Printed in U.S.A.

66-WA/PT-9

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MEAR-WH 66-0471

Reaction Technique at High Pressure for Low-Boiling Materials

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A technique is described wherein low-boiling gases may be exposed to pressures of 40 kilobars and temperatures of 500 C.

Contributed by the Research Committee on Pressure Technology for presentation at the Winter Annual Meeting and Energy Systems Exposition, New York, N. Y., November 27-December 1, 1966, of The American Society of Mechanical Engineers. Manuscript received at ASME Headquarters, August 1, 1966.

Copies will be available until September 1, 1967.

THE AMERICAN SOCIETY OF MECHANICAL ENGINEERS, UNITED ENGINEERING CENTER, 345 EAST 47th STREET, NEW YORK, N.Y. 10017

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INTRODUCTION

In our research on the reactions of organic fluorocarbons at pressures in the 10 to 40 kbar range, it was necessary to develop a method of handling mixtures of low-boiling liquids and gases. It was desirable to encapsulate compounds boiling at low as -100 deg C so that they could be heated in piston-cylinder equipment. Definite amounts of reactants must be monitored into the capsule, exposed to pressure and temperature, and then recovered. Furthermore, the capsule used should have sufficient volume to contain adequate material for characterization of the product.

Workers in this field, for example Bengelsdorf (1),[1] have exposed high-boiling organic liquids to pressures of 50 kbars at temperatures of 350 deg C, using lead containers. H. T. Hall (2) has described a container for liquids but this appears unsuited to low-boiling materials. A. P. Young and coworkers (3) have described a container for low-boiling liquids to be used in belt equipment. However, this unit contains only a little sample and recovery of gaseous products after a run is difficult. The more volatile fluorocarbons can generate more than 500 psia at room temperature. Also our type of filling and recovery technique for samples permits handling gases which do not solidify during the reaction.

PISTON-CYLINDER EQUIPMENT

Our piston-cylinder equipment was of the two-ram variety described by Boyd and England (4) and modified by Kennedy (5). One furnace assembly holding 0.5 grams was used with the 1/2-in. piston and cylinder. Here the pressure plate and piston assembly was similar to Kennedy's. However, for cases where larger quantities of material were needed, we developed a 1-in. pressure plate using a 1-in. piston and a furnace assembly holding a capsule containing 5 grams of material. The 1-in. pressure plate, Fig.1, consisted of two Vascojet 1000 (Vanadium Alloy Steel Company) binding rings and a steel shim, to match to the tungsten-carbide core. We were very successful with a pressure plate containing a Vasco Supreme steel inner tube

