Containing Hydrogen Deflagrations

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MISSOURI S&T
University of Science & Technology

BLUEFIELD
PROCESS SAFETY

Presented by

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What we’re covering

- **The hazards of hydrogen, especially its flammability**
- **Hydrogen deflagration pressure, P_{EX}**
- **The meaning of “containment” as it relates to the MAWP of hydrogen vessels**
- **An example that applies these concepts**

Hydrogen is Dangerous

- **Asphyxiant**
- **Cryogen**
  - **Frostbite**
  - **Cold embrittlement**
- **Hydrogen embrittlement**
- **Flammable!**

Thank you, Captain Obvious

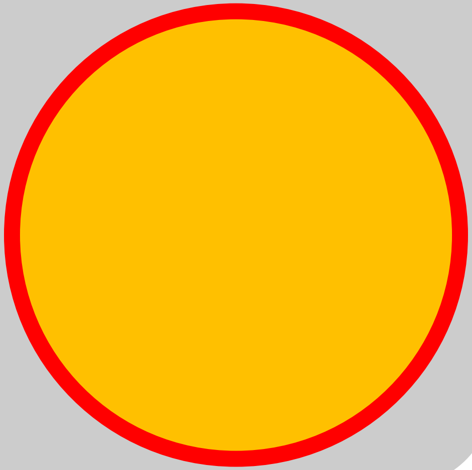
- **Flammable limits**
  - **4% to 75% in air**
  - **4% to 94% in O_2**
  - **5% to 95% in Cl_2**
- **Ignition energy**
  - **0.02 mJ**
  - **Compare to**
    0.29 mJ for methane
    0.24 mJ for gasoline

Then why contain it?

- **Reactant**
  - **Haber-Bosch: $N_2 + 3\ H_2 \rightarrow 2\ NH_3$**
  - **Hydrogenation**
  - **Hydrocracking**
  - **Dealkylation and desulfurization**
- **Product**
  - **Reforming: $CH_4 + H_2O \rightarrow CO + 3\ H_2$**
  - **Electrolysis:**
    $2\ NaCl + 2\ H_2O \rightarrow 2\ NaOH + Cl_2 + H_2$
- **Fuel**

What is a deflagration?

- **Flame front propagates via heat transfer, bringing the material before the front to its autoignition temperature**
- **Flame front propagates at subsonic velocities**

