



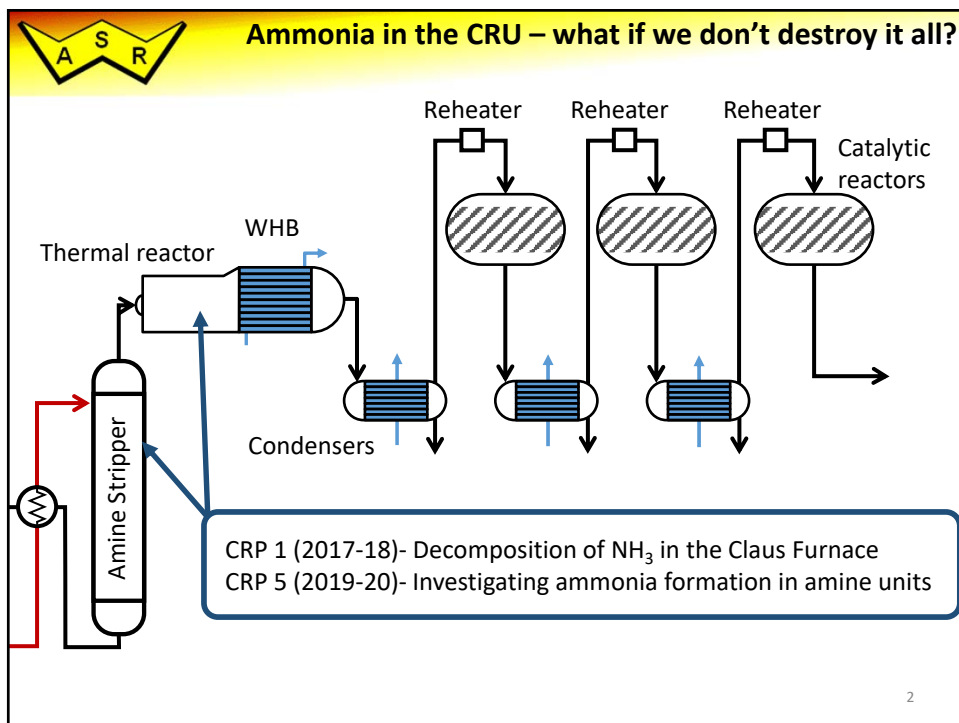
Ammonium salt vapour pressures: what conditions lead to ammonium salt deposition?

R. A. Marriott, M. Madekufamba and K. L. Lesage

Vail Brimstone Symposium, Virtually in Vail, Colorado

September 14, 2021

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ASR Ammonium salt within lines leading to the thermal oxidizer

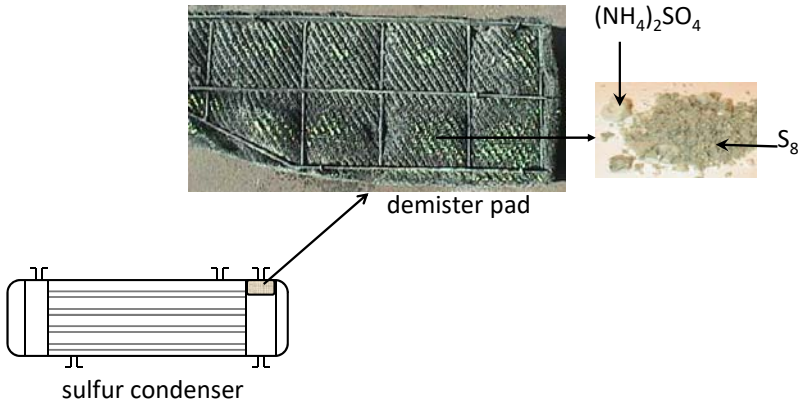


Deposition problem: Plugging
(no corrosion was evident with these deposits)

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ASR Ammonium salts on demister pads



