

# The Galileo Probe Mass Spectrometer: Composition of Jupiter's Atmosphere

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The composition of the jovian atmosphere from 0.5 to 21 bars along the descent trajectory was determined by a quadrupole mass spectrometer on the Galileo probe. The mixing ratio of He (helium) to  $H_2$  (hydrogen), 0.156, is close to the solar ratio. The abundances of methane, water, argon, neon, and hydrogen sulfide were measured; krypton and xenon were detected. As measured in the jovian atmosphere, the amount of carbon is 2.9 times the solar abundance relative to  $H_2$ , the amount of sulfur is greater than the solar abundance, and the amount of oxygen is much less than the solar abundance. The neon abundance compared with that of hydrogen is about an order of magnitude less than the solar abundance. Isotopic ratios of carbon and the noble gases are consistent with solar values. The measured ratio of deuterium to hydrogen (D/H) of  $(5 \pm 2) \times 10^{-5}$  indicates that this ratio is greater in solar-system hydrogen than in local interstellar hydrogen, and the  $^3\text{He}/^4\text{He}$  ratio of  $(1.1 \pm 0.2) \times 10^{-4}$  provides a new value for protosolar (solar nebula) helium isotopes. Together, the D/H and  $^3\text{He}/^4\text{He}$  ratios are consistent with conversion in the sun of protosolar deuterium to present-day  $^3\text{He}$ .

Determination of the composition of Jupiter's atmosphere should constrain the relative importance of direct contributions to the atmosphere from the solar nebula itself, on the one hand, and from large icy or rocky objects present in the early outer solar system, on the other. The contribution of these "planetesimals" could have been in the form of an early atmosphere around Jupiter's primitive solid core or in the form of volatiles they carried to the planet after it began to acquire its atmosphere of  $H_2$  and He from the solar nebula (1, 2). The degree of resemblance between the sun's atmosphere and that of Jupiter in the abundances relative to  $H_2$  of elements such as C, N, and O should be decisive in providing the required constraints.

Before the direct, in situ measurements reported here, remote spectroscopic sensing from Earth and from spacecraft had indicated that the relative abundances of C (in  $\text{CH}_4$ ) and N (in  $\text{NH}_3$ ) were greater than the solar abundances (3, 4). Phosphine and water vapor had been detected, but their abundances below the clouds were uncertain, and  $\text{H}_2\text{S}$  and the noble gases other

than He had not been detected at all. Definitive data to replace these tantalizing clues to the sources of volatile compounds in Jupiter's atmosphere were not available before descent of this probe.

An accurate direct measurement of the abundances of He and the other noble gases is important for understanding how Jupiter has processed its constituents. Abundances less than the solar values would signal the formation, in the metallic interior of the planet, of a separate He phase, some of which has precipitated deeper into the interior. Remote sensing had indicated a modest depletion of He, but this indirect result is much less satisfactory than the direct sensing by two of the Galileo instruments reported here.

The Galileo probe mass spectrometer (GPMS) was designed to measure the mixing ratios of major and minor species while determining the isotopic ratios of their constituent elements (5). Signals were recorded from over 6000 individual values of mass-to-charge ratio ( $m/z$ ). The data returned by the instrument have led to the discovery of six new atmospheric constituents and the measurement of numerous abundances and isotopic ratios. The gas sampling system admitted the jovian atmosphere through low-conductance leaks to the ion source of a quadrupole mass analyzer. The ion source was pumped by a getter and the analyzer volume pumped to a much lower pressure by a getter backed by a sputter-ion pump. One inlet (direct leak 1; DL1) was open from 0.52 to 3.78 bars; the other inlet (DL2) functioned from

8.21 bars to the end at about 21 bars (6).

Figure 1 shows a sample mass spectrum from the 3-bar region at 228 K, before any significant water cloud was expected, and another one from the 11-bar region, where the 350 K temperature ensures that the probe was far below any water condensation level. Comparison of the two spectra shows a large increase in the second direct leak of  $\text{H}_2\text{O}$  and  $\text{NH}_3$ . In fact, the design of the leak 1 sampling system, with a relatively long vacuum path to the ion source, precludes a sensitive detection of the surface active species  $\text{H}_2\text{O}$  and  $\text{NH}_3$  in the atmospheric region sampled by this leak. Raw counts shown in these spectra must be corrected for the counting system dead time. The efficiencies of the ion source and of the pumping system vary from species to species, and the sensitivity factors, which are different for the two direct leaks, must be individually determined. In most cases, we used preflight calibrations, but for the most important species we were able to do some recalibrations on the spare instrument. With the direct-leaks, the background level was typically between 0 and 3 counts. Two background measurements demonstrated that the instrument arrived at Jupiter in a very clean state and quickly lost its memory of almost all gases contributed by DL1.

