DVS Vacuum
Dynamic Gravimetric Sorption

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Product specialist

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All current vacuum sorption instruments operate in a **static** mode

- The sorbate enters the sample chamber, the chamber is sealed and the experiment occurs under static conditions, i.e. no gas flow.
- The system pressure can change for various reasons, but commonly due to vacuum leaks.
- Studying dynamic processes is not possible.

**Why is Vacuum desirable?**

- Materials such as microporous solids, nanomaterials, chemical adsorbents and strong hydrates need extensive drying/outgassing, which is not possible with traditional methods such as dry gas flow and thermal convection heating.
- Guarantee of clean and dry environment for air or moisture sensitive samples.
- Gas and vapor adsorption at low relative pressures (e.g. water adsorption at 25°C from 0.1 to 5%P/Po in 0.1% step).
- Solely water vapor or organic vapour adsorption.
Dynamic Gravimetric Sorption

Sub-atmospheric vapor sorption technique that measures the uptake and loss of vapor/gas using micro-balance in dynamic mode.

- Controls both upstream rates of sorbate entry and the downstream rates of sorbate exit by dynamic butterfly valve on the exit side of the system.
- Permits control over the residence time of the sorbate in the chamber.
- Estimates amount of sites that are accessible to organic or water vapors at ambient temperatures which is not possible with traditional volumetric methods (nitrogen adsorption at 77K).
Principle of Dynamic Gravimetric sorption

(1) Chamber evacuation
Downstream pumping
Downstream sealed
Sample pan
Upstream sealed

(2) Filling with sorbate
Downstream sealed
Mass flow controllers opened

(3) Steady-state
Downstream opened
Upstream opened

Scheme of DVS vacuum
Measurable Physisorption Properties

- Adsorption and desorption Isotherms (T constant, P variable)
- Adsorption Isobars (T variable, P constant)
- BET (Brunauer, Emmett and Teller) Surface Area
- Micro/meso-pore size distributions
- Diffusion coefficients
- Heat of sorption
Benefits of DVS Vacuum

✓ The use of the same chamber for *in-situ* activation/outgassing immediately followed by sorption measurements

✓ Sorption measurements from very low up to atmospheric pressures using step size of 0.1% P/Po

✓ Wide range of sample and vapor temperatures (20 to 400°C). Isothermal control of entire system; no condensation issues.

✓ Real time sorption kinetics

✓ Wide range of sorbate molecules (Benzene, Toluene, Xylene, Aldehydes, Alcohols, H₂S, NH₃, CO₂)

✓ Competitive adsorption of two probe molecules
  (H₂O-CO₂, H₂O- NH₃, H₂O-MeOH)

✓ Multiple sorption/desorption/outgassing cycles in one experiment

✓ Sorbate molecules residence time control
DVS vacuum system

Vacuum pumps assembly

Data acquisition station

Incubator
DVS vacuum system

- Turbo pump
- Rotary pump
- Pressure controller
- 972 Pressure controller
- Pre-heater temperature controller
- Pre-heater switch
- Incubator switch
- Incubator door
- Cooler
- Incubator temperature controller
- Butterfly valve
- Cooling Fun
- Manual (speedi) valve
- Turbo pump controller
DVS vacuum stand

10 Torr Baratron → 1000 Torr Baratron

Sample side

Vacuum gas manifold

UltraBalance hat

Reference side

Gas

Vapour
High temperature pre-heater

Miniature radiator style pre-heater for outgassing samples up to 400°C

Sample pan

Pre-heater
✓ Dynamic (or static) operational mode
✓ Upstream and downstream vapor/gas flow controls
✓ Temperature controlled incubator operating in the range from 20 (15) to 70°C
✓ *In-situ* sample pre-conditioning /activation up to 400°C (using pre-heater) and high vacuum
✓ Multi vapor and/or gas injection system for sorbates (2 gasses or 2 vapors or 1 gas and 1 vapor)
✓ Water vapor adsorption up to 90 %P/P₀ up to 70°C and up to 150°C up to 7%P/P₀
✓ Highly accurate baratrons for pressure measurements (0.005 to 10 Torr and 0.01 to 1000 Torr)
✓ Cold cathode/ MicroPirani transducer from very low (10⁻⁸ Torr) to atmospheric pressure measurements
Low end P/Po control
Vacuum and preheater drying of 5A zeolite
Initial mass: 33.1724mg
Drying kinetics of hydrates

