

# REVIEW OF NEW SOLUBILITY DATA FOR CERTAIN HYDROCARBONS IN LIQUID OXYGEN

W. L. Ball  
Air Products and Chemicals, Inc.  
Allentown, Penn.

Accurate solubility data for hydrocarbons in liquid oxygen are recognized by all as a prerequisite for the safe design and operation of air separation units. Solubility data developed by Air Products research laboratories has been reported and quoted on a number of occasions in discussions concerning air separation plant safety. Because of questions raised concerning certain relatively low solubility materials, we recently undertook a program to review this data, taking advantage of improved techniques particularly in methods of analysis. (Discussion of this analytical technique was presented by our Dr. H. Linde at the 1965 Cryogenic Engineering Meeting.) The new data developed by this work is of particular importance because we found that the improved techniques gave us solubility values in some cases almost an order of magnitude less than the values previously reported.

## Test apparatus

The apparatus used for this work is shown in Figure 1. The saturator consisted of two 6-in. lengths of 3/8 in. O.D. x 1/4-in. I.D. copper tubing packed with

six 1-in. long plugs of stainless mesh separated by 1-in. long spacers of copper tubing. The two saturators were placed in series and were arranged so that the liquid flow was from bottom to top. The vaporizer was a 10-in. length of 1-in. O.D. copper pipe, heated on the outside by two 44-watt heating tapes. A 1/8-in. O.D. copper tube passed into the vaporizer, and this tube was bent at the end so that the LOX stream would contact the warm walls and vaporize immediately. The vapor then passed to the chromatograph for analysis. The temperature bath consisted of boiling liquid oxygen for all liquid solubility determinations.

## Experimental procedure

The steps of the experimental procedure are outlined below:

1. The saturator assembly was filled through the upstream side to about 30 lb./sq. in. gauge with the test gas.
2. The temperature bath was raised so that only the saturator was immersed in the bath liquid, and the test gas frozen or condensed.

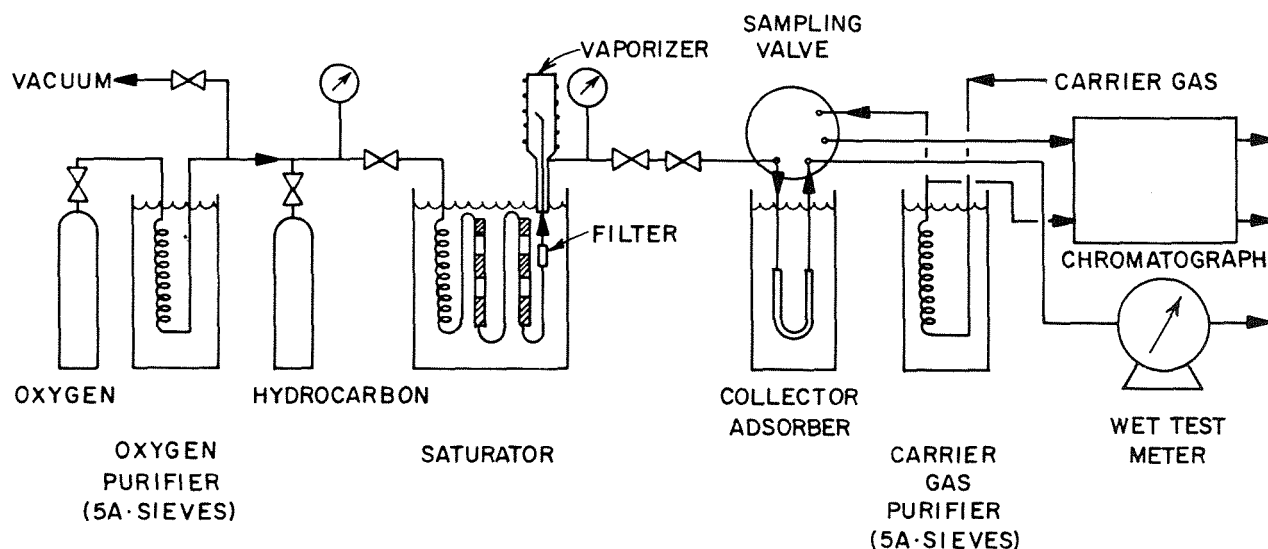


Figure 1. Liquid phase solubility apparatus.

3. The temperature bath was raised into place, and the system brought to operating temperature. The saturator assembly was briefly evacuated and isolated. The test gas was evacuated from all upstream lines.
4. Oxygen flow was started at the desired pressure through the saturator and continued for 5 to 10 min. Experience with duplicate runs showed that steady state was reached within this time. Duplicate runs also showed that flow rates between 1.7 and 4.3 liter/min. did not affect results. All runs were made at a vapor flow of 4.2 liter/min.
5. Analysis was accomplished by flowing the effluent from the saturator through the collecting adsorber at  $-110^{\circ}\text{F}$ . When the desired volume of gas (up to 50 liters, depending upon concentrations expected) had passed through the collector, the sampling valve was rotated, directing the carrier gas through the collector and into the chromatograph. The collector

was immediately heated to  $90$  to  $95^{\circ}\text{C}$  by a hot water bath to desorb the collected sample. The total volume of gas passed through the collector was determined by initial and final wet test meter readings. The amount of sample desorbed was determined from the chromatogram.

By knowing the amount of test gas desorbed from the collector, and the total amount of gas passed through the collector, the concentration can be calculated. The lowest concentration measured by this method was 40 ppb.

## Data scatter

Results for liquid phase solubilities as determined in this manner are compared with previous data (McKinley, C., and E. S. J. Wang, Proc. 1958 Cryo. Eng. Conf., p. 11-25) in Table 1. Factors which might contribute to the observed scatter include the possibility that the filter occasionally may have passed some tiny solid particles, and the possibility that temperature fluctuations occurred in the saturator. The solubilities were determined at pressures between 30 and 90 lb./sq.in. abs.; no effect of pressure on the results were observed. Other causes of the data scatter could be the possibility of very small amounts of test gas freezing out downstream of the filter (although precautions were taken to avoid this) and possible upset of the chromatograph when switching the collector column into the carrier gas. In addition, some scatter was present in the chromatograph calibrations particularly for pentane and hexane.

TABLE 1. LIQUID PHASE SOLUBILITIES  
IN MOLAR PPM.

	APCI-1958	APCI-1965
Acetylene	5.2	2- 4.6
n-Butane	800	115- 240
Isobutane	2000	1600-2400
1,3-Butadiene	20	2.5- 4
n-Pentane	40	8.5- 9.7
Isopentane	-	80- 300
n-Hexane	6	0.16- 1.8
Ammonia	-	0.065- 0.25