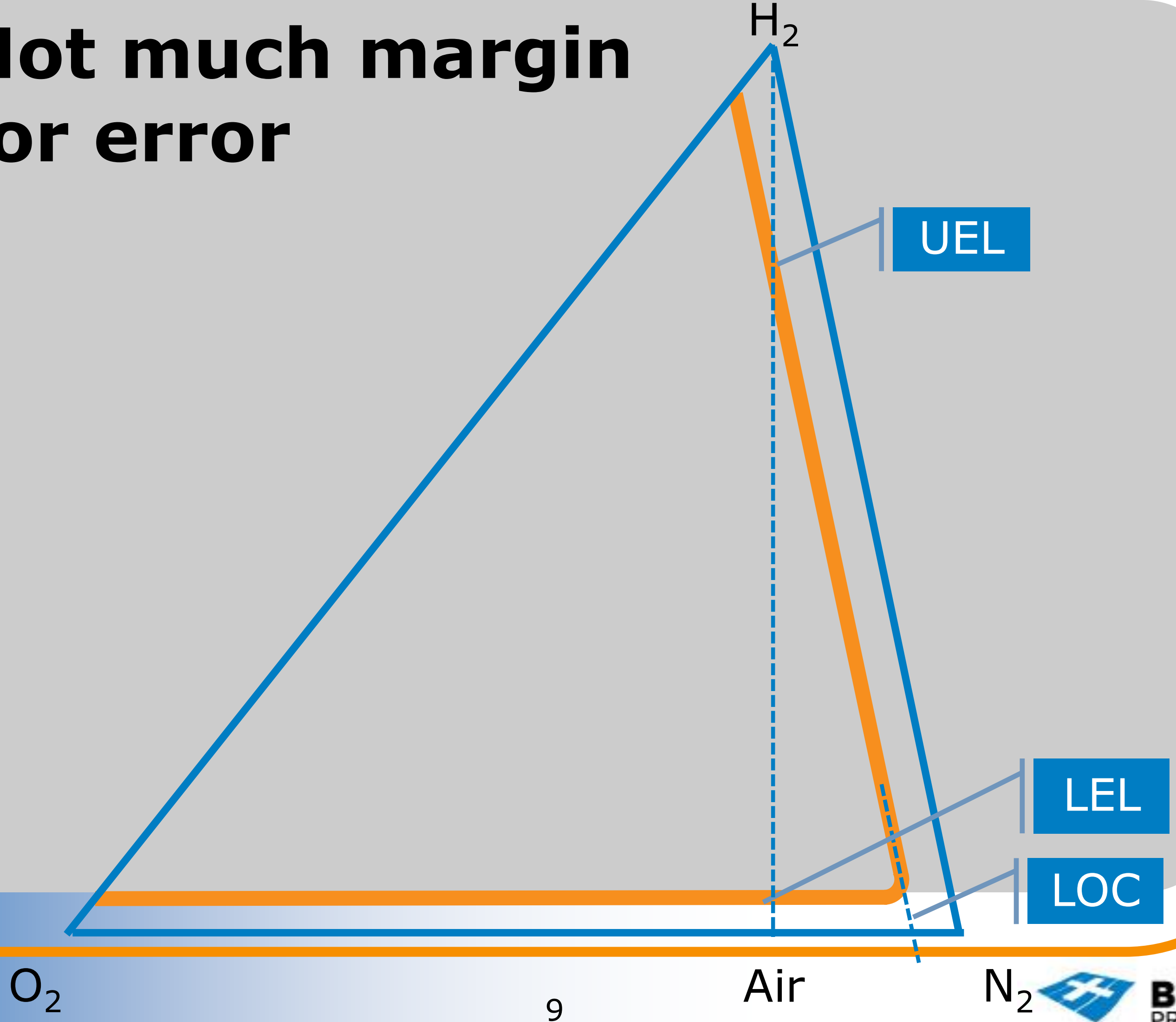


Avoiding harmful deflagrations

- **Avoid flammable mixtures**
- **Avoid ignition**
- **Contain the deflagration**

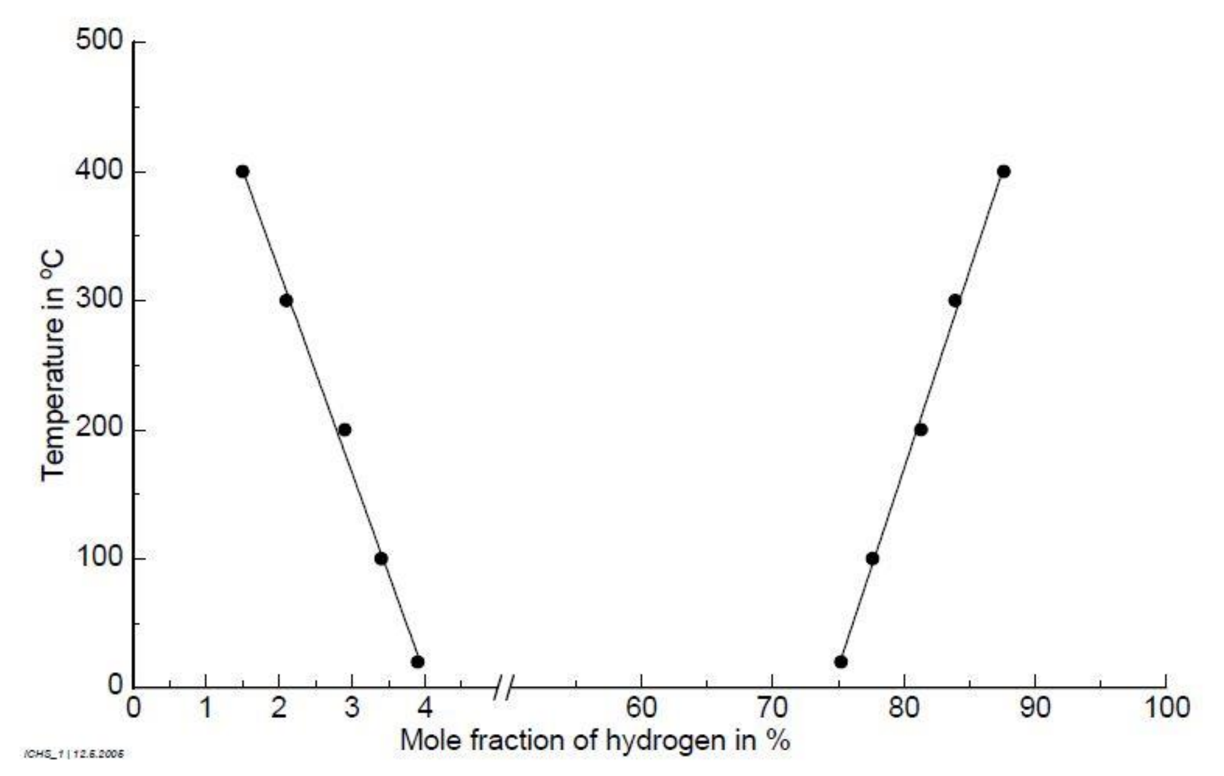
Avoid flammable mixtures?

