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Investigation of Mixed Gas Sorption in Lab-Scale

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Technical Necessity:



Application of porous Materials as Adsorbents

Fine cleaning of Gases (i.e. purification of H_2 , natural gas, bio methane...)

Waste air treatment, respiratory protection, solvent recovery, removal of pollutants...)

Gas separation (i.e. Air separation...)



Modern and effective materials should have high sorption capacities, high selectivities, and a good kinetic performance.





For such applications, one must consider gas mixtures and their sorption properties in any case.

Characterization of Adsorbents





Characterization of Adsorbents





Why are Textural Properties not enough...?



Textural properties of adsorbents:

- BET-Surface
- Pore Size Distribution
- Micropore Volume





- Textural properties allow only limited qualitative statements regarding:
 - expected sorption capacity (Micropore volume)
 - rough assessment of general sorption properties from pore size distributuion
- Textural properties do not allow quantitative statements regarding:
 - sorption affinity
 - selectivity
 - no sufficient information of surface chemistry



Often different definition of selectivity (separation factor)!

Thermodynamic selectivity and limit of selectivity (p \rightarrow 0) α

Difference of shape of isotherms and of loadings important [1]

$$\alpha_{CO_2,CH_4} = \frac{Y_{CH_4}}{Y_{CO_2}} \frac{X_{CO_2}}{X_{CH_4}} \qquad \qquad \alpha_{CO_2,CH_4} (p \to 0) = \frac{H_{CO_2}}{H_{CH_4}}$$

Y... mole ratio in gas phase

X... mole ratio in adsorbed phase

H... Henry constants

Sorbent selection parameter of Rege and Yang [2]

$$S = \frac{\Delta q_{CO_2}}{\Delta q_{CH_4}} \alpha_{CO_2, CH_4}$$

 $\Delta q \dots$ difference in loading between adsorption and desorption

Kinetic separation faktor β

Difference of sorption rates important [3]

$$\beta_{CO_2,CH_4} = \frac{H_{CO_2}}{H_{CH_4}} \cdot \sqrt{\frac{D_{CO_2}}{D_{CH_4}}} \qquad \text{H... Henry constants}$$
$$D... \text{ Diffusion coefficients}$$

R.T. Yang, *Gas separation by adsorption processes*, Imperial College Press, London, **1987** S.U. Rege, R.T. Yang, *Sep. Sci. & Technol.*, **2011**, *36*, 3355-3365
 D.M. Ruthven, S. Farooq, K.S. Knaebel, *Pressure Swing Adsorption*, Wiley-Verlag, New York **1994**.

Mixture Equilibria - Basics



Dependence of partial and total adsorption amounts



- - partial loadings, - total loading

General:

$$n_{CO_2,CH_4,total} = FKT(Y_{CO_2}, Y_{CH_4}, p)$$

Investigation along:

THE READ LINE – Case A

$$n_{CO_2,CH_4,total}(p=const.) = FKT(Y_{CO_2},Y_{CH_4})$$

THE BLUE LINE – Case B $n_{CO_2,CH_4,total}(Y_{CO_2}, Y_{CH_4} = const.) = FKT(p)$

Mixture Equilibria - Basics



Typical presentation of sorption capacities for binary mixtures

Case A – variable gas composition



p=const. (1 bar), CO_2 , CH_4 on D55-1.5

Case B – variable pressure



Y=const. (50:50), CO₂,CH₄ on D55-1.5

X-Y-Plot with statement to the composition of adsorbed phase at constant pressure

n-p-Plot with statement to the composition of amount of adsorbed at constant composition of the gas phase

Mixture Equilibria - Basics



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n-Y-Plot with statement to the partial loading at constant pressure

n-p-Plot with statement to the composition of amount of adsorbed at constant composition of the gas phase



Relationship between loading - mole fraction - selectivity

- 1. Calculation of **mole fractions of adsorbed phase** from partial loading
- 2. Calculation of **mole fraction of gas phase** from partial pressures
- 3. Calculation of selectivity
- 4. Check **plausibility with** help of **limit for selectivity** (for IAST-Calculations)

$$X_{CO_2} = \frac{n_{CO_2}}{n_{CO_2} + n_{CH_4}} \qquad Y_{CO_2} = \frac{p_{CO_2}}{p_{CO_2} + p_{CH_4}}$$

$$\alpha_{CO_2,CH_4} = \frac{Y_{CH_4}}{Y_{CO_2}} \frac{X_{CO_2}}{X_{CH_4}} \qquad \alpha_{CO_2,CH_4}(p \to 0) = \frac{H_{CO_2}}{H_{CH_4}}$$



