$MgCl_2(2\text{-}6)NH_3$ sorption behaviour

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Ryuichi IWATA*, Takafumi YAMAUCHI, Yasuki HIROTA, Masakazu AOKI and Takashi SHIMAZU

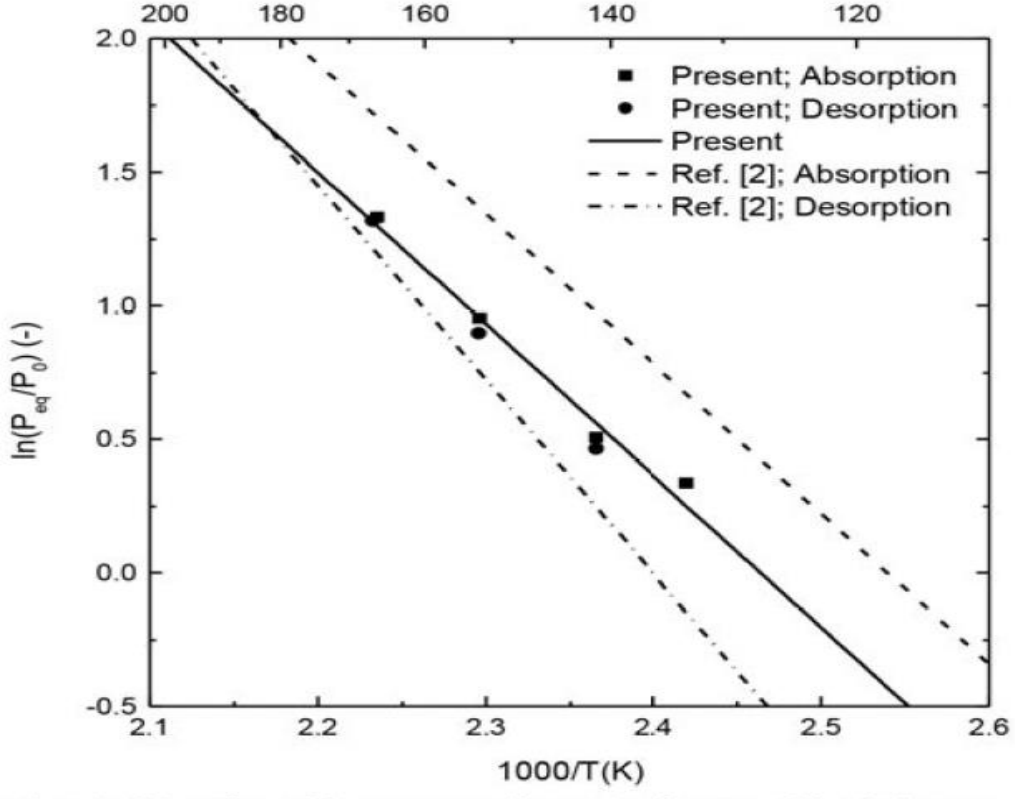


Fig. 3 Clausius-Clapeyron diagram for $MgCl_2 \cdot 2/6NH_3$.

Repeated DSC measurements on $MgCl_2$

- Goal: to understand equilibrium & kinetic behaviour $MgCl_2(2\text{-}6)NH_3$

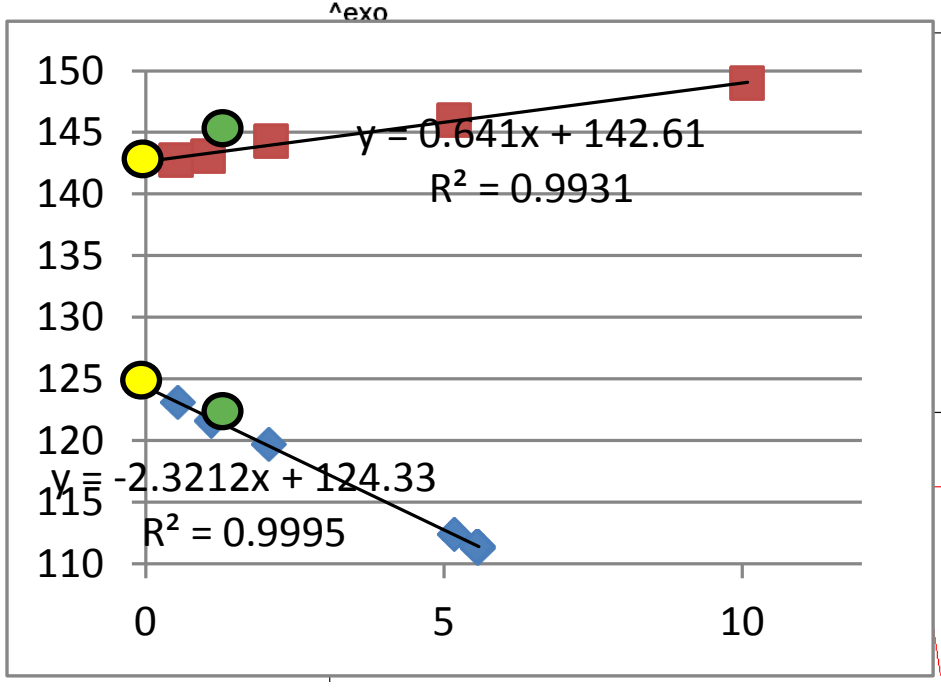
- Approach:

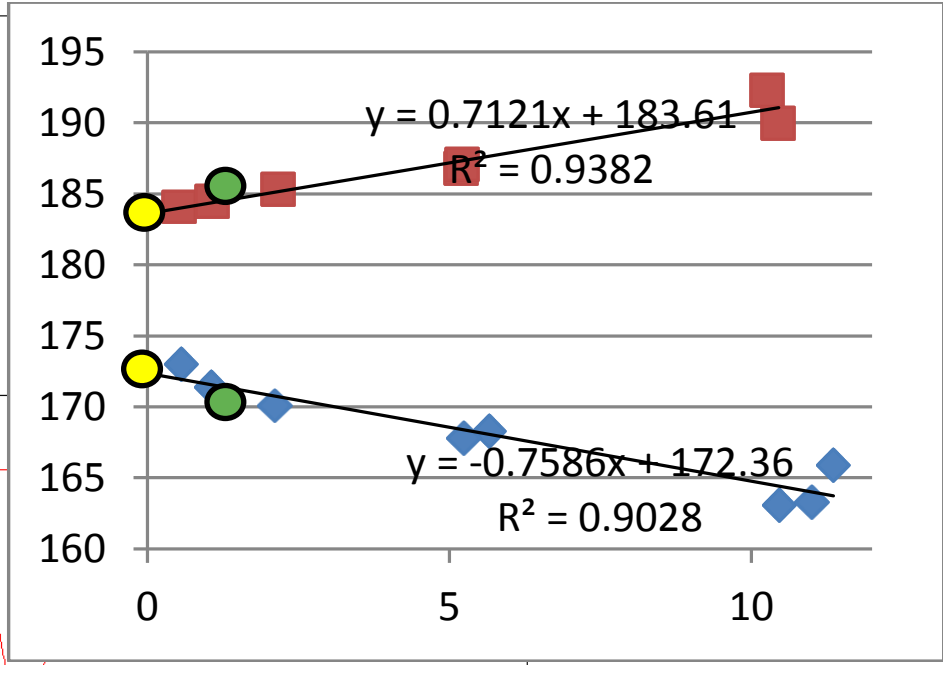
  for equilibrium conditions & thermodynamic properties:
  - Measure HP-DSC signal for a range of DSC-scanning rates (0.5 to 10 K min^{-1})
  - Determine on-set temperatures of peaks
  - Assume: on-set temperature of sample is independent of scan-rate

  $\Rightarrow$ if measured T_{onset} varies with scan-rate: extrapolate to scan-rate = 0 to obtain the sample's onset-temperature = equilibrium temperature
  - Clausius-Clapeyron + onset temperatures & pressures yield ΔS & ΔH values

  for kinetics:
  - Use LDF-model based on pressure difference between eq pressure and actual pressure
  - Determine *k*, E_a and *n*: $dx/dt = k*(1-x)^n*e^{-Ea/RT}*\ln(P_{eq}/P_{dsc})$

DSC results – equilibrium points





On-set temperature(°C) as a function of scan-rate (K/min) for synthesis (blue) and decomposition of $MgCl_2(2\text{-}6)NH_3$ at 1(left) and 5(right) bar NH_3

Eq values Bevers

Eq values ECN

REACTION KINETICS OF AMMONIA ABSORPTION/DESORPTION OF METAL SALTS

Ryuichi IWATA*, Takafumi YAMAUCHI, Yasuki HIROTA, Masakazu AOKI and Takashi SHIMAZU

