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ABSTRACT

An apparatus is described for the complete degassing of liquids which have low vapor pressures at their freezing points. A modification of the apparatus for the complete recovery of traces of dissolved gases in liquids has been illustrated with the recovery of 0.126 millimole of a mixture of propene, propane, isobutene and isobutane from di-isopropyl ether.

A Method of Degassing Liquids

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In experiments on the radiolysis of alcohols and ethers using very low energy input, and therefore very low product yield, it was found that traces of air in the liquids markedly influenced the results. In addition, the quantitative recovery of very small amounts of gaseous products, especially the higher boiling hydrocarbons such as propane and the butanes, was quite difficult. In order to simplify both these operations, a method has been devised whereby the liquid can be refluxed under vacuum while pumping on it either with a regular vacuum pump for de-aerating, or with a Toepler pump for collecting dissolved gases.

In essence, the apparatus is a low-temperature reflux condenser in which the liquid can be refluxed at a temperature at which its vapor pressure is negligible (<1 mm). The method for de-aerating is limited to those materials, which have low vapor pressures at temperatures above their melting points, thereby excluding such compounds as water, benzene, and glacial acetic acid. In principle, dissolved gases can be determined in these high melting liquids by forming a low-melting eutectic with a previously degassed liquid of lower boiling point and refluxing this mixture under vacuum. This has been illustrated with benzene.

EXPERIMENTAL

Degassing Liquids.--The apparatus used by this author for refluxing liquids under vacuum is shown in Fig. 1. It was set up with the receiving flasks sealed in place on the line. The liquid to be degassed was introduced into the flask F using a narrow-necked funnel which passes through the constriction C. Flask F was then cooled with ice, the sidearm gently flamed and then sealed off at the constriction. The flask F was cooled with dry ice and the reflux condenser filled with a dry-ice and trichlorethylene slurry. The trap T was cooled with liquid nitrogen and the system evacuated through A and B. The dry-ice bath in F was then removed and the boiling liquid refluxed in the condenser. It is necessary to pre-cool the flask F to prevent violent bumping when the system is evacuated. Pumping was continued until the pressure in the connecting vacuum system was down to less than about 1 micron (as measured by a vacuum thermocouple gauge). Further, the pressure in the vacuum system beyond the nitrogen trap showed no change when stopcock A was turned off for 10 or 15 minutes and then opened. For 250 ml of liquid, starting at atmospheric pressure, this process required from one to two hours.

Stopcock B was then turned off, a dry-ice-trap was placed around R, and the dry-ice slurry removed from the reflux condenser D. The dry ice removal is readily accomplished by removing the dry ice with a long-handled spoon and removing the trichlorethylene with a pre-cooled syringe. Flask F was then warmed and the liquid distilled into R until the desired amount was transferred. The flask, F, was again

cooled, and R sealed off. Stopcock B can be opened during the sealing off if it is desired to remove any gases evolved by the glass during the sealing operation. The rest of the bulbs are filled in a similar manner.

The system is not limited to dry-ice cooling; any cooling agent which gives a temperature above the melting point of the solvent, yet low enough to reduce the vapor pressure to a reasonable value, may be used. A fairly high vapor pressure can be tolerated if the size of the liquid nitrogen trap is increased and some loss of material can be tolerated. A carbon disulfide slush bath (m.p. -110°C) has been used quite successfully in degassing diethyl ether.

Recovery of Gases from Liquids.--The system for the quantitative recovery of dissolved gases from liquids is essentially the same, but if gases as high boiling as butanes are to be recovered an additional step is necessary. The setup is shown in Fig. 2. The gas sample was sealed to the sidearm of flask F (samples used by this author are contained in flasks with break-seals) and the system thoroughly evacuated through stopcocks G, H, E and D. The condenser was then filled with dry ice and trichlorethylene slush, the flask F was cooled with dry ice, stopcock D closed and the sample was introduced to F, in this case by use of a magnet to raise the iron hammer against the break-seal. The glass-wool plug serves as a shock absorber for the hammer on its return. The system was allowed to come to temperature equilibrium and the dry-ice bath was removed from flask F. Liquid nitrogen traps were placed around A and B, stopcock G closed, and the

Toepler pump started in operation. When stopcock D is opened, the non-condensable gases are collected by the Toepler pump while all condensable gases, together with a small amount of solvent are collected in trap A. When no further gas can be collected with the liquid nitrogen traps on, any higher boiling gas can be fractionated from the small amount of material collected in trap A.