$(\text{NH}_4)_2\text{SO}_4$

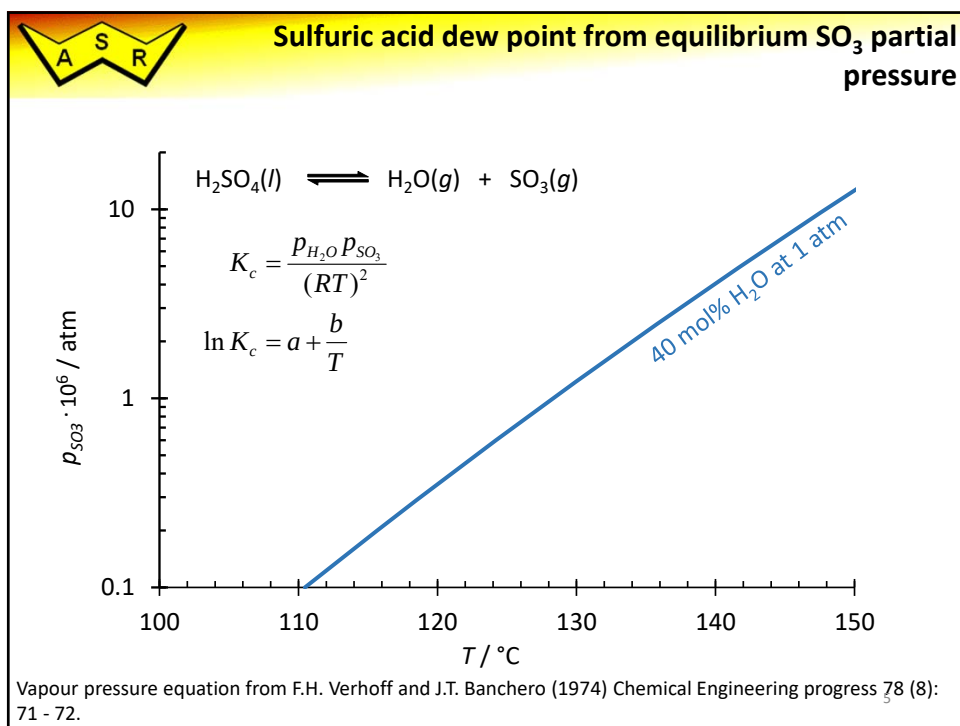
S_8

demister pad

sulfur condenser

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Atmospheric stability of ammonium salts

Decomposition temperatures for ammonium salts (1 atm)⁽¹⁻⁴⁾

Compound		Decomposition Temperature
(NH ₄) ₂ SO ₄	sulfate	235-280 °C
NH ₄ HSO ₄	bi-sulfate	< 235-280 °C
(NH ₄) ₂ S ₂ O ₃	thiosulfate	150 °C
(NH ₄) ₂ SO ₃	sulfite	60-70 °C
NH ₄ HSO ₃	bi-sulfite	< 150 °C (Subl. in N ₂ at 150 °C)
NH ₄ NH ₂ CO ₂	carbamate	40 °C

1. Clark P.D., Dowling N., Huang M., Bernard F., and Lesage K.L. Deposition of ammonia in Claus systems; Theoretical and practical considerations. ASRL Quarterly Bulletin 136. Vol XLII No.4 January - March 2006 p 1-34.
 2. Handbook of Chemistry and Physics, 80th Ed., CRC Press, Inc., Boca Raton, Florida, USA, 1999-2000.
 3. The Merck Index, 12th Ed., Merck and Co. Inc., Whitehouse Station, NJ, USA 1996
 4. Aldrich Handbook of Fine Chemicals and Laboratory Equipment, Sigma Aldrich Fine Chemicals, Canada, 2000-2001

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Studying ammonium salt vapour pressures

T control

Gas Flow

Saturation bed

$(\text{NH}_4)_2\text{S}_2\text{O}_3$
 $(\text{NH}_4)_2\text{SO}_3$
 $(\text{NH}_4)_2\text{SO}_4$

Gas phase analyses

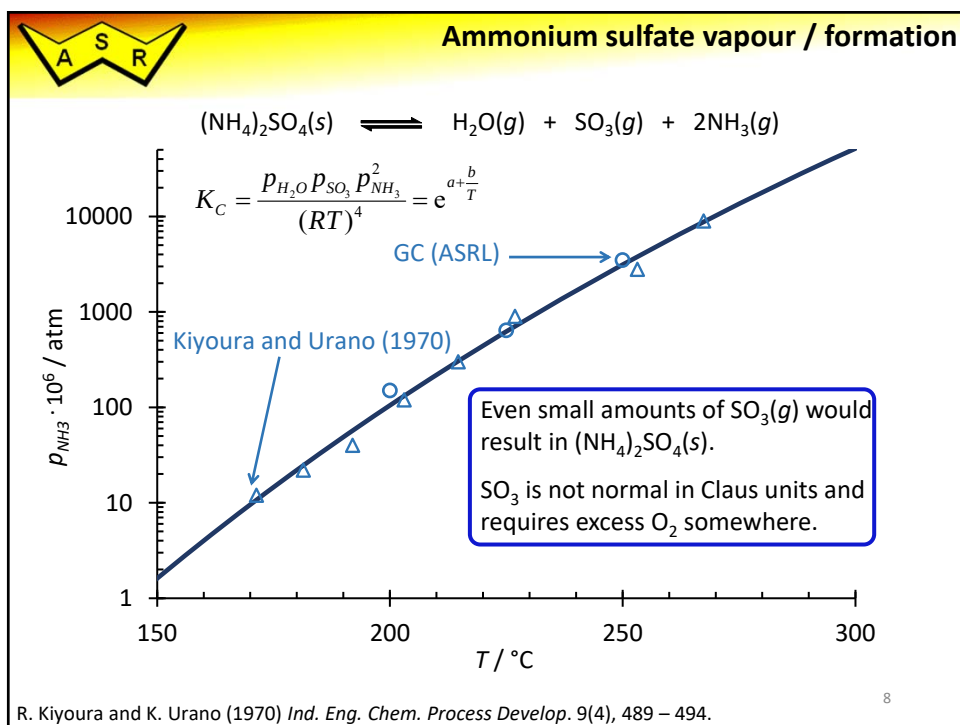
- Cold trap (mass)
- Acid traps (NH_3 only by IC of wash)
- GC (NH_3 only)
- Hiden Mass Spectrometer (gas)
- (residual sulfur on salt)

