Physikalisch-Technische Bundesanstalt
Braunschweig und Berlin
Nationales Metrologieinstitut

MetHyInfra

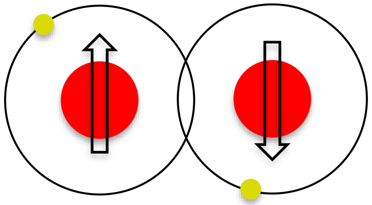
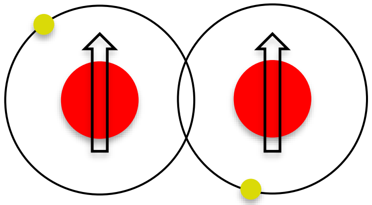
Good practice to ensure complete conversion of para to ortho hydrogen

"State-of-the-art in traceable cryogenic flow measurement training"

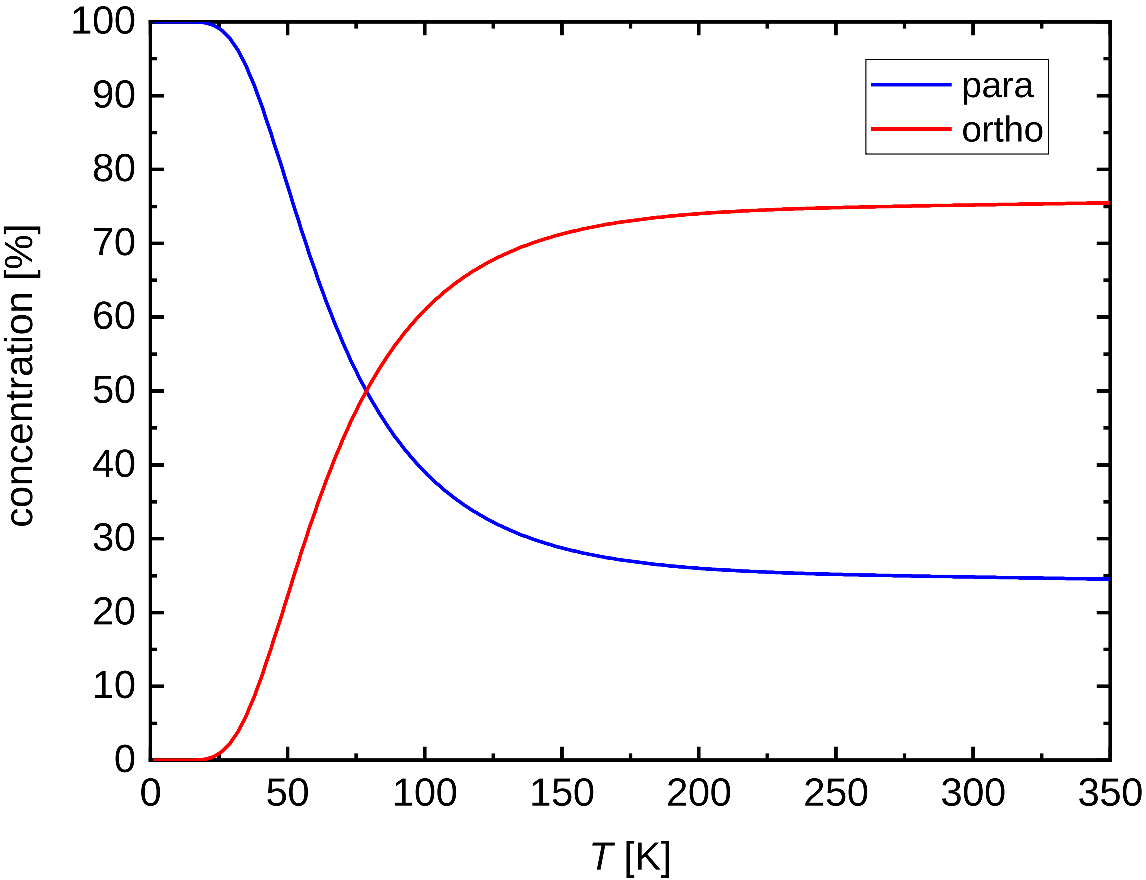
16th of February 2022

Christian Günz

1. Para and ortho hydrogen

	para hydrogen:	ortho hydrogen:
		
core spin orientation:	anti-parallel	parallel
core spin quantum number:	0 (=1/2-1/2)	1 (=1/2+1/2)
rotational quantum number J:	even J=2(n-1)	odd J=2n-1
lowest energy state:	J=0 (singulett state)	J=1 (triplett state)
magnetic moment:	no	yes

1. Para and ortho hydrogen



Distribution equilibrium H_2:

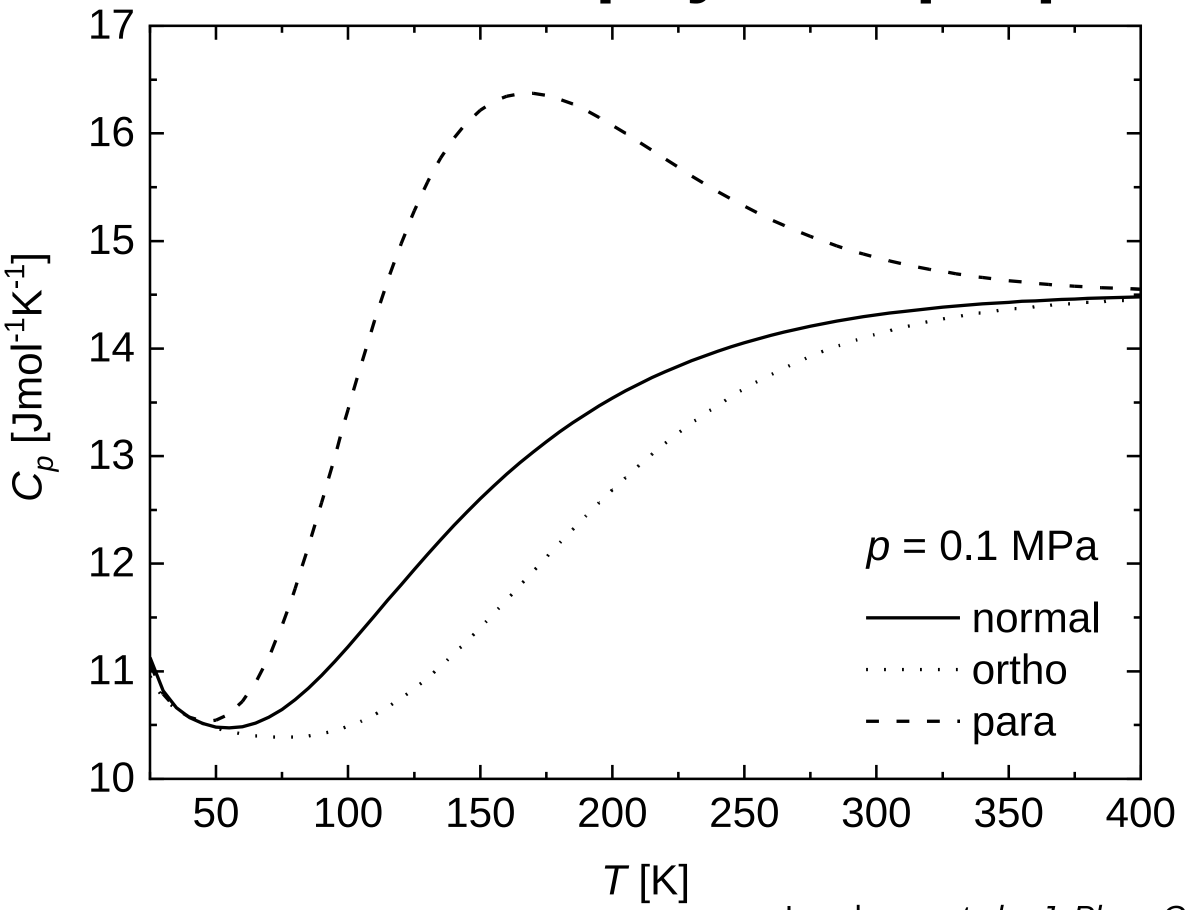
$$\frac{\chi_{\text{para}}}{\chi_{\text{ortho}}} \approx \frac{1}{3} \frac{1 + 5e^{-\frac{6B}{T}}}{3e^{-\frac{2B}{T}} + 7e^{-\frac{12B}{T}}}$$

$$B = \frac{h^2}{8\pi^2 I_{\mathrm{H}_2} k} = 86.2\ \mathrm{K}$$

normal H_2:

25% para + 75 % ortho
(at all temperatures)

