MoO_2Cl_2 and the Art of Gas Delivery: Pressure, Flow, and Stability

A Game Changer in Deposition Processes: Next-Generation Process Material Molybdenum and Advanced Delivery Systems

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Agenda

01 **Sand-to-Science – Gratitude For The Times We Live In!**

02 **States of Matter – Getting to Gas - Complexities of Various States of Matter**

03 **Solid Sublimation Deep Dive – Containers, and Delivery**

04 **Chemistry of MoO_2Cl_2**

05 **Why Can Merck Operate At Higher Temps?**

06 **Merck Solution**

- MoO_2Cl_2 Stability
- Pressure and Flow Stability
- CK Vapor Deep Dive

Sand-to-Science

01

From Sand-to-Science

- 1600-1700s – emergence of organized scientific communications
- 1830s – mass communication through print
- Early 1900s – Public libraries and standardized curricula
- 1940s-50s – Broadcast media and growth of specialty knowledge
- Early 1969 – birth of internet
- 1990s-2000s – search engines and digital repositories explode
- 2010-2020 – online learning, democratized content
- **2020s-Present – Broad, internet scale access to expert level input**
- What’s next?!

- Going from sand to expert advice is a miracle! Think of the collaboration and all that has to go right?!
- Anyone with internet has expert level advice on any topic. Your curiosity is the limit!
- Putting so much information and expertise in the hands of everyone WILL lead to humanity flourishing

States of Matter And Delivery

02

Pattern → Etch → Fill → CMP

MERCK

Semi Materials Supply Chain – Simplified PFD

Merck (and my) Expertise

- A good semi supplier allows chip manufacturers to do what they do best – carry out the most advanced manufacturing process known to man on a daily basis
- A good semi supplier manages everything upstream to ensure high quality – which leads to best-in-class uptime – materials and delivery
- How does the Merck solution bring forth best cost of ownership for MoO_2Cl_2 – best utilization, best flow and pressure stability, least frequent cylinder exchanges? **No news is good news on startup**!

  - Merck has leveraged **first-principal engineering** and **deep chemistry expertise** to provide the overall solution

States of Matter – Back to The Basics

FUN FACT CHECK!

What’s the most abundant state of matter?

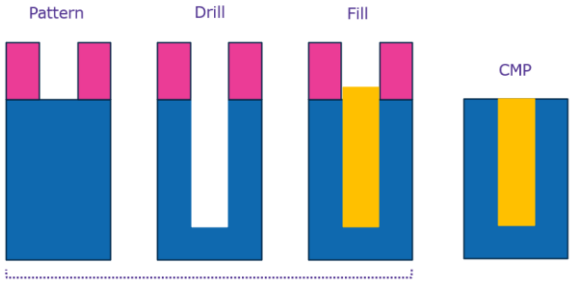
- Gas
- Liquid
- Solid

FUN FACT CHECK!

What's the most abundant state of matter?

- Gas
- Liquid
- Solid
- Plasma!

States of Matter – Back to The Basics
Gas Delivery – <u>Gas</u> Vs Liquid Vs Solid

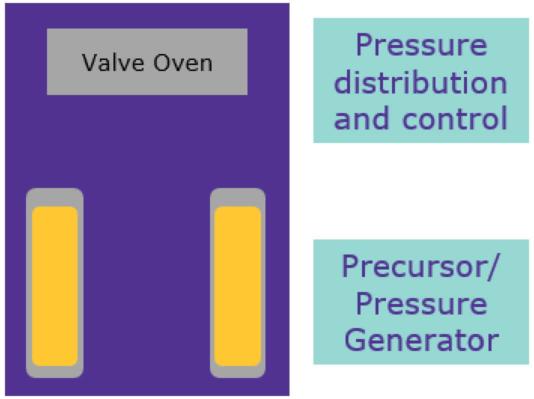


Requires GAS DELIVERY

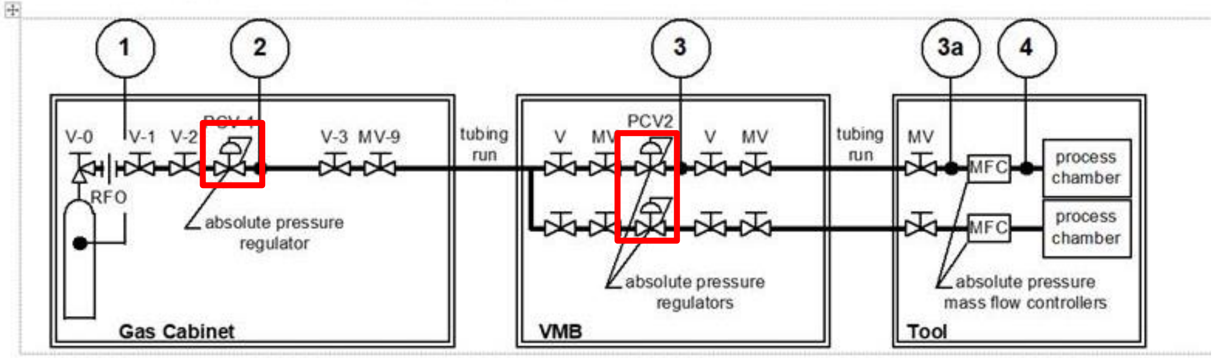
GAS

- Easiest to deliver. Comes down to gas management
  - Down regulation of pressure, pressure monitoring, redundant valves for safety
- WF_6 Case Study - Multi-stage regulator system to get from 800 torr to 400 Torr and below for tool operating pressures


The Versum Materials' eV* Temperature Control System provides tighter, more precise control that will lead to more consistency for your process.



5.3 Pressure Reduction System Diagram: The following diagram shows a typical system (see paragraph 7.1 for the diagram legend).



