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Technical Report 32-1236

Technique for Determining Gases Dissolved in Fuels, Oxidizers, and Liquids in General

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Abstract

A simple, direct method is described, as used at the Jet Propulsion Laboratory for determining the dissolved pressuring gases in oxidizers and fuels. The method consists in pumping the gases from repetitively frozen samples, measuring the volume manometrically, and sampling the collected gases for analysis.

Technique for Determining Gases Dissolved in Fuels, Oxidizers, and Liquids in General

I. Introduction

For some time, there has been an interest in gases dissolved in fuels and oxidizers.

Liquid fuels and oxidizers used aboard spacecraft and stored in bladders housed in pressurized tanks contain dissolved, pressurizing gas which has permeated the bladders. This dissolved gas comes out of solution when the fuels or oxidizers undergo pressure drops across metering valves, orifices, and so forth, and causes an unsteady engine thrust. A relatively simple, direct method has been used at the Jet Propulsion Laboratory (JPL) for determining dissolved gases. The preparation of this technical report has been prompted by this current interest and the past requests for the JPL technique for determining dissolved gases.

II. Apparatus

Figure 1 shows schematically the apparatus used to pump off the dissolved gas from the frozen phase, measure manometrically the collected gas and, finally, sample the gas for analysis.

The fixed zero-reference manometer, shown in the sketch, is described in the reference[1] which also covers an electronic circuit incorporating an electron-ray tube for setting the zero reference of the manometer more accurately than can be achieved by a direct visual setting. Electrical Connections 1 and 2, in the figure, are used for this circuit with Contact 1 being the manometer zero level.

The Toepler pump is operated automatically through the use of Electrical Connections 3, 4, and 5, in Fig. 1. The circuit selected for operating the automatic Toepler pump should be one drawing very little current so that if combustible gas mixtures are being pumped, the danger of an explosion will be minimized.

The 100-ml flask, containing a glass-enclosed stirring bar and into which the fuel or oxidizer is transferred, is constructed of heavy-wall, Pyrex glass. Kjeldahl flasks have the required wall thickness and can be used for

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[1] Barr and Anhorn, *Scientific and Industrial Glass Blowing and Laboratory Techniques*, p. 264 and pp. 276–279, Instruments Publishing Co., Pittsburgh 12, Pa., 1949.