- **Not much margin for error**



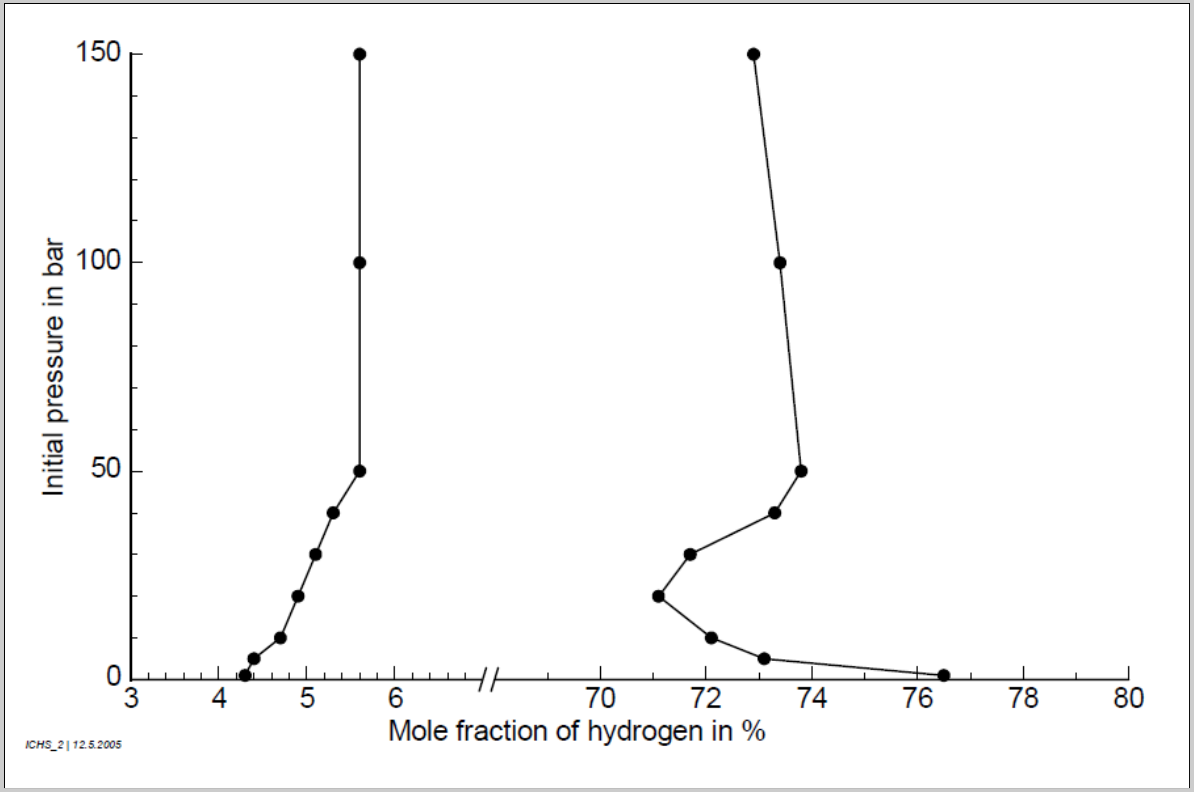
Flammable limits widen…

… as temperature increases

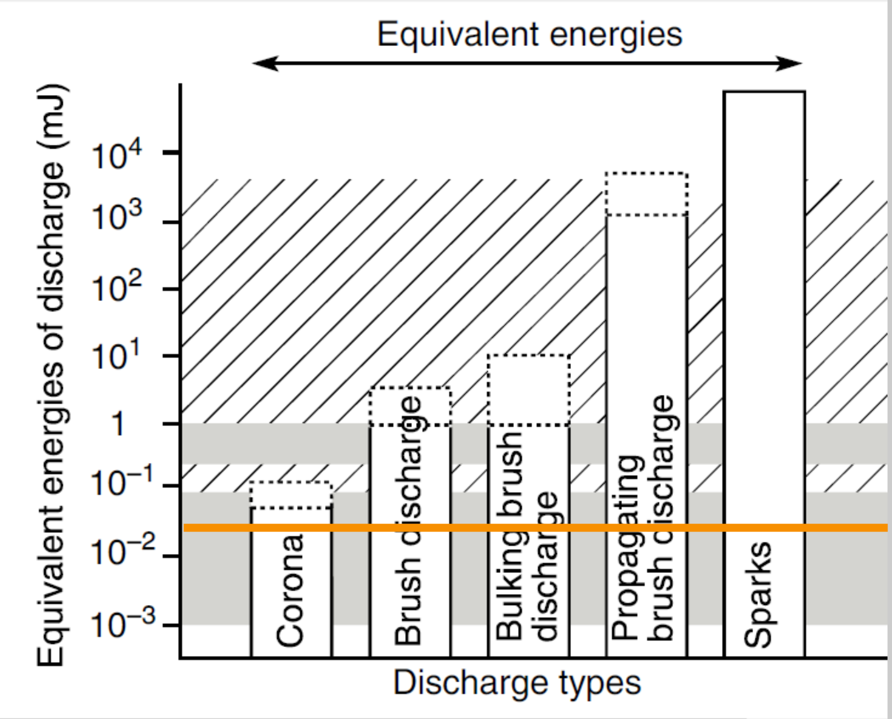


But narrow slightly as…