This distillate may be cut into as many fractions as desired, but all further steps involve simple 1- or 2-plate distillations. If only two cuts are desired, stopcock D is closed, a new collector is put on the Toepler pump, and traps A and B are surrounded with dry-ice baths. After closing stopcock E, trap C was cooled with dry ice and volatile materials from traps A and B were pumped into trap C with liquid nitrogen. The material collected in trap C was later pumped into a gas burette and a collection bottle. The exact procedure is not critical as long as it leads to the desired separation. The material in trap A is transferred to trap B while pumping, thus achieving a fast one-plate separation with the more volatile material being collected in trap C. Stopcock E can then be closed off, the bulk material transferred back from B to A with liquid nitrogen, more volatile material taken out of the reflux condenser by opening D for several minutes, and the process may be repeated. After two such cycles almost nothing will be collected during the transfer of the solvent from A to B, although a trace of solvent is always collected if its vapor pressure is at all appreciable at the trap temperature used.

As a check on this procedure, 0.126 millimole of a mixture of isobutane, isobutene, propane, and propylene (Phillips Petroleum Company,

Research Grade hydrocarbons) was added to 50 ml of degassed isopropyl ether by liquid nitrogen transfer from a gas burette. It was degassed by the procedure outlined above (Fig. 2) and the gases from the Toepler pump were collected over mercury in a gas burette. The added gas and the final recovered gas were analyzed using a Consolidated Engineering Corporation model 21-103 mass spectrometer. The recovery is shown in Table 1.

Table 1

Recovery of Gases from Di-isopropyl Ether

Component	Millimoles added	Millimoles found*	Δ Millimoles
propene	0.0482	0.0485	+0.0003
propane	0.0320	0.0323	+0.0003
isobutene	0.0309	0.0296	-0.0013
isobutane	0.0149	0.0156	+0.0007
total	0.126	0.126	

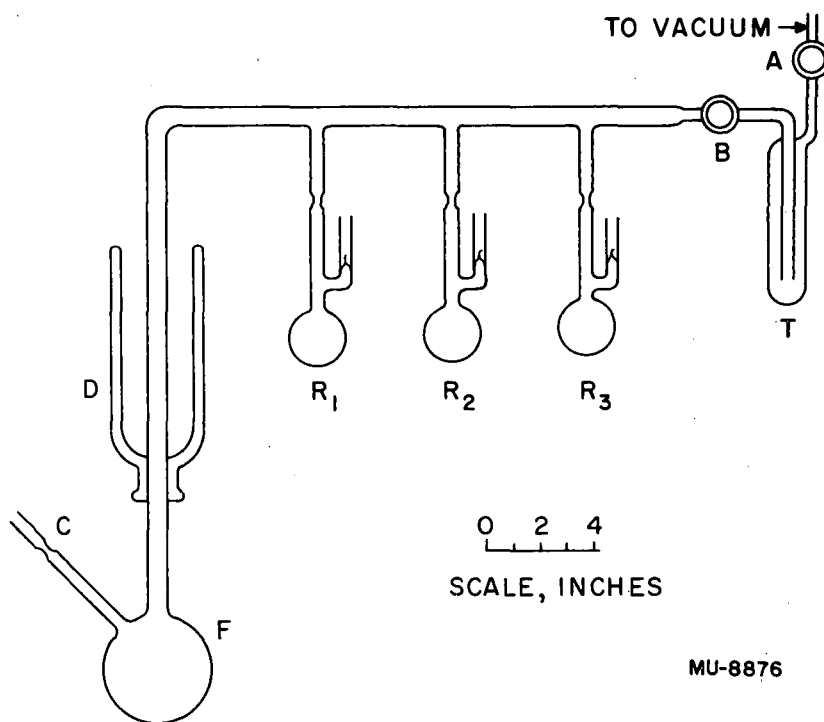
*The recovered gas also contained 0.0114 millimole of di-isopropyl ether (8.3% of the total gas collected).