States of Matter – Back to The Basics
Liquid Delivery – Gas Vs <u>Liquid</u> Vs Solid

LIQUID

- Liquid delivery complexity increases significantly relative to gas – <u>but ultimately you need gas in the deposition chamber</u>
- Precursor Considerations
  - **Stability - Many organometallic precursors lack thermal stability**
    - Require near-tool vaporization – DLI as an example
  - Precursor degas
  - As an example, a more complex system is needed for **1)** Bulk **2)** distribution and **3)** final vaporization – primarily due to thermal stability of materials
- Container Design
  - Bubbler – enables lower temperatures for lower vapor pressure materials and thermal sensitivity
- Heat tracing lines often required to prevent condensation

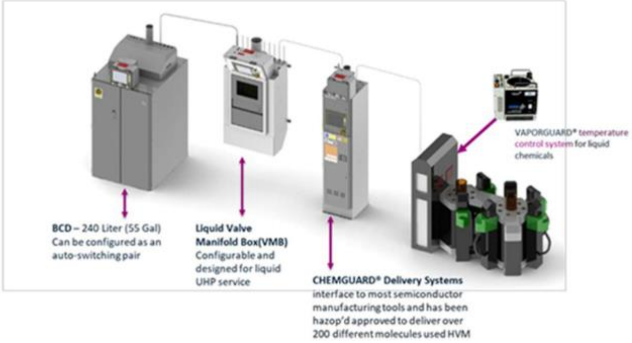
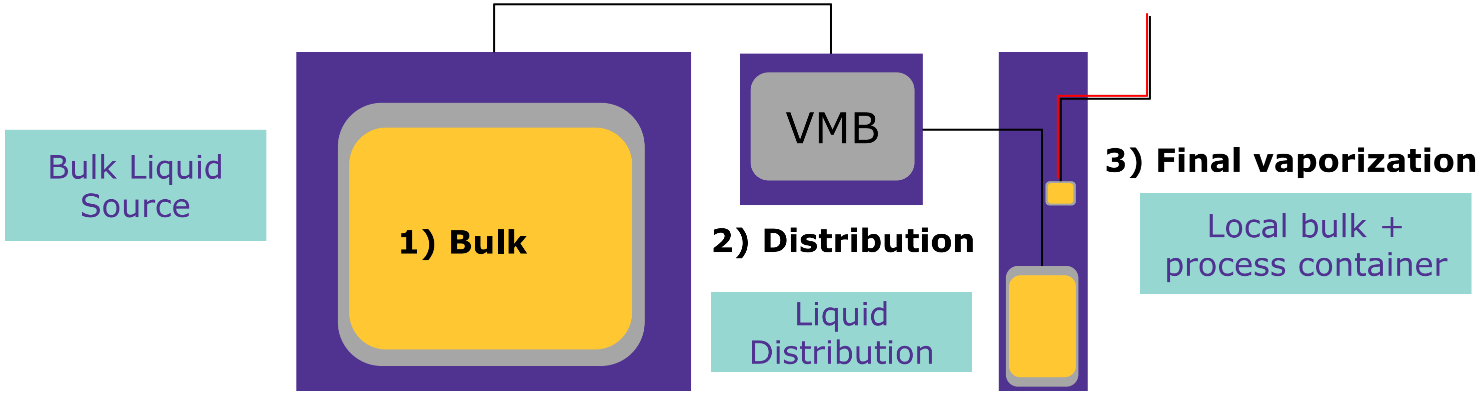


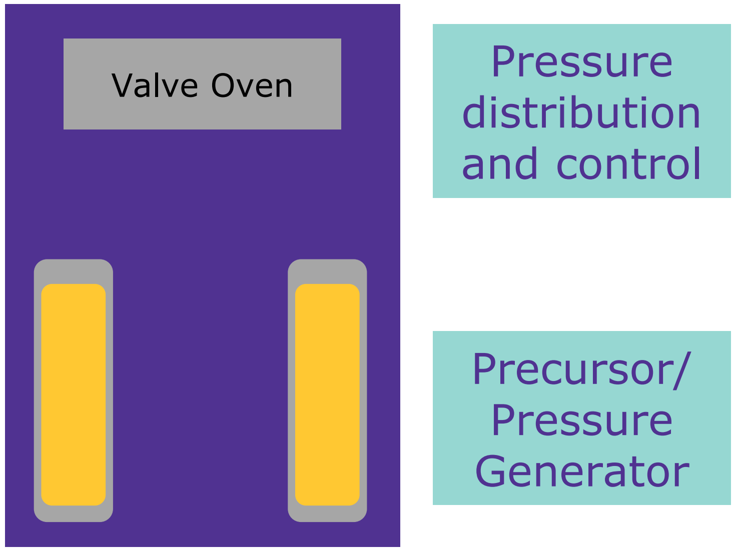
Figure 5-1: CHEMGUARD® GenIII

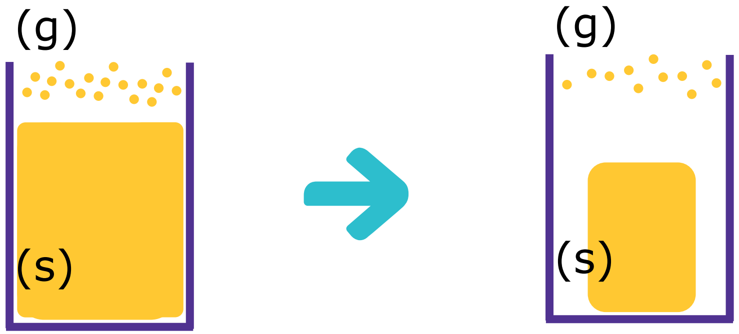


States of Matter – Back to The Basics
Solid Delivery – Gas Vs Liquid Vs Solid

SOLID – Difficulties of Solid Delivery

- Difference between gas and solid delivery? Primary difference is container complexity (and higher temperature components)
- Sublimation vs Boiling
  - Container design is critical for sublimation – significant increase in container complexity. **Source of pressure for the process**
    - **- Heat and mass transfer more of a problem in sublimation than boiling – especially in high flow regimes**
    - - Evaporative cooling with limited heat transfer – driving heat into bed of solid is critical factor for stable flow and pressure delivery
  - Which is better for heat transfer (pressure and flow stability)? Sublimation vs boiling?