Our goal was to measure vapour pressure and develop an expression for the temperature dependant equilibrium constant

- The initial intention was to do this by mass difference / balance
- Vapour pressure could have sensitivity to $[\text{NH}_3]$, $[\text{H}_2\text{S}]$, $[\text{SO}_2]$, $[\text{SO}_3]$ and $[\text{H}_2\text{O}]$

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Ammonium sulfate formation

40% H₂O and 1 ppm NH₃ would form solid with only 0.001 ppm SO₃ at T = 150°C.

Formation of ammonium sulfate seems inevitable if SO₃ is present.

- At 130°C [90/10 acid gas/SWS] (150 ppm NH₃ survival)
 - 10⁻¹⁵ to 10⁻¹⁹ atm SO₃ leads to (NH₄)₂SO₄ (s) (~1 molecule / mL)
- 1 ppb SO₃ [90/10 acid gas/SWS] (150 ppm NH₃ survival)
 - T < 191 °C

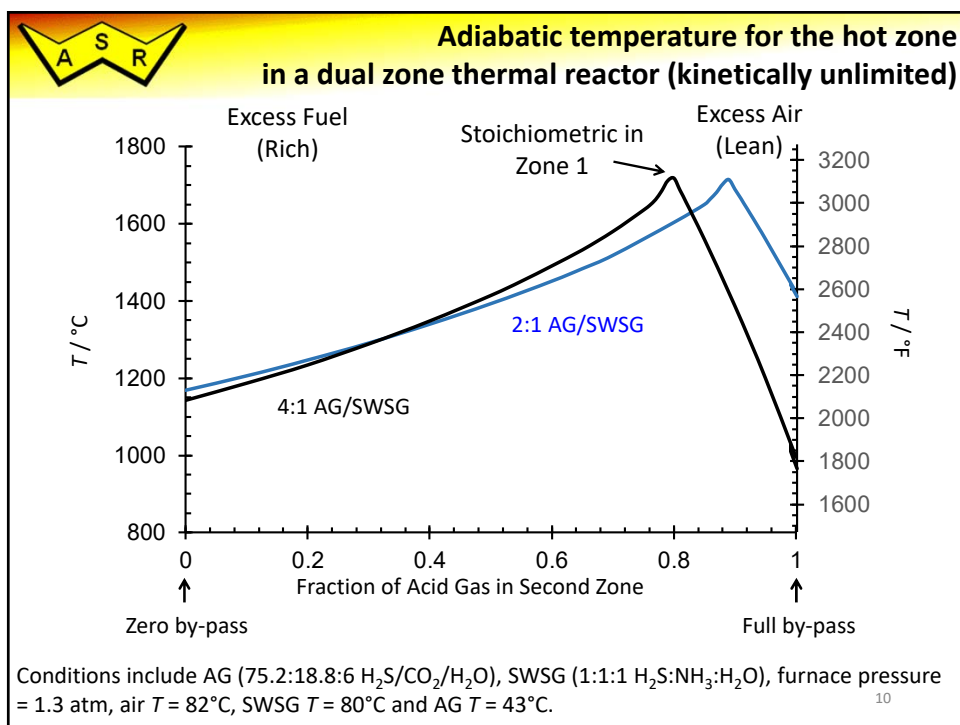
Where would SO₃ come from?

