Advanced Topics
Active Area, Thermodynamics, and Pore Size
Adsorption Sites

- On Top
- 2-Fold Bridge
- 4-Fold Hollow

- Short Bridge
- 2-Fold Hollow
- Long Bridge
Stoichiometry

- Associative chemisorption
  \[ Pt_s + CO \rightarrow 1Pt_s^{\text{CO}} \]

- Dissociative chemisorption
  \[ 2Pt_s + H_2 \rightarrow 2Pt_s^{\text{H}} \]

- Surface reactions
  \[ \frac{4}{3}Pt_sH + O_2 \rightarrow \frac{4}{3}Pt_s^{\text{O}} + \frac{2}{3}H_2O \]
  \[ \frac{2}{3}Pt_sO + H_2 \rightarrow \frac{2}{3}Pt_s^{\text{H}} + \frac{2}{3}H_2O \]
Chemisorption - Metal Catalysts

- In-situ preparation
- Degasing to remove weakly bound water or adsorbed molecules
- Calcination to remove ligands or ions (may be corrosive)
- Reduction to activate the catalyst
- Chemisorption isotherm - total chemisorption
- Repeat analysis - reversible adsorption
Chemisorption

- Stainless steel construction
- Quartz reactor
- 1100°C furnace

- 12 analysis gases
- 1000, 10, 1, and vacuum gauge
- Dry vacuum system
Typical Analysis of Pt on Alumina

- Evacuate sample at 100 C
- Flow hydrogen
  - Temperature program to 400 C
  - Hold for 30 min
- Evacuate at 400 C
- Cool to 35 C
- Sorb hydrogen
  - Evacuate for 30 min
  - Repeat hydrogen sorption
Chemisorption

- Associative
- CO

\[ Pt_s + CO \rightarrow 1Pt_s^{CO} \]
Chemisorption

- Associative
  - Assess monolayer using Langmuir Isotherm
  - 0.4 m²/g

\[
\theta = \frac{bP}{1 + bP}
\]

\[
P = \frac{1}{bn_m} + \frac{P}{n_m}
\]
Chemisorption

- Dissociative
- $\text{H}_2$

$$2Pt_s + H_2 \rightarrow 2Pt_s^H$$
Chemisorption

- Dissociative
- $\text{H}_2$
- $0.41 \, \text{m}^2/\text{g}$

$$\theta = \frac{\sqrt{bP}}{1 + \sqrt{bP}}$$

$$\frac{\sqrt{P}}{n} = \frac{1}{n_m \sqrt{b}} + \frac{\sqrt{P}}{n_m}$$
BET surface area
Pt/Al$_2$O$_3$

**Summary**
- BET Surface Area: 101.3868 ± 0.1919 m$^2$/g
- Slope: 0.042522 ± 0.000080 g/cm$^2$ STP
- Y-Intercept: 0.000415 ± 0.000015 g/cm$^2$ STP
- C: 103.506416
- Qm: 23.2901 cm$^3$/g STP
- Correlation Coefficient: 0.999994
- Molecular Cross-Sectional Area: 0.1620 nm$^2$
Summary

- Chemisorption
- Reversible
- Irreversible
- Sample preparation (for physisorption) removes chemisorbed molecules
Thermodynamics
Model-less Assessments

- Free energy
\[ \Delta G = RT \ln \frac{P}{P_r} \]

- Total Free Energy
\[ \Delta G^{int} = nRT \ln \frac{P}{P_r} \]

- Differential Free Energy
\[ \Delta G^{diff} = nRT \frac{d \ln P}{dn} + \Delta G \]
Carbon SWNT
Carbon SWNT Surface Area

- BET area
  - 850 m²/g

- Area from Differential Free Energy
  - 414 m²/g
  - 840 m²/g
Estimate $\Delta H$ and $\Delta S$ from Two Isotherms