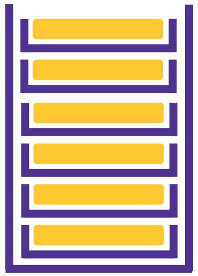
1. **Heat transfer area to Material ratio**
2. **Material closest to sidewalls sublimes first**
3. **Constant temperature, sublimation rate decreases over time**

Solid Sublimation Deep Dive – Container Design

03

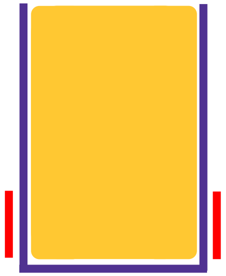
Delivering Solids – Sublimation Vs Boiling
Heat Transfer Strategies

High Surface Area



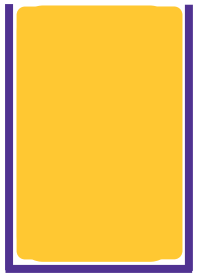

- Low volume efficiency
- Difficult to load/clean
- Constantly changing HX efficiency

Local Heat Flux Control




- Thermal variation inside container
- Solids pull away from hot walls
- Behavior changes with fill level

Increase Heat Transfer Coefficient




- Convert to liquid
- High interface heat transfer
- Reduced thermal gradients
- Constant source pressure
- High utilization possible

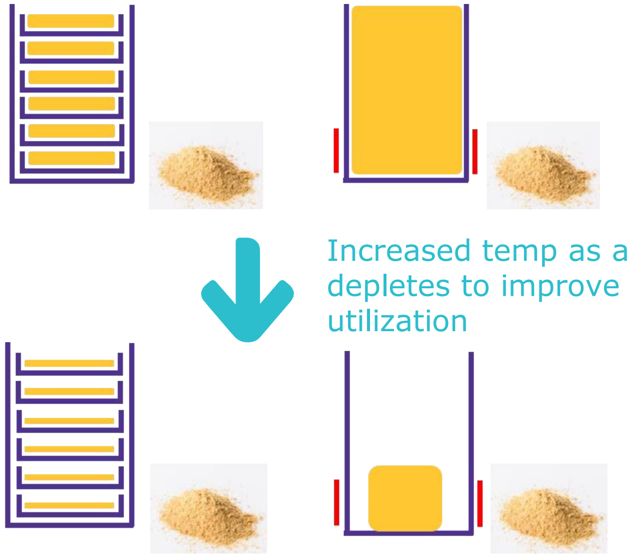
$$Q = cA\Delta T$$

Challenges of Sublimation – Decreased Rate Over Time

1. **Heat transfer area to Material ratio**
2. **Material closest to sidewalls sublimes first**
3. **Constant temperature, sublimation rate decreases over time**

SOLID – Difficulties of Solid Delivery

- Heat transfer is limiting
  - Surface area for heat transfer and interfacial heat exchange degrade as solid sublimes
- As material is depleted, less heat flux means pressure and flows drop
  - **Requires increase in temperature to maintain sublimation rate**



$$Q = cA\Delta T$$

Chemistry of MoO_2Cl_2

Moisture Contamination Pathway

$$MoO_2Cl_2(H_2O)_2 \xrightarrow{60\ ^\circ C} MoO_2Cl_2(H_2O) + H_2O$$

$$MoO_2Cl_2(H_2O) \xrightarrow{80\ ^\circ C} HMo_9O_{27}Cl + HCl$$

$$\underline{\mathbf{H}}Mo_9O_{27}\underline{\mathbf{Cl}} \xrightarrow{>150\ ^\circ C} HCl\ (g)$$ (1974, Chem Letters)

04

Deep Dive Into Decomposition of MoO_2Cl_2 Hydrate

MoO_2Cl_2 – Hydrate Decomposition

Thermal decomposition of MoO_2Cl_2 happens in 3 reactions

- First decomposition is removal of H_2O at relatively low temperatures
- Second decomposition is degradation of core molecule and generation of HCl
- Third and final decomposition happens at higher temperatures

Moisture Contamination Pathway

$$MoO_2Cl_2(H_2O)_2 \xrightarrow{60\ °C} MoO_2Cl_2(H_2O) + H_2O$$

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Sublimation temps – HCl Remains!