$$2 \text{SO}_2 + \text{O}_2 \rightleftharpoons 2 \text{SO}_3$$

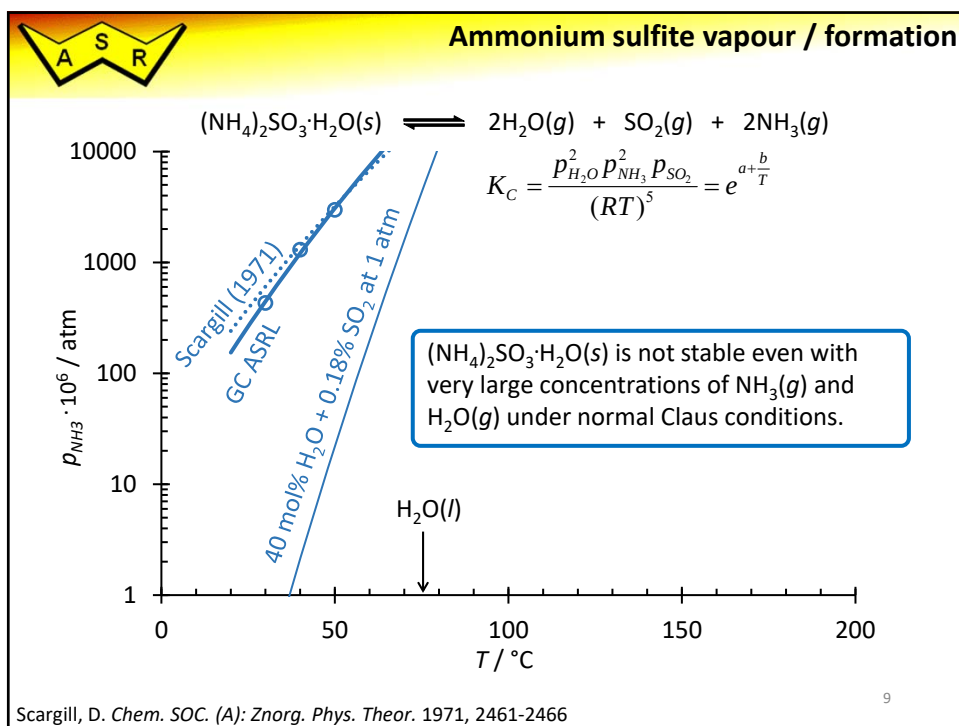
What happens to SO₃ as it passes over a typical Claus catalysts?

P.D. Clark, N.I. Dowling, M.M. Huang, F. Bernard and K.L. Lesage (2006) ASRL QB XLII Vol 4, 1-34. 10
 M. Madekufamba, K. L. Lesage, N. I. Dowling and R. A. Marriott (2021) ASRL QB LVIII Vol 1, 16-32.

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Ammonium sulfate formation *via* the thiosulfate

Previous experiments with Claus species showed that the dominant salt was thiosulfate $[(\text{NH}_4)_2\text{S}_2\text{O}_4]$ for $T < 100^\circ\text{C}$. Newer experiments have reproduced these results.

Experiments have shown that Al_2O_3 can be used to induce ammonium thiosulfate formation, but what are the volatile species or the initial salt?

$$\text{SO}_3^{2-} + \text{S}^0 \longrightarrow \text{S}_2\text{O}_3^{2-}$$

$$\text{S}_2\text{O}_3^{2-} + \text{H}_2\text{O} \rightleftharpoons \text{SO}_4^{2-} + \text{H}_2\text{S}$$

In the presence of S^0 , sulfite would exist as thiosulfate; exposure to liquid water could then cause disproportionation to sulfate.

P.D. Clark, N.I. Dowling, M.M. Huang, F. Bernard and K.L. Lesage (2006) ASRL QB XLII Vol 4, 1-34.
 M. Madekufamba, K. L. Lesage, N. I. Dowling and R. A. Marriott (2021) ASRL QB LVIII Vol 1, 16-32.

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Formation and decomposition of ammonium thiosulfate

Ammonium thiosulfate decomposes to the hydrosulfite and sulfur. For this reason, low quantities of weak acid ammonium salts (less than 0.01%) are often added to thiosulfate to stabilise it, Ziegler (1967).