- Estimate the heat of adsorption from isosteres
- Estimate the entropy

\[
\frac{\partial \ln P}{\partial \frac{1}{T}} = -\frac{q}{R}
\]

\[
\Delta S = \frac{\Delta H - \Delta G}{T}
\]
Carboxen 1012
Surface Area

- BET area
  - 1700 m²/g
- NLDFT
  - 1488 m²/g
- ΔS
  - 1464 m²/g
Overview

- Materials
  - Carbon
  - MOF
  - Pt, Pd, Ru/Pt on carbon
- Probe Molecules
  - CH$_4$, CO$_2$
  - H$_2$, O$_2$, CO
  - Surface Reaction
- Techniques
  - Manometric Adsorption
  - Differential Calorimetry
- Compare Heat of Adsorption calculated from adsorption isotherms and measured via microcalorimetry
Adsorption

Heat

Model
Physical Adsorption
Techniques for estimating heat of adsorption

- Clausius Clapeyron
  - Interpolation of isotherms to isosteres
- Virial-type expansion
  - Fit the isotherms and then estimate HOA from the derivative of the VTE
Clausius Clapeyron

\[ \frac{\partial \ln P}{\partial (1/T)} \bigg|_n = -\frac{q^{st}}{R} \]

- Calculated from adsorption isotherms at several temperatures
- Differential enthalpy \( q^{st} \) is assumed to have weak temperature dependence over a narrow temperature range
- Requires interpolation of adsorption isotherms at constant coverage \( V \) to estimate \( P_V \) and \( T_V \)
Virial-type expansion

\[
\ln P = \frac{1}{T} \sum_{i=0}^{n_1} c_{1,i} V^i + \sum_{j=0}^{n_2} c_{2,j} V^j + \ln V
\]

\[
\frac{\partial \ln P}{\partial (1/T)} = \sum_{i=0}^{n_1} c_{1,i} V^i
\]

- Fit a virial-type expression to the isotherm data
- Estimate the differential enthalpy \(q^s\) from partial derivative of the VTE
- Provides an estimate of \(q^s\) at \(V=0\)
CH₄ Adsorption

- Adsorption isotherms
- 15, 25, 40°C
- 3 - 4 days per material
\[
\ln P = \frac{1}{T} \sum_{i=0}^{n_1} c_{1,i} V^i + \sum_{j=0}^{n_2} c_{2,j} V^j + \ln V
\]

\[
\frac{\partial \ln P}{\partial (1/T)} = \sum_{i=0}^{n_1} c_{1,i} V^i
\]
Isosteric Heat

- Strongest interaction
- Grouping

\[
\ln P = \frac{1}{T} \sum_{i=0}^{n_1} c_{1,i} V^i + \sum_{j=0}^{n_2} c_{2,j} V^j + \ln V
\]

\[
\frac{\partial \ln P}{\partial (1/T)} = \sum_{i=0}^{n_1} c_{1,i} V^i
\]
Evaluate Classic versus Virial Expansion

- MOF
  - Commercially available
- Commonly used techniques for evaluating materials
CO$_2$ adsorption
$\text{CO}_2$ adsorption
NH₃ adsorption
NH₃ adsorption
NH₃ adsorption
Techniques for estimating heat of adsorption

- **Clausius Clapeyron**
  - Interpolation of isotherms to isosteres

- **Virial-type expansion**
  - Fit the isotherms and then estimate HOA from the derivative of the VTE

- **Microcalorimetry**
  - Simultaneous measurement of the isotherm and heat evolved during the equilibrium of the sorption
Clausius Clapeyron

\[ \frac{\partial \ln P}{\partial (1/T)} \bigg|_n = -\frac{q_{st}^*}{R} \]

- Calculated from adsorption isotherms at several temperatures

- Differential enthalpy \((q_{st}^*)\) is assumed to be have week temperature dependence over a narrow temperature range

- Requires interpolation of adsorption isotherms at constant coverage \((\psi)\) to estimate \(P_{\psi}\) and \(T_{\psi}\)
\( \frac{\partial \ln P}{\partial (1/T)} \bigg|_n = \frac{-q^{st}}{R} \)
CO$_2$ adsorption
CO₂ adsorption
CO$_2$ adsorption
Virial-type expansion

\[
\ln P = \frac{1}{T} \sum_{i=0}^{n_1} c_{1,i} V^i + \sum_{j=0}^{n_2} c_{2,j} V^j + \ln V
\]

\[
\frac{\partial \ln P}{\partial (1/T)} = \sum_{i=0}^{n_1} c_{1,i} V^i
\]