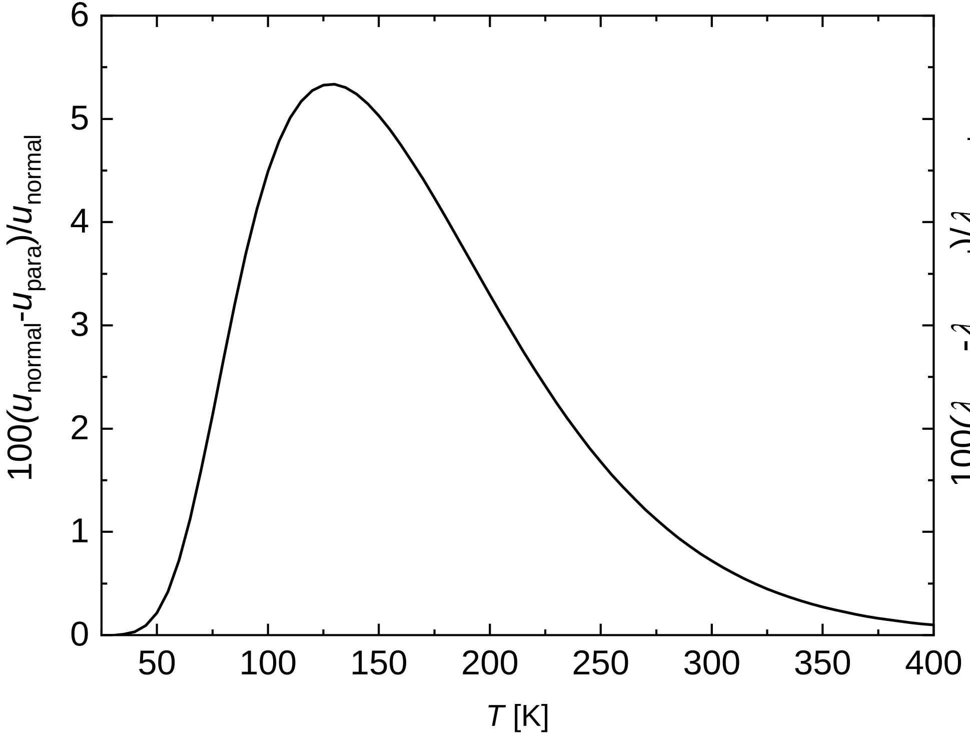
1. Differences in thermophysical properties



Leachman *et al.*, *J. Phys. Chem. Ref. Data* **38**, 721 (2009)

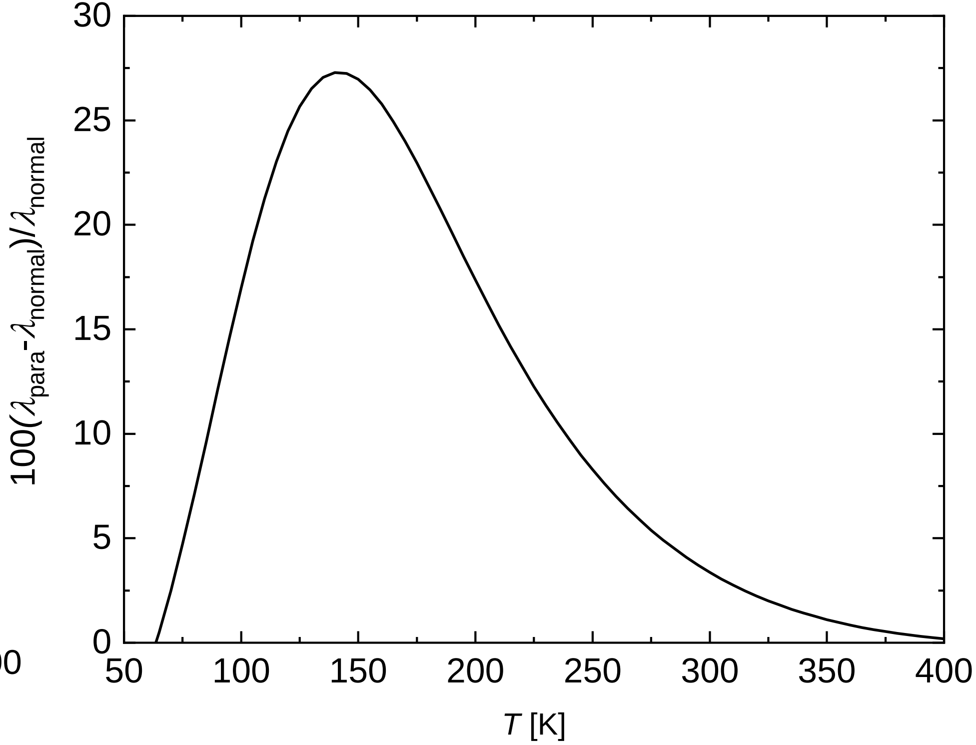
1. Differences in thermophysical properties

speed of sound



Leachman *et al.*, *J. Phys. Chem. Ref. Data* **38**, 721 (2009)

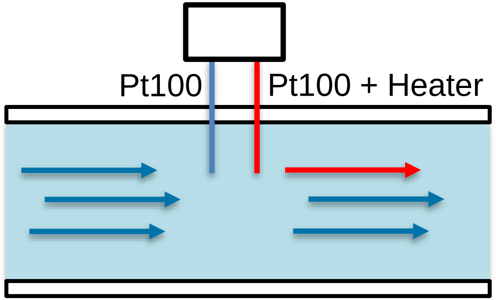
thermal conductivity (0.1 MPa)



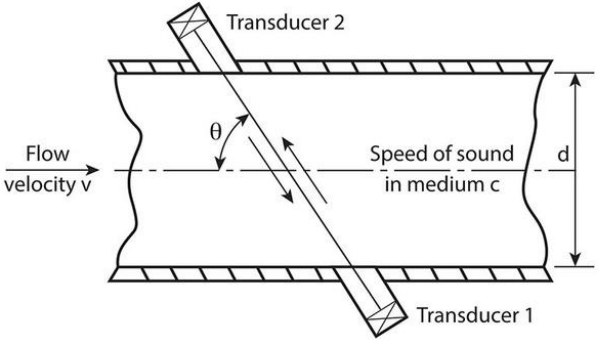
Assael *et al.*, *J. Phys. Chem. Ref. Data* **40**, 033101 (2011)