50% CO₂,50% CH₄ on NaMSX, IAST with Toth



- Limit of selectivity can be used to check the results of IAST-Calculations (only for models with Henry range)
- Often Limit of selectivity do not reflect the selectivity for the real separation process, therefore a single consideration is not enough

Mixture Equilibria - Models





[1] R.T. Yang, *Gas Separation by Adsorption Processes*, Imperial College Press, **1987**[2] A.L. Myers, J.M. Prausnitz, *AIChe Journal*, **1965**, *11*, 129
[3] W. Kast, *Adsorption aus der Gasphase*, 1.Aufl., VCH Wiley Verlag, Weinheim, **1988**

Mixture Equilibria - Models







Calculations of mixture data with dynaSim – Recommendations for pure components

- 1. Fitting of pure component data at same temperature for all components
- 2. All data as table pressure / bar (mbar) and adsorbed amount / mmol g⁻¹
- 3. All components must be fitted with same isotherm model



TYP I: Langmuir, SIPS, Toth, DSLangmuir, DSLangmuirSIPS

Typ II: (Freundlich)

Typ IV, V: DSLangmuirSIPS, (DSLangmuir), (SIPS)



Calculations of mixture data with dynaSim - fitting of pure components

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| Datei Zwischenablage Ansicht Einheiten Hilfe | | | | | | | | | | | | | |
| Isother | Isothermendaten Graph | | | | | | | | | | | | |
| | Druck [bar] | adsorbierte Menge [mmol/g] | Menge (Modell) [mmol/g] | Druck [bar] | adsorbierte Menge [mmol/g] | Menge (Modell) [mmol/g] | Druck [bar] | adsorbierte Menge [mmol/g] | Menge (Modell) [mmol/g] | sothermenmodel | e | | |
| • | 0.000458011 | 0.004757015 | | 0.006865849 | 0.002470565 | | | | | SIPS | | | |
| | 0.003472018 | 0.468592639 | | 0.020603231 | 0.007696778 | | | | | Henry ≡ LAI | | | |
| | 0.012477618 | 1.048656684 | | 0.031250407 | 0.01175837 | | | | | Toth | | | |
| | 0.03730939 | 1.601237634 | | 0.041363275 | 0.015613759 | | | | | Freundlich | | | |
| | 0.036144854 | 1.619471556 | | 0.050962239 | 0.019286592 | | | | | Dual Site Lang DS Langmuir S | muir IPS | | |
| | 0.043990056 | 1.732073998 | | 0.061246217 | 0.023211446 | | | | | D'o canginair o | | | |
| | 0.055453544 | 1.865050588 | | 0.071227353 | 0.027015401 | | | | | TZ A. damati | also Chadaaada | | |
| | 0.065057526 | 1.964831458 | | 0.07 | | !! | : ; | المام مم | - f | | ארדי 📗 | | |
| | 0.074561942 | 2.053023595 | | 0.08(| CODV | ⁄ equi | IDriu | m dat | a fror | り とえし | ノヒL 📗 | | |
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| | 0.094028598 | 2.211579629 | | 0.091023877 | 0.034547452 | | | | | Annitatskons | tante (17bal) | N. | |
| | 0.189961926 | 2.674189991 | | 0.204665945 | \sim | | - (- | | | - (] | | 1.1 | |
| | 0.310146866 | 3.001565847 | | 0.300663825 | 2) C | noice | e or a | suita | DIE ISC | otherr | n moc | | |
| | 0.404448286 | 3.172821526 | | 0.399927085 | _/ ~ | | | | | | | | |
| | 0.495526066 | 3.299733552 | | 0.496237265 | 0.184869878 | | | | | 0 | | | |
| | 0.577835466 | 3.39292191 | | 0.603080425 | 0.222805196 | | | | | | | | |
| | 0.686582746 | 3.494381728 | | 0.696559505 | 0.255432838 | 3) Fitt | ina tl | ne Ma | ndel ta |) aet r | nodel | narame | eter |
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| - Is | otherme 1 | | | Isotherme 2 | | | Isotherme 3 | | | Temperatura Exponenten | bhängigkeit des | | |
| A | finitätskonstante [1/b | ar] 5.3 | 346338 | Affinitätskonstant | e [1/bar] | 0.149988 | Affinitätskonsta | ante [1/bar] | 0 | ✓ | | | |
| м | aximalbeladung (mmo | l/g] 5.3 | 304088 | Maximalbeladung | [mmol/g] | 3.137722 | Maximalbeladu | ing [mmol/g] | 0 | V | | | |
| Т | oth/Sips/Freundlich E | xponent 0.5 | 5224 | Toth/Sips/Freund | llich Exponent | 1.0781 | Toth/Sips/Free | undlich Exponent | 0 | V | | | |
| | | | | | | [] | | | | | | | |
| Т | emperatur [°C] | | ÷ | Temperatur [°C] | | ÷ | Temperatur [°C |] | 40.0 🚖 | | | | |
| Modellanpassung R ² = 0.998590 Modellanpassung R ² = 0 Modellanpassung | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |
| | | | | | | | | | | | | | |

