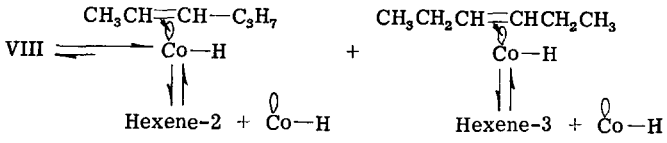
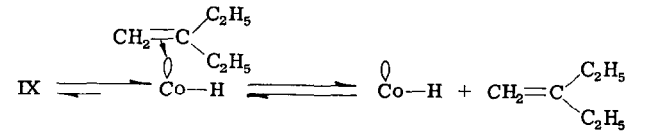


[9]



[10]

similar to those previously proposed [(*1*); see also ref. (*4*) for a discussion of insertion reactions]. This mechanism is detailed below for the case of ethylene oligomerization [Eqs. (2)–(10)]. Sequential insertion of ethylene could occur to form the observed butene-1 and hexene-1 [Eqs. (2)–(6)]. Partial isomerization [Eqs. (1), (4), (6)] could account for the observed butene-2 and hexene-2. The best way to account for the formation of the abnormally large quantities of hexene-3 and for the formation of 3-methylpentenes is by the reinsertion of butene-1 into the ethyl cobalt intermediate [Eqs. (8)–10)]. Additional amounts of 3-methylpentenes could be formed by ethylene insertion into the *sec*-butylcobalt (V) formed during partial isomerization [Eq. (7)].

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Received November 8, 1966; revised December 8, 1966

Density Measurements at Low Temperatures

Applications

Density measurements with liquid nitrogen may have advantages in some cases:

(a) if a small molecule is needed to penetrate into narrow pores while water is not suitable; i.e., density measurements of water-soluble substances or of substances (like coal), which are not wetted by water; diameter H_2O molecule: 2.90 Å; diameter N_2 molecule: 3.15 Å;

(b) if the exact volume of a sample with a small surface area is needed at 78°K for adsorption measurements;

(c) if density measurements are to be carried out in a reproducible way without affecting the properties of the sample; fol-

lowing the method described here the sample will lose all adsorbed nitrogen after being heated to room temperature.

Description of the Apparatus

The apparatus consists of the following elements (see Fig. 1):

1. A manometer with mercury filling device and reference point. This point can be either a (colored) glass needle for visual adjustment or a metal needle (with vacuum-tight seal) for more accurate electric adjustment.

2. A thermostated 250-ml vessel, accurately gauged between two reference points, fitted with a mercury filling device; this is the so-called "burette."

3. A pycnometer (volume ~ 5 ml) with fused ground glass joint B-10, connected by a capillary tube and stopcock M to the apparatus. The pycnometer joint is greased with silicone grease, which gives a vacuum-tight connection even when immersed in liquid nitrogen.

4. A Dewar vessel with observation hole for observation of the reference mark of the pycnometer; this model is commercially obtainable.

5. A system of capillary glass tubing connected to a high-vacuum line and to a nitrogen cylinder as shown in figure.

The apparatus can be assembled quite easily by adding the elements 2, 3, and 4 to an existing volumetric adsorption apparatus. For standard BET surface area measurements an adsorption vessel is substituted for the pycnometer and connected by a capillary tube to the apparatus. Our custom is to immerse this vessel together with the glass joints in liquid nitrogen.

Measurement Procedure

1. Grease the pycnometer with a minimum quantity of silicone grease.

2. Outgas the apparatus at 10^{-4} torr (dependent on nature of sample); close stopcock M.

3. Immerse the pycnometer in liquid nitrogen.

4. Adjust the mercury level in the burette on the lower reference point.

5. Add N_2 to about 78 cm Hg pressure;

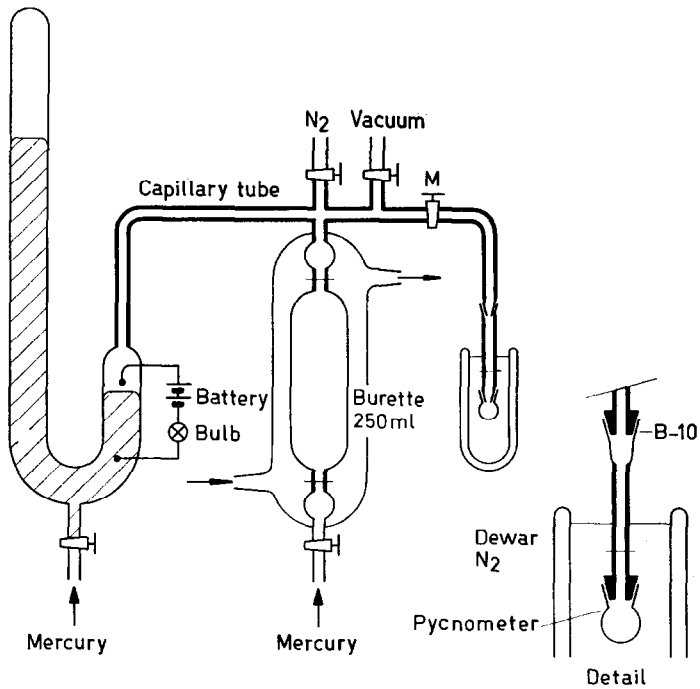

Fig. 1.

adjust the manometer to the reference point; note the pressure reading.

6. Open stopcock M; raise carefully the mercury in the burette up to the higher reference point; N_2 condenses in the pycnometer.

7. Close stopcock M; note the pressure reading.

Actions 4 to 7 are repeated until the pycnometer is nearly filled with liquid nitrogen. Condensation of the final quantity must take place at a pressure which is not more than 1–2 cm higher than the condensation pressure. This is carried out by raising the mercury in the burette very slowly.

When the liquid nitrogen level reaches the mark in the pycnometer stem (to be determined visually), stopcock M is closed. The mercury in the burette is adjusted at the lower reference point and the pressure reading noted.

The volume of the pycnometer empty or filled with as much solid material as possible is calculated from the difference between the total quantity of gaseous nitrogen added and the quantity of gas, which is not condensed at the end point. It is necessary to keep both burette and Dewar vessel at constant temperature.

At a total pressure of 