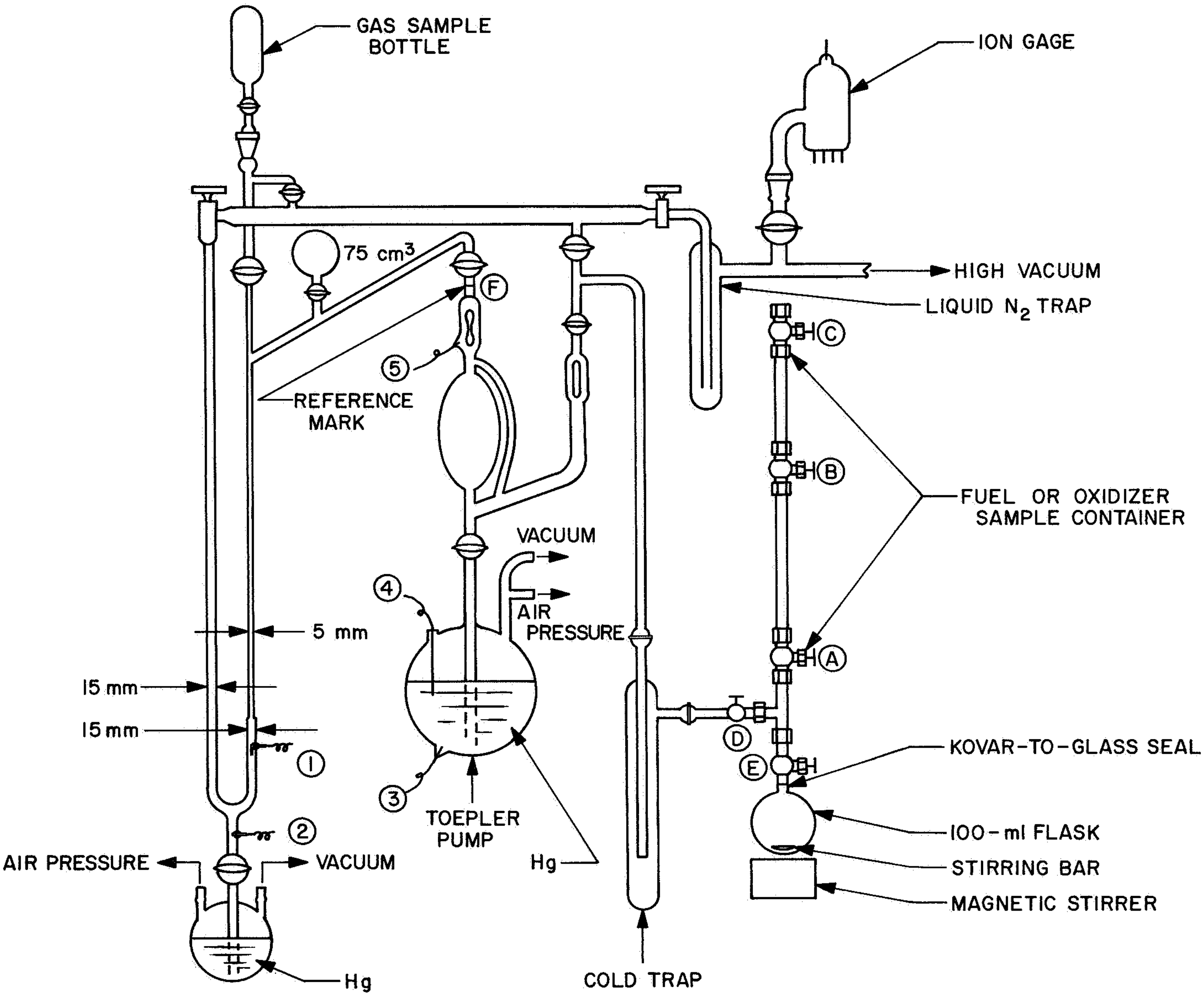

Fig. 1. System for pumping, collecting, and measuring dissolved gases

fabricating these flasks. The valve and flask assembly should be light enough so that the loaded flask can be weighed on an analytical balance. Commercially available ¼-in. Swagelok valves are too bulky for this application. Suitable valves have been fabricated from Teflon-packed stainless steel, ⅛-in. Hoke valves by replacing the ⅛-in. male pipe thread with a ¼-in. male Swagelok fitting using heliarc welding. The metal wall in the ¼-in. Kovar-to-Pyrex seal used on the flask should be at least 0.01 in. thick. Such seals are capable of withstanding hundreds of pounds of pressure, though in this application pressures experienced will be quite low.