Example: CO_2 , CH_4 on NaMSX at 40°C



Calculations of mixture data with dynaSim - fitting of pure components

| 일 Mod | 🖉 Modellanpassung an Reinstoffisothermen 💦 👘 👘 👘 | | | | | | | | | | | | |
|---------|--|-------------------------------|----------------------------|--------------------|-------------------------------|----------------------------|----------------------|--|----------------------------|---------------------------------|---------------------------------------|----------------|--------|
| Datei | Datei Zwischenablage Ansicht Einheiten Hilfe | | | | | | | | | | | | |
| Isother | Isothermendaten Graph | | | | | | | | | | | | |
| | Druck [bar] | adsorbierte Menge [mmol/g] | Menge (Modell) [mmol/g] | Druck [bar] | adsorbierte Menge [mmol/g] | Menge (Modell) [mmol/g] | Druck [bar] | adsorbierte Menge [mmol/g] | Menge (Modell) [mmol/g] | Isothermenm | odelle | | |
| • | 0.000458011 | 0.004757015 | 0.219836972685 | 0.006865849 | 0.002470565 | 0.001887379064 | | | | SIPS | ▼ | | |
| | 0.003472018 | 0.468592639 | 0.587605206783 | 0.020603231 | 0.007696778 | 0.006162695239 | | | | = | | | |
| | 0.012477618 | 1.048656684 | 1.037118364080 | 0.031250407 | 0.01175837 | 0.009645705421 | | | | | | | |
| | 0.03730939 | 1.601237634 | 1.5968827596546 | 0.041363275 | 0.015613759 | 0.013035548287 | | | | 0 -0 | $(K \cdot p)^{\mathfrak{e}}$ | | |
| | 0.036144854 | 1.619471556 | 1.578453456595 | 0.050962239 | 0.019286592 | 0.016307394203 | | | | Yeq - Y | $\max 1 + (K \cdot p)^{\mathfrak{c}}$ | | |
| | 0.043990056 | 1.732073998 | 1.6945422740491 | 0.061246217 | 0.023211446 | 0.019858850912 | | | | | | | |
| | 0.055453544 | 1.865050588 | 1.836999615455 | 0.071227253 | 0.027015401 | 0 023342941761 | | | | TT A.da | anationka Ctadurada | | |
| | 0.065057526 | 1.964831458 | 1.938443462812 | 0.07 | | | | 1 | | ! | | | |
| | 0.074561942 | 2.053023595 | 2.026878798225 | 0.08(| Cnec | ck of c | Oemi | cient | or det | ermi | nation | R ² | |
| | 0.084486444 | 2.135270805 | 2.109241579301 | 0.09 | | | | | | - | | | |
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| | 0.189961926 | 2.674189991 | 2.662767881467 | 0.204665945 | | | | | r | | | | |
| | 0.310146866 | 3.001565847 | 3.000354018334 | 0.300663825 | 2) E | ventu | ally (| choice | e of ar | n and | other n | nodel | |
| | 0.404448286 | 3.172821526 | 3.179180630646 | 0.399927085 | _/ _/ | | | | | | | | |
| | 0.495526066 | 3.299733552 | 3.312785951456 | 0.496237265 | 0.184869878 | 0.179740874680 | | | | 0 | | | , |
| | 0.577835466 | 3.39292191 | 3.4115935486045 | 0.603080425 | 0.222805196 | | | _ | | | | | |
| | 0.686582746 | 3.494381728 | 3.519784950198 | 0.696559505 | 0.255432838 | 3) Pai | rame | ter fo | r mixti | Ire e | anilipi | ria ava | ilahle |
| | 0.778699066 | 3.566393691 | 3.596808896610 | 0.787867705 | 0.28679448 | | unic | | | | yumor | | nabic |
| leathe | 0.895358046 | 3 643961114 | 3 680126062005 | 0 884453785 | 0 319480955 | 0 319327272921 | | | | 0 | | | |
| - Is | otherme 1 | | | Isotherme 2 | | | Isotherme 3 | | | Tempera Exponen | aturabhängigkeit des nten | | |
| A | finitätskonstante [1/b | ar] 5.3 | 346338 | Affinitätskonstant | e [1/bar] | 0.149988 | Affinitätskonsta | nte [1/bar] | 0 | 0 | | | |
| м | aximalbeladung [mmo | 1/a] 5. 3 | 304088 | Maximalbeladung | [mmol/a] | 3.137722 | Maximalbeladur | na [mmol/a] | 0 | 7 | | | |
| Т | oth/Sins/Freundlich F | xponent 0! | 5224 | Toth/Sips/Freund | llich Exponent | 10781 | Toth/Sips/Freu | ndlich Exponent | 0 | 7 | | | |
| | | | | | | | | | | | | | |
| т | Temperatur [°C] | | | Temperatur (°C) | | | Temperatur [*C] 40.0 | | | | | | |
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Calculations of mixture data with dynaSim – fitting of pure components