Table 1 shows the mixing ratios (number densities relative to  $\text{H}_2$ ) of species that were detected and for which reliable measurements could be made. Error estimates are roughly  $1\sigma$  and represent the data scatter about the average value. Some of the observed mixing ratios can be compared with those for the solar system as compiled by Anders and Grevesse (7), commonly referred to as the solar abundances. Also shown are results of earlier analyses based on Voyager or Earth-based spectra.

The jovian  $\text{He}/\text{H}_2$  ratio,  $0.156 \pm 0.006$ , is the average of 14 individual measurements from DL1 ( $0.157 \pm 0.006$ ) and 4 from DL2 ( $0.151 \pm 0.004$ ). All the other noble gases were detected, and they are elementally fractionated. The Ne ratio to  $\text{H}_2$  is about an order of magnitude less than the solar ratio, whereas for Ar the ratio is slightly greater. Kr and Xe were clearly detected; upper limits on the mixing ratios are respectively 5 and 50 times the solar values. For all four of the heavier noble gases, the isotopic ratios are close to the solar values.

The  $^3\text{He}/^4\text{He}$  and the D/H ratios were determined from an analysis of the 3 amu (atomic mass unit) data. This analysis is complicated by the need to correct for  $\text{H}_3^+$  produced in the ion source and to distinguish between the contributions of HD and  $^3\text{He}$ .  $\text{H}_3^+$  is generated by two mechanisms: the dissociative ionization of  $\text{CH}_4$  and two-body ion-molecule reaction between  $\text{H}_2^+$  and  $\text{H}_2$ . The efficiency of  $\text{H}_3^+$  production

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could be determined during the second background study when little  $\text{H}_2$  and He, but a considerable amount of  $\text{CH}_4$ , existed in the ion source and  $\text{CH}_4$  was the only important source of 3-amu ions. During pre-flight calibration, when the  $\text{H}_2$  pressure in the GPMS was varied over a large range, the  $\text{HD}/\text{H}_2$  ratio for the laboratory  $\text{H}_2$  sample and the efficiency of  $\text{H}_3^+$  production in DL1 and DL2 were separately determined. During probe descent, the  $^3\text{He}/^4\text{He}$  ratio was determined from 3-amu and 4-amu data obtained with the noble gas cell (NGC) sample (6). Hydrogen was effectively absent from this gas sample. The result,  $1.1 \times 10^{-4}$  (Table 1), indicates that He in the jovian atmosphere has a smaller proportion of  $^3\text{He}$  than the protosolar He found in meteorites, where  $^3\text{He}/^4\text{He} = (1.5 \pm 0.3) \times 10^{-4}$  (8). Evidently, the "protosolar" He isotopes in meteorites do not, in fact, reflect the values that existed in the solar nebula.

With the He mixing ratio and  $\text{H}_3^+$  production efficiencies in hand, the  $\text{HD}/\text{H}_2$  ratio was determined from the DL1 and DL2 data at 3 amu and 2 amu. During DL2 sampling, the electron energy in the ion source was reduced at times from 75 eV to 25 eV or 15 eV. Few and no He ions, respectively, were produced under these conditions, and the ratios of the 3-amu rate to the 2-amu rate provided an upper limit to  $\text{HD}/\text{H}_2$  (assuming no  $\text{H}_3^+$  production) of  $(1.1 \pm 0.3) \times 10^{-4}$ . The average value of  $\text{HD}/\text{H}_2$ , measured from inlet 2 data, was just at this limit. The ratios measured in inlets 1 and 2 were almost precisely the same. The  $^{12}\text{C}/^{13}\text{C}$  isotopic ratio was determined with high precision in DL1 data where the contribution of  $\text{NH}_3$  at 17 amu was negligible. The ratio is exactly that of the solar values.