Ammonium hydrosulfite can further decompose to produce sulfur dioxide.

$$\begin{aligned}
 (\text{NH}_4)_2\text{S}_2\text{O}_3(\text{s}) &\rightleftharpoons \text{NH}_3(\text{g}) + \text{NH}_4\text{HSO}_3(\text{s}) + 1/8 \text{S}_8 \\
 \text{NH}_4\text{HSO}_3(\text{s}) &\rightleftharpoons \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{SO}_2(\text{g}) \\
 \hline
 (\text{NH}_4)_2\text{S}_2\text{O}_3(\text{s}) &\rightleftharpoons 2 \text{NH}_3(\text{g}) + \text{H}_2\text{O}(\text{g}) + \text{SO}_2(\text{g}) + 1/8 \text{S}_8
 \end{aligned}$$

Ziegler, H.B., Method of preventing decomposition of anhydrous ammonium thiosulfate., United States Patent Office, Patent No. 3,350,168, Oct, 1967

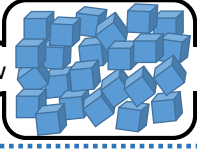
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The Hyden HPR 20 Mass Spectrometer

T control (HP 6890)

Saturation bed



Gas Flow

$(\text{NH}_4)_2\text{S}_2\text{O}_3$

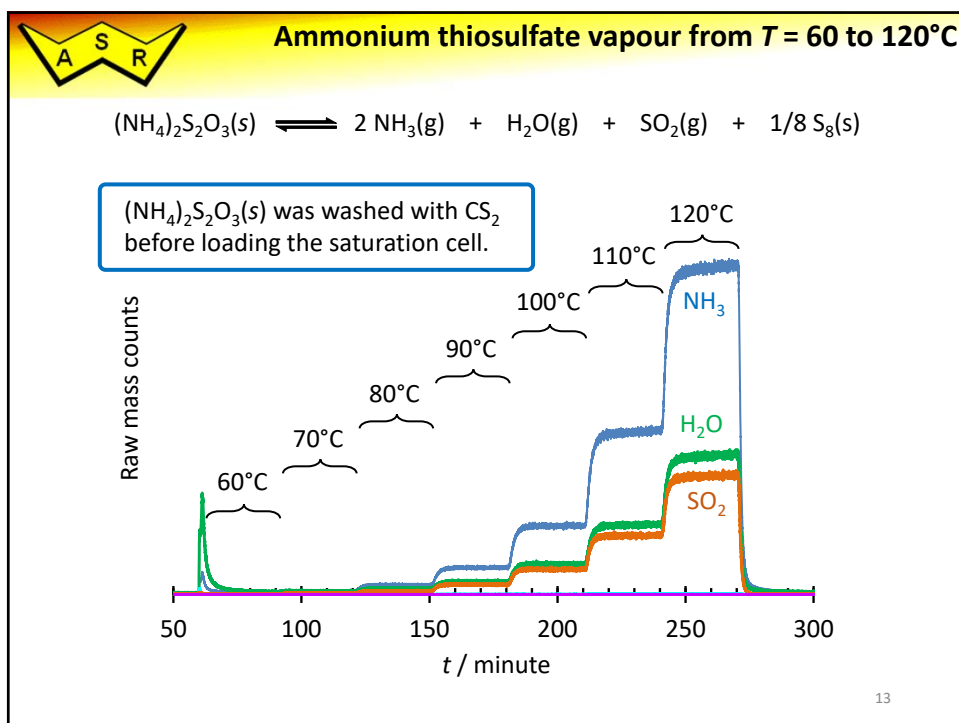


Heated capillary inlet probe

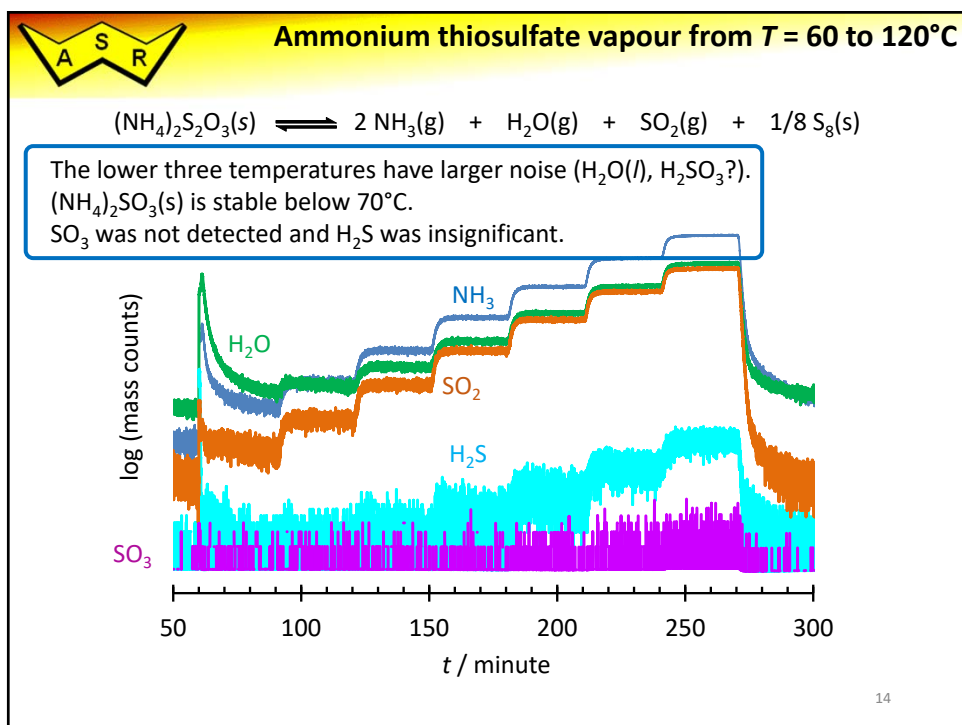
Carrier: He at 6 Scm³ min⁻¹
Monitoring: SO₂, SO₃, H₂O, H₂S and NH₃