Calculations of mixture data with dynaSim – fitting of pure components





Calculations of mixture data with dynaSim – calculation of mixture data

| 9. Berechnung der Gleichgewichtsdaten von Gemischen | | | | | | | | | |
|--|--|---|--|--|--|--|--|--|--|
| Datei Zwischenablage Hilfe | | | | | | | | | |
| Berechnung Graph | | | | | | | | | |
| Isothermenparameter und Molenbrüche Affinitätskonstante [1/bar] 0.000 * Maximalbeladung [mmol/g] 0.000 * Toth/Sips Exponent 1.000 * Molenbruch in der Gasphase 0.000 * | Variante Komponenten Komponente 3 Komponente 3 | Bedingungen für die Berechnung mponente 4 0 0 0 0 0 0 Bereich für die Berechnungen Variable Komponente Minimum 0.00 0 Maximum 0.00 Komponente 2 | | | | | | | |
| Gesamtdruck [bar] 0.00 1 Choice of a isotherm model for mixture Anzahl der Komponenten [stothermenmodel] Anzahl der Komponenten SIPS detieren editieren ed | | | | | | | | | |
| Gesamtdruck (bar) Y Multicomponent DSLangmuir IAST with DSLangmuir | | | | | | | | | |
| AST with DSLAISIPS | 3) Choic (p=cor | e of calculation type st. or Y=const.) | | | | | | | |
| | m | • | | | | | | | |
| Berechnungsmodell für die Gemischberechnung : Multikomp | onenten SIPS | | | | | | | | |



The selected mixture model must include the pure component isotherm model!