Reasonably good agreement was found for  $\text{CH}_4$  mixing ratios in DL1 and DL2, within the calibration uncertainty of  $\pm 20\%$ . This determination indicates that

atmospheric  $^{12}\text{C}$  is more abundant by a factor of 2.9 relative to  $\text{H}_2$  than in solar system material. The measured mixing ratio of  $\text{H}_2\text{S}$  in the well-mixed atmosphere between 8 and 11 bars increased by a factor of 4 with depth. There was a tentative detection of HCl. Water vapor and  $\text{NH}_3$  are readily adsorbed on metal surfaces, and their densities in the ion source may lag behind those in the gas stream. The measurements made while DL2 was open should be the most reliable, but they were made just after enrichment cell 1 (EC1) was closed. Some of the  $\text{NH}_3$  and  $\text{H}_2\text{O}$  detected in DL2 may therefore have been contributed by outgassing of this adsorbed gas in the presence of abundant  $\text{H}_2$  and He (9). Hence, for the present, only upper limits can be set for these molecules. The constraint for  $\text{NH}_3$ , 16 times the solar value, is weaker than the existing estimate, 1 to 1.3 times the solar value, from analysis of Jupiter's microwave emission spectrum (10). The limit on water vapor, 0.2 times the solar value, is significant in view of the solar or greater values found

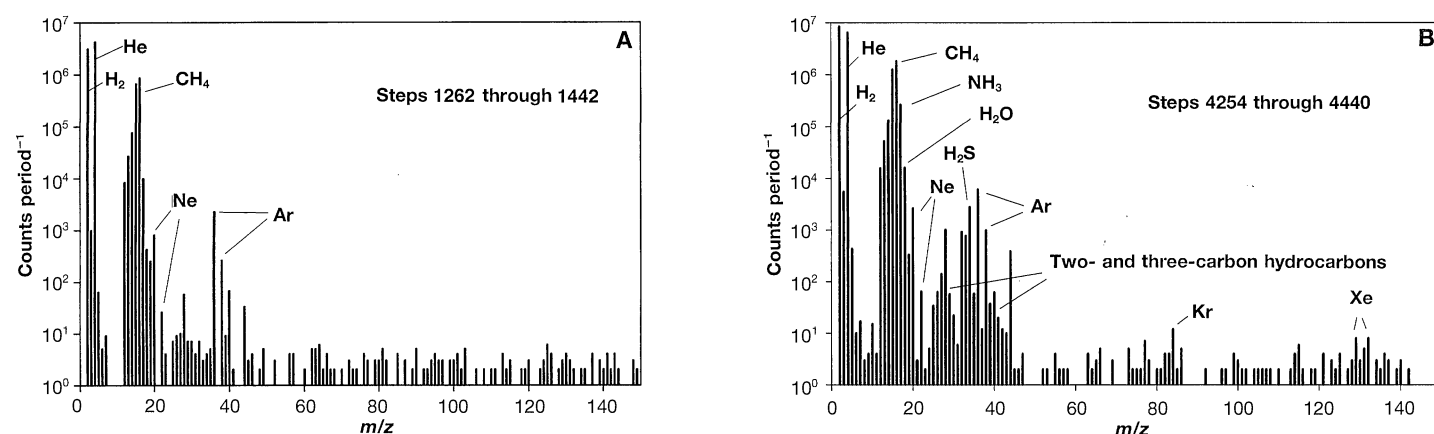
for the other volatiles C, N, and S.

Hydrocarbons containing two or three C atoms appeared to be present. The direct leaks showed no sign of any heavier hydrocarbons. Upper limits for the mixing ratios of these heavy hydrocarbon species are  $\sim 1$  ppb.

Our  $\text{He}/\text{H}_2$  ratio (0.156) agrees almost exactly with the ratio of 0.157 obtained by the helium abundance detector (HAD) on the Galileo probe (11); some of the implications of this measurement are discussed elsewhere (11). This value is considerably larger than the value of 0.11 obtained from Voyager data (12), but is little (if any) less than the value for the present sun. The protosolar value, deduced from evolutionary models of the sun, is probably a more relevant standard and is 18% greater (11). It is widely believed that Saturn's atmosphere, with a  $\text{He}/\text{H}_2$  ratio about one-fifth of the protosolar value, has been depleted of He by rain-out of He droplets in the interior (13, 14). The GPMS and HAD results agree with the Voyager data in suggesting that the same process must operate at Jupiter,

**Table 1.** Mixing ratios to  $\text{H}_2$  and isotopic ratios in the jovian atmosphere. Blank spaces indicate lack of prior results.