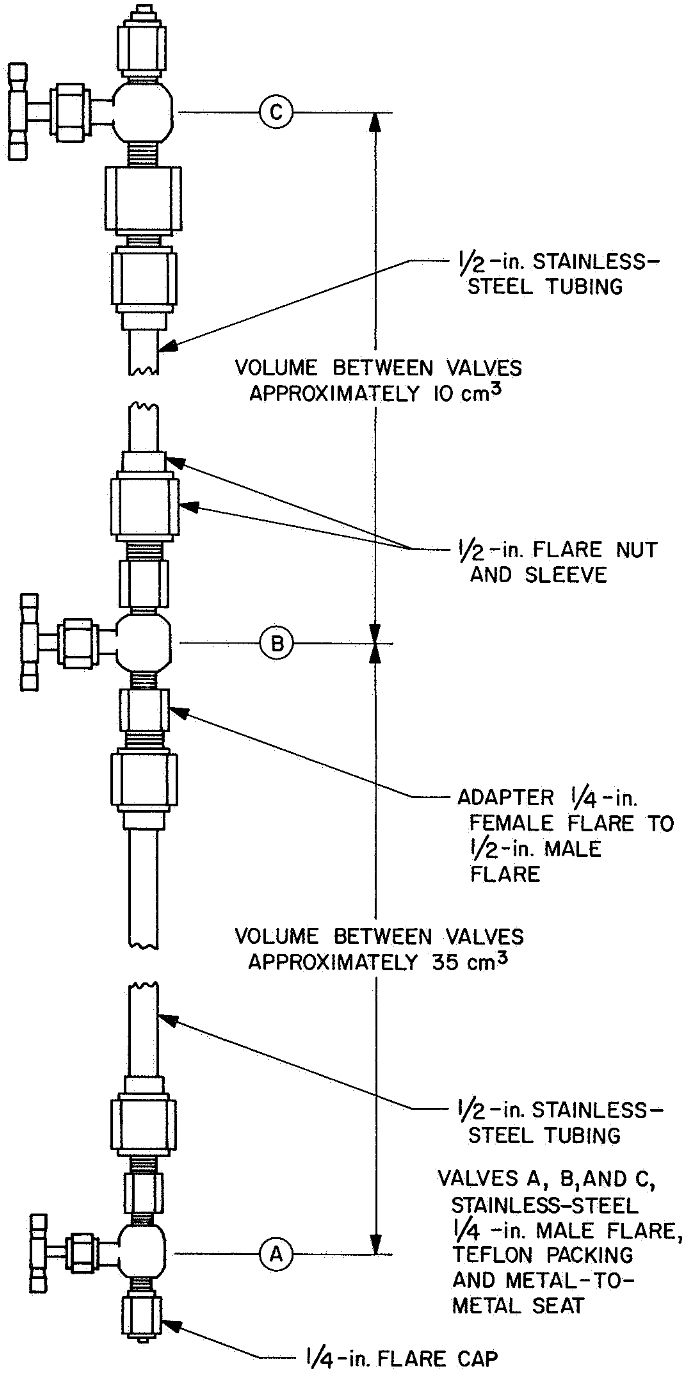

Fig. 2. Sample holder

The gas-measuring portion of the apparatus is calibrated by pumping a known volume of gas at a known pressure from a calibrated glass bulb fitted with a stopcock. The supplementary volume of approximately 75 cm^3 was calibrated with water prior to its installation.

Figure 2 shows the sample container designed by Larry K. Jones of JPL. This container holds about 35 cm^3 of liquid sample. Let us now consider the actual steps in making a measurement.

III. Gas Solubility Procedures

The most critical operation is that of sampling. The loss of dissolved gases must be avoided as well as the inadvertent introduction of air. The following procedure should provide a meaningful sample.

The carefully cleaned sample container should be connected as close as possible to the valve on the fuel or oxidizer tank to be sampled. Valves A, B, and C are opened and the attached assembly pumped down to the tank valve. The pump-down should be by means of a properly trapped pump capable of attaining 50 μm of Hg pressure or less as read on a Pirani gage. A valve isolating the vacuum pump is desirable so that the system can be checked for leaks by means of the Pirani gage.

With a suitably evacuated system, Valves B and C are closed and the tank valve opened to allow the liquid to enter the volume between Valves A and B. After a while the tank valve and Valve A are closed, and Valve B is opened to the evacuated ullage volume. The sample container is removed and the ends are capped off, with the precaution taken of blowing off, with dry nitrogen gas, any liquid residue present on the fitting of Valve A. Hopefully, none of the gases coming out of solution during sampling have been left trapped between the tank valve and Valve A. A short ⅛-in. tubing interconnecting the tank valve and Valve A on the upwardly sloped sample container would tend to minimize this possibility. So much for the sampling technique.

Assuming there is a representative sample, the sample container, the 100-ml flask, and the cold trap are interconnected by means of suitable hardware. Liquid nitrogen is used for cooling when collecting dissolved noncondensible gases, such as oxygen, nitrogen and helium.

The various stopcocks and valves are arranged so that all components are evacuated up to Valve A on the sample container. The ready attainment of pressure in the 10^{-6} torr region as read on the ion gage is taken as an indication of a tight system.

With a vacuum in the 10^{-6} torr region, Valve D is closed and Valve A is opened to allow the sample to drain into the flask. The drained sample is frozen in liquid nitrogen.

When the liquid nitrogen surrounding the flask has become quiescent, which indicates a completely frozen sample, mercury is driven up into the manometer and the Toepler system isolated from the high-vacuum manifold. The pumping is initiated by activating the Toepler pump and opening Valve D. For small gas volumes, the 75-cm^3 volume is excluded, which leaves only about 25 cm^3 in the measuring system.