…pressure increases



Avoid ignition?

- **Ignition energy for H_2 is 0.02 mJ**
- 

- **“Ignition is free”**

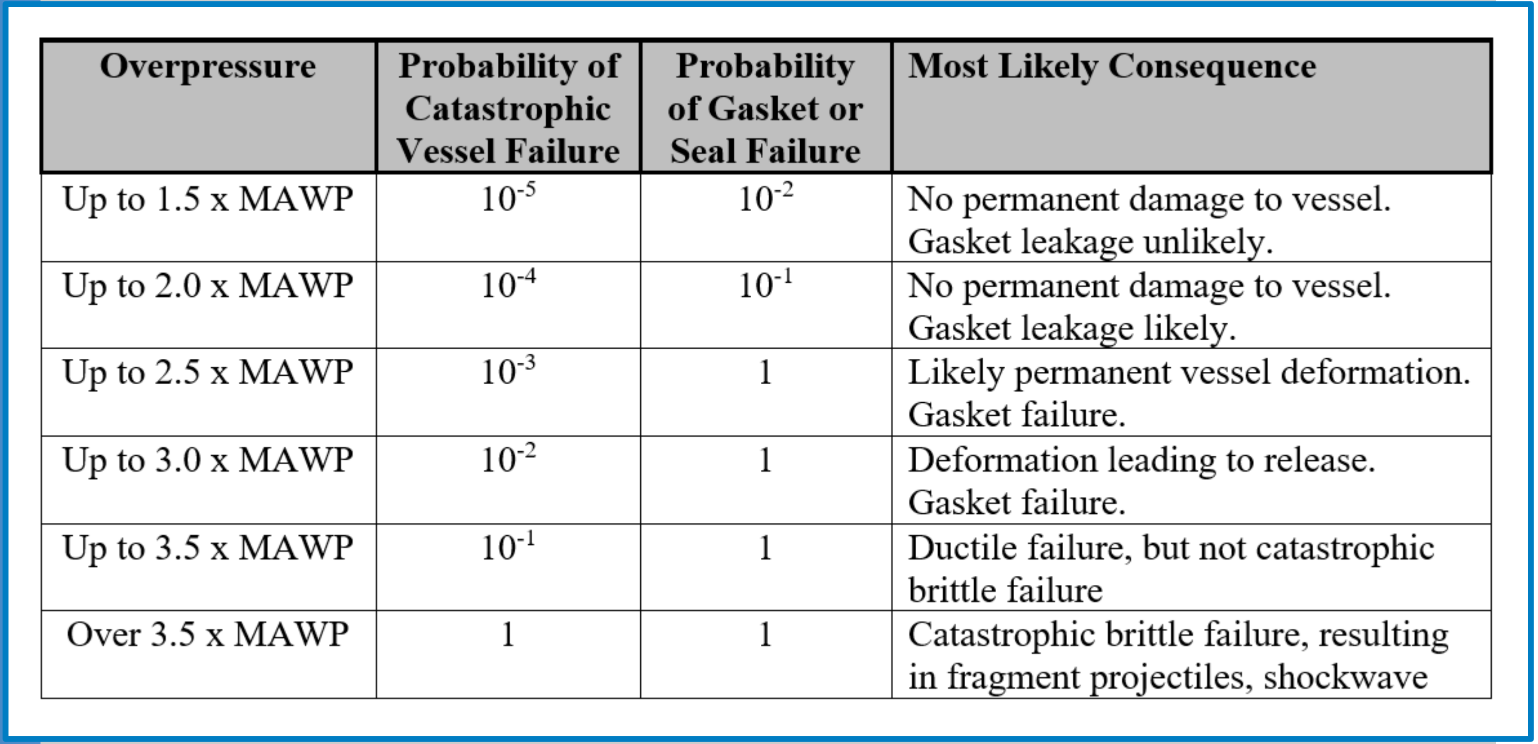
Can deflagrations be contained?