| Species                       | Jovian atmosphere                    | Ratio to solar value | Prior results               | References |
|-------------------------------|--------------------------------------|----------------------|-----------------------------|------------|
| $^4\text{He}$                 | $0.156 \pm 0.006$                    | 0.80                 | 0.11                        | (12, 13)   |
| $^{20}\text{Ne}$              | $(2.3 \pm 0.25) \times 10^{-5}$      | 0.10                 |                             |            |
| $^{36}\text{Ar}$              | $(1.0 \pm 0.4) \times 10^{-5}$       | 1.6                  |                             |            |
| $^{84}\text{Kr}$              | $\leq (8.5 \pm 4) \times 10^{-9}$    | $\leq 5$             |                             |            |
| $^{132}\text{Xe}$             | $\leq (5 \pm 2.5) \times 10^{-9}$    | $\leq 50$            |                             |            |
| $\text{CH}_4$                 | $(2.1 \pm 0.15) \times 10^{-3}$      | 2.9                  | $2.2 \times 10^{-3}$        | (3, 4)     |
| $\text{H}_2\text{O}$          | $\leq (3.7 \pm 0.35) \times 10^{-4}$ | $\leq 0.2$           |                             |            |
| $\text{NH}_3$                 | $\leq (3.5 \pm 0.3) \times 10^{-3}$  | $\leq 16$            | $2.5 \times 10^{-4}$        | (10)       |
| $\text{H}_2\text{S}$          | $(7.7 \pm 0.5) \times 10^{-5}$       | 2.2                  |                             |            |
| D/H                           | $(5 \pm 2) \times 10^{-5}$           |                      | $(2.0, 3.6) \times 10^{-5}$ | (17-19)    |
| $^3\text{He}/^4\text{He}$     | $(1.1 \pm 0.1) \times 10^{-4}$       |                      |                             |            |
| $^{13}\text{C}/^{12}\text{C}$ | $0.0108 \pm 0.0005$                  | 1.0                  |                             |            |



**Fig. 1.** Sample mass spectra. The spectra in (A) were obtained through DL1 between pressures of 2.72 and 3.05 bars, with ambient temperature at 228 K. The spectra in (B) were obtained through DL2 between pressures of 10.6 and 11.3 bars, with ambient temperature at 350 K. No corrections have been made for dead time or for different efficiencies at different masses.

though not to the same extent. This loss of He is a likely explanation of the Ne depletion observed by the GPMS, if the solubility of Ne in He is as large as has been suggested (15).

The value of  $(5 \pm 2) \times 10^{-5}$  deduced for D/H from HD/H<sub>2</sub> is higher than the ratios derived from Earth-based spectroscopic observations (16, 17):  $(2 \pm 1) \times 10^{-5}$  from CH<sub>3</sub>D/CH<sub>4</sub> and  $(2 \pm 1) \times 10^{-5}$  from HD/H<sub>2</sub>. It agrees well with the value found in a recent analysis of Voyager infrared spectra (18):  $(3.8 \pm 0.5) \times 10^{-5}$ . The jovian D/H ratio should be the same as the protosolar or solar-nebular value because the nebula was the source of Jupiter's hydrogen. [The terrestrial ratio is  $1.6 \times 10^{-4}$ .] The sun converted all its D to <sup>3</sup>He early in its history; thus, Geiss (8) argued that the original D/H in the solar nebula should be equal to the difference between the <sup>3</sup>He/<sup>4</sup>He ratios in the solar wind and in meteorites, which should contain nebular He (19). Geiss's value for protosolar D/H is  $(2.6 \pm 1.0) \times 10^{-5}$ , and this overlaps the GPMS value. Substituting the new determination of protosolar <sup>3</sup>He/<sup>4</sup>He =  $(1.1 \pm 0.2) \times 10^{-4}$  for the meteoritic one, the same argument would yield D/H =  $(3 \pm 1) \times 10^{-5}$ , a value that is closer to that derived directly from HD. It is clear that D/H on Jupiter is distinctly higher than the value of  $(1.6 \pm 0.1) \times 10^{-5}$  found in local interstellar H (20), as expected from the steady destruction of D in the galaxy by stellar nucleosynthesis during the last  $4.5 \times 10^9$  years.