When the mercury level in the manometer has reached a static position, Valves A, D, and E are closed, the frozen material in the flask is thawed, stirred, refrozen, and any released gases pumped off. Usually several millimeters of additional pressure are realized as a result of thawing, stirring, and refreezing.

With the mercury level in the manometer again static, the mercury in the Toepler pump is placed at its Reference Mark F, located above the mercury check valve, by means of the stopcock located above the Toepler mercury reservoir. The mercury in the manometer is brought down to its zero reference in the right leg and the height in the left leg is then read by means of a cathetometer.

After making the manometric measurement on the collected gas, the gas is admitted into the evacuated sample bottle for compositional analysis. For this, at JPL, a mass spectrometer is available. With good sampling, the collected gases assay in excess of 95% for the pressurizing gas used. Analysis is required to be sure that leaks have not vitiated the results.

The weight of fuel or oxidizer is determined by reweighing the flask containing the thawed material. The material in the flask is available for assay.

The volume of gas collected is calculated from the manometer pressure and the volume between Reference Mark F and Contact 1. The solubility results can be expressed as cm^3 (STP) of dissolved gas per gram of liquid.

Figure 3 shows some results obtained on helium-saturated mixed oxides of nitrogen containing 9.23 wt % of nitric oxide (MON-10). Figure 4 shows a plot of MON-10 vapor pressure vs temperature.

Figure 5 shows data obtained on helium-saturated monomethylhydrazine monohydrate ($MMH \cdot H_2O$).

The two sets of solubility data show increasing helium solubility with increasing temperature. Helium is appreciably more soluble in MON-10 than in $MMH \cdot H_2O$.