i.e.: with SIPS only the Multicomponent-SIPS approach is available



Calculations of mixture data with dynaSim – calculation of mixture data

| <u>84</u> I | Berechnung der Gleichgewich | ntsdaten von Gen | nischen | | | | | | | | | | × |
|--|-----------------------------|------------------|------------------|------------------------------|--------------------|-----------|----------------|---------|-----------|----------------------|------------------------|---------------------|-----------------|
| Serechnung der Gleichgewichtsdaten von Gemischen | | | | | | | | | | | | | |
| | Datei Zwischenablage Hilfe | | | | | | | | | | | | |
| Ľ | Berechnung Graph | | | | | | | | | | | | |
| | lsothermenparameter und | Molenbrüche | | Parameter der einzelr CO2 | nen Kompone CH4 | nten | - Komponente 3 | Kompone | ente 4 | Bedingungen für die | Berechnung | | |
| | Affinitätskonstante [1/bar | 0.000 | * | 5.346338 | 0.149 | 988 | 0 | 0 | | konstante Gas | szusammensetzung, va | niabler Druck | |
| | Maximalbeladung (mmol/c | . 0.000 | | 5.304088 | 3,137 | 722 | 0 | 0 | | konstanter Dr. | uck, variable Gaszusar | nmensetzung | |
| | Teth /Ciss Evenenant | 1.000 | × | 0.5004 | 1.070 | | 0 | 0 | | Bereich für die Bere | echnungen | variable Komponente | |
| | Toth/Sips Exponent | 1.000 | | 0.5224 | 1.078 |)1 | U | U | | Minimum | 0.00 | @ CO2 | |
| | | | Le I | | | | | | | Maximum | 1.00 | © CH4 | |
| | Molenbruch in der Gasph | ase 0.000 | ÷ | 0.5 | 0.5 | | 0 | 0 | | Maximum | 1.00 | Komponente 3 | |
| | Gesamtdruck [bar] | 1.00 | * * | | | | | | | Anzahl der Berech | n. 50 🚔 | Komponente 4 | |
| | Anzahl der Komponenten | Isothermer | nmodell | 🗸 übemehme | 🖌 üb | emehme | V übernehme |) 🗸 üb | emehme | | | | |
| | 2 - | Multikomponen | ten SIPS 🔻 | / editieren | 1 | editieren | / editieren | | editieren | berechne | | | |
| | | | | | <u></u> | | | | | | | | onent isotherms |
| | | | | | | | | | | | | | |
| | Gesamtdruck (bar) | Y1 | Y2 | Y3 | Y4 | X1 | X2 | | X3 | X4 | n1 (mmol/g) | n2 (mmol/g) | |
| l h | ▶ 0.000 | 0.500 | 0.500 | | | 0.000 | 0.0 | 00 | | | 0.000 | 0.000 | E |
| | 0.020 | 0.500 | 0.500 | | | 0.998 | 8 0.0 | 02 | | | 0.943 | 0.002 | |
| | 0.040 | 0.500 | 0.500 | | | 0.996 | 6 0.0 | 04 | | | 1.257 | 0.005 | |
| | 0.060 | 0.500 | 0.500 | | | 0.995 | 5 0.0 | 05 | | | 1.470 | 0.007 | |
| | 0.080 | 0.500 | 0.500 | | | 0.995 | 5 0.0 | 05 | | | 1.633 | 0.009 | |
| | 0.100 | 0.500 | 0.500 | | | 0.994 | 4 0.0 | 06 | | | 1.767 | 0.011 | |
| | 0.120 | 0.500 | 0.500 | | | 0.993 | 3 0.0 | 17 | | | 1.879 | 0.013 | |
| | 0.140 | 0.500 | 0.500 | | | 0.993 | 3 0.0 | 17 | | | 1.977 | 0.014 | |
| ų | 0.160 | 0.500 | 0.500 | | | 0.992 | 2 0.0 | 38 | | | 2.063 | 0.016 | |
| Be | • | | | 1 | m | | | | | | | | |
| | | | | | | | | | | | | | |
| | Berechnungsmodell für die | Gemischberechnu | ung : Multikompo | onenten SIPS | | | | | | | | | |

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Calculations of mixture data with dynaSim - calculation of mixture data



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Static versus Dynamic Methods



Static-volumetric Method

- Sorption in closed chamber
- Measurement of pressure drop
- Pure component isotherms, mixed gas sorption hard to realize
 - Standard characterization (BET, Pore volume, pure component isotherms)

Dynamic Method

- Sorption in an open system at constant pressure
- Time resolved measurement of effluent gas composition
- Mainly for mixed gas sorption, pure component data only with some approaches possible
- Technical processes in "Labscale"
 - Investigations to technical relevant parameters (selectivity, sorption kinetic, regenerability, cycle stability ...)