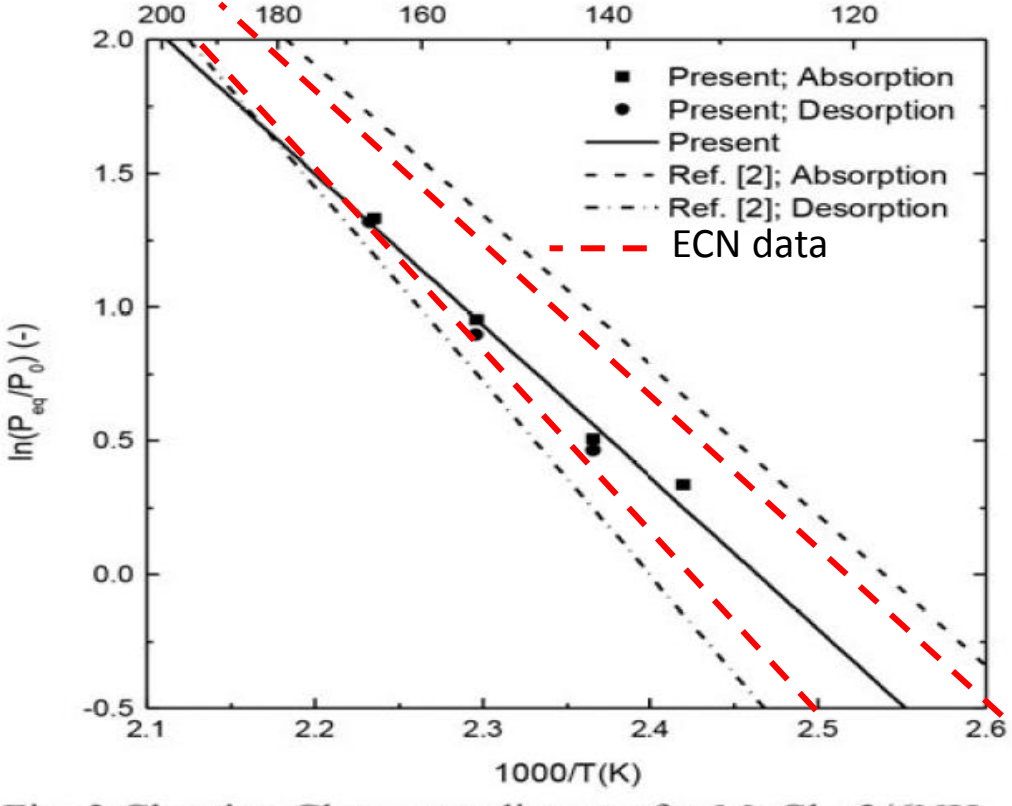


Fig. 3 Clausius-Clapeyron diagram for $MgCl_2 \cdot 2/6NH_3$.

Data ECN: Clear effect of hysteresis

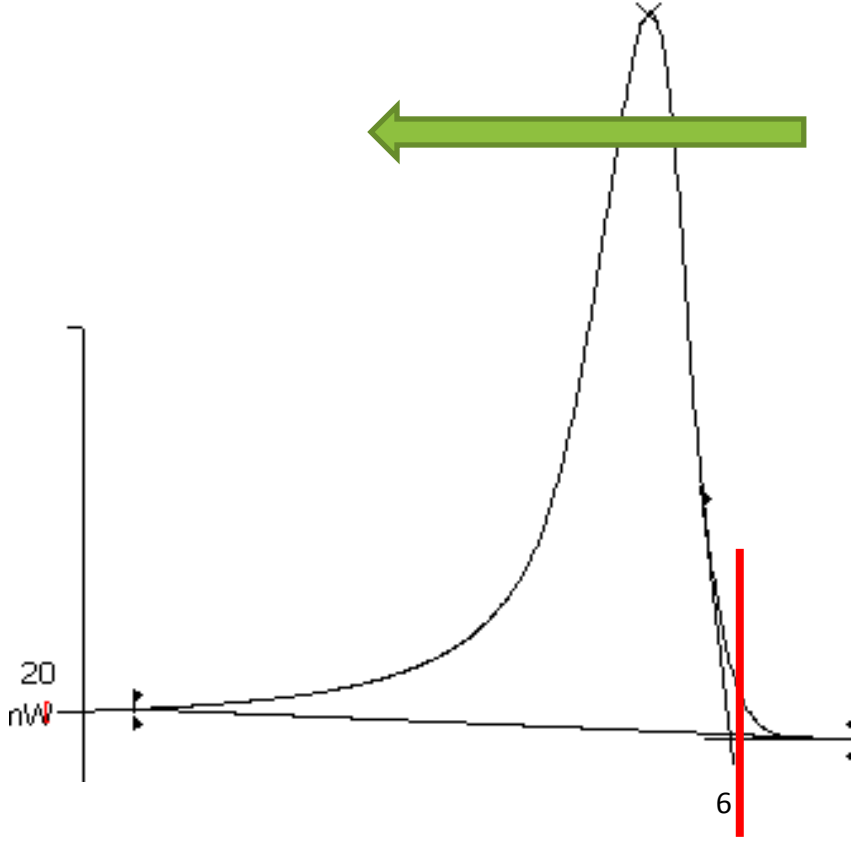
Data Iwata: no hysteresis

What causes this difference?

Comparing measuring techniques

Bevers/ECN: HP-DSC: Equilibrium value is found by taking the on-set temperature of DSC-peak:

This gives the temperature at which the $MgCl_2$ **starts** to adsorb/desorb NH_3



Comparing measuring techniques

Iwata: Fixed volume is filled with ammonia and then connected to a volume containing to $MgCl_2$ sample

The pressure is measured as function of time until equilibrium pressure has been reached, i.e. the pressure at the **end** of the sorption process