For comparison with ordinary methods of degassing, 100 ml of di-isopropyl ether was saturated with methane at room temperature. It was then degassed by cooling with dry ice and pumping on it for 30 minutes. The ether was further divided into 2 parts by vacuum distillation of 1/2 of it into a second dry-ice cooled trap consisting of a U trap in the vacuum line with a volume at the bottom of the U for collecting the

liquid. Pumping was continued during the entire transfer process. Both traps were then cooled with dry ice and sealed off. Dissolved gas in each fraction of the isopropyl ether was then determined by the procedure outlined. In this case, for the Toepler pump to collect the gas, it was expedient to add a small quantity of air (0.05 millimole) to the system. From the residual 50% of the ether, 0.0006 millimole of methane was recovered, and from the distilled 50% ether 0.0003 millimole of methane was recovered. This shows incomplete degassing by even a rigorous application of a "normal" degassing procedure.

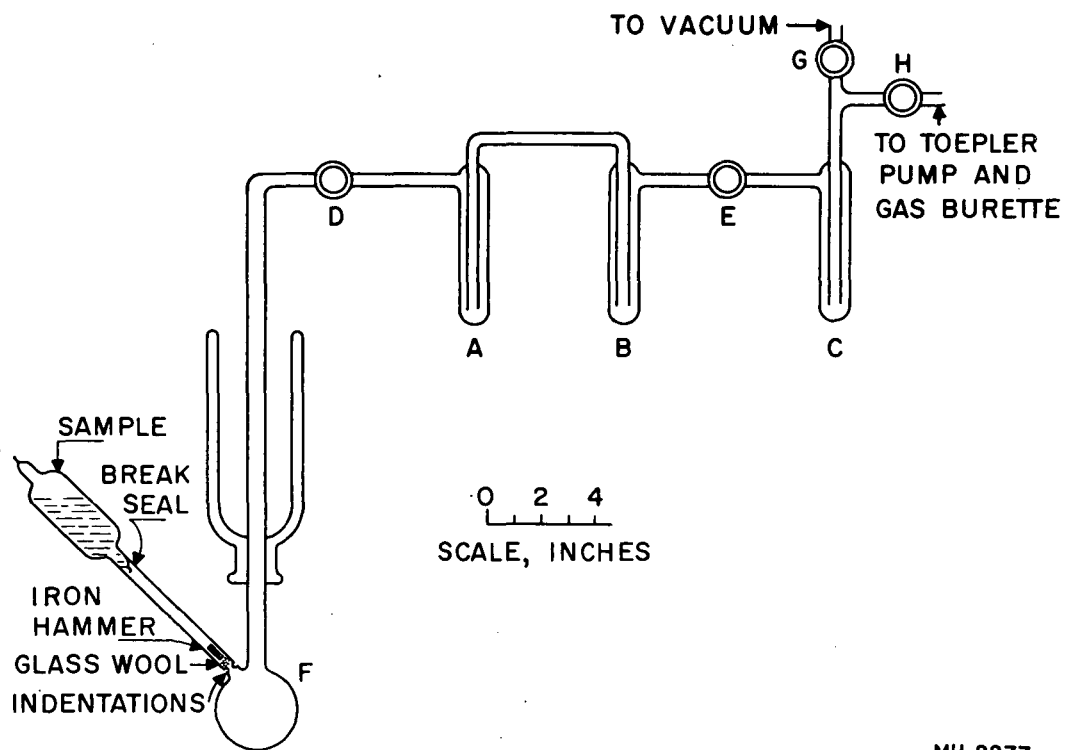
Application to High Melting Solvent.--Pure solvents which have high vapor pressures at their melting points cannot be degassed by this procedure, but in principle, gases may be recovered from such solvents, e.g., benzene, by adding the solvent to flask F in which there is another previously degassed solvent of lower boiling point which will form a low-melting mixture with the high-melting solvent in question. As an example, benzene was distilled from sodium under an argon atmosphere, then degassed by repeated freezing and melting under vacuum. It was frozen 5 times and after the second time no gas evolution was noted during the freezing process. As a final step about 20% of the material was vacuum distilled. Some 50 ml of the residual benzene was added to 50 ml of degassed n-hexane in apparatus II and the noncondensable gases were collected. Some benzene precipitated in flask F during the operation, but the precipitated benzene was kept fairly well washed down from the condenser by the refluxing liquid. The 0.003 millimole of gas collected was 46% argon, 39.5% nitrogen and 14.5% oxygen. The high argon content proved the gas was dissolved in the benzene. No tests on recovery of added gases in benzene were made.

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Fig. 1. Apparatus for degassing liquids.



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Fig. 2. Apparatus for recovering gases from liquids.