- Fit a virial-type expression to the isotherm data
- Estimate the differential enthalpy \((q^{st})\) from partial derivative of the VTE
- Provides an estimate of \(q^{st}\) at \(V=0\)
\[
\ln P = \frac{1}{T} \sum_{i=0}^{n_1} c_{1,i} V^i + \sum_{j=0}^{n_2} c_{2,j} V^j + \ln V
\]

\[
\frac{\partial \ln P}{\partial (1/T)} = \sum_{i=0}^{n_1} c_{1,i} V^i
\]
CO$_2$ adsorption
CO₂ adsorption
CO$_2$ adsorption
CO$_2$ adsorption
Microcalorimetry

- Manometric adsorption
- ASAP 2020
- Differential calorimeter
- 3D heat flow sensors
- Micro-dosing
- Solid state calibration
Microcalorimetry

• Restricted to dosing small quantities of gas
• Heat flow must be due to adsorption not heat transfer of the entering fluid
• Careful evaluation of the data

• Forward difference - limited use and “noisy data”
  \[ q^s_t = \frac{\Delta H_{MC}}{\Delta V_{ads}} \]

• Lagrange polynomial - estimate of the \( q^s_t \) at \( V=0 \)
  \[ q^s_t = h_{i-1} \frac{2v - v_i - v_{i+1}}{(v_i - v_{i-1})(v_i - v_{i+1})} + h_i \frac{2v - v_{i-1} - v_{i+1}}{(v_i - v_{i-1})(v_{i+1} - v_i)} + h_{i+1} \frac{2v - v_{i-1} - v_i}{(v_{i+1} - v_{i-1})(v_{i+1} - v_i)} \]
CO₂ heat flow and adsorption isotherm
\[ q_{vl} = h_{i-1} \frac{2v - v_i - v_{i+1}}{(v_{i-1} - v_i)(v_i - v_{i+1})} + h_i \frac{2v - v_{i-1} - v_{i+1}}{(v_i - v_{i-1})(v_i - v_{i+1})} + h_{i+1} \frac{2v - v_{i+1} - v_i}{(v_{i+1} - v_i)(v_{i+1} - v_i)} \]
$\text{CO}_2$ calorimetry, VTE, and CC
CO$_2$ calorimetry, VTE, and CC
NH₃ - q after initial activation of sample
NH$_3$ - $q$ after initial adsorption and subsequent evacuation at 40°C
NH$_3$ - q after regeneration at 200C and repeat adsorption at 40C
# Reversibility

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Typical Analysis of Supported Metals - Pt, Pd, Ru/Pt

- Evacuate sample at 100 C
- Flow hydrogen
  - Temperature program to 400 C
  - Hold for 30 min
- Evacuate at 400 C
- Cool to 35 C
- Sorb active gas
  - Evacuate for 30 min
- Repeat sorption
Temperature Programmed Reduction

\[ MO_{(s)} + H_2(g) \rightarrow M_{(s)} + H_2O_{(g)} \]

- Convert a metal oxide to a metal
- Metal oxides demonstrate unique reduction profiles
- The reducibility of the metal oxide
Free energy Change for TPR

\[ MO(s) + H_2(g) \rightarrow M(s) + H_2O(g) \]

\[ \Delta G = \Delta G^\circ + RT \ln \left( \frac{P_{H_2O}}{P_{H_2}} \right) \]
0.5% Pd

Graphs showing the adsorption of hydrogen on 0.5% Pd-alumina at different temperatures and pressures.
1% Pd

Graphs showing the relationship between P (mmHg) and V (cm³/g) for H₂ adsorption on 1% Pd-alumina at different temperatures and pressures.
5% Pd
Pd summary

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<td>120</td>
<td>6.5</td>
<td>17.1</td>
<td>29.1</td>
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Palladium on Carbon