$$MoO_2Cl_2(H_2O) \xrightarrow{>150\ °C} \mathbf{H}Mo_9O_{27}\mathbf{Cl} + HCl$$

Deep Dive Into Decomposition of MoO_2Cl_2 Hydrate

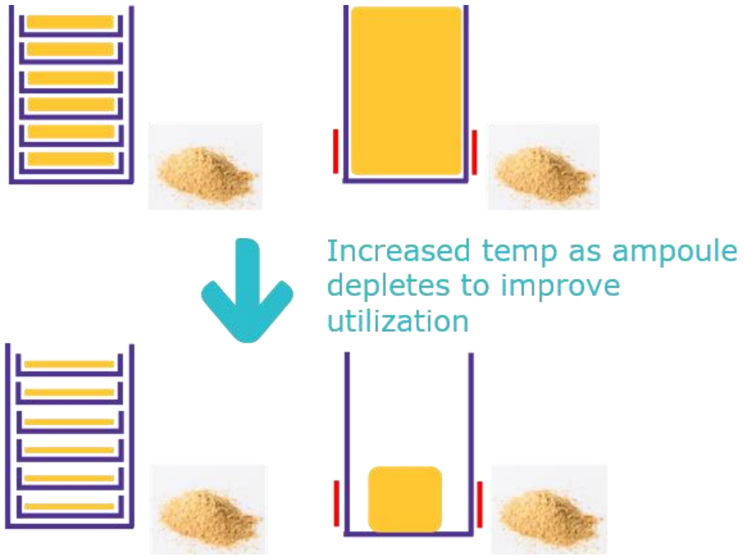
MoO_2Cl_2 – Hydrate Decomposition

- Solid state MoO_2Cl_2 delivery still has **HCl** tied up in $\mathbf{H}Mo_9O_{27}\mathbf{Cl}$!
- As container depletes, increase in temperature to maintain pressure means **more HCl generation**

Sublimation temps – HCl Remains!

$$MoO_2Cl_2(H_2O) \xrightarrow{\mathbf{80\ °C}} \mathbf{H}Mo_9O_{27}\mathbf{Cl} + HCl$$

$$\underline{\mathbf{H}}Mo_9O_{27}\underline{\mathbf{Cl}} \rightarrow HCl\ (g)$$



Deep Dive Into Decomposition of MoO_2Cl_2 Hydrate

MoO_2Cl_2 – Hydrate Decomposition

- In order to successfully leverage high temperature operation, **you must have hydrate free material**

High Surface Area

- Low volume efficiency
- Difficult to load/clean
- Constantly changing HX efficiency

Local Heat Flux Control

- Thermal variation inside container
- Solids pull away from hot walls
- Behavior changes with fill level

Increase Heat Transfer Coefficient

- Convert to liquid
- High interface heat transfer
- Reduced thermal gradients
- Constant source pressure
- High utilization possible

$$Q = cA\Delta T$$

Why Can Merck Operate At Higher Temps?

Moisture Contamination Pathway

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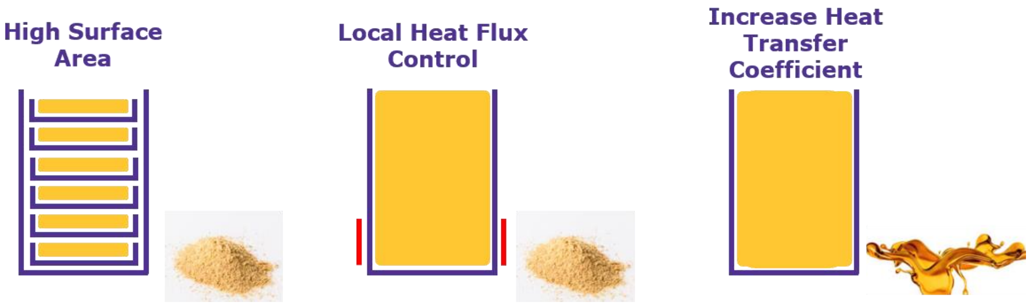
05

MoO_2Cl_2 – Merck Solution
Thermal Stability of MoO_2Cl_2

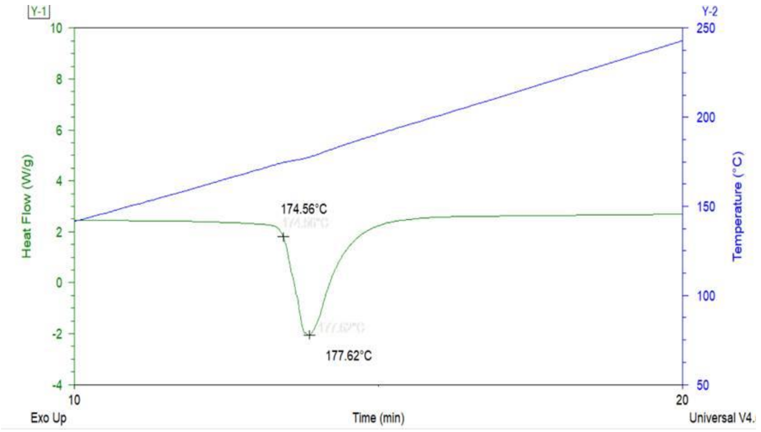


Is MoO_2Cl_2 Thermally Stable?

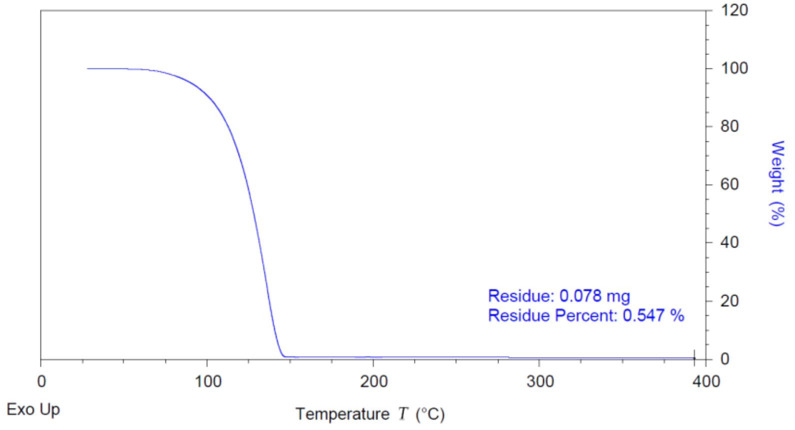
- No observable MoO_2Cl_2 decomposition observed between RT and 250 °C
- No observable difference in residue after heating at 200 °C for 12 months

Conclusion: **MoO_2Cl_2 is thermally stable. Why not go hotter for delivery?**

DSC up to 250 °C



TGA after heating at 200 °C for 12 months



MoO_2Cl_2 – Merck Solution
HCl Facilitates Corrosion

Corrosion Triangle

- What about for MoO_2Cl_2, Ni and HCl?

