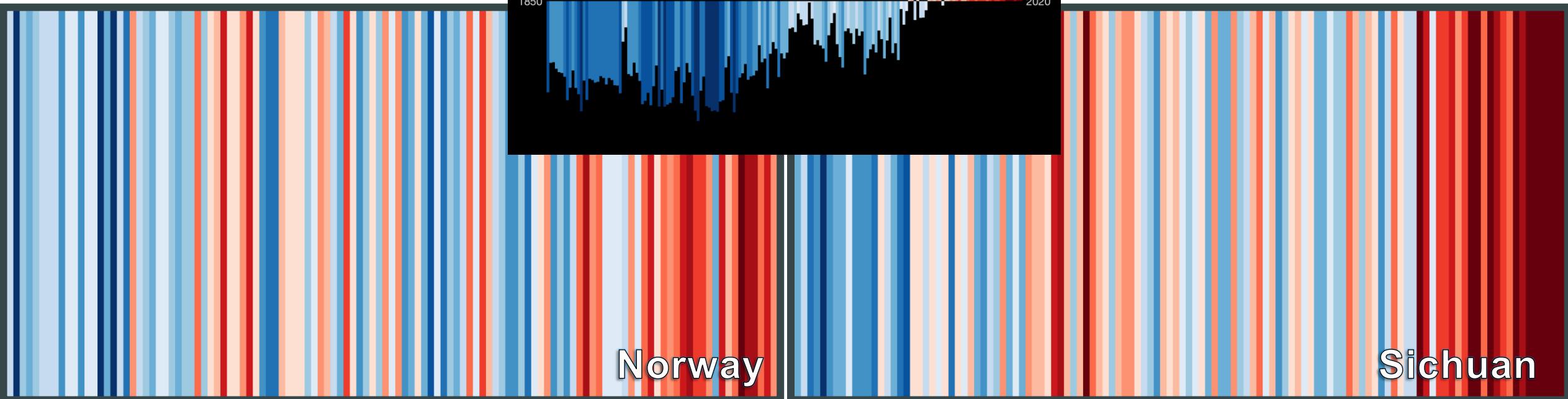
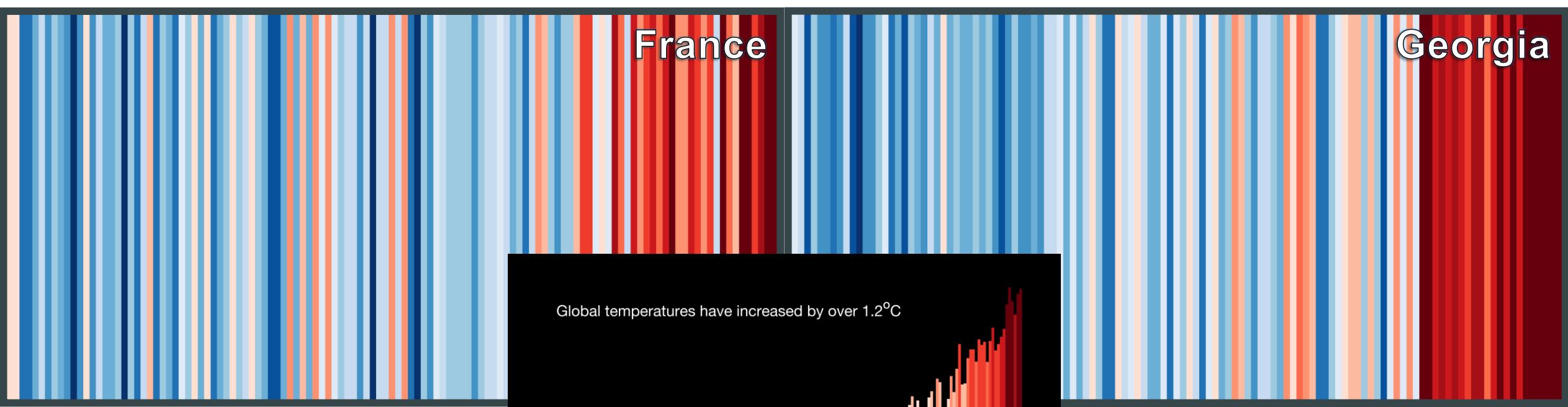
Empirical
expressions



Energy
Clausuis
Clapeyron
Virial



Selectivity
IAST
(or other
selectivity
calculations)



Thank you for your attention & stay safe

<https://showyourstripes.info/>