- Hydrogen sorption
- Chemisorption
  - Irreversible
  - Reversible
- Stoichiometry
- Hydride Formation
Palladium

- H$_2$ chemisorption and hydride
  - Irreversible monolayer forms at < 1 mmHg
  - Hydride formation above 10 mmHg
Palladium

- Temperature dependence
  - Irreversible monolayer forms at low pressure
  - Hydride formation has a strong temperature dependence
  - Hydride is reversible
Estimate $\Delta H$ for the Hydride

- Hydride is reversible
  - Calculate $\Delta H$ from van’t Hoff
    - $-\Delta H = 35 \text{ kJ/mol}$

![Graph showing $\Delta S_A = -85.7 \text{ J/mol K}$, $\Delta H_A = -35.1 \text{ kJ/mol}$, $\Delta S_W = -97.6 \text{ J/mol K}$, $\Delta H_W = -41.0 \text{ kJ/mol}$]
Estimate $\Delta H$ for the Hydride

- Hydride is reversible
  - Calculate $\Delta H$ from van’t Hoff
    - $-\Delta H = 35 \text{ kJ/mol}$
  - Calculate $\Delta H$ from isosteres
    - $-\Delta H = 36 \text{ kJ/mol}$
Microcalorimetry

- Manometric adsorption
- Differential calorimeter
- Micro-dosing

🔥 Irreversible component of adsorption
Estimate $\Delta H$ for the Hydride

- Hydride is reversible
  - Calculate $\Delta H$ from van’t Hoff
    - $\Delta H = 35 \text{ kJ/mol}$
  - Calculate $\Delta H$ from isosteres
    - $\Delta H = 36 \text{ kJ/mol}$
  - $\Delta H$ from Micro-calorimetry
- H/Pd = 0.116
  - Traditional diff method
- H/Pd = 0.113
  - Micro-cal minimum
Chemisorption and Surface Reactions

\[
Pt_s + CO \rightarrow Pt_s^{\text{CO}}
\]

\[
2Pt_s + H_2 \rightarrow 2Pt_s^{\text{H}}
\]

\[
2Pt_s + O_2 \rightarrow 2Pt_s^{\text{O}}
\]

\[
\frac{2}{3}Pt_sO + H_2 \rightarrow \frac{2}{3}Pt_s^{\text{H}} + \frac{2}{3}H_2O
\]
CO Chemisorption on 0.5% Pt

\[ Pt_s + CO \rightarrow Pt_s^\text{CO} \]
TPR of Pt/Carbon
20 Ru/10 Pt - CO Chemisorption
TPR of Pt-RuCarbon
Pd - CO Chemisorption
H₂ Chemisorption on 0.5%Pt

\[ 2Pt_s + H_2 \rightarrow 2Pt_s^\text{H} \]
20 Ru/10 Pt - H₂ Chemisorption
H$_2$ Chemisorption on 5\%Pd
O₂ Chemisorption on 0.5%Pt

\[ 2Pt_s + O_2 \rightarrow 2Pt_s^O \]
H₂-O₂-H₂ Titration on 0.5%Pt

\[
\frac{2}{3} \text{Pt}_8O + H_2 \rightarrow \frac{2}{3} \text{Pt}_s^H + \frac{2}{3} H_2O
\]
Adsorption on 0.5%Pt

- Hydrogen
  - Total adsorption
  - Reversible adsorption
- Oxygen
  - Total adsorption
- Titration
  - H₂ uptake on Pt-O
Heat Flow from Micro-calorimetry

- Hydrogen
  - Total adsorption
  - Reversible adsorption
- Oxygen
  - Total adsorption
- Titration
  - $\text{H}_2$ uptake on Pt-O
Differential Heat from Micro-calorimetry

- **Hydrogen**
  - $\Delta H_{T,0} = 102 \text{ kJ/mol}$
  - $\Delta H_{R,0} = 58 \text{ kJ/mol}$