Electron Source · Electron Sink · Product

$$\mathbf{Ni + MoO_2Cl_2 \rightarrow NiCl_2}$$

- HCl acts as a facilitator of the reaction, rapidly etching the protective oxide
- In the absence of HCl, rely on direct etch and diffusion (slow)

Electron Source · Electron Sink · Product

$$Fe + O_2 \rightarrow FeO_2$$

H_2O enables reaction

O_2

- H_2O acts as a facilitator of the reaction, allowing ions/electrons to conduct for the reaction to proceed.
- In the absence of water, rely on diffusion (which is slow below 570 C)

HCl enables reaction

MoO_2Cl_2

MoO_2Cl_2 – Merck Solution
HCl Free Performance

Moisture Contamination Pathway

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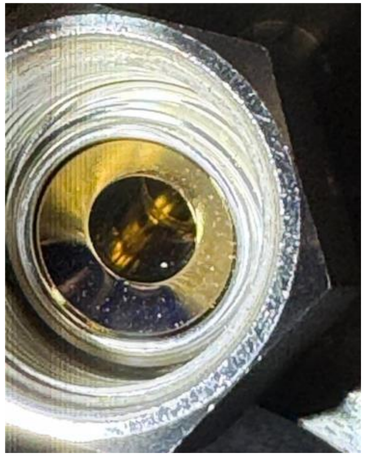
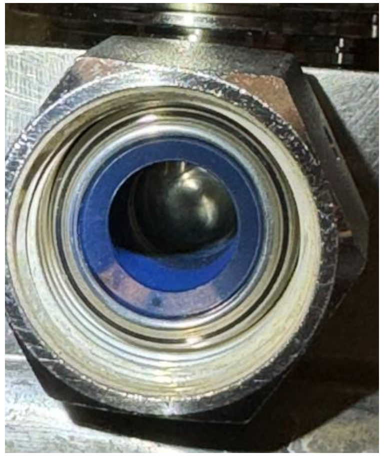
Merck MoO_2Cl_2

- Merck process ensures **best-in-class HCl** – this is a chemical fact
  - Long term operation in the absence of HCl – **<u>NO Residue!</u>**

> 6 Months of operations at 200 C – Low HCl



1 month of operation at 200 C – elevated HCl



- Any residual hydrates or HCl will lead to corrosion of container and delivery systems
- **Merck REMOVES hydrate and HCl – most thoroughly dried material!**
- **No corrosion**

Merck Delivery Solution – Enabling Performance

Stable Flow
Stable Pressure
>99 % utilization

06

Merck Solution

RECAP

- Complexity of delivery
  - Gas < Liquid ≤ Solid
- Sublimation requires highly specialized containers to drive heat into solid – heat transfer MUCH less efficient than in a liquid
- Increase in temperature towards end of ampoule life is often needed for improved utilization – as powder levels decrease, surface-area-to-solid contact area reduces, higher temperature required to maintain same pressure
- Higher temperature generates HCl from hydrates
  - **Merck's process eliminates HCl formation, reduces corrosion**

WHERE TO NEXT?

- Merck Approach – First principals design of chemistry and delivery system
  - Requirements/Problem statement
    - Stable flow and pressures for near 100 % of ampoule ✓✓✓
    - Stable quality throughout delivery ✓
    - Maximize fill weights in allocated footprint ✓

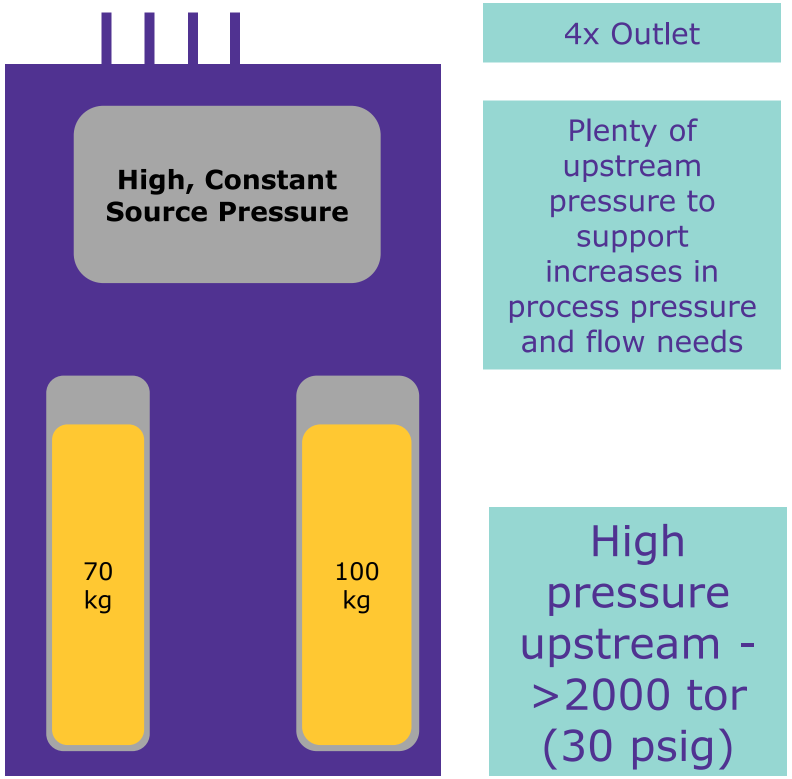
Merck Solution

MoO_2Cl_2 Delivery – Theory of Operation – Today's Offering is HVM Ready

Merck Approach – First Principal Design of chemistry and delivery system

- Can we treat MoO_2Cl_2 as a gas?! Higher operating temperatures → plenty of upstream pressure (like WF_6!)
- MoO_2Cl_2 is thermally stable, and higher temperature operation is better for HCl contamination.