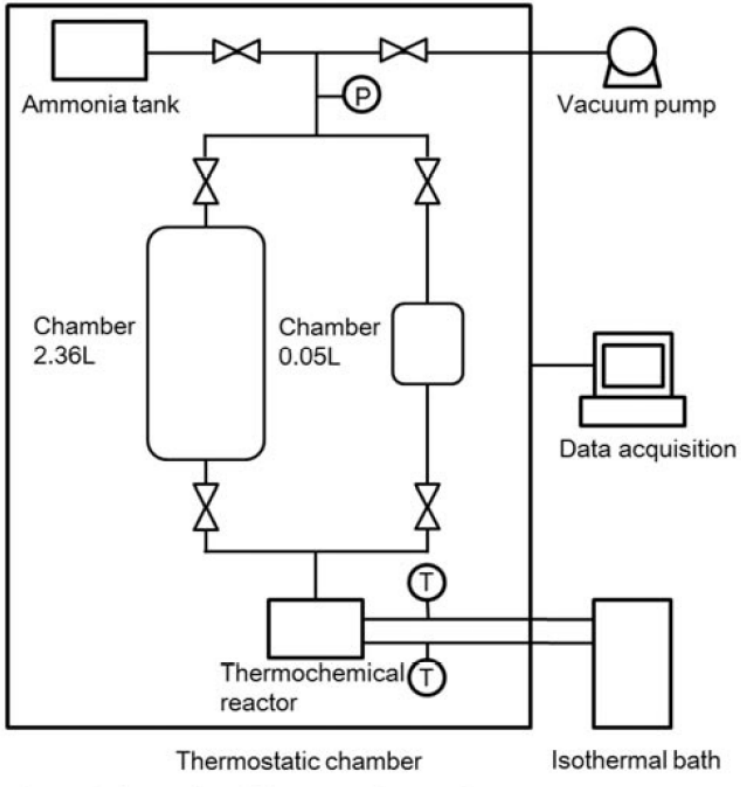
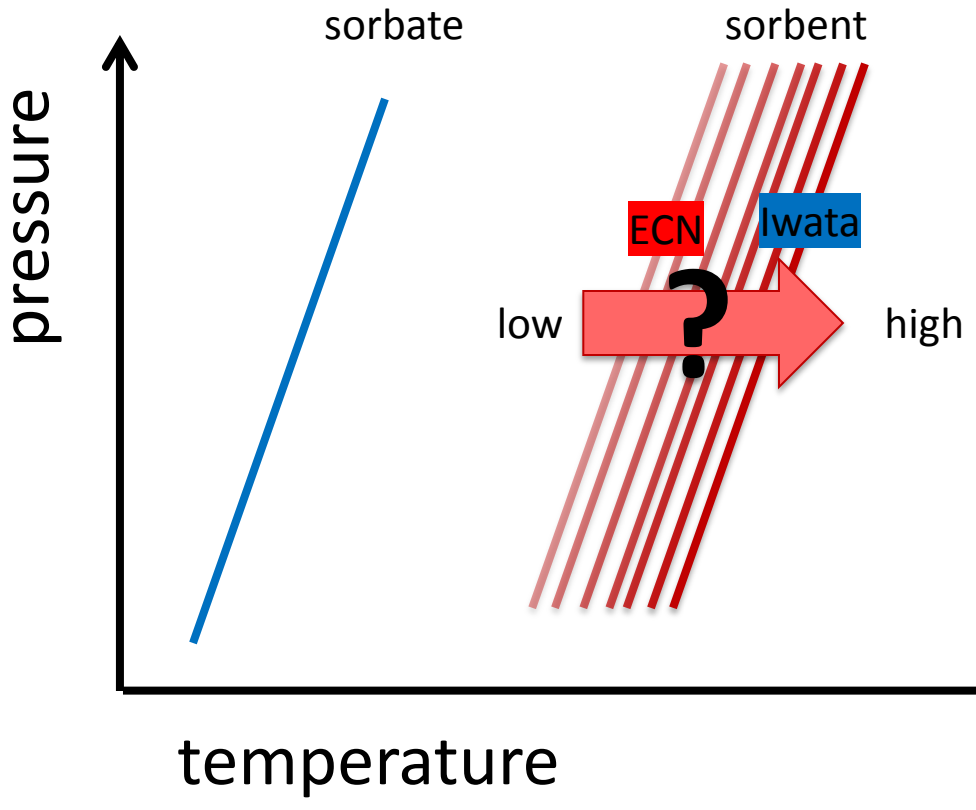


Fig. 2 Schematic of the experimental set-up.