- **Deflagration pressure, P_{EX}, is not infinite**
- **Two questions:**
  - **What will the P_{EX} of a deflagration be?**
  - **What vessel design pressure will contain the P_{EX} while resulting in no more harm than is tolerable?**

What does containment mean?

- No leakage
  - Gaskets leak
  - Gaskets fail
- No permanent vessel damage
  - Deformation
  - Ductile Failure
  - Catastrophic Brittle Facture

What is the risk of overpressure?

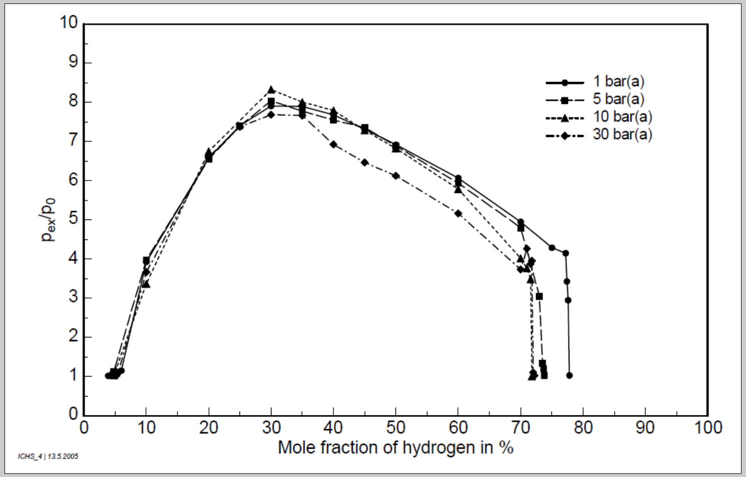


Overpressure	Probability of Catastrophic Vessel Failure	Probability of Gasket or Seal Failure	Most Likely Consequence
Up to 1.5 x MAWP	10^{-5}	10^{-2}	No permanent damage to vessel. Gasket leakage unlikely.
Up to 2.0 x MAWP	10^{-4}	10^{-1}	No permanent damage to vessel. Gasket leakage likely.
Up to 2.5 x MAWP	10^{-3}	1	Likely permanent vessel deformation. Gasket failure.
Up to 3.0 x MAWP	10^{-2}	1	Deformation leading to release. Gasket failure.
Up to 3.5 x MAWP	10^{-1}	1	Ductile failure, but not catastrophic brittle failure
Over 3.5 x MAWP	1	1	Catastrophic brittle failure, resulting in fragment projectiles, shockwave

What will P_{EX} be?

- **Deflagration pressure, P_{EX} , depends on initial pressure, P_O**
- **Normalized deflagration pressure, P_{EX}/P_O , is independent of P_O**
- **P_{EX}/P_O , is a function of flammable mixture composition**