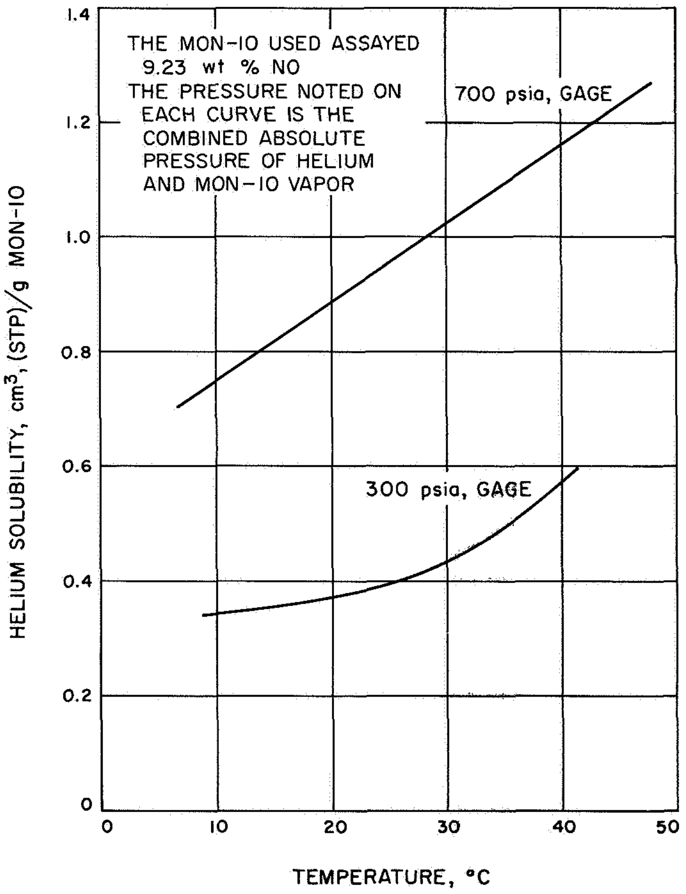

Fig. 3. Helium solubility in MON-10

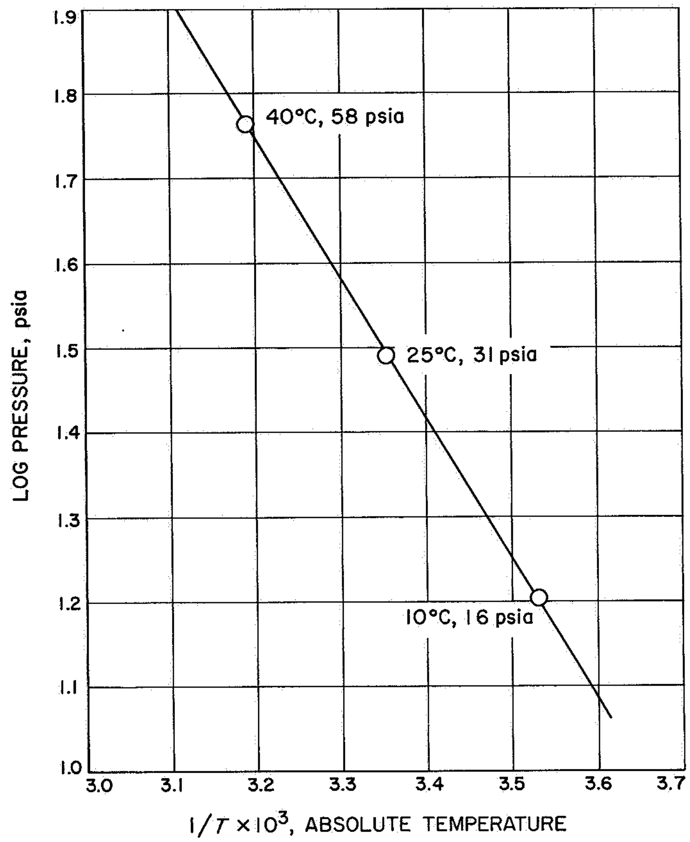

Fig. 4. Vapor pressure of MON-10, 9.23 wt % NO

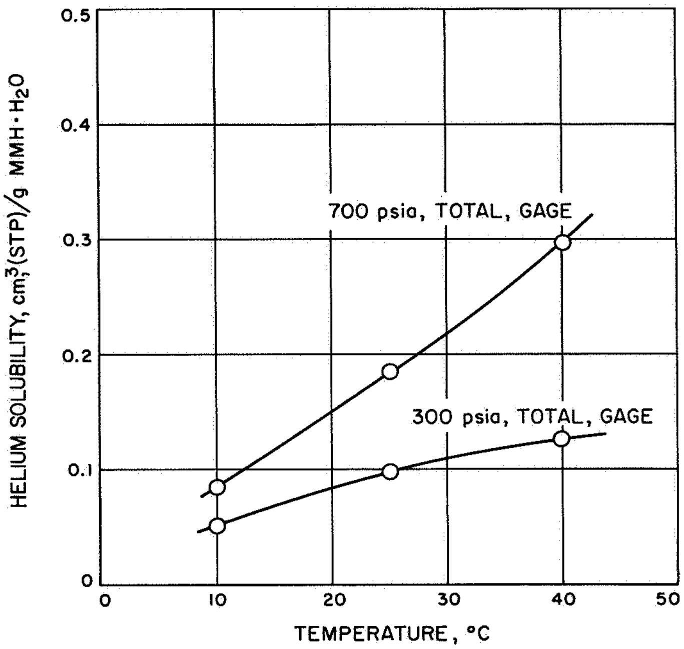

Fig. 5. Helium solubility in MMH·H_2O, 71.8 wt % MMH, 28.2 wt % H_2O

IV. Safety Precautions

Oxidizer sample containers, prior to use, should be carefully cleaned to LOX standards. The containers should be color coded and carefully labeled so that fuel and oxidizer samples are not confused.

Hydrocarbon lubricants must be avoided with oxidizer samples. Both N_2O_4 and MON-10 contaminated with hydrocarbons are shock sensitive. Sparing use of Teflon spray dispersions on valve threads to prevent galling is feasible. Kel-F greases are inert toward N_2O_4 and MON-10, but are decomposed by hydrazine fuels. Hydrocarbon greases are compatible with hydrazine fuels. The perfluorinated grease, Du Pont PR-240AC, is compatible with both the oxidizers and hydrazine fuels.

Both N_2O_4 and MON-10 are highly toxic. For greater safety the 100-ml glass flask can be replaced by a stainless steel container, but this is heavier and does not permit visibility.

V. Conclusion

The technique described is a general one for determining gases dissolved in liquids. The CO_2 content in MON-10 has also been determined using the described technique. Dry ice–acetone is used instead of liquid nitrogen for freezing and trapping when determining the CO_2 content.