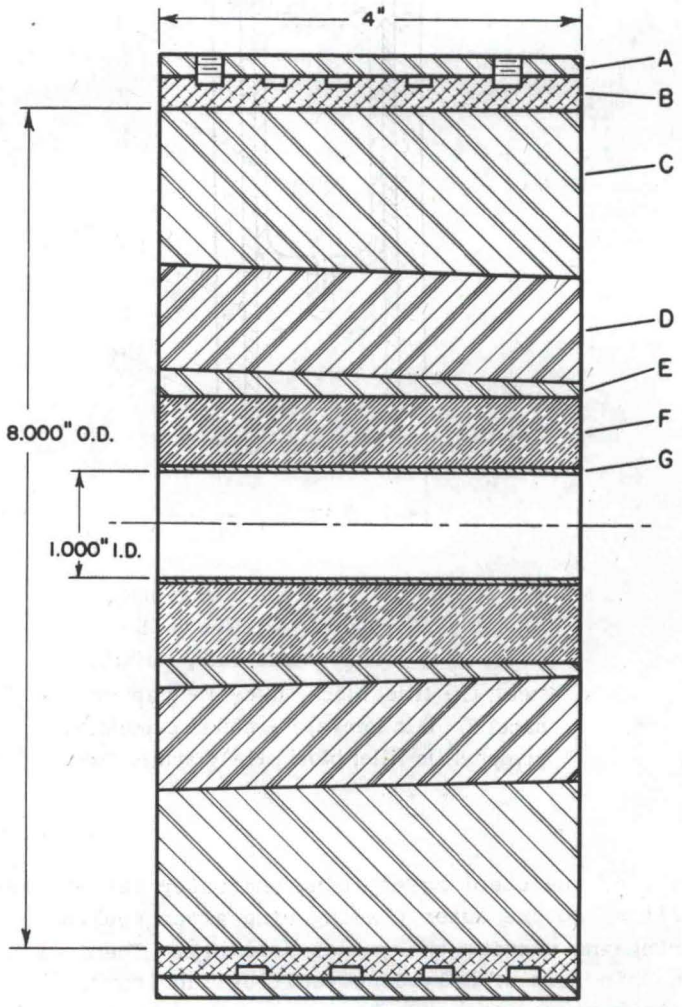

Fig. 1 One-inch pressure plate: A - Soft-steel safety ring; B - aluminum water jacket; C - Vascojet 1000, 8-in. binding ring RC 35, $1^1/2$ deg taper; D - Vascojet 1000, 5-in. binding ring RC 45, $1^1/2$ deg taper; E - Vega steel, 3-in. shim RC 60; F - tungsten-carbide core, 2.5 in. 6 percent Co binder; G - Vasco supreme inner liner, 1.067 in. od RC 68; interference C/D = 0.020 in. in diameter and D/E = 0.015 in. in diameter before installation

to serve as a replaceable lining for the tungsten-carbide core. For pressures up to 25 kbars, a Vega steel core in place of a tungsten-carbide one was satisfactory. In assembling the pressure

[1] Numbers in parentheses designate References at the end of the paper.

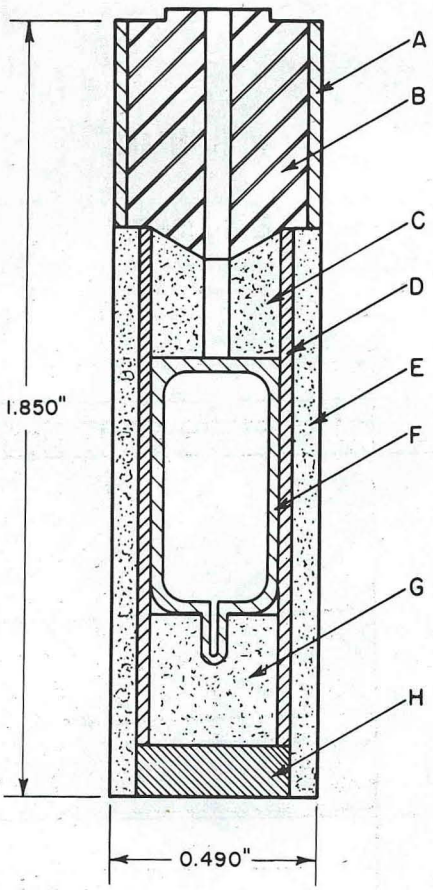

Fig. 2 One-half inch-diameter furnace assembly: A - Pyrophyllite sleeve; B - power lead, thermocouple inlet, stainless steel; C - filler block, talc; D - graphite furnace; E - talc sleeve; F - nickel capsule; G - pryophyllite filler block; H - graphite disk

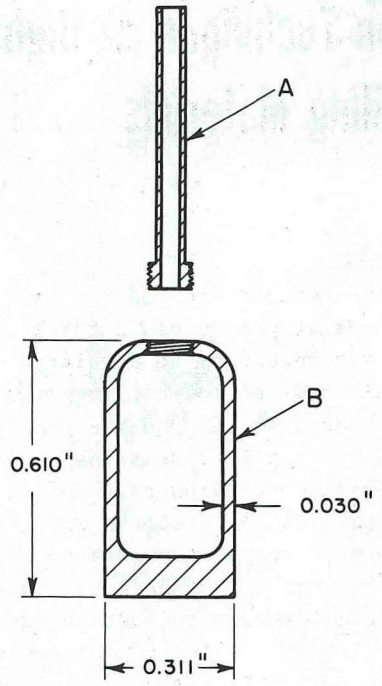

Fig. 3 Capsule for 1/2-in. furnace assembly: A - Stem, od 0.070 in., id 0.046 in.; B - capsule body, grade A nickel

plate, the steel safety ring and water jacket were fitted to the outer binding ring after cooling the ring and warming the jacket assembly. Then, with a thin film of molybdenum-sulfide lubricant, the other rings were assembled from the outside in, pushing them together with the end-load ram of the piston-cylinder press. Prior to pushing in the tungsten-carbide core, the Basco Supreme liner was inserted. After assembly, the inner hole was ground to 1.000 + 0.001-0.000 in. The piston was a cylinder 2.000 in. long, 1.000 in. in diameter, of Plansee Metalwerke grade 850 tungsten carbide containing 6 percent cobalt. A steel disk, (AISI 4340, id 0.995 in., od 2.500 in., 0.125 in. thick), supported the 1-in. piston at its bottom, using 0.005-in. interference.

ONE-HALF-INCH FURNACE ASSEMBLY AND CAPSULE

The small furnace assembly, Fig.2, for the 1/2-in. pressure plate was a modification of one by Boyd and England (4). To contain the nickel capsule it was necessary to use a thinner graphite furnace.

The small furnace assembly contained a small annealed-nickel capsule, Fig.3, equipped with a filling tube, 0.046 in. id and 0.070 in. od. It could be screwed into the capsule and silver soldered. This 0.070-in. tube is designed to be crimped and silver soldered after filling. The capsule itself with its 0.030-in. wall held our 0.3 cc of material satisfactorily. Using a factor of safety of 4 and a tensile strength for nickel of 67,000 psi, a safe pressure of 3600 psi is calculated for this capsule.

ONE-INCH FURNACE ASSEMBLY AND CAPSULE

While satisfactory for the preliminary exploratory work, the sample capacity of the small capsule is usually too small for adequate characterization of polymers. Also some improvement in measurement of reaction temperature is needed, since in the small capsule the temperature of the capsule face is observed. Therefore, we designed a larger nickel capsule, Fig.4, holding 5 cc of sample and equipped with a thermocouple well. Here on the same basis as the small capsule, the safe working pressure is 2000 psi.

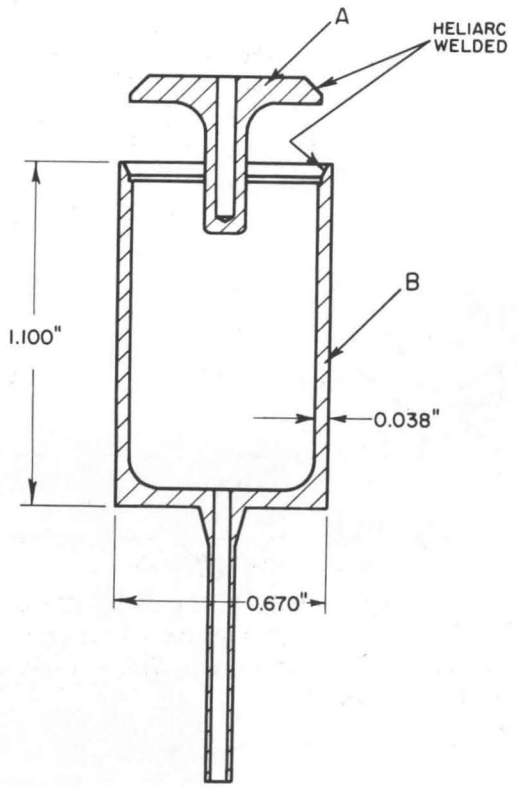

Fig. 4 Capsule for 1-in. furnace assembly equipped with thermocouple well: A - Base with thermocouple well; B - body of capsule with filling tube, grade A nickel

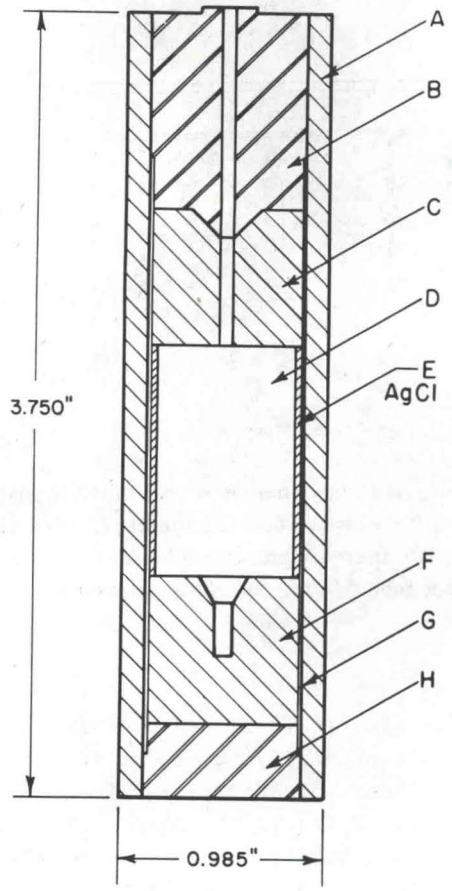

Fig. 5 One-inch-diameter furnace assembly: A - pyrophyllite sleeve; B - power lead, thermocouple inlet, stainless steel; C - pyrophyllite filler block; D - nickel capsule; E - silver-chloride capsule sleeve; F - pyrophyllite filler block; G - stainless-steel furnace; H - stainless-steel power lead, all pieces slide fit

In this case, a pyrophyllite outer furnace assembly, Fig.5, and stainless-steel heater were more convenient to use. To reduce friction during pressure release, we surrounded the capsule by a silver-chloride sleeve.

CAPSULE FILLING LINE

In order to handle gases boiling as low as -100 deg C, some vacuum technique was needed to monitor gases into the capsule, and to recover them after a run. A simple vacuum line with gas pipette, manometers, sample inlets, and a test tube in which to insert the capsules for gas recovery after a run, served our purpose. A 1/4-in.. copper tube equipped with a Swagelok top fitting connected the capsule to the vacuum line. Its lower end was constricted by spinning so that the capsule filling tube could easily be silver soldered to it.

CAPSULE FILLING TECHNIQUES

Capsules were filled utilizing the manifold described, Fig.6. The gases should be monitored carefully into the container. Overfilling will cause liquid pressure to bulge the capsule, and a bulged capsule will not fit the furnace assembly. The optimum fill would be a little under 100 percent capacity at room temperature. Since the thickness of the ends of the large capsule is about the same as the sides, some pressure relieves itself by bulging the ends, though this seldom is necessary.

In a typical run, the quantity of sample needed is calculated from the ideal gas law and from a knowledge of the liquid density of the sample. The capsule is silver soldered to the sampling line, evacuated, cooled with liquid nitrogen, and the measured sample is condensed into it. Any solid catalysts are added before soldering to the line, but in this case the capsule body is cooled in ice during the soldering to prevent catalyst decomposition. When the proper amount of sample

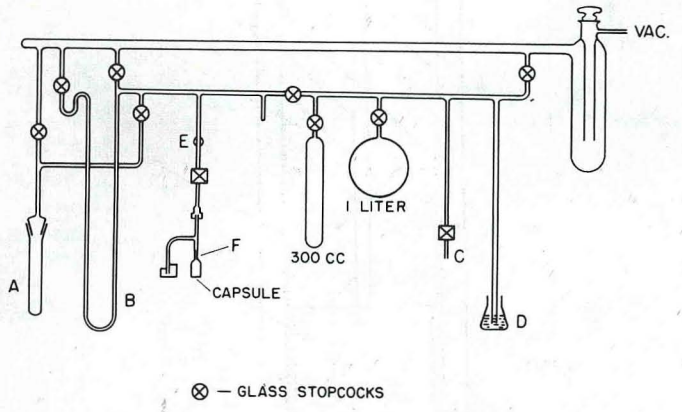

Fig. 6 Capsule handling line: A - Test tube for gaseous product recovery; B - closed-end manometer; C - sample inlet for reactants; D - mercury pressure release; E - kovar to glass seal F - copper tube 1/4 in. for connecting capsule

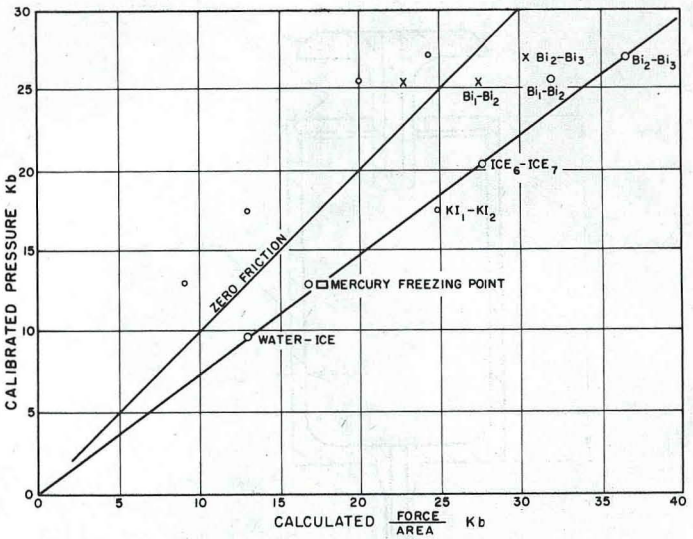

Fig. 7 Calibration experiment for Ni capsule: □ - Compression (large capsule); 0 - compression (small capsule); O - release (small capsule); X - bismuth slug with no capsule. Graph taken from LaMori (6)

is in the capsule, it is closed by crimping. Then, still in liquid nitrogen, it is cut from the line and quickly silver-soldered closed in a metal dewar flask, full of liquid nitrogen. With such a procedure, we can easily handle vapors boiling as low as -100 deg C. BF_3 (bp - 101 deg C) is the lowest boiling material we have handled to date.

RUN AND RECOVERY OF SAMPLE

In making a run, the filled capsule is placed in the furnace assembly which is then exposed to the desired pressure and temperature for the designated time. Experiments of several hours in length can conveniently be made. A quick reduction in temperature followed by slow pressure release ends the run. The sample assembly can then be pushed from the pressure plate and the capsule is usually recovered intact. With the model of capsule used in the 1-in. pressure plate, over 95 percent of the runs permitted quantitative recovery of the reaction products.

To remove the sample from the intact capsule, it is chilled in liquid nitrogen and its neck cut open. Then the capsule containing sample is placed in the precooled container on the vacuum line and held at liquid-nitrogen temperature while the air and nitrogen is removed. Should it be undesirable for oxygen to come in contact with the sample, this step could occur in a nitrogen atmosphere. After the air is removed, the sample is allowed to warm up and the residual gases from the reaction are condensed in the vacuum line. Here they can be analyzed in the usual way by vapor chromatography and infrared spectroscopy. After removing the gases, the capsule can be cut open for recovery and characterization of any involatile residues.

In some cases the capsule may crack open after the run, on release of pressure. Losses arising from this may be minimized by chilling the whole furnace assembly in liquid nitrogen prior to opening and capsule removal.

CALIBRATION OF THE CAPSULE

Temperature may be measured fairly accurately by thermocouples, except for the effect of pressure on thermocouple EMF. This error is believed to be small however. The thermocouple well of the large capsule should result in an average temperature of the reactants. The situation is worse in the small capsule since there is a rapid decrease in temperature towards the ends of the furnace (6). This is about 15 deg C at 450 deg C and 40 kbars, a quarter-inch away from the capsule.

For pressure calibration, a technique described by P. N. LaMori (6) was utilized. Here, the volume change of various calibration standards indicated the pressure inside the capsules. Ram travel indicated volume change as the piston advanced or retracted. When plotted against pressure, inflection points occurred as the various high-pressure phases formed. Since the compression stroke only was used to compress the furnace assembly in actual runs, the calibration for friction was computed from the phase transitions on the up stroke only. For a check on friction owing to the furnace assembly alone, a bismuth slug was

substituted for the capsule. All data were taken at ambient room temperature, about 25 deg C. Calibration (6) for the nickel capsule is shown in Fig.7.

From the data presented it is evident that the overall friction owing to the capsule and furnace assembly is 22 percent and that the friction owing to the furnace assembly alone is 10 percent, leaving 12 percent due to the small capsule. Using the freezing point of mercury as reference, the large capsule and assembly similarly show a combined 22 percent friction.

CONCLUSIONS

This technique should be feasible with any gas which does not react with the nickel. It should be possible by the volume-pressure plot to observe freezing points and other phase changes. Gases boiling as low as -100 deg C have been handled by this technique.

ACKNOWLEDGMENTS

This work was partially supported by the U.S. Army Research Office, Durham, N. C., to whom grateful acknowledgment is made. Acknowledgment is also made to Messrs. K. P. Murphy and P. N. LaMori who carried out work of the calibration experiments on the capsules.

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