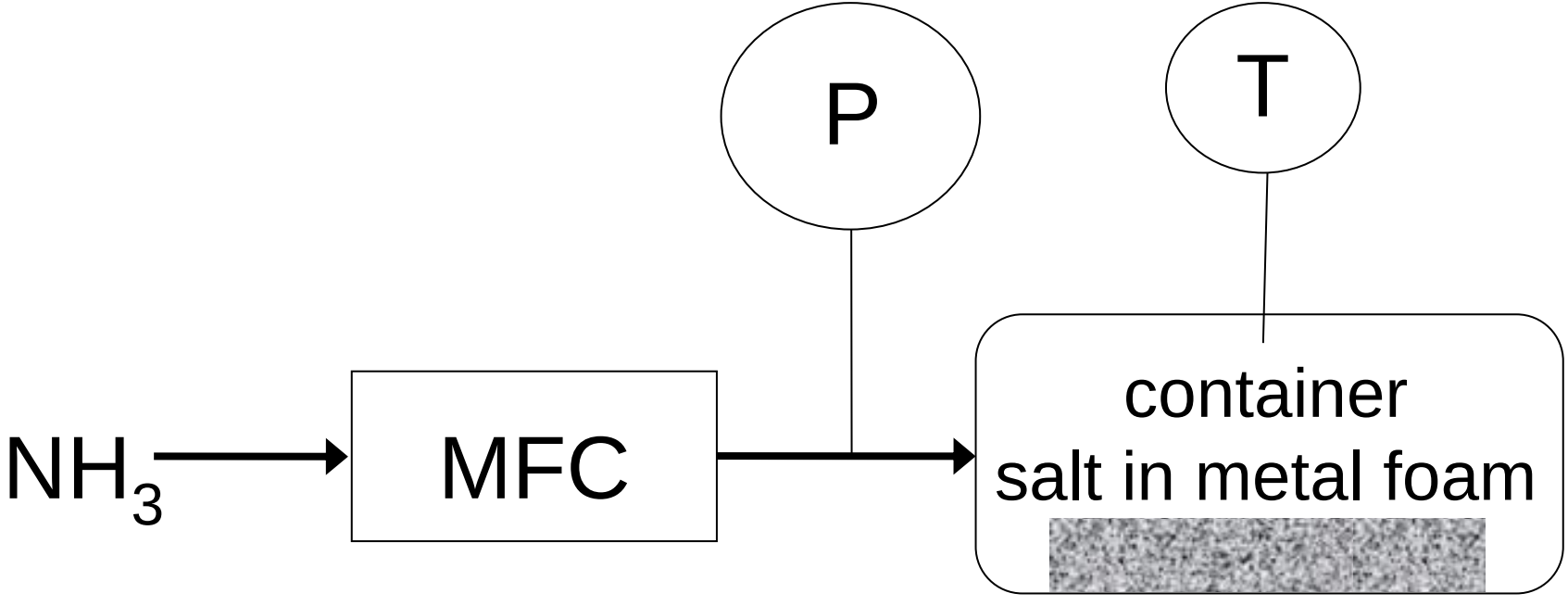
If you put this in a CC diagram (adsorption)



Behavior opposite to:

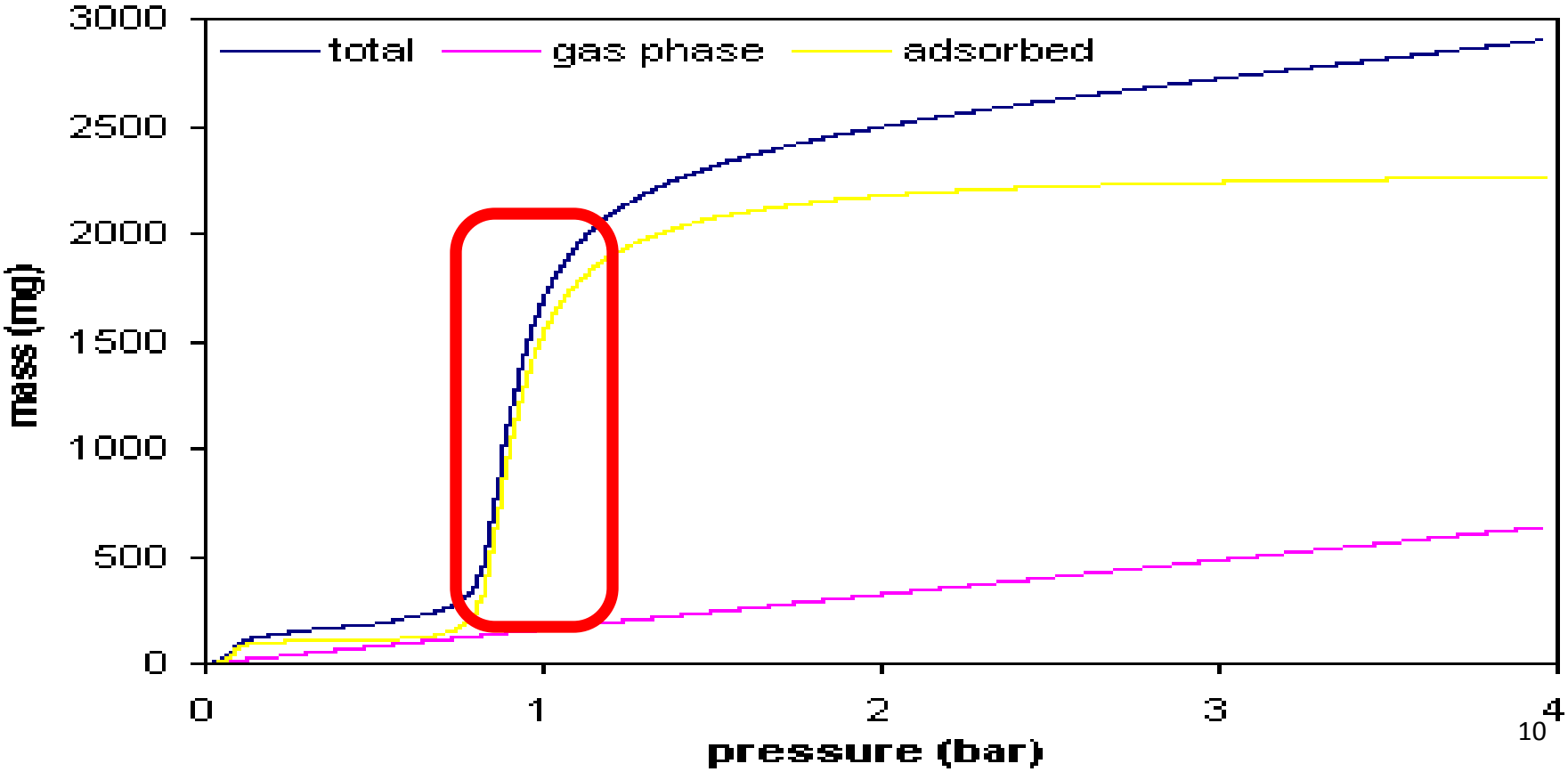
- Absorption
- Physisorption (isosteres)
- Metal hydrides (slope)