2. Motivation - effect on flow measurement

thermal flow meters

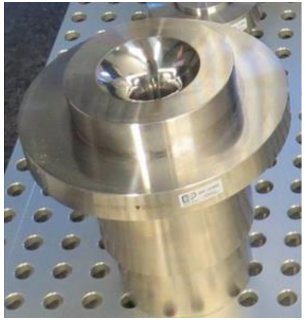


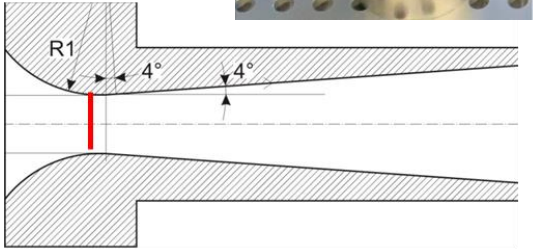
ultra sonic flow meters



taken from: http://flowmeters.co.uk/low-flow-rate-ultrasonic-liquid-flow-meter-a-novel-approach/#prettyPhoto

critical flow venturi nozzles





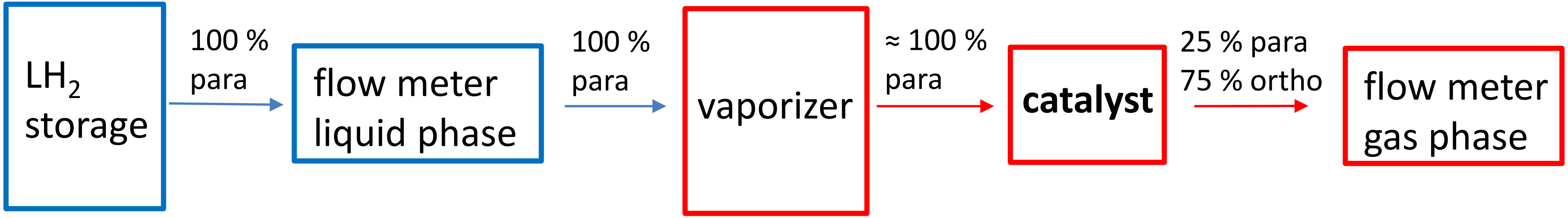
differences for other properties:

density (very small): Leachman *et al.*, *J. Phys. Chem. Ref. Data* **38**, 721 (2009)

viscosity (small): Mehl *et al.*, *Int. J. Thermophys.* **31**, 740 (2010)

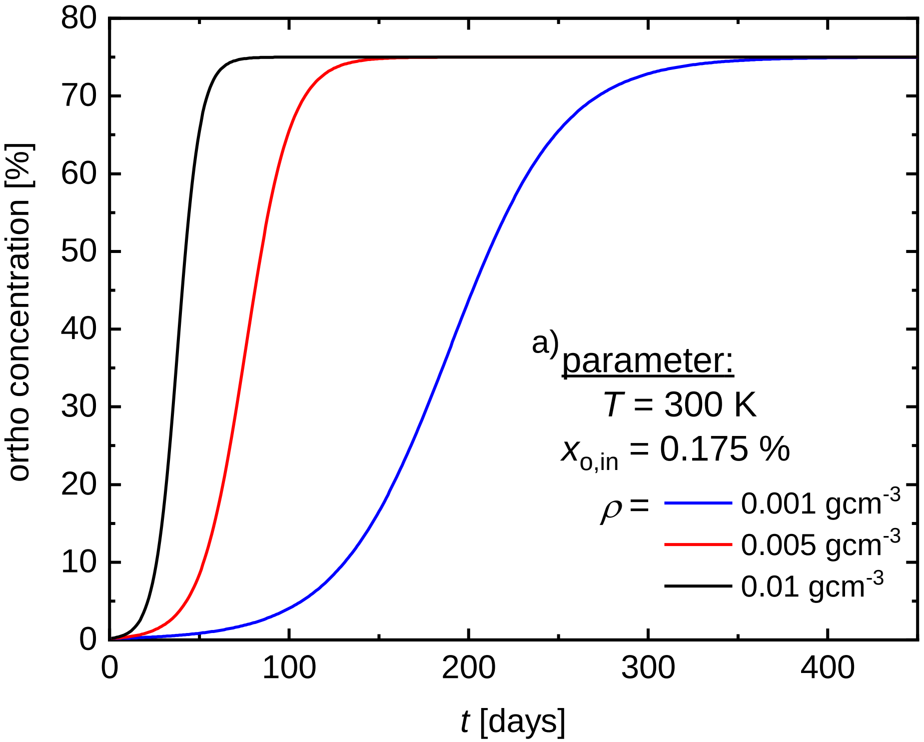
2. Motivation – vaporization test rig

How to ensure traceable calibration at cryogenic temperatures?