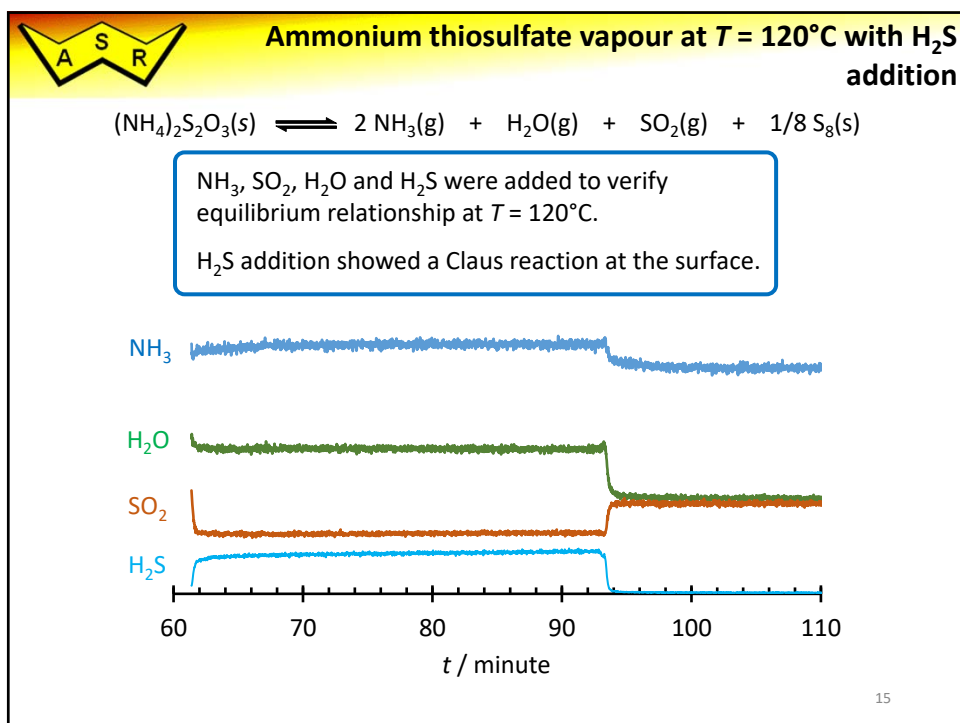
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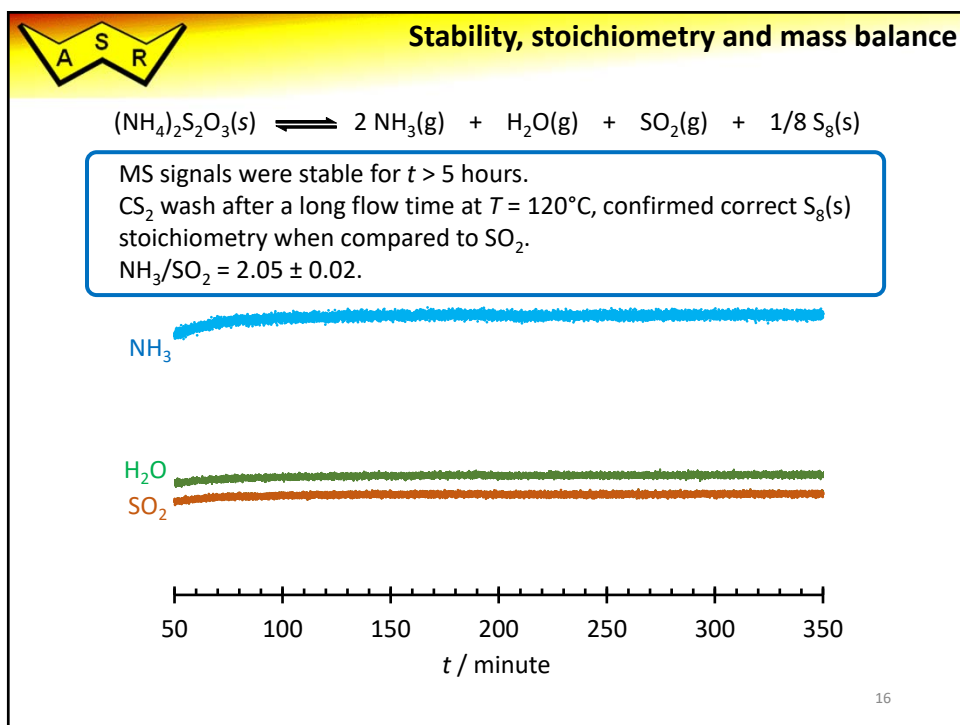
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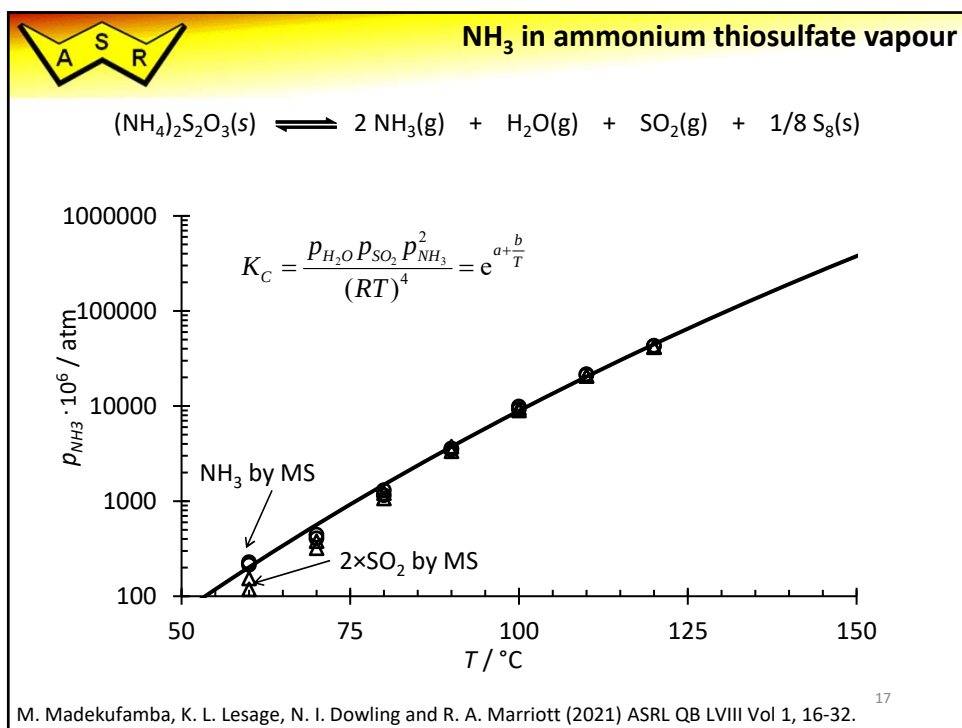
