Elemental Sulfur – What is it, Where is it Found?

1. Occurs naturally as elemental sulfur

2. Sulfide ores e.g.
   - Galena PbS
   - Pyrite FeS₂
   - Pyrrhotite Fe₁₋ₓS

3. Sulfate minerals e.g.
   - Barytes BaSO₄
   - Epsomite MgSO₄·7H₂O

4. Sulfur removal: By-product of natural gas and petroleum industries
Sulfur Crystals

SEM image 300x

3200x
Gas reservoir

- Sulfur, $S_8$
- Polysulfanes, $H_2S_y$  $H$-$S$-$S$-$S$-$S$-$S$-$S$-$H$ (Unstable) $\rightarrow H_2S + S$

Chemical reactions

- Oxidation of $H_2S$
  $2H_2S + O_2 \rightarrow 2S + 2H_2O$
  (Oxygen in natural gas $<10$ ppm vol)
UK Network Entry Specification

Safety Limits
- Calorific value
- Wobbe number
- Hydrogen Sulfide, $H_2S$
- Hydrocarbon dewpoint
- Water dewpoint

UK Network Limits
- Total sulfur
- Oxygen
- Inerts ($CO_2$ & $N_2$)
- Delivery temperature
- Contaminants
- Odour

Gas Safety (Management) Regulations 1996

“No person shall, subject to paragraphs (2) to (4), convey gas in a network unless the gas conforms with the requirements specified in Part I of Schedule 3”
**GS(M)R 1996, Part I Schedule 3**

### Physical Properties

<table>
<thead>
<tr>
<th></th>
<th>Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wobbe Number</td>
<td>47.2 – 51.41 MJ/m³</td>
</tr>
<tr>
<td>Incomplete Combustion Factor</td>
<td>≤ 0.48</td>
</tr>
<tr>
<td>Soot Index</td>
<td>≤ 0.60</td>
</tr>
</tbody>
</table>

Gas below 7 barg will have a stenching agent added to give a characteristic, distinctive odour

### Natural Gas Composition

<table>
<thead>
<tr>
<th></th>
<th>Limit</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydrogen</td>
<td>≤ 0.1 mol%</td>
</tr>
<tr>
<td>Oxygen</td>
<td>≤ 0.2 mol%</td>
</tr>
<tr>
<td>Impurities</td>
<td>Not contain solids or liquids that may interfere with integrity or operation of the network or appliances</td>
</tr>
<tr>
<td>Hydrocarbons &amp; Water Dewpoint</td>
<td></td>
</tr>
<tr>
<td>Hydrogen Sulfide, H₂S</td>
<td>≤5 mg/m³ (~ 3.3 ppmv)</td>
</tr>
<tr>
<td>Total Sulfur (including H₂S)</td>
<td>≤50 mg/m³</td>
</tr>
</tbody>
</table>

**No limits for elemental sulfur**
What’s the Problem? Deposition of Solid Sulfur

- Gas fired power stations
- Blockage of orifices, valves, fuel jets
- Turbine blade impairment
- Transmission & distribution systems – certain pressure reduction stages possibly at risk
- Pipework, filters, valves
Gas Control Valve Cage
Turbine Blades
Burners
Deposition in Gas Regulators

- Pressure reduction
- 300 psi to 30 psi

- Temperature reduction
- 20 °C to 10 °C
Gas Regulator Orifice and Seat
Gas Offtakes
Hong Kong
Pressure Reduction to 38 bar, 40.6 °C Sulfur Deposits
Confirmation of Sulfur – Chemical Analysis Techniques

SEM/EDX (Kα X-ray 2.3 keV)  
Gas chromatography–mass spectroscopy (GC-MS)  
Mass spectrum $S_8$ (m/e 256)
X-ray Diffraction

Operations: Smooth 0.049 | Background 1.000,1.000 | Import

Lin (Counts)

2-Theta - Scale

YELLOW - File: YELLOW.raw - Type: 2Th/Th locked - Start: 5.000 ° - End: 80.002 ° - Step: 0.014 ° - Step time: 0.2 s - Temp.: 20 °C - Time Started: 11 s - 2-Theta: 5.000 ° - Theta: 2.500 ° - Chi: 0.00 ° - Phi: 0
Operations: Smooth 0.049 | Background 1.000,1.000 | Import

01-078-1888 (D) - Sulfur - alpha-S8 - Y: 74.98 % - d x by: 1. - WL: 1.5406 - Orthorhombic - a 10.46460 - b 12.86600 - c 24.48600 - alpha 90.000 - beta 90.000 - gamma 90.000 - Face-centered - Fddd (70) - 1
Modelling of Sulfur Solubility in Natural Gas
# Sulfur ($S_8$) Properties

<table>
<thead>
<tr>
<th>Physical Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>256.520 g/mol</td>
</tr>
<tr>
<td>Boiling Point</td>
<td>444.6 °C (717.8 K)</td>
</tr>
<tr>
<td>Monoclinic ($\beta$)</td>
<td>$&lt;115.2$ °C (388.33 K)</td>
</tr>
<tr>
<td>Rhombic ($\alpha$)</td>
<td>$&lt; 95.3$ °C (368.46 K)</td>
</tr>
<tr>
<td>Vapour Pressure at 15 °C</td>
<td>$2.0 \times 10^{-4}$ Pa ($1.5 \times 10^{-6}$ mmHg)</td>
</tr>
</tbody>
</table>
## Sulfur Solubility

### Liquid-Solid Solubility (20 °C)

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Solubility wt% in soln.</th>
<th>Solvent</th>
<th>Solubility wt% in soln.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hexane</td>
<td>0.30</td>
<td>Benzene</td>
<td>1.70 (20 °C)</td>
</tr>
<tr>
<td>Heptane</td>
<td>0.33</td>
<td>Toluene</td>
<td>1.83 (20 °C)</td>
</tr>
<tr>
<td>Octane</td>
<td>0.36</td>
<td>Methanol</td>
<td>0.03 (18 °C)</td>
</tr>
<tr>
<td>Nonane</td>
<td>0.39</td>
<td>Ethanol</td>
<td>0.05 (18 °C)</td>
</tr>
<tr>
<td>Decane</td>
<td>0.40</td>
<td>Diethyl ether</td>
<td>0.28 (18 °C)</td>
</tr>
<tr>
<td>Water</td>
<td>&lt;0.01</td>
<td>Acetone</td>
<td>2.65 (23 °C)</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>1.02 (22 °C)</td>
<td>CS$_2$</td>
<td>30.0 (20 °C)</td>
</tr>
</tbody>
</table>
Sulfur Phase Diagram

- Pressure / kPa vs. Temperature / K
- Points:
  - Rhombic Solid
  - Monoclinic Solid
  - Vapour
  - Liquid

Legend:
- Rhom-Vap
- Mono-Vap
- Rhom-Mono
- Rhom-Liq
- Mono-Liq
- Vap-Liq
- Points

Graph shows different phases and transitions of sulfur under varying pressure and temperature conditions.
Solubility of Sulfur in Natural Gas
Solubility in Natural Gas

10^{-8} moles S_8 in 100 moles Natural Gas is equivalent to:
- 0.0001 ppm(v) or 0.0008 ppm (H_2S equivalents)
- 0.0026 mg
- 0.0011 mg/scm
- 0.000068 lb/Mscf

500 mL/min gas flow rate is equivalent to:
- 500 x 10^{-6} x 60 x 24 scm/day
- 0.00079 mg-S_8/day

Joule-Thomson cooling from 15 °C, 68.9 bar (1000 psia) to -28.3 °C, 1.01325 bar (1 atm)

Typical level of H_2S is 3 ppm(v)
Chemical Analysis

- Sulfur in natural gas – very low concentrations ~0.001 ppm (vol)
- Conventional gas chromatography
  - Sulfur not easy to chromatograph (bp 444 °C)
  - Detection limits insufficient
  - Gas bomb gas volumes – too small (0.5 L at 70 bar = 35 L at 1 bar). Need 1000 L
- Other methods (total sulfur, H₂S) not sensitive enough
- Need sensitive and selective method
Triphenyl Phosphine (TPP)

**Physical Properties of TPP (C\textsubscript{18}H\textsubscript{15}P)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>262.29 g/mol</td>
</tr>
<tr>
<td>Melting temp.</td>
<td>81.3 °C (354.4 K)</td>
</tr>
</tbody>
</table>

Section: Reaction of triphenyl phosphine with sulfur to form triphenyl phosphine sulfide (TPPS):

\[
8 \text{C}_6\text{H}_5\text{P} + \text{S}_8 \rightarrow 8 (\text{C}_6\text{H}_5)_3\text{P}=\text{S}
\]

- 0.00079 mg S\textsubscript{8} reacts with 0.0065 mg TPP

**Physical Properties of TPPS (C\textsubscript{18}H\textsubscript{15}PS)**

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>MW</td>
<td>294.35 g/mol</td>
</tr>
</tbody>
</table>
Sampling of High Pressure Natural Gas

![Image of high pressure natural gas sampling equipment]

Diagram showing the flow from NTS to vent, with Dreschel bottles and a wet gas meter.

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[Image of pressure gauge]

[Image of Dreschel bottles filled with liquid]

[Image of wet gas meter reading]
Gas Sampling

Solution of TPP in dimethyl formamide

Requires sampling large gas volumes ~500–1000 litres

Sampling times typically 8 hours at 2 L/min
Mass Spectrum TPPS

- Selective ion monitoring of 294+ ion
- Sensitive
- Part per billion (solution)
- $10^{-7} - 10^{-8}$ mol% (gas)
Mitigation of Elemental Sulfur Deposition

- GasVLe
- Models phase equilibria in natural gas
- Study pressure reduction in gas regulators
- Risk assessment of assets
Conclusion

- Elemental sulfur deposition – problem for some gas assets
- Analytical method for elemental sulfur – very low concentrations in natural gas
- Solution to the problem experienced by gas assets using solubility curves and an understanding of Joule-Thomson effect. Installation of pre-heaters.