iSorb HP 1



Measurement Methods – Static Volumetry





- > Dosing and **mixing of a predefined gas mixture** in V1 by circulation pump
- Switch to adsorption chamber V2 and continuous mixing by circulation pump
- Recording of pressure drop and analysis of gas phase after achievement of equilibrium
- Calculation of partial loading based on mass balance

→ Precalculations necessary for a desired equilibrium point

Measurement Methods – Headspace

Headspace Method (HS):

- Special case of a static-volumetric setup
- Higher sample throughput as classical volumetry
- Primarily for vapor mixtures suitable

Principle:

- \blacktriangleright Regeneration under N₂ at 150 °C (AC)
- > Sometimes preloading with component 1 (i.e. H_2O)
- Loading of HS-Vial with sample and VOC (with µl-Syringe)
- Equilibration for several days in tempered bath
- Analysis of gas phase via GC and performing of a mass balance

Headspace GC at INC e.V.

Vials

Measurement Methods – Dynamic Setup

Flow plot of a setup for the dynamic method

- Flow through the regenerated sample with a predefined gas mixture
- Measurement of equilibrium data at a specified pressure and gas composition

→ Advantage over static volumetry, no precalculations necessary

Measurement Methods - Overview

| Static-Volumetric | Headspace Method | Dynamic Method |
|--|---|---|
| Closed Chamber | Closed Chamber | > Open System |
| no carrier gas necessary | no carrier gas necessary | carrier gas necessary, depending on the routine |
| Suitable for gas mixtures and vapors | Mainly for vapors | Suitable for gas mixtures and vapors |
| Experimentally complex | Precalculations necessary | No precalculations necessary |
| Precalculations necessary | Sequenced experiments hard to perform | Sequenced experiments easy to perform |
| Sequenced experiments hard to perform | | Experiments along the "Lines" possible |

Measurement Methods - Overview

| Static-Volumetric | Headspace Method | Dynamic Method |
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Measurement Methods – Dynamic Technique

Balancing of breakthrough experiments

• Widely used approach and simplification for high diluted systems:

$$\dot{V}_{Out}(t) = \dot{V}_{In}(t) = const.$$

Small changes in concentration minimize this error

Quantach

particle characterization

Measurement Methods – Dynamic Technique

- binary mixture:
 - CO₂/He (non-adsorbable carrier gas)
 - \rightarrow Pure component equilibria
 - CO₂/CH₄ (adsorbable carrier gas)
 - \rightarrow Preloading of sample with pure CH₄
 - → Incomplete Determination of the system

(evaluation mostly simple)

→ Partial loading for CO₂ (mixture sorption data)

Quantach

particle characterization

• ternary mixture:

 $CO_2/CH_4/He$ (non-adsorbable carrier gas) Displacement of less adsorbed component

- → Partial Desorption, Role-Up Effects
- → Complete Determination (evaluation complex)
- $CO_2/CH_4/N_2$ (adsorbable carrier gas)
 - \rightarrow Preloading of sample with pure N₂
 - \rightarrow Partial loading for CO₂ and CH₄
 - → Incomplete ternary mixture data

Calculation of mixture data desired (Y/N)?

 \rightarrow Pure component isotherms necessary

> Definition of total flow, measurement temperature etc.

→ Sample must be under "thermodynamic control" (always)

Is a complete determination of the system desired?

→ determination of all partial loadings, diluting with Helium-carrier gas (Y/N)

Which concentration range is relevant?

 \rightarrow Calibration of suitable analytic technique (always)

 \rightarrow Check if any approach is valid, i.e. constant gas velocity ...(always)

Sample preparation and definition of preparation conditions

 \rightarrow Temperature, carrier gas (always)

Build up of a measurement routine

→ pressurization, Helium or Adsorptive 1 (Helium for complete determination)

Evaluation of the experiment

Task: Investigation of a binary system

Activated Carbon, CO_2 (25%), CH_4 (75%), complete determination at 5 bar

- 1. Weighting the sample and sample preparation at 120°C, He-flow 200 ml min⁻¹ (STP)
- **2.** Definition of partial pressures: 1,25 bar CO_2 ; 3,75 bar CH_4 ; 5 bar He; $\Sigma 10$ bar
- **3.** Gas flows: 11 min⁻¹ (STP) He, 0,75 I min⁻¹ (STP) CH₄, 0,25 I min⁻¹ (STP) CO₂
- 4. Pressurization with Helium up to 10 bar
- 5. Start of measurement by simultaneous dosing of CO2 and CH4 in Helium
- 6. Recording of effluent gas composition via MS (all components!)
- 7. After breakthrough, regeneration of sample for determination of activated mass

