

Occupational & Public Health Developments Concerning Exposure to Hydrogen Sulphide

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Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

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S - sulphur or sulfur?

For chemistry the standards are agreed by IUPAC [International Union of Pure and Applied Chemistry]. In 1990 it was recommended by IUPAC that the spelling of sulfur would use 'f' instead of 'ph' ...

Interestingly, in 18th and 19th century Britain it was commonplace for sulfur to be spelt with either an 'f' or 'ph'.

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

The 'ultras' of chemical nomenclature will
Reprinted from Chemistry in Britain (May

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Group 6, main group elements
 - Oxygen, Sulfur, Selenium, Tellurium
- ◆ Sulfur oxidation states are -2 to $+6$
 - Sulfate ($+6$) SO_4^{2-}
 - Sulfur dioxide ($+4$) SO_2
 - Elemental sulfur (0), cyclo- S_8
 - Disulfides (-1), $\text{CH}_3\text{-S-S-CH}_3$
 - Hydrogen Sulfide, (-2) H_2S

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Compounds of Oxygen and Sulfur
- ◆ Water H_2O and Hydrogen Sulfide H_2S
 - H_2O_2 and H_2S_2 , H_2S_3 , ... the sulfanes
- ◆ Alcohols and Thiols or Mercaptans
 - $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{SH}$

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Ethers and Sulfides
 - $C_2H_5OC_2H_5$ and $C_2H_5SC_2H_5$
- ◆ Peroxides and Disulfides
 - t-Bu-O-O-t-Bu, and $CH_3-S-S-CH_3$
 - Easy to oxidize thiols to disulfides and reduce disulfides
- ◆ Carbon Dioxide $O=C=O$
 - Carbonyl Sulfide $O=C=S$
 - Carbon Disulfide $S=C=S$

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Occurrence of reduced sulfur compounds
 - Minerals
 - ◆ Ores, volcanic activity (Hot vents)
 - ◆ Oil & gas, coal
 - Biological materials
 - ◆ Amino acids (protein)
 - Cysteine 2 amino, 3 mercapto-propanoic acid
 - Cystine (oxidized cysteine with a disulfide bridge)
 - Activities giving rise to H₂S
 - ◆ Acid and sulfides
 - ◆ Hydrolysis of mercaptans and sulfides
 - ◆ Anerobic bacterial decomposition of biomass

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Types of industry where H₂S is found
 - Coke ovens, asphalt, oil and gas
 - Tanneries, food processing
 - Sewage, wastewater
 - Kraft Paper mills
 - Rayon manufacture
- ◆ Depending upon the source, there may be substantial amounts of other reduced sulfur compounds present

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Properties of Hydrogen Sulfide
 - Boiling point -61 C
 - Density relative to air, $34.1/28.5 = 1.2$
 - ◆ Air at -20 C has density of 1.2 compared to +20C
 - ◆ 70% H₂S/30% methane same density as air
 - ◆ H₂S, once mixed with air, does not separate under t
 - Separation requires substantial energy to overcome the en

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Hydrogen sulfide dissolves in water
 - About 200 ml of gas dissolves in 100 ml of water at atmosphere pressure
 - Henry's Law calculation
 - ◆ 2 ul of gas in 100 ml of water corresponds to 10^{-5} a of H₂S
 - ◆ Expressed in weight percent, 3×10^{-6} wt%
 - Solubility in oil is similar
- ◆ Mercaptans partition into an oil phase

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Hydrogen sulfide is a weak acid
 - Hydrosulfide ion HS^-
 - ◆ $\text{pK}_{\text{a}1} = 7.04$, slightly weaker than CO_2 ($\text{pK}_{\text{a}1} 6.37$)
 - Sulfide ion S^{2-}
 - ◆ $\text{pK}_{\text{a}2} = 17$, long thought to be 11.96
 - Both easily oxidized by air
 - ◆ Iron sulfide can be pyrophoric
 - ◆ Common in oil and gas operations

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species



Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Hydrogen sulfide and reduced sulfur compounds are highly and unpleasantly odorous
- ◆ Much odour and taste research is done by the industry and is proprietary
- ◆ Tabulated results are highly variable and not understood

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Presentation of test samples
 - May be in air, but also in water and other media
 - Usually presented in three samples, spot the difference
 - Detection and recognition thresholds
 - ◆ Recognition is commonly 10x higher

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

◆ References:

- ◆ Odor Thresholds for Chemicals with Established Occupational Health Standards, W.S.Cain, A.Turk, *J Air Pollut Control* 1985, 115-126
- ◆ Smell of danger: An analysis of LPG-gas odorization, W.S.Cain, A.Turk, *J Air Pollut Control* 1985, 115-126
- ◆ Variation in recognition odor threshold of a panel, F.V.Wilby, *J Air Pollut Control* 19 (2), 1969, 95-100
- ◆ Handbook of Environmental data on organic chemicals, K.Verschueren, Ed 1996
 - Latest Edition Jan 2001, 2,800 pages and costs \$800

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Values of odour thresholds (AIHA)
 - Hydrogen Sulfide
 - ◆ Detection (Geo. Mean) 9.4 ppb
 - ◆ Recognition (geo. Mean) 4.5 ppb
 - ◆
 - ◆ Range of values from acceptable studies
 - 1.0 to 130 ppb

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ Values of odour thresholds (AIHA)
 - Methyl Mercaptan
 - ◆ Detection (Geo. Mean) 0.5 ppb
 - ◆ Recognition (geo. Mean) 1.0 ppb
 - ◆
 - ◆ Range of values from acceptable studies
 - 0.0002 to 41 ppb

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ "Clean" natural gas has poor warning properties
 - LPG commonly scented at around 40 ppm H₂S/mercaptan
- ◆ Want people to recognize the smell well before explosive concentrations build up
 - For LPG in air, 10% LEL is 0.2% v/v
 - Dilution by a factor of 500 gives 80 ppb S
- ◆ Ref: Toxicology of gas odorants and odorization issues 921, J.S.Roberts, (1998) API document No 4602703

Chemistry of Hydrogen Sulfide and Reduced Sulfur Species

- ◆ H₂S causes fatigue of the olfactory system
 - H₂S has poor warning properties so air-purifying cannot be used
 - Lethal effects can occur without any warning by
- ◆ The odour of H₂S can be masked and changed by low molecular weight hydrocarbons. Chevron letter to April 4, 1985