Key question: How much and which catalyst is required to ensure complete conversion from para to normal hydrogen?

3. Natural conversion – is very slow [a)]



boil-off loss for normal liquid hydrogen:

40% of liquid H2 will be lost after 100 hour storage time

The corresponding plot can for instance be seen in:
Schmauch and Singleton, *Ind. Eng. Chem.* **56**, 20 (1964)

→ possible alternative approach: measure para hydrogen gas flow

a) Extrapolation of reaction constant by:
Milenko and Sibileva, *J. Low Temp. Phys.* **107**, 77 (1997)

4. Catalytic conversion

7 steps of the heterogenic catalytic reaction:

1. Diffusion to catalyst
2. Diffusion into pores
3. Adsorption
4. Conversion - 1st order
5. Desorption
6. Diffusion out of pores
7. Diffusion to gas stream

rate determing step and corresponding reaction kinetics:

Steps 3–5: Langmuir-Hinshelwood

Keeler *et al.*, in: *Adv. Cryo. Eng.*, **Vol 5**, 511 Plenum Press NY (1960)
Schmauch and Singleton, *Ind. Eng. Chem.* **56**, 20 (1964)

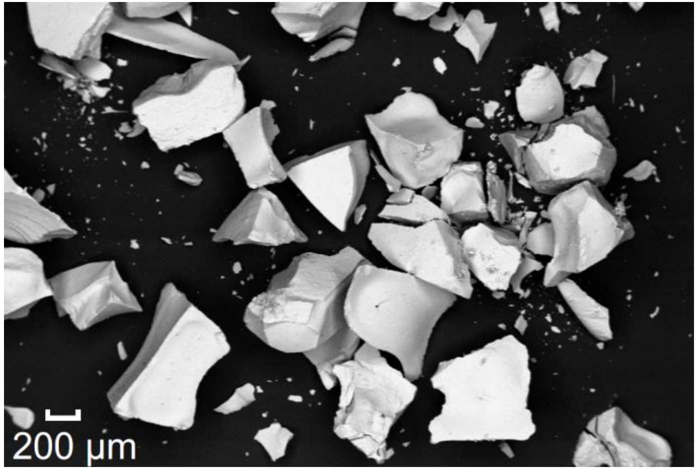
4. Which catalyst? - HFO

Hydrous **F**erric **O**xide (Fe_2O_3) – IONEX® type O-P (by Molecular Products) (currently only commercially available option)

Key question: How much?
→ data of incomplete conversion (300 K)

<u>data evaluation with 1st order rate reaction[a]:</u>

$$k_V = \frac{\dot{n}}{V_{\mathrm{cat}}} \ln\left(\frac{1 - \frac{\chi_{\mathrm{para,in}}}{\chi_{\mathrm{para,eq}}}}{1 - \frac{\chi_{\mathrm{para,out}}}{\chi_{\mathrm{para,eq}}}}\right)$$



taken with kind permission from: Jürgen Essler, PhD thesis, TU Dresden, Dresden (2012)

[a]Zhuzhgov *et al.*, *Catalysis in Chemical and Petrochemical Industry* **10**, 9 (2018)

4. Data on HFO – available literature data

ortho → para:

plenty

- Manufacturer
- Donaubauer *et al.* 2019
- Zhuzhgov *et al.* 2018
- Hutchinson *et al.*1971
- Hutchinson PhD 1966
- Keeler *et al. 1960*
- Weitzel *et al. 1957*

para → ortho (T<90K):

some ***T*** **constant**

- Hutchinson *et al.*1971
- Hutchinson *et al.*1967
- Hutchinson PhD 1966
- Hutchinson *et al. 1965*
- Hutchinson Master Thesis 1964

40 K < *T* < 80 K

para → ortho (T>90K):

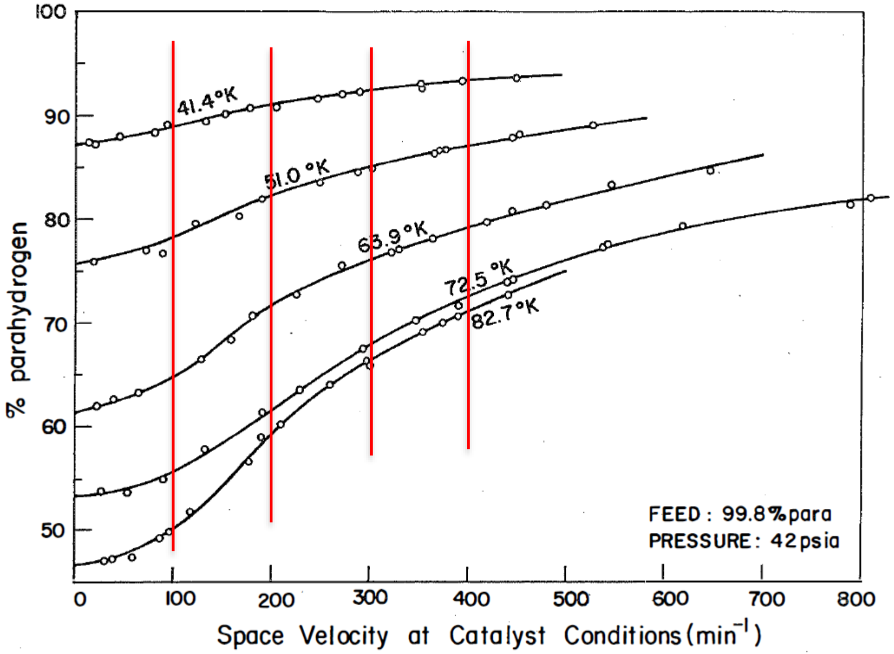
one?