MoO_2Cl_2 Theory of Operation

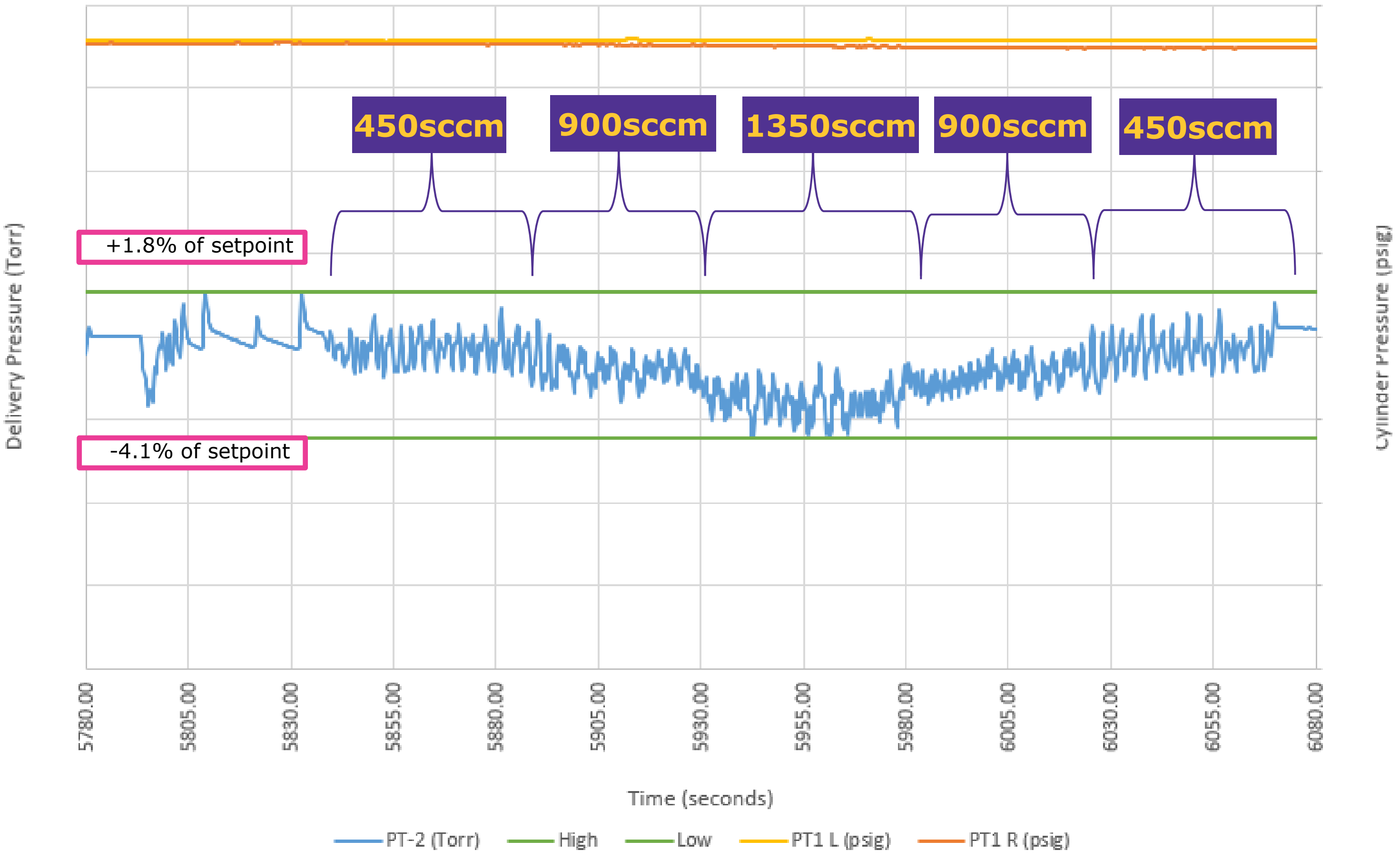


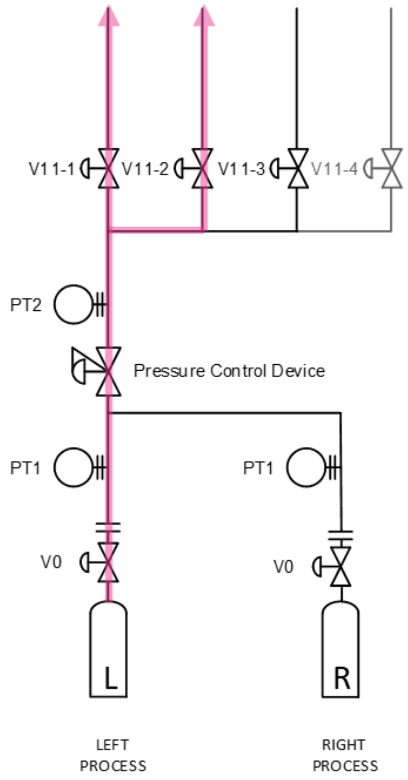
1. **Merck's system generates high upstream pressure – acts like a gas for delivery!**
2. **Regulate downstream delivery pressure within a tight window**
3. **Stable pressure and flow throughout vessel life**
4. **>99 % utilization of material in container**
5. **Enables auto-crossover when container is empty**