Task: Investigation of a binary system

Activated Carbon, CO₂ (25%), CH₄ (75%), complete determination at 5 bar

Result:

Breakthrough curve with "Role-Up"

Effect

- Includes all partial loadings
- Reference on p_{CO2}=0,25 bar and
 P_{CH4}=3,75 bar
- Mole ratios: y_{CO2}=0,25; y_{CH4}=0,75
- Helium will not be considered! Integration of areas:

> n(CO₂); n(CH₄); n(total); α

Measurement Method – Dynamic Technique

Sequence of several breakthrough curves on Activated Carbon D 55-1.5

Conditions:

- 20 °C, 2 L min⁻¹
- 10 bar (pressurization with N₂)

Quantach

particle characterization

- Concentrations:
 - 5 % CO₂ 80 % CO₂ in N₂

Procedure:

- Start further breakthroughs after equilibrium before
- Integration and summation results in partial loading data of CO₂
- Volume ratio and total pressure defines the partial pressure of CO₂
- \rightarrow Mixed isotherm data of CO₂ in N₂

Measurement Method – Dynamic Technique

Measured partial loading data for CO₂ on Activated Carbon D 55-1.5 at 10 bar

- Dynamic measured data (red)
- IAST-Model (Ideal Adsorbed Solution Theory) based on pure component isotherms (lines)

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particle characterization

Mixture of CO₂ and N₂ shows ideal behavior on AC

Determination of partial loading data of CO_2 on AC D 55-1.5 by performing sequentially experiments along constant total pressure.

$$n_{CO_2,N_2,total}(p=const.) = FKT(Y_{CO_2},Y_{N_2})$$

Measurement Method – Dynamic Technique

Sequence of several breakthrough curves on Activated Carbon D 55-1.5

Assumption of **non-adsorbable Gas**, i.e. Helium 10 loading q / mmol g⁻¹ as carrier gas will lead to pure component equilibria. Other, adsorbable gases results in mixture 0.1 iSorb HP sorption data. Toth model dynamic experiment 0.01 0.01 CO₂/He 0.1 1 10 pressure p / bar 100 10 80 mole fraction $y(CO_2) / \%$ 8 60 loading q / mmol g⁻¹ 6 40 CO_2/N_2 IAST total loading IAST partial loading CO 20 IAST partial loading N exp. CO_loading 0 3000 6000 9000 12000 0.2 0.4 0.6 0.8 0.0 1.0 time-on-stream t / s mole fraction $y(CO_{2})$

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Your partner in particle characterization

An Incomplete Determined System...

5% CO₂ 95% N₂ at 40°C, 5 bar, 2000 ml min⁻¹ on D 55/1.5

System is only incomplete determined. Model is confirmed by experiment.

A Complete Determined System...

System is complete determined, good agreement confirmed ideal behavior.

Measurements of Vapor Mixtures...

Very high selectivity of model confirmed by experiment

Measurements of Vapor Mixtures...

Deviation between model and experiment → no prediction, experiment necessary!

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Comparable Measurements of Mixtures

15% Propane 45% Propylene in He at 25°C, 5 bar, 1000 ml/min on A1, A2, A3

Statements on selectivity also possible without modeling from pure component data

Determination of sorption capacities and selectivities, recording of kinetic

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Summary

- > Equilibria of mixtures and selectivities are important for applications
 - Knowledge of such data are highly valuable and of great interest
- however much more difficult to measure as pure component equilibria
 - There is a lack of data in literature
- Mixture equilibria can not calculated by textural properties but partial predictive from pure component isotherms based on classical thermodynamic Models.
- ➢ Predictions have some limits! → Number of components, vapors, nonideal systems...
- ➤ Investigation of mixture sorption by dynamic method easy possible and should be favored (→ sequential experiments possible).
- We can support you and offer commercial measurement capabilities.

Thank you for your attention!

www.dynamicsorption.com

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