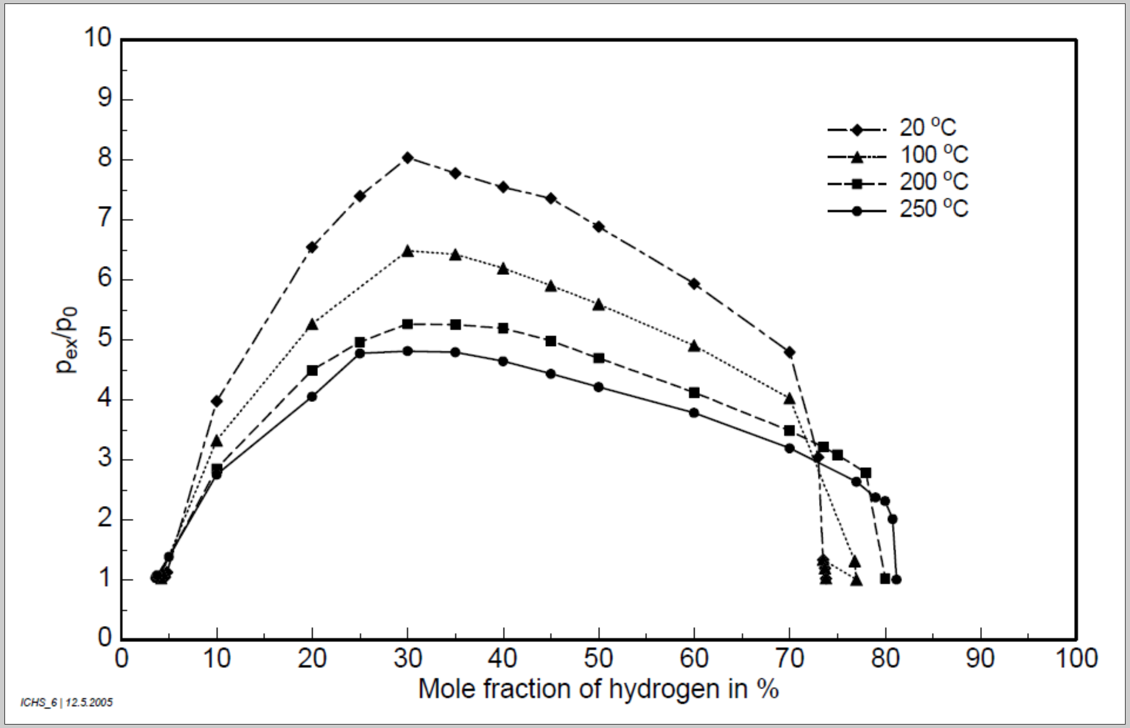
A function of composition

- **A stoichiometric mixture of air and hydrogen is 29.6 mol% H_2**
- 

- **Stoichiometric mixtures give peak P_{EX}/P_O**
- **$P_{EX}/P_O = 1$ at flammable limits**