Earth-based imaging (21) and the remarkably small number of cloud particles detected by the nephelometer experiment (22) indicate that the probe may have descended into an unusually clear part of the jovian atmosphere. An obvious explanation is that the region was one of subsidence, like most clear regions on Earth. Our H<sub>2</sub>O abundance value, then, may be less than the planetary average, although this interpretation is unlikely. In a cloud, the relative humidity should be just over 100%, and this is consistent with the comprehensive analysis of Voyager spectra by Carlson *et al.* (18). The corresponding profile of water vapor has a scale height of about 3 km. If, for example, the relative humidity is reduced by a downdraft from 100% to 90%, the amount of subsidence required is  $3 \ln(90/100)$  km, or a mere  $-0.3$  km. Our measurements were made at far greater depths than the expected condensation level (5 or 6 bars); to perturb the humidity at such a deep level would require a downdraft extending over a range of well over a scale height, far more than needed simply to clear out the clouds. There remains the possibility of a global-scale circulation, perhaps upward at

high latitudes and downward at low.

The large atmospheric abundance of C suggests that sources other than the gas of the solar nebula contributed a significant share of the volatiles in the envelope of Jupiter. These elements and water should have been in the condensed phase in the neighborhood of the accreting Jupiter. One possible explanation for a deficiency of water was proposed by Gautier and Owen (3): most of the planetesimals accreted to the rocky, icy core of the embryo planet rather than being collected after the planet began to amass its gaseous envelope from the neighboring solar nebula. Water vapor, being the least volatile, remained close to the core, whereas gases like CO, CH<sub>4</sub>, and N<sub>2</sub> could mix with the nebula-derived envelope, enriching it in C and N. Although this scenario could reproduce the observed abundances, it must be tested by rigorous modeling. If there was a large mass of late-accreting planetesimals, the low relative abundance of atmospheric H<sub>2</sub>O requires them to have been rich in carbonaceous materials and deficient in O. It has been customary to assume that outer solar system planetesimals resemble the least-altered carbonaceous chondrites that fall to Earth, which contain more O than C (23), but there are many that are much drier. The mean densities observed for many satellites in the outer solar system have been explained by assuming a rock:ice ratio of order unity, but perhaps much of the low-density material is carbonaceous rather than icy.

If our results are representative of the entire planet (24), they preclude models in which several Earth masses of late-accreting, water-rich planetesimals deliver volatiles to the jovian envelope (1). There is no sign of the dense water cloud, or the corresponding vapor, invoked to explain waves spreading from the Shoemaker-Levy 9 impacts (25). Water vapor observed in the impact plumes probably came from the impactors, not Jupiter, as suggested (26).

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system were designed and fabricated by Aker Industries in Oakland, CA. The capillary leak arrays and secondary electron multiplier detector were manufactured by Galileo Electro Optics in Sturbridge, MA. The chemical getter material was provided by the SAES Getter of Milan, Italy. M. Wong of the University of Michigan participated in the data analysis. We also

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## The Helium Mass Fraction in Jupiter's Atmosphere

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On 7 December 1995, the NASA Galileo probe provided in situ measurements of the helium abundance in the atmosphere of Jupiter. A Jamin interferometer measured the refractive index of the jovian atmosphere in the pressure region from 2 to 14 bars. These measurements indicate that the atmospheric helium mole fraction is  $0.136 \pm 0.004$ . The corresponding helium mass fraction is slightly below the presolar value, which suggests that separation of helium from hydrogen in Jupiter's interior is only in its early stages.

In 1977, when the instruments for the Galileo probe were chosen, it was generally thought that the He abundance in the jovian atmosphere was the same as that which was created in the Big Bang and was later present in the solar nebula from which the sun and the planets were formed (1). An accurate measurement, therefore, would tell us something about conditions at the instant of the universe's creation. But later, Voyager results for Saturn (2) and Uranus (3), as well as more detailed knowledge of Jupiter (2, 4) and the sun (5), all suggested that processes in Jupiter could have modified the original ratio. An accurate measurement of the He abundance in the jovian atmosphere is now viewed as providing information about the origin and evolution of the planet itself. The purpose of the He abundance detector (HAD) (6) aboard the Galileo probe was to determine as accurately as possible the abundance ratio of He to H in Jupiter's atmosphere.