Ammonia-salt experiment from 2008 (ISHPC2008, Seoul)

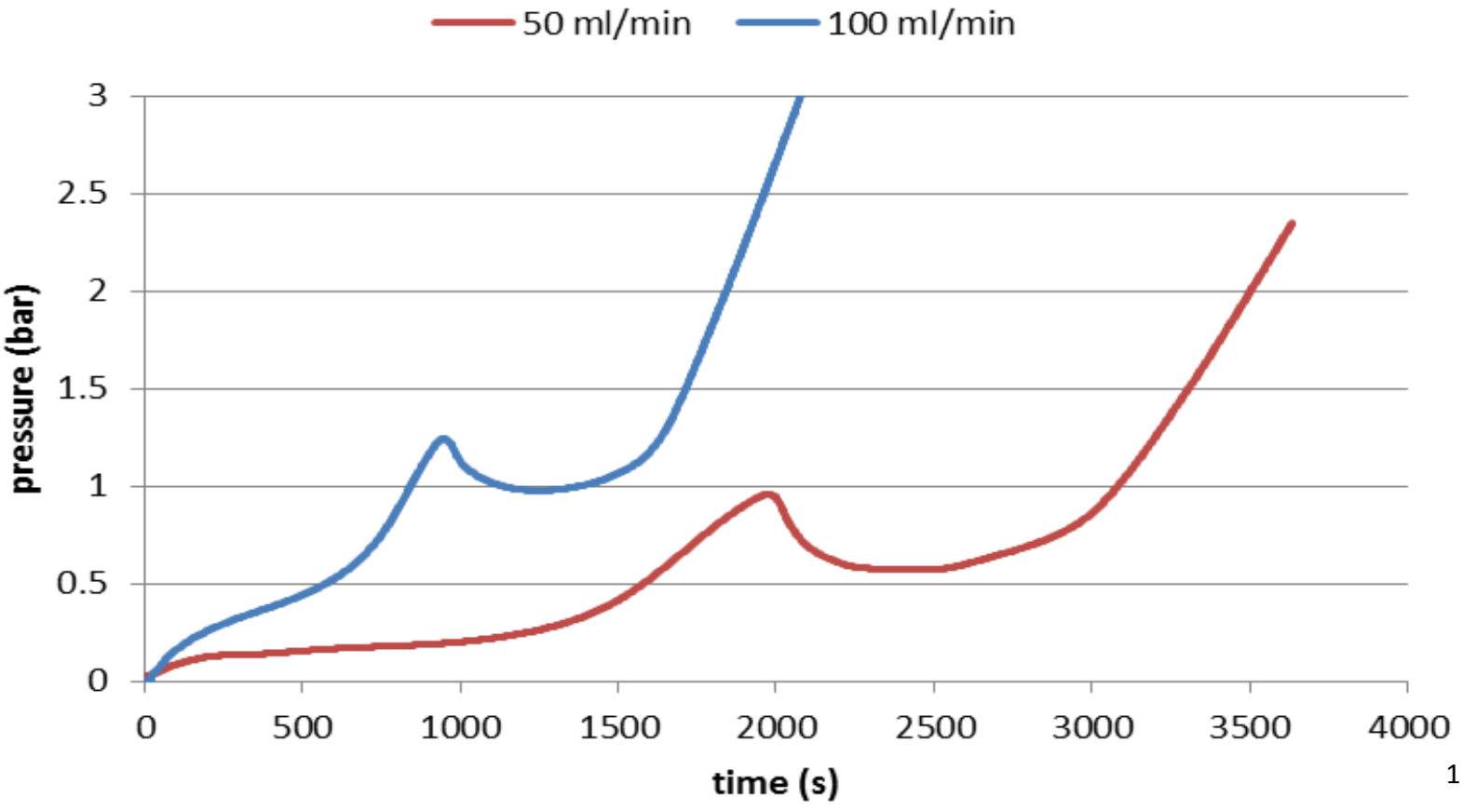


flow NH_3: 50 to 250 ml_n/min

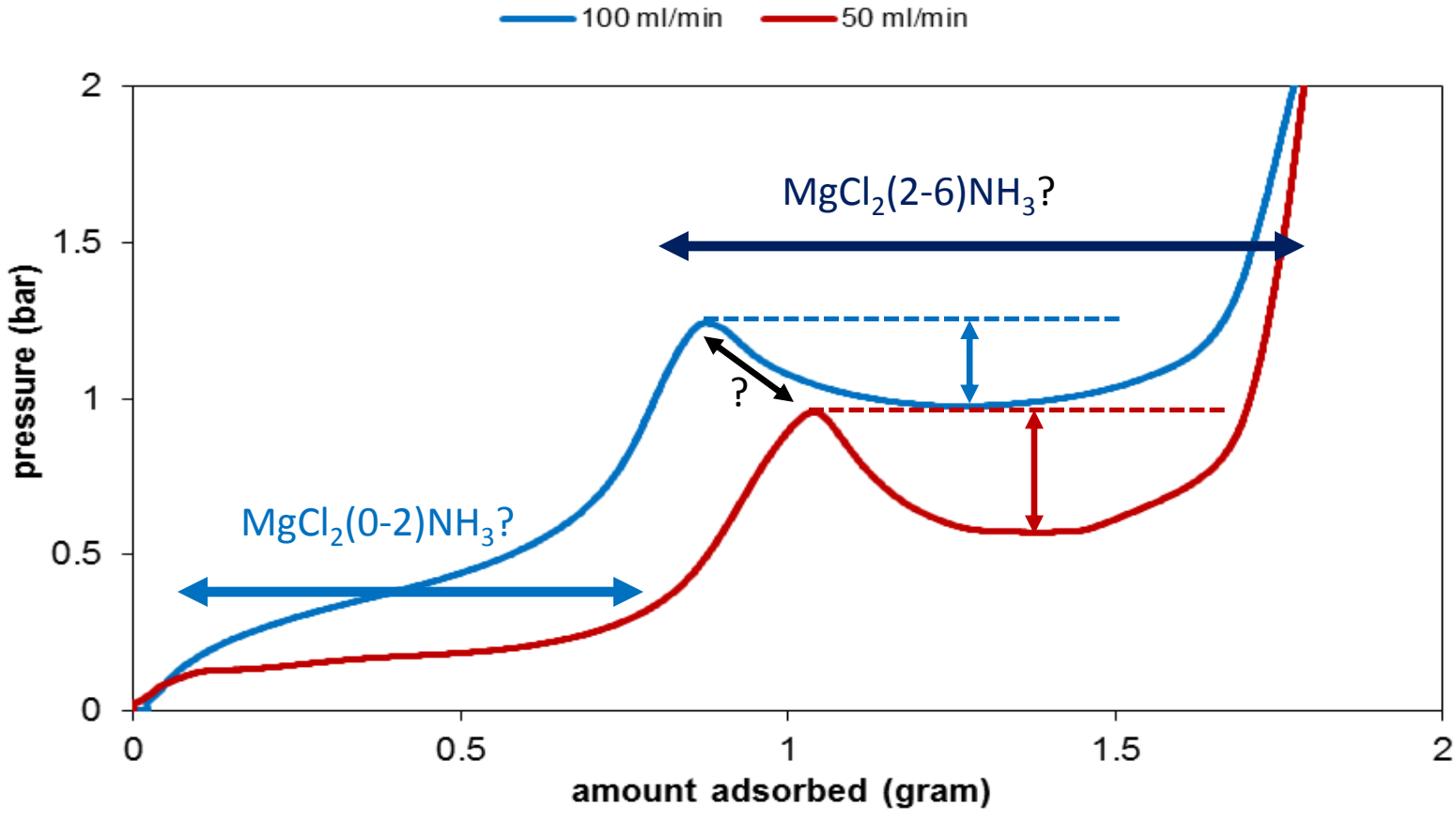