- Weitzel *et al.*1957

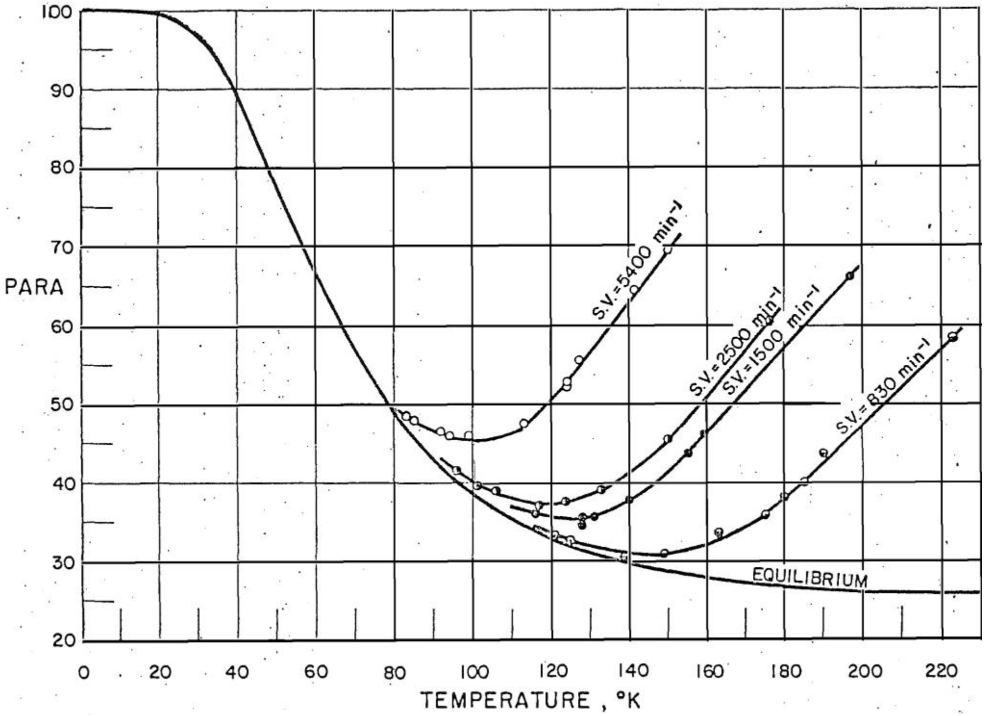
85 K < *T* < 220 K

unknown reaction kinetics

4. HFO – para to ortho conversion

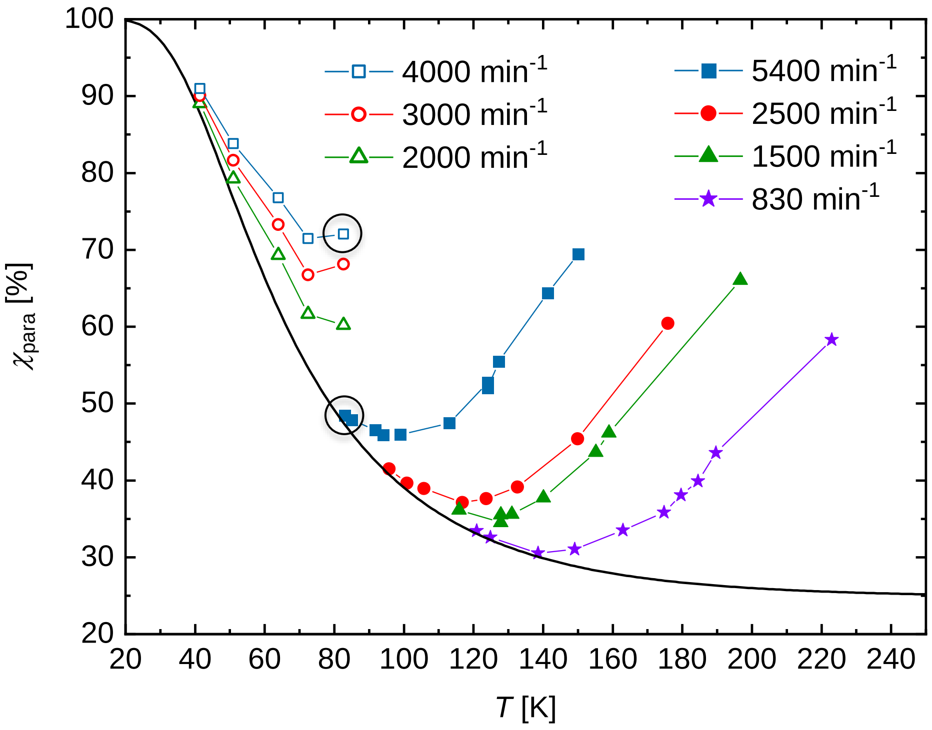


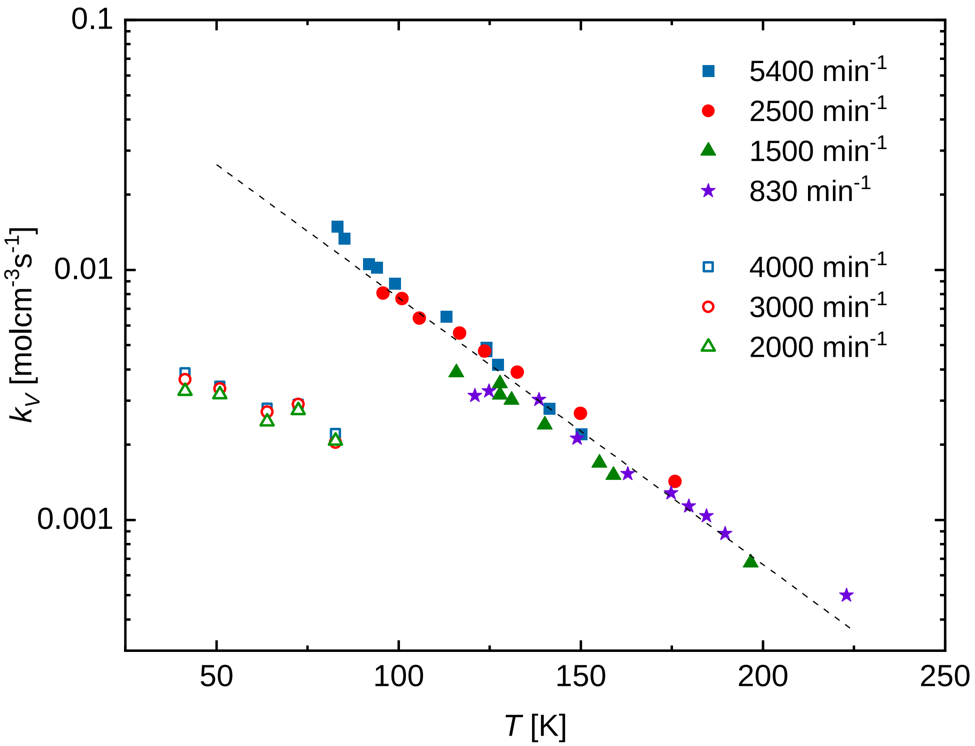
taken from:
Hutchinson *et al.*, *Adv. Cryo. Eng.* **10**, 190-196
edited by Timmerhaus (1965)



taken from:
Weitzel, Valin and Draper, *NBS Report* **5515**, 1 (1957)

4. HFO – para to ortho conversion





linear fit: $k_V = 0.09 * e^{-0.0246*T}$

5. Example of calculation

specify:

- T = 300 K
- mass flow = 4 kg/h
- $\chi_{para,out}$ = 27 %
- $\chi_{para,in}$ = 99.8 %

calculate:

- $\chi_{para,eq}$ = 24.8 %
- k_V = 5.69*10^{-5} mol/(cm^{3}s)
- molar flow $\dot{n}$ = 0.551 mol/s

$$V_{cat} = \frac{\dot{n}}{k_V} \ln\left(\frac{1-\frac{\chi_{para,in}}{\chi_{para,eq}}}{1-\frac{\chi_{para,out}}{\chi_{para,eq}}}\right) \approx 34200\ \text{cm}^3$$