- **Carbon Monoxide**
  - $\Delta H_0 = 140 \text{ kJ/mol}$

- **Oxygen**
  - $\Delta H_0 = 265 \text{ kJ/mol}$

- **Titration**
  - $\Delta H_0 = 150 \text{ kJ/mol}$
Differential Heat vs X/Pt

- Hydrogen
  - H/Pt = 0.35
- Carbon Monoxide
  - CO/Pt = 0.33
- Oxygen
  - O/Pt = 0.33
- Titration
  - H/Pt = 0.35
Summary

- Microcalorimetry can be used to verify the reversibility.
- Simultaneous determination of differential enthalpy and adsorption isotherm is in good agreement with traditional isosteric methods.
- Use of Lagrange polynomial provides a useful estimate of the differential enthalpy at infinite dilution.
Porosity
Porosity

- Macro
  - mm to 50nm
- Meso
  - 50nm to 2 nm
- Micro
  - < 2nm
Macro-porosity

- Characteristics of macro-porous materials
  - Favorable transport properties
    - Bulk diffusion
  - Large pore volumes
  - Low surface area
- Mercury Intrusion is often used for characterization
Meso-porosity

- Characteristics of meso-porous materials
  - Favorable transport properties
  - Knudsen diffusion
  - Large pore volumes
  - Large surface area
- Mercury Intrusion and Physical Adsorption are used for characterization
Hg Intrusion

❖ Hg - non wetting fluid - we must apply force to “push” the mercury into the sample pores

❖ Pressure (force) is inversely proportional to pore size

\[ d \propto \frac{1}{p} \]
Hg Intrusion

**Applied Force**

\[ F_i = P \times A \]
\[ F_i = P \times \pi \frac{d^2}{4} \]

**Friction - Resistance**

\[ F_e = \gamma \times \ell \cos \theta \]
\[ F_e = \gamma \times \pi d \cos \theta \]

**Force Balance**

\[ P \times \pi \frac{d^2}{4} = -\gamma \times \pi d \cos \theta \]

**Washburn Equation**

\[ d = -\frac{4\gamma \cos \theta}{P} \]
Washburn Equation

- Surface tension - $\gamma$ - property of liquid Hg
- Contact angle - $\theta$ - property of the surface (solid)
- Pressure - $P$ - measured
Measurement

Two basic measurements

• Pressure
• Pore size
• Capacitance
• Intrusion volume
• Macro and meso porosity
Hg Intrusion P vs V
4mm Alumina Bead
Bead vs Powder

[Graph showing the comparison of Bead and Powder cummulative intrusion volume against pressure in MPa.]
Porosity

- Between particles (void space from packing)
  - porosity of beds
- Within a particle
  - porosity of the material
Differential vs Log-differential Pore Size Distribution

\[ \frac{dV}{d(\log D)} = D \frac{dV}{dD} \]
Differential Pore Size Distribution

VS

Log-differential Pore Size Distribution

\[
\frac{dV}{d(\log D)} = D \frac{dV}{dD}
\]
Pore Area vs BET Area

 Worm Hg Pore Area

\[ a_{Hg} = \frac{-\int_0^V PdV}{\gamma \cos \theta} \]

雄厚 Based upon a work function

 Exclamation BET Area

\[ a_m = \frac{n_m N_a \sigma}{m} \]

 Exclamation Based upon the area occupied by adsorbed nitrogen (krypton)

\[ \cos \theta = \frac{-\int_0^V PdV}{a_{Hg} \gamma} \rightarrow \cos \theta_{eff} = \frac{-\int_0^V PdV}{a_{BET} \gamma} \]


\\
\[ a_{Hg} \cos \theta = a_{BET} \cos \theta_{eff} \]
BJH - PVD
Pt/Al$_2$O$_3$
BJH & MIP - PVD
Pt/Al$_2$O$_3$
Contact Angle: Mercury Intrusion

Params
- BET Surface Area = 101.2
- Hg Pore Area = 116.2
- theta = 130.0
- theta effective = 137.6

Contact Angle: Mercury Intrusion

Isotherm
Contact Angle: Mercury Intrusion

Pore volume, ml/g

$d$, nm

θ, θ$_{eff}$

Intrusion
Thank-you