MERCK

CHEMKEEPER® Vapor 200 - Flow Step Test – Multiple Chamber On/Off in HVM

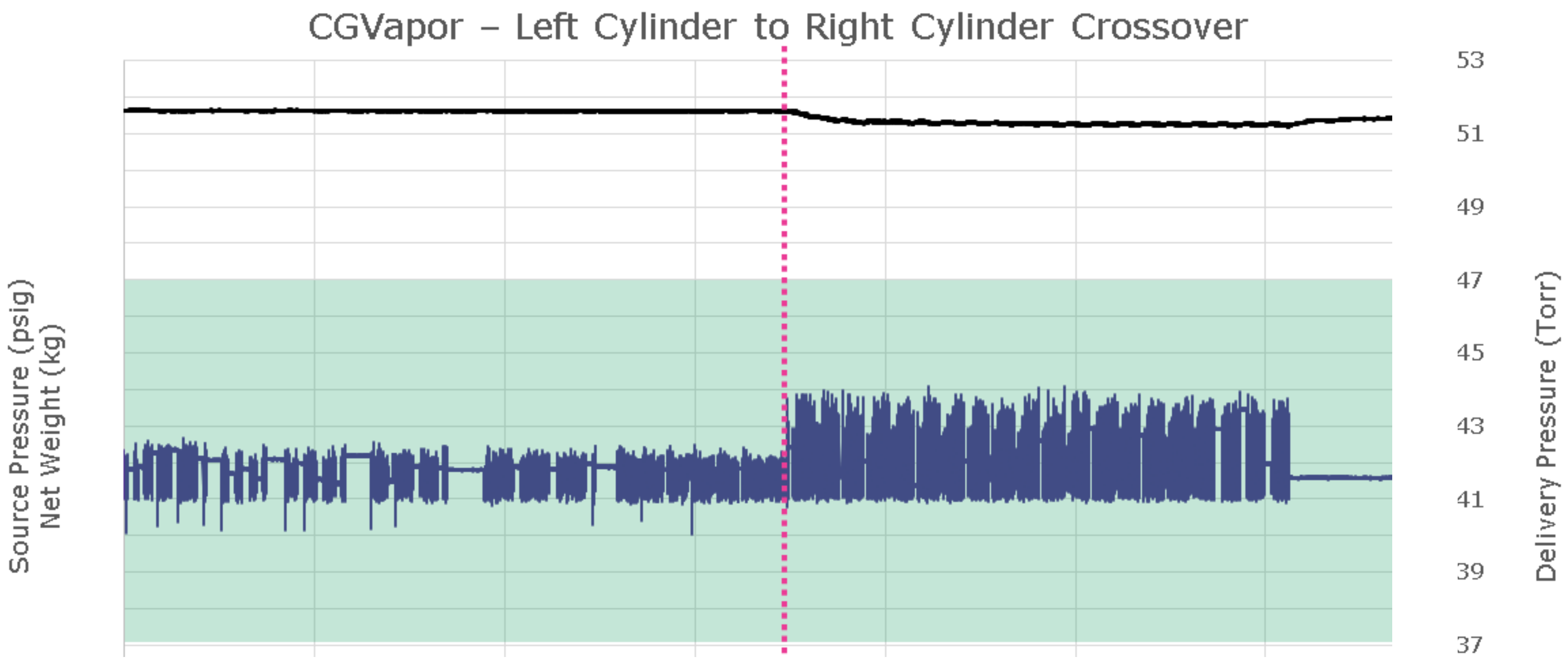
- System reacts quickly to sudden flow demand changes
- Constant pressure across wide range of flows
- Test was conducted through two sticks to simulate multi-chamber operation





System can accommodate multiple chambers on/off with impact to pressure

CHEMKEEPER® VAPOR 200
Cylinder Depletion & Crossover Testing



> 99%
Utilization

1. **CGVAPOR auto-switches from left to right container when container is empty**
2. **No disruption in supply flow or pressure during or after changeover**
3. **Utilization verified on external scale**

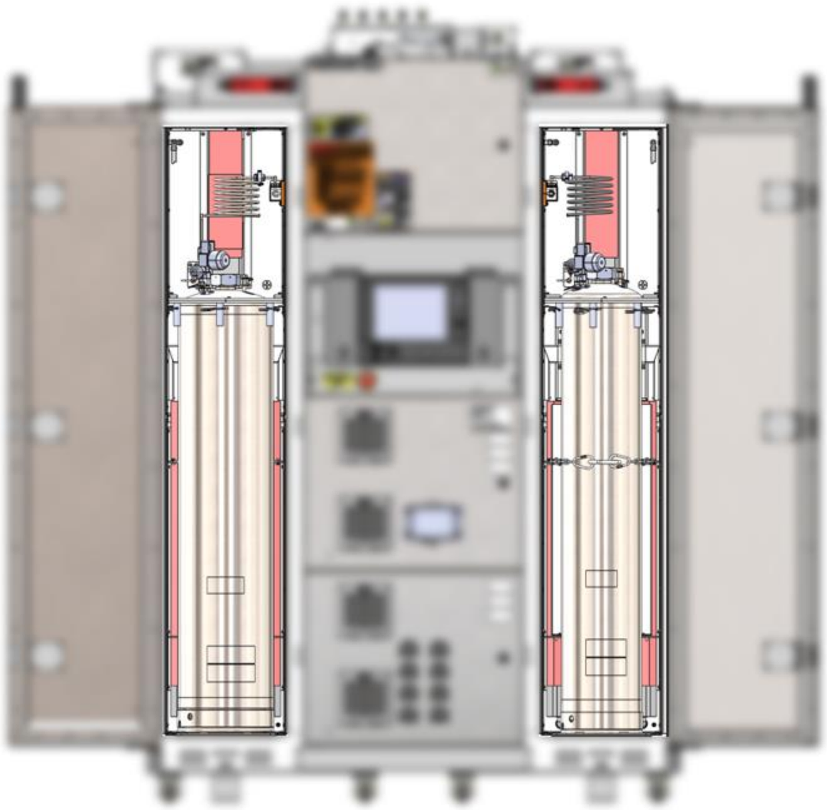
MERCK

CHEMKEEPER® VAPOR 200

MoO_2Cl_2 – Merck Solution – The Benefits Keep Coming! 100 kg

Next Gen Offering

- ✓ **No Change** in cabinet externals – small changes to internals
- ✓ **100 Kg** per cylinder oven with automatic crossover functionality
- ✓ **200 Kg** per system
- ✓ Same footprint and performance as 70 kg offering