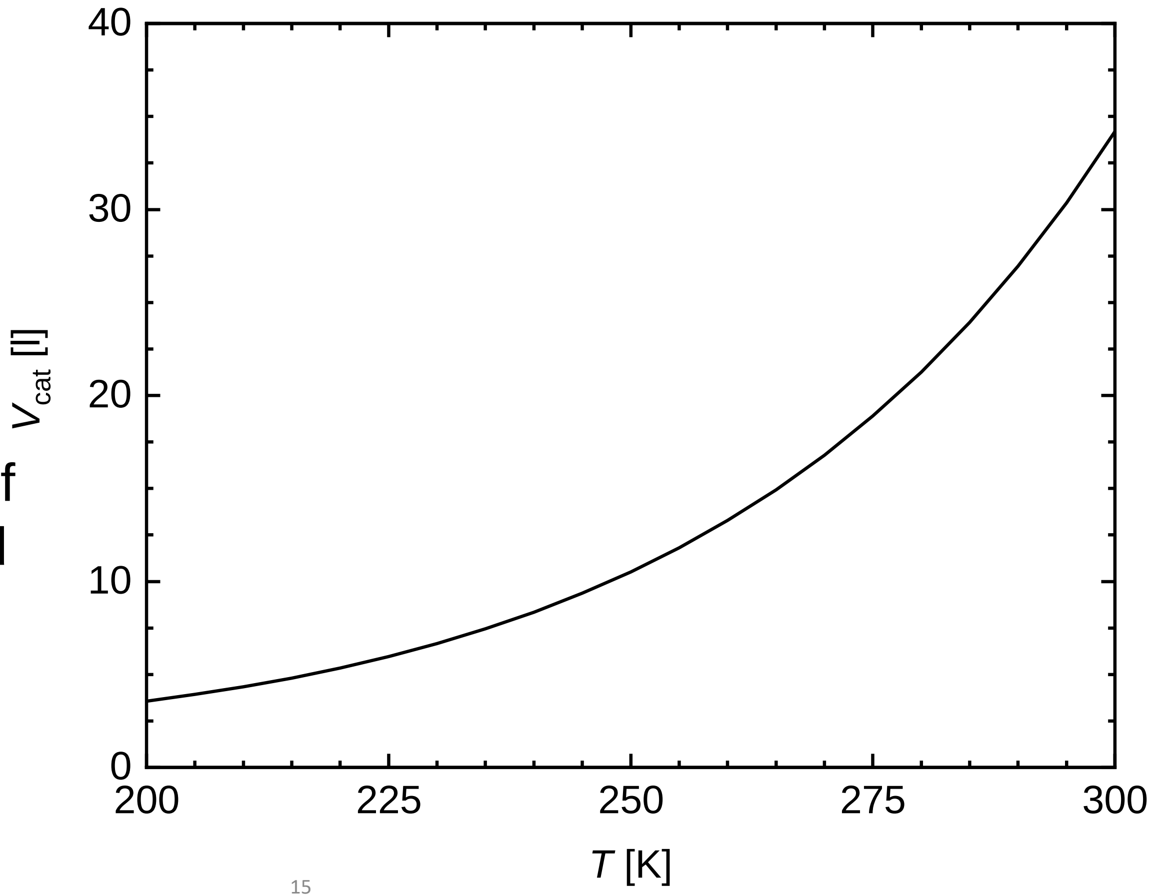
5. Example of calculation – variation of *T*

specify:

- T = 200 K - 300 K
- mass flow = 4 kg/h
- $\chi_{para,out}$ = 27 %
- $\chi_{para,in}$ = 99.8 %

→ for 200 K the amount of catalyst can be reduced by a factor of 10

→ but 200 K is difficult to maintain



5. HFO - further aspects and literature

- isothermal vs. adiabatic conversion [1]
- particle size: smaller particles have a higher catalytic activity [2]
- activation of the catalyst: alternatives to procedure by manufacturer [3]
- pressure influence [4]
- other catalyst „APACHI“ more suitable? [5]

1) Weitzel, Valin and Draper, *NBS Report* **5515**, 1 (1957)
   Weitzel *et al., Advances in Cryogenic Engineering* **4**, pp. 286-295 Plenum Press NY (1960)
2) Keeler *et al., Advances in Cryogenic Engineering* **5**, pp. 511-517 Plenum Press NY (1960)
3) Jürgen Essler, PhD thesis, TU Dresden, Dresden (2012)
4) Hutchinson *et al.*, *Advances in Cryogenic Engineering* **10**, 190-196 edited by Timmerhaus (1965)
   Harold Lee Hutchinson, Master Thesis, University of Colorado, Boulder, (1964)
5) Schmauch and Singleton, *Ind. Eng. Chem.* **56**, 20 (1964)

6. Summary

- ortho and para H_2 differ in properties relevant for flow measurement (speed of sound, thermal conductivity and heat storage capacity)
- the equilibrium composition changes with temperature
- natural conversion is slow → measurement of pure para H_2 after vaporization is possible
- conversion can be accelerated by catalysts →HFO is available but not ideal
- an example for the estimated amount of catalyst was given

This project (20IND11 MetHyInfra) has received funding from the EMPIR programme co-financed by the Participating States and from the European Union's Horizon 2020 research and innovation programme.

The EMPIR initiative is co-funded by the European Union's Horizon 2020 research and innovation programme and the EMPIR Participating States

Physikalisch-Technische Bundesanstalt
Braunschweig and Berlin
Abbestraße 2-12
10587 Berlin

Dr. Christian Günz
Telephone: +49 30 3481 7796
E-mail: christian.guenz@ptb.de
www.ptb.de