Example result for $LiCl(1\text{-}3)NH_3$



Results for $MgCl_2$ @90°C



Results for $MgCl_2$ @90°C



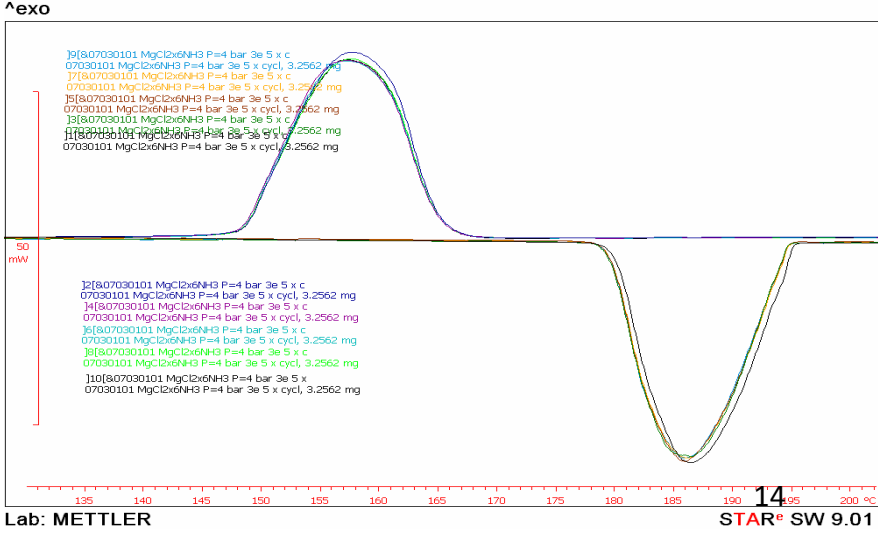
So what do we know?:

- DSC measurements show hysteresis for $MgCl_2(2\text{-}6)NH_3$
- Iwata measurements show no hysteresis
- Apparently hysteresis occurs at start of sorption
- Pressure measurements with MFC are in line with these observations:

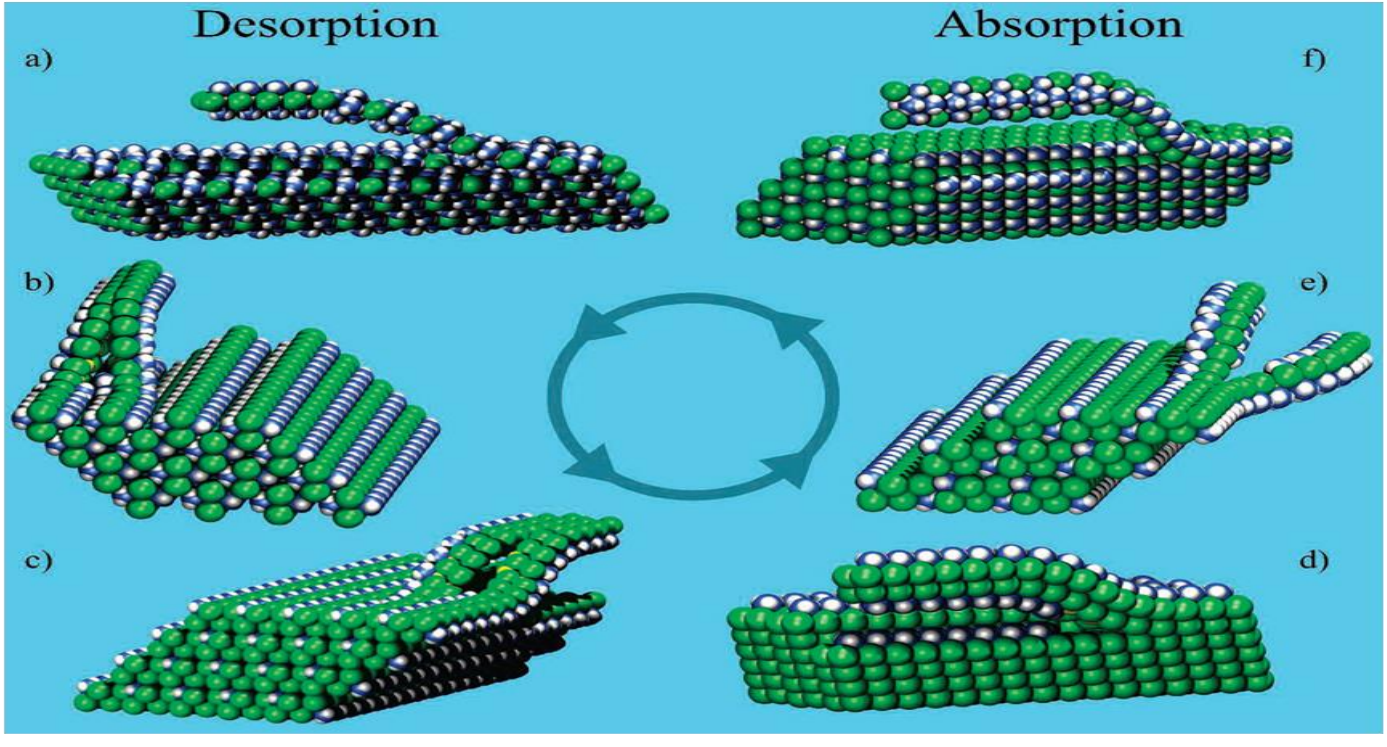
  (if $P_{eq} \downarrow$ after initial adsorption, driving force $(P\text{-}P_{eq}) \uparrow$, $dNH3_{sorbed}/dt \uparrow$ and if $dNH3_{sorbed}/dt >$ MFC => $P \downarrow$)

What causes this behavior?

- Poor kinetics?: if so, why no (big) difference in effect of scan-rate for 1 vs 5 bar (i.e. relative low vs high T)?: k = k0 exp(-Ea/RT) and why hysteresis when extrapolating to scan-rate is 0?
- Some sort of crystal structure change?: if so: why do repeated measurements show very similar HP-DSC curves? (whilst the average crystal size reduces over # of cycles)
- Or … ?



Can it be explained from this?



Mechanistic model for the sequence of $MgCl_2$-NH_3 sorption reactions. A-F refer to the $MgCl_2(6\text{-}2)NH_3$ reactions. source (Sørensen et al., 2008)

To wrap it up:

- Hysteresis in $MgCl_2(2\text{-}6)NH_3$ sorption confirmed (but slightly less than reported by Bevers, 2007)
- Hysteresis effect apparently only for the first amounts of NH_3 adsorbed (down to a few %?)
- Hysteresis seems quite independent of temperature so should we exclude kinetics?
- Could it be related to (change in) crystal structure/reaction mechanism?

Application(s):

- Are there other materials that show similar behavior?
- What would be an accurate method for determining P-T diagram as a function of amount adsorbed? Is it/can it be a function of state at all??
- Can we somehow take advantage of this behavior?
- Sorption heat pump performance better if 0>>x>>1 ?!


~~Questions?~~Answers!?

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