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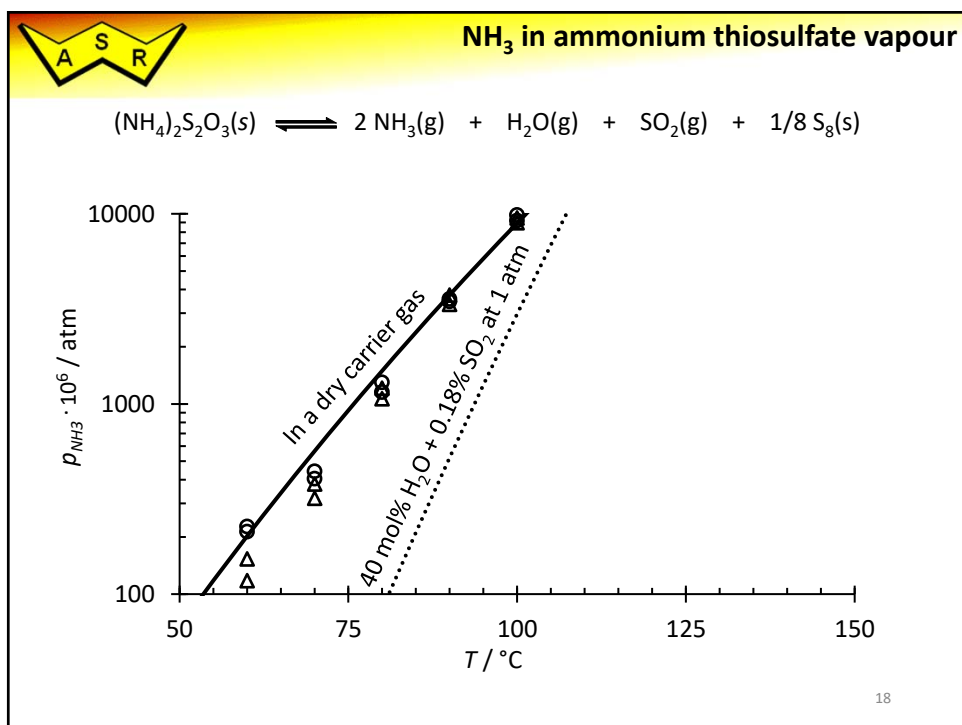
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Could we achieve ammonium thiosulfate solidification? (no SO₃)