An unexpected dependence…

- **The hotter the mixture, the lower the P_{EX}/P_O**



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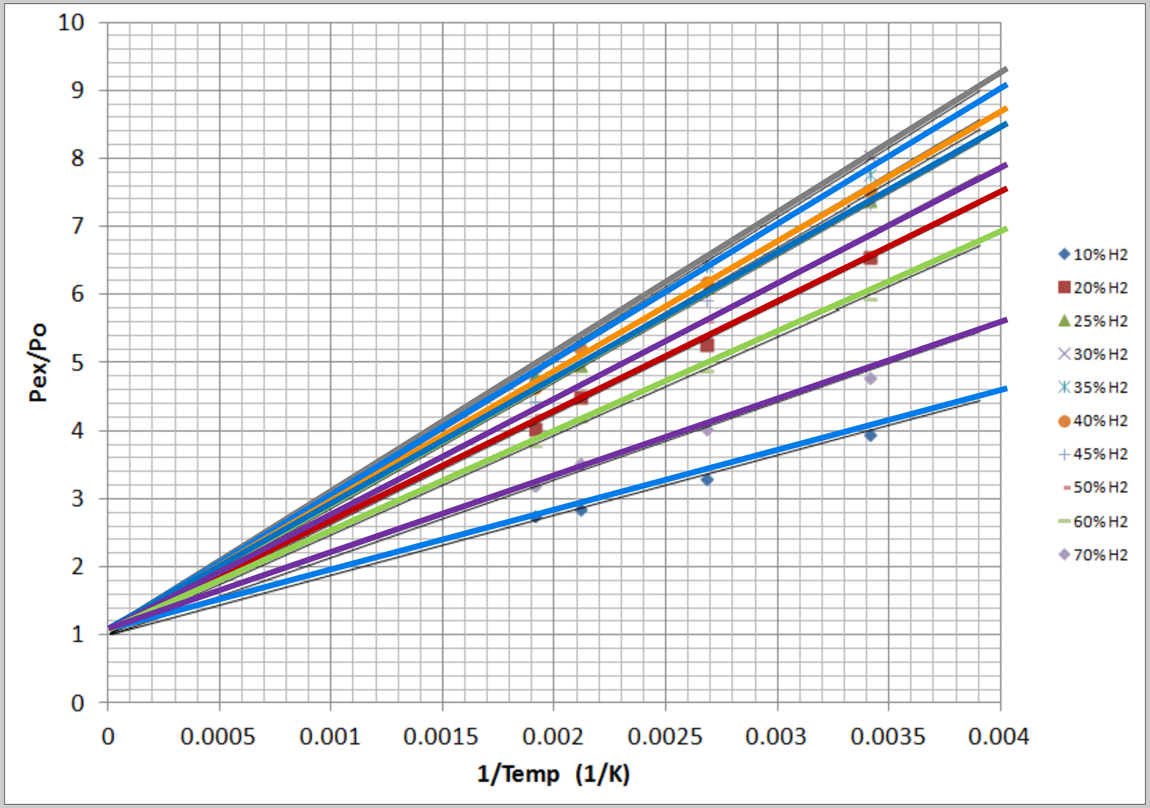
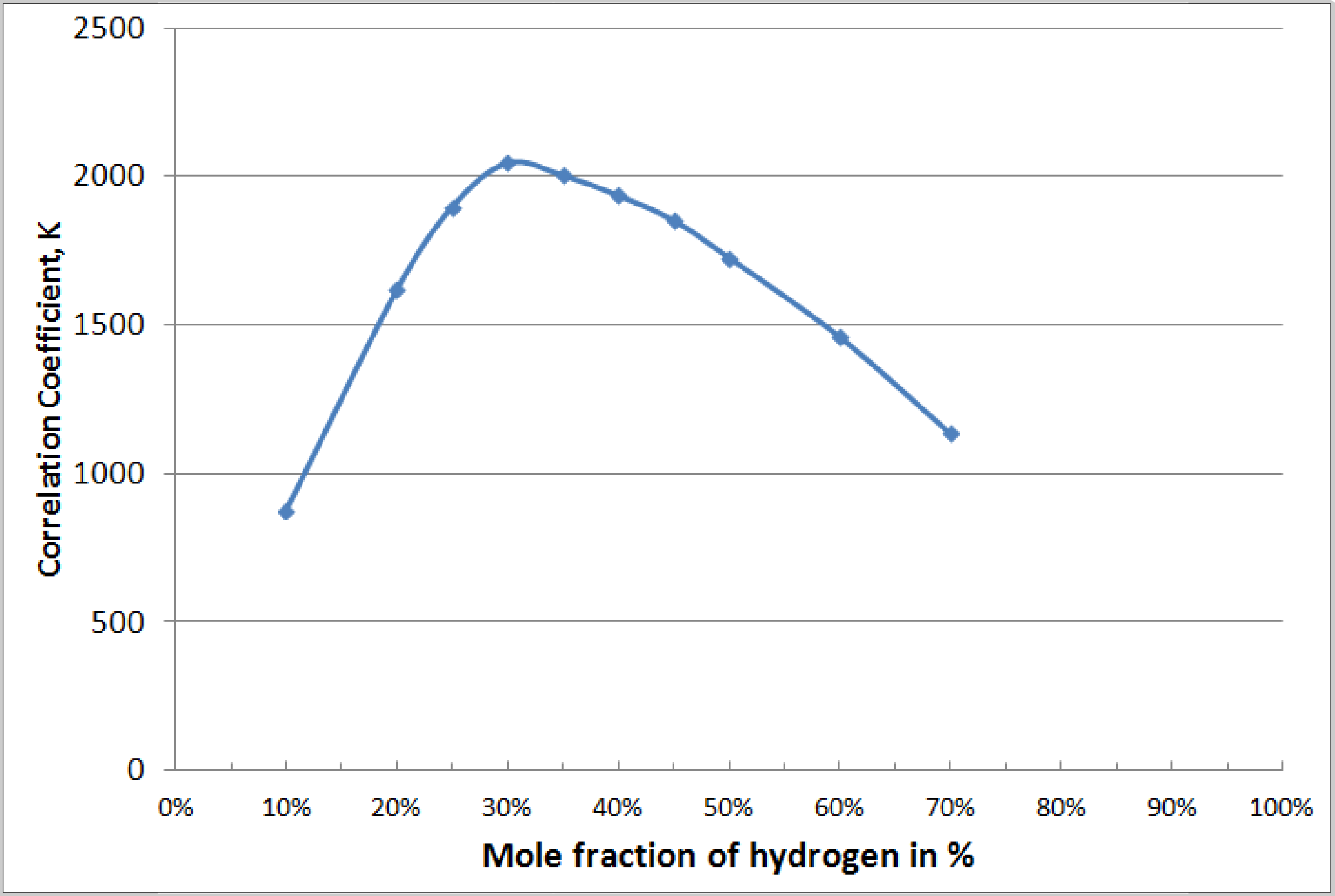
…suggesting $P_{EX}/P_O = f(1/T_O)$