More than 99.5 mole percent of the jovian atmosphere consists of  $H_2$  and He. Hence, to a first approximation, this atmosphere can be considered to be a binary gas mixture, for which the mole fraction  $q_{He}$  of He can be derived from the ratio of refractive indices

$$q_{He} = \frac{n_{H_2} - n_s}{n_{H_2} - n_{He}} \quad (1)$$

where  $n_{He}$  is the refractive index of He,  $n_{H_2}$  is the refractive index of  $H_2$ , and  $n_s$  is the refractive index of the sample gas (jovian

gas). We use the word "sample" because the refractive index of this jovian gas is measured inside the HAD instrument and at sample gas pressures and temperatures that differ from conditions in the ambient jovian atmosphere.

For an accurate measurement of the refractive index of the jovian gas, the Galileo HAD used a two-arm Jamin interferometer (7). It produces a fringe pattern on an array of nine photodiodes (PDA), which does not change if both cells are filled with gas mixtures having the same refractive index. However, any difference between the refractive indices of the sample and the reference gas causes a continuous shifting of the fringe pattern with increasing pressure (that is, as the entry probe penetrates deeper into the jovian atmosphere). The signals from eight of the nine photodiodes are combined electronically inside the HAD to monitor in digital form the direction and number  $F$  of interference fringes displaced across the PDA in multiples of one-eighth of the fringe separation. The output signal of the ninth diode is used in analog form.

During launch and cruise of the Galileo spacecraft toward Jupiter, the HAD entrance orifice was closed by a thin metal diaphragm. This diaphragm was designed to burst when an outside jovian pressure of about 2 bars was reached. Subsequently, the ambient pressure operated a needle device that punched a hole in a second diaphragm that previously had closed off the reference gas in its storage volume. The reference gas passed into its interferometer reference gas cell (RGC) through a membrane valve that kept the pressure difference between cells SGC (sample gas cell) and RGC near 80 mbars. This pressure difference was also measured

sure sensor. Measurement of the subsequent fringe motion continued until the reference gas was expanded to the local ambient pressure.

A complete calculation of the He mole fraction  $q_{He}$  needs to take into account quantitatively (i) the pressures of the sample gas  $P_s$  and the reference gases  $P_r$  (or instead of the latter, the pressure difference between sample and reference gases) at the start (i) and end (e) of the measurement in the jovian atmosphere; (ii) the absolute temperatures of the sample gas  $T_s$  and the reference gas  $T_r$  at the start (i) and the end (e) of the measurement; (iii) the Lorentz-Lorenz function that connects the refractive index  $n$  of a nonpolar gas with its mass density  $\rho$ ; (iv) the non-ideal gas characteristics of  $H_2$ , He, Ar, and Ne as described by their compressibilities  $Z$  and virial coefficients  $B(T)$ ; and (v) the effects of an absorber in front of the SGC, which eliminates the traces of jovian methane from the measured gas sample. The aggregate equation for calculating  $q_{He}$  contains four terms, shown below as  $f_1$ , through  $f_4$ ; the mole fraction is (8):

$$q_{He} = f_1(n_r) + f_2(F^e - F^i) + f_3(P_s^{e,i}, T_s^{e,i}) + f_4(q_{He}, T_{absorber}) \quad (2)$$

where  $f_1$  is dominated by the refractive index  $n_r$  of the reference gas,  $f_2$  represents the contribution from the observed fringe displacement  $DF = F^e - F^i$ ,  $f_3$  is dominated by the pressure difference  $P_s - P_r$ , and  $f_4$  represents an empirical correction required by the presence of absorbers for the trace gases  $H_2O$ ,  $NH_3$ , and  $CH_4$ , which absorb small amounts of  $H_2$  too. These terms are of the order 0.11, 0.03, 0.0005, and  $-0.004$ , respectively.

The HAD instrument was designed to perform best in the pressure range from 2 to 12 bars (6). During the descent of the probe, the reference gas storage volume

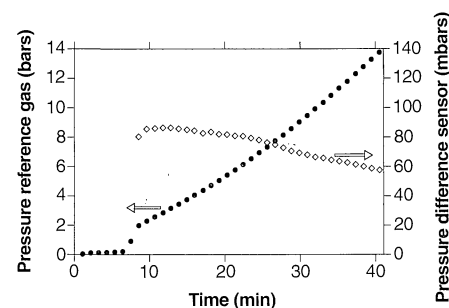


Fig. 1. Pressure inside the reference gas in the RGC (left ordinate) and the pressure difference between the SGC and the RGC (right ordinate) versus time [for definitions, see (7) and text] during the descent into Jupiter's atmosphere. The opening of the reference gas reservoir is notable close to 7 min.

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