Current Offering

- ✓ **70 Kg** per cylinder oven with automatic crossover functionality
- ✓ **140 Kg** per system
- ✓ High pressure cylinder when at temperature (>2000 Torr) ensures high flow rates while maintaining delivery pressure ± 5T
- ✓ **200C oven** guarantees ***uniform heating*** and ***eliminates moisture***

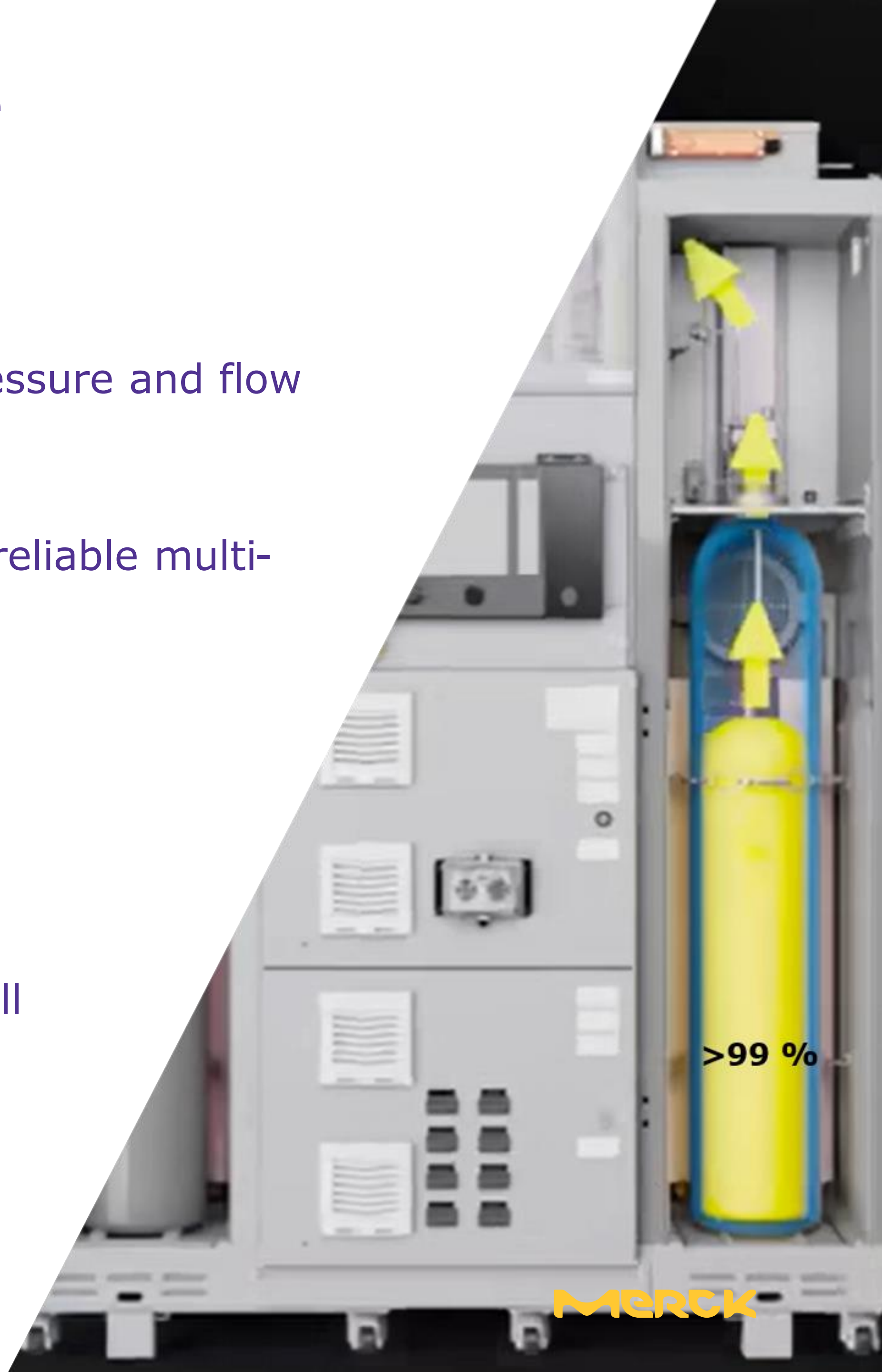
MoO_2Cl_2 Delivery: Stable, Efficient, and Predictable
Conclusion

KEY TAKEAWAYS

- First-principles design yields near 100 % usage with stable pressure and flow across the container life
- High-purity material eliminates corrosion
- Merck solutions reduce complexity, improve COO, and enable reliable multi-chamber operation

KEY BENEFITS

- CG/CK Vapor offers high utilization (>99 %), tight pressure control and robust crossover handling
- Fundamental shift in theory of operation enables simplified container design - reducing maintenance, variability and overall COO
- Scalable, cost-efficient delivery aligned with manufacturing uptime goals



Benjamin Garrett, PhD

Head of New Product Introduction
Innovation team of Specialty Gases and
Delivery Systems and Services

Scan to explore our innovative topics in integrated solutions!