- $P_{EX}/P_O \rightarrow 1$ as $T_O \rightarrow \infty$

$P_{EX}/P_O = 1 + K/T_O$, $K = f([H_2])$



An example

- Dehydrogenation process yields aqueous solution and hydrogen
- Process runs at 40 C and slightly higher than 1 atm
- Hydrogen is vented and flared
- Plant lore says that any hydrogen deflagrations will be contained as long as it is designed to 50 psig MAWP

Tolerable consequences

- **Plant lore says that any hydrogen deflagration will be contained as long as equipment is designed to 50 psig MAWP**
- **After deflagration event, however, equipment will need to be inspected and may need to be replaced**
- **No one recalls basis for criteria**

50 psig MAWP vs. P_{EX}

- **"After deflagration event, however, equipment will need to be inspected and may need to be replaced"**
- **Suggests a P_{EX} of**
  - **2.0 · MAWP → Gasket damage → P_{EX} < 100 psig**

  OR

  - **2.5 · MAWP → Vessel deformation → P_{EX} < 125 psig**

Assume peak P_{EX}/P_O (Stoichiometic)

- $P_{EX}/P_O = 1 + 2050\ K^{-1} / T_O$
- $P_O = 15$ psia
- $T_O = 40\ C = 313\ K$

- $P_{EX}/P_O = 1 + 2050\ K^{-1} / 313\ K = 7.55$

- $P_{EX} = 7.55 \cdot P_O = 113.25$ psia $= 98.55$ psig

P_{EX} vs. 50 psig MAWP

- **99 psig vs. 2.0 · MAWP**
  → May avoid gasket damage
- **99 psig vs. 2.5 · MAWP**
  → Probably avoids permanent vessel deformation

- **Plant lore is valid AT 40 C and 0.3 psig (15 psia)**

What if conditions change?

- "Any hydrogen deflagration will be contained as long as equipment is designed to 50 psig MAWP"
- Consider modest changes:
  - Increasing operating pressure from 0.3 psig to 10 psig
  - Lowering operating temperature from 40 C to 35 C

Again, stoichiometric P_{EX}/P_O

- $P_{EX}/P_O = 1 + 2050\ K^{-1} / T_O$
- $P_O = 10$ psig = 24.7 psia
- $T_O = 35$ C = 308 K

- $P_{EX}/P_O = 1 + 2050\ K^{-1} / 308\ K = 7.66$

- $P_{EX} = 7.66 \cdot P_O = 164.4$ psia = 149.7 psig

P_{EX} vs. 50 psig MAWP

- **150 psig is 3.0 · MAWP**
  - **Gasket damage nearly certain**
  - **Permanent vessel deformation almost certain**
  - **Modest probability (≤ 0.1) of ductile vessel failure**
  - **Low probability (≤ 0.01) of catastrophic brittle fracture**
- **Plant lore is not valid at 35 C and 10 psig**

Designing to reduce risk

- Understand the consequences to avert
  → Affects the multiple, N, of MAWP to use as basis
- Understand the normal and upset conditions at the point of deflagration
  → Affects the P_{EX} to use as basis
- Set MAWP to meet tolerable risk
  → MAWP $\geq P_{EX}/N$

Summary

- While avoiding flammable H_2 mixtures is the first objective, once one forms, ignition is hard to avoid
- This can result in hydrogen deflagrations, overpressures that vessels may be able to contain
- "Containment" must be defined in terms of tolerable consequences
- P_{EX}/P_O is a function of $[H_2]$ (peaking for stoichiometric mixtures) and goes down when operating temps increase

Acknowledgment

This work is almost entirely the result of analyzing data presented by Schroeder and Holtappels at the International Conference on Hydrogen Safety, held in Pisa, Italy in September 2005

Questions?