$$(NH_4)_2S_2O_3(s) \rightleftharpoons 2 NH_3(g) + H_2O(g) + SO_2(g) + 1/8 S_8$$

$$(NH_4)_2S_2O_3(s) + H_2O \longrightarrow (NH_4)_2SO_4(s)$$

- [90/10 acid gas/SWS] (150 ppm NH₃ survival)
 - $T < 84^\circ C$ (89°C with 100% O₂ enrichment)
- Upset with 2 % SO₂ (150 ppm NH₃ survival)
 - $T < 90^\circ C$ (98°C at 2 atm)
- $T = 130^\circ C$ with 2% SO₂
 - 100,000 ppm NH₃

Analysis of a deposit would show thiosulfate + sulfate or just sulfate (with S₈)

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Conclusions

NH₃ vapour has been measured for pure ammonium sulfate [(NH₄)₂SO₄] and sulfite [(NH₄)₂SO₃].

An MS technique was used to measure NH₃, SO₂, H₂O, H₂S and SO₃ vapour for [(NH₄)₂S₂O₃].

$$(NH_4)_2S_2O_3(s) \rightleftharpoons 2 NH_3(g) + H_2O(g) + SO_2(g) + 1/8 S_8$$

$$(NH_4)_2SO_4(s) \rightleftharpoons 2 NH_3(g) + H_2O(g) + SO_3(g)$$

$$(NH_4)_2SO_3 \cdot H_2O(s) \rightleftharpoons 2 NH_3(g) + 2 H_2O(g) + SO_2(g)$$

Using our vapour pressure expressions, sulfite and thiosulfate are too volatile to be considered for ammonium deposition at typical plant temperatures ($T > 130^\circ$).

M. Madekufamba, K. L. Lesage, N. I. Dowling and R. A. Marriott (2021) ASRL QB LVIII Vol 1, 16-32. ¹⁹

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Conclusions

No SO₃ and no cold-spots ($T < 98^{\circ}\text{C}$) should lead to no ammonium salt deposition.

- How much SO₃ could desorb from a catalyst surface?
- What happens to SO₃ on different catalysts (if anything)?

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Thank you

- Abu Dhabi National Oil Company (ADNOC)
- Ametek Process Instruments/Controls Southeast Inc.
- Arkema
- Axens
- Bechtel Hydrocarbon Technology Solutions, Inc.
- Brimstone STS Ltd.
- Bryan Research & Engineering, LLC
- Cenovus Energy
- CES Energy Solutions/PureChem Services
- Chevron Energy Technology Company
- Con-Sul, Inc.
- ConocoPhillips
- Energy Transfer Canada ULC
- Euro Support BV
- ExxonMobil Upstream Research Company
- Flint Hills Resources
- Haldor Topsoe
- HEC Technologies
- Hexion Inc.
- Honeywell UOP
- Houston Refining, LP (a LyondellBasell company)
- Industrial Ceramics Ltd.

- KT – Kinetics Technology SPA
- Lummus Technology
- Nasato Consulting Ltd.
- Nova Chemicals
- OMV Exploration and Production GmbH
- P. Scott Northrop, Ph.D.
- PetroChina Southwest Oil and Gas Field Company/RINGT
- Phillips 66 Company
- Porocel Industries, LLC
- Porter McGuffie, Inc.
- Saudi Arabian Oil Company (Saudi Aramco)
- Secure Energy
- Shell Canada Limited
- Sulfur Recovery Engineering
- Sulphur Experts Inc.
- Sultran
- Suncor Energy Inc.
- TC Energy
- Technip Energies
- TotalEnergies
- UniverSUL Consulting
- Worley Comprimo





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