Drying Behaviour of Pharmaceutical Hydrates: Carbamazepine (CBZ) dihydrate

Pressure: $10^{-3}$ Torr

Very strong kinetic dependence of drying rate with temperature and level of vacuum for CBZ dihydrate
Benzene sorption of porous material at 25°C

DVS Isotherm Plot

- Cycle 1 Sorp
- Cycle 1 Desorp

DVS Change In Mass (ref) Plot

- dm - dry
- Target % P/Po

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Pt-SiO$_2$ toluene sorption at 55°C

P/P$_0$ increased in 0.2 %
Comparison of isotherms for Pt-SiO$_2$ Toluene sorption at 25$^\circ$C (adsorption in green and desorption in purple) and 55$^\circ$C (adsorption in red and desorption in blue)
### Cyclohexane and methanol adsorption

#### Surface area (m²/g)

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<thead>
<tr>
<th></th>
<th>MOR</th>
<th>FER</th>
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<tr>
<td>N₂</td>
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<tr>
<td>Methanol</td>
<td>422</td>
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<td>Cyclohexane</td>
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<td>148</td>
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<td>n-Octane</td>
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#### Micropore volume (cm³/g)

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<td>Cyclohexane</td>
<td>0.14</td>
<td>0.09</td>
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---

### DVS Isotherm Plot

- **Temp:** 25.0 °C
- **Meth:** Meth: MRef: 31.2818

![DVS Isotherm Plot](image1)

### DVS Change In Mass (ref) Plot

- **Temp:** 25.0 °C
- **Meth:** Meth: MRef: 31.2818

![DVS Change In Mass (ref) Plot](image2)
Acetaldehyde and benzene sorption

Benzene sorption at 20°C

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface Area [m²/g]:</th>
<th>Monolayer Capacity [Mol/g]:</th>
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<tr>
<td>MOF beads</td>
<td>1035</td>
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<tr>
<td>Beads</td>
<td>293</td>
<td>0.0011</td>
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</table>

Acetaldehyde sorption at 17°C

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<td>Beads</td>
<td>654</td>
<td>0.002</td>
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Water sorption isotherm of freeze-dried polymer at 40°C

Adsorption/desorption cycles showing water sorption kinetics 40°C ($P_0 = 55.3$Torr).
Ionic liquid water sorption at 25°C
Sylosiv A10 water sorption at 40°C

DVS Change In Mass (ref) Plot

Date: 11 Dec 2011
Time: 10:46 am
File: Sylosiv A10 water 40C_2cycles Sylosiv A10 water 40C_2cycles 05-12-2014 18-36-36_DVS.xlsb
Sample: Sample: Sylosiv A10 water 40C_2cycles
Temp: 40.0 °C
Meth: 
MRef: 21.9039

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Sylosiv A10 water sorption at 40°C

DVS Isotherm Plot

Temp: 40.0 °C
Meth: 
MRef: 21.9039
SAPO-34 water adsorption isobars at 27°C

**Graph Details:**
- **Axes:**
  - Horizontal: Time (minutes)
  - Vertical: Mass (mg), Temperature (°C), P/Po (%)
- **Legend:**
  - Red: Mass (mg)
  - Blue: Temperature (°C)
  - Green: P/Po (%)
- **Data Values:**
  - Temperature: 27.0 °C
  - Meth: MRef: 25.1724

**Note:**
- The graph illustrates the adsorption isotherms of water on SAPO-34 at 27°C, showing changes in mass, temperature, and P/Po over time.
- The data points and trends indicate the sorption behavior of the material under the given conditions.
SAPO-34 water adsorption isobars at 27°C

DVS Isobar Plot

- Cycle 1 Increasing T
- Cycle 1 Decreasing T
- Cycle 2 Increasing T
- Cycle 2 Decreasing T
- Cycle 3 Increasing T
- Cycle 3 Decreasing T
- Cycle 4 Increasing T
- Cycle 4 Decreasing T

% P/Po: 48.28%
Meth: MRef: 25.1724

Cycle 1: 8.01 Torr
Cycle 2: 13.35 Torr
Cycle 3: 21.36 Torr
Cycle 4: 25.37 Torr
Cyclohexane carbon sorption at 25°C
Cyclohexane carbon sorption at 25°C

BET Surface area determination

<table>
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<tr>
<th>Sample</th>
<th>Surface Area [m²/g]:</th>
<th>Monolayer Capacity [Mol/g]:</th>
<th>Sorption constant</th>
<th>R [%]</th>
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<td>Carbon</td>
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<td>0.003</td>
<td>-23.2</td>
<td>99.2</td>
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</table>

BET plot
DMMP carbon sorption at 25ºC
Partial Pressure Control up to 1Torr

Dimethyl methylphosphonate

Actual Pressure [Torr] vs Time/mins graph for Dimethyl methylphosphonate.
Dynamic adsorption of 2-hexanol on activated carbon

Normal static vacuum methods suffer from the effect of system leak rates for sorption at low pressures, resulting in the system pressure not equalling the vapour pressure.

Dynamic vacuum overcomes this problem by continuously bleeding the vapour into the system and continuously taking vapour out using the downstream butterfly controlled vacuum.
Comparison of water-octane co-adsorption and water adsorption on activated carbon coated with chitosan at 25 deg C

- Water partial pressure = 6.10 torr
- Octane partial pressure = 3.40 torr
- Total partial pressure = 9.50 torr

- Water partial pressure = 7.48 torr
- Octane partial pressure = 2.02 torr
- Total partial pressure = 9.50 torr

- Water partial pressure = 9.50 torr
Hydroxides can be potentially used for CO$_2$ capture for environment protection.
Adsorption heat pumps (AHPs) are alternative to conventional vapor compression based heating, ventilation and air conditioning systems.

Benefits of AHPs

✓ Energy efficient and environmentally friendly
✓ Minimal electricity consumption
✓ Small CO$_2$ footprint
✓ Use sustainable energy sources such as solar or geothermal energies or waste heat from industrial processes

The AHP rely on the reversible physisorption of the adsorptive (a refrigerant vapor) on porous material (the adsorbent). The adsorption cycle is driven by temperature swings applied to the adsorbent.
Requirements for the adsorbent in AHPs

- high water uptake capacities to maximize heating and cooling efficiencies
- Rapid adsorption desorption kinetics

Zeolites are promising adsorbent materials because of their high surface area, tuneable hydrophilicity/hydrophobicity, uniform pore size, high adsorption capacity and shape/size selectivity.

The aim of the work is to measure adsorption isotherms which are required to understand physisorption properties of the adsorbents.
NaY water sorption at 25 and 65°C

Development of adsorption based thermal batteries (MIT)

Very good reproducibility

Sample regenerated for 8h at 370°C
13x Zeolite outgassing at high temperature and vacuum

Outgassing: 250min at 370°C using the pre-heater and high vacuum
13x Zeolite water sorption at 25°C

Adsorption/desorption cycles showing water sorption kinetics 25°C (P₀ = 23.8Torr).
13x Zeolite water sorption isotherm at 25°C
Surface area is derived from water sorption isotherm.

Surface Area: 698 m$^2$/g, Monolayer Capacity: 0.011 [Mol/g], Sorption Constant: -162, R: 0.999
SO$_2$ gas sorption on three different Zeolites at 25$^\circ$C

Result shows typical Type I isotherms. Sorption was found to be irreversible at 25$^\circ$C, i.e. desorption could not be achieved by vacuum alone.
BET surface area measurement of 13x Zeolite using SO\textsubscript{2} gas at 25°C.

BET surface area of a 13x Zeolite measured by DVS Vacuum using SO\textsubscript{2} gas. The result correlates well with the established value of 750m\textsuperscript{2}/g, measured using N\textsubscript{2} at –196°C.
Water/Ethanol Zeolite Sorption Isotherms at 130°C

Molecular sizes:
- Water: 0.28nm
- Ethanol: 0.44nm
Drying of 4A zeolite at 70°C

Outgassing: 7 hours at 300°C using the pre-heater and high vacuum
Adsorption/desorption cycles showing water sorption kinetics at 70°C ($P_o = 233.7$Torr).
Partial pressure control of water vapor at 70°C
4A Zeolite water sorption isotherm at 70°C

DVS Isotherm Plot

- Temp: 70.0 °C
- Meth:
- MRef: 46.4147

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4A water sorption isotherms at 25 and 70°C
Prior to determination of isotherms at 25°C (P_o=23.7 Torr) and 140°C the sample was outgassed at 300°C for 5 hours and high vacuum. In 2nd cycle sample was kept at 140°C using the pre-heater, while the incubator temperature was maintained at 70°C throughout experiment. (P_o (water at 70°C)= 233.7Torr). The P/ P_o of 7.6 % at 90 % was reached.
4A Zeolite water sorption isotherms at 25, 70 and 140°C

 Isotherm plot

- Adsorption 25°C
- Desorption 25°C
- Desorption 70°C
- Adsorption 70°C
- Adsorption 140°C
- Desorption 140°C

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CO$_2$ Adsorption/Desorption Isotherms for 4 samples
## Sample B BET Surface Area

**Experimental Parameters**
- Molecular weight: 44,0088 g/mol
- Effective molecular area: 20.34 Å²
- Adsorbate: Carbon Dioxide
- Temperature entered by user

**Calculation Options**
- P/Po fraction lower limit range: 0.05
- P/Po fraction higher limit range: 0.30
- % P/Po type: Target
- Half cycle: Sorption
- Isotherm cycle 1

**Analysis Results**
- \( V_m \): 36.75 cm³/g
- \( c \): 9.988
- Specific surface area: 20009 m²/g
- R-squared of line fit: 99.846 %

![DVS BET Plot](image1.png)

## Sample C BET Surface Area

**Experimental Parameters**
- Molecular weight: 18.02 g/mol
- Effective molecular area: 20.34 Å²
- Adsorbate: Carbon Dioxide
- Temperature entered by user

**Calculation Options**
- P/Po fraction lower limit range: 0.05
- P/Po fraction higher limit range: 0.30
- % P/Po type: Target
- Half cycle: Sorption
- Isotherm cycle 1

**Analysis Results**
- \( V_m \): 76.43 cm³/g
- \( c \): 11.52
- Specific surface area: 4178 m²/g
- R-squared of line fit: 99.878 %

![DVS BET Plot](image2.png)
### Sample B Diffusion Calculations
61.92 micron particle diameter used

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<th>R-sq. (%)</th>
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CH₄ Adsorption Isotherm
CO₂ and CH₄ Isotherms
### Heat of Sorption for alumina

**Sample:** alumina 25°C, alumina 60°C  
**Temp (°C):** 24.30, 59.23  
**M(0):** 46.2162, 54.3436

<table>
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<th>dm (%)</th>
<th>Interpolated P/mm Hg</th>
<th>Heat of Sorption (J/mol)</th>
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<td>9.76</td>
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- **ΔH\text{\textsubscript{sorp}} Moisture**

- **ΔH\text{\textsubscript{vap}} = 41kJmol\textsuperscript{-1}**

- **ΔH\text{\textsubscript{vap}} = 41kJmol\textsuperscript{-1}***
Knudsen Effusion Method

Gravimetric measurement of the weight loss by evaporation through a small orifice into vacuum.

Clausius-Clapeyron equation:

\[ \ln p = -\frac{\Delta H_{\text{sub}}}{RT} + C \]
Vapor pressure measurements

Material held in a cell, with an orifice of known dimensions will effuse through the hole via sublimation, under vacuum which prevents “back scattering” by air molecules.

Through measurement of the rate of mass loss, temperature, molecular weight and orifice dimensions, the Knudsen equation can be applied to provide vapour pressure data.

\[ P = \sqrt{\frac{2\pi RT}{M}} \left( \frac{dm}{dt} \right) \]

\[ \log(P) = b + a \]

- \( \frac{dm}{dt} \) is the rate of mass loss
- \( P \) is the vapour pressure of the solid
- \( R \) is the universal gas constant (8.314 \( m^3.Pa.K^{-1}.mol^{-1} \))
- \( T \) is temperature in Kelvin
- \( A \) is the area of the orifice
- \( M \) is the molecular weight of the solid
- \( \Delta H \) is heat of sublimation
- \( a \) and \( b \) are constants
Vapor pressure of benzoic acid
## Vapor pressure of benzoic acid

<table>
<thead>
<tr>
<th>Temperature [°C]</th>
<th>DM/DT [mg/min]</th>
<th>Vapour Pressure [Pa]</th>
<th>Vapour Pressure* [Pa]</th>
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Note: The cell orifice size was 167micron

Experimental values are in very good agreement with literature data * published by:
Vapor pressure of naphthalene

Vapor pressure at 25°C:
Measured value: 11.08 Pa
Environmental Protection agency value: 11.60 Pa
Daryl Williams, Imperial college London, UK
Evelyn Wang and Xiansen Li, MIT, USA
Patrick Ruch, IBM, Zurich, CH