HD gas purification for polarized HDice target production at Jefferson Lab

Overview

• Commercial HD Gas contains 0.5-2.0% $H_2$ and $D_2$
• To produce targets, the $H_2$ and $D_2$ must be reduced
  – Require small, carefully controlled concentrations
• Isotopic separation is done using distillation
  – Operate at low temperature to liquefy and obtain good boiling point (partial pressure) differences
  – Apply heat to boil the liquid
  – Use a packed column for good efficiency
• Gas monitoring
  – Residual Gas Analyzer
  – Gas chromatography
  – Raman Scattering
Isotopic Separation

$H_2$, HD, and $D_2$ have significantly different vapor pressures at low temperature.

This allows separation using distillation techniques.
Low Temperature Distillery
Mechanical refrigerator
- Two-stage system
  - 1\textsuperscript{st} stage: \(\sim 35\) K
  - 2\textsuperscript{nd} stage
    » \(T_{\text{min}} = 11\) K
    » \(T_{\text{oper}} = 18\) K

Temperature control & boil-up power supply
- Typical boil-up power \(\sim 2.3\) W
  - \(18\) K \(\rightarrow\) \(P \sim 260\) mbar
  - Extraction rate = 1 mole/day
Packed Distillation Column

• Heli-pak
• Improves efficiency
  – http://www.wilmad-labglass.com/Products/LG-6730-104/

Windows in vacuum container and thermal shield permit viewing the boiling liquid hydrogen

...has often enabled system debugging
Gas Handling

• Manifold with 2-mole stainless tanks
• Gas moved between tanks using LHe and a cold trap
• Long term storage at low pressure in Al tanks
Essentially all $H_2$ extracted.

Extraction ends (pot empty)

System hold-up ~3.5 moles ($D_2$-rich gas)

Purified HD gas ~7 moles

Initially, 12 moles in the system

Inferred $D_2$ increase

Observed $H_2$ decrease

Schematic of Extraction Process

HD Concentration

% Concentration

Moles Extracted
Distillery Operation

Beginning of JMU 6.0

RGA Monitoring of Gas Extraction

All $H_2$ is extracted as measured by GC

"$H_2$ Rich"

2-mole tanks filled to $\sim$260 mbar each

Limit of RGA sensitivity

$H_2$ / HD ratio (%)

Gas Extracted (moles)
Low Temperature Gas Chromatography

Measuring the relative concentration of H2 and D2 in HD gas with gas chromatography
Whisnant, Hansen, and Kelley
Rev. Sci. Inst. 82, 024101 (2011)
Chromatography Column

- Off-the-shelf PLOT 5A capillary column
  - ValcoPLOT® VP-Molesieve GC Capillary Column
  - Length=30 m, ID=0.53 mm, Film Thickness=50μm

- Column operated between T≈115K - 130K
  - Immersed in a roughly equal mixture of LN₂ and iso-pentane
  - ΔT during a run is 1-2K
  - Run-to-run variation is larger as LN₂ boils away
  - As T increases: separation and retention time decreases
Monitoring with Gas Chromatography

For accurate results, sample must be run several times and averaged
- Gas sample collected in 75 ml bottle at 2 ATM
  - Yields ~ 3-4 injections
- TCD gives a H$_2$ and D$_2$ detection threshold of a few $\times 10^{-3}$
  - Limited by noise
  - Noise is primarily microphonics
- Precision is improved by averaging the results of several runs

- Raw Gas
- para-H$_2$
- ortho-H$_2$
- D$_2$
- HD

JMU 6.0 - Tank 4

~ 30 minutes
**Raman spectroscopy: laser scattering from rotational states**

Raman spectroscopy does not dissociate HD molecules and it is used to provide measurements of H$_2$ and D$_2$ relative concentrations in HD gas at the 10-5 level.

Molecular rotational energy levels are given by:

$$E_R = \hbar^2 \frac{J^2}{2I} = hcb_0J(J + 1)$$

where:

$$b_0 = \frac{h}{8\pi^2 I}$$

and $I$ is the molecule moment of inertia.

Distance among levels is higher for lighter molecules.

Raman scattering occurs when Laser light is absorbed and re-emitted by a molecule while the rotational state changes: the scattered light is shifted from the Laser energy by:

$$\Delta E = hcb_0(J + 2)(J + 3) - hcb_0J(J + 1) = hcb_0(4J + 6)$$

Selection rules $\Delta J=\pm2$ connect ortho- to ortho- and para- to para- molecular states.
Raman set-up

- The gas to be analyzed is used to fill the cell.
- The Laser light is focused at the center of the cell and reflected back by a mirror to increase the useful incoming power.
- The scattered light is reflected by a mirror and expanded in a parallel beam to enter the monochromator slit.

The scattered light spectrum is detected by a cooled CCD and recorded by a PC.
Counts/s

Pure H$_2$ Raman Spectrum

$J=0 \rightarrow J=2$

$J=1 \rightarrow J=3$
ortho-H$_2$

$J=2 \rightarrow J=4$
ortho-lines are higher because of higher nuclear states multiplicity

$J=3 \rightarrow J=5$
ortho-H$_2$

$J=4 \rightarrow J=6$
para-H$_2$

Lines are equally spaced

para-H$_2$

ortho-H$_2$
Counts/s

![Pure D₂ Raman Spectrum](image)

**orthobands are higher because of higher nuclear states multiplicity**

Lines are equally spaced and are closer than H₂ lines.
H$_2$ and D$_2$ lines are present as well.

Distance among HD lines is higher than H$_2$ and lower than D$_2$ ones.
Three \( \text{H}_2 \) and seven \( \text{D}_2 \) lines are visible and well separated from the main five HD ones.
Raman spectrum analysis

• The relative content of $H_2$ and $D_2$ contaminants in HD gas is determined fitting all the peaks in the frequency range between 100 and 1000 cm$^{-1}$ higher than the original Laser frequency (stokes lines).

• Peaks intensities are determined from the Gaussian fit parameters

• By studying the dependence upon the temperature and upon the index $J$ of each rotational level it is possible to determine the relative number of molecules in the sample for the different chemical species.

• The minimum relative amount that may be detected is lowered by increasing the Laser power and by reducing the background fluctuations

we use a 15 Watts Laser and we integrate the spectrum over 1 hour to average over noise fluctuations
Comparing Raman and GC

• Raw HD before purification:
  – Raman
    • $\text{H}_2/\text{HD} = (7.0 \pm 0.6) \times 10^{-3}$
    • $\text{D}_2/\text{HD} = (8.0 \pm 0.07) \times 10^{-3}$
  – GC
    • $\text{H}_2: (7.0 \pm 0.14) \times 10^{-3}$
    • $\text{D}_2: (11.0 \pm 0.22) \times 10^{-3}$
JMU 5 – tank 2

Ion-Ar Laser: 12 W power

\[ \frac{H_2}{HD} = (61 \pm 2) \times 10^{-5} \]

\[ \frac{D_2}{HD} = (5 \pm 3) \times 10^{-5} \]

H₂ and D₂ peaks were not visible in the chromatogram
Summary

• Low-temperature distillation permits separation of $H_2$, HD, and $D_2$ to a few parts in $10^{-4}$ or better
• Measurement techniques available for monitoring purity (in increasing sensitivity and complexity)
  — Residual gas analysis
  — Gas chromatography
  — Raman scattering
• Gas production underway
The Need for Purity

Creating a frozen spin target with significant relaxation time requires that $H_2$ and $D_2$ concentrations be small and carefully controlled.

Longitudinal relaxation time $T_1^H$

\[ \frac{1}{T_1^H} \propto \left( c_1^H \right)^{2.1} \left( c_1^D \right)^{1.6} \]
Gas is stored at < 2 ATM in specially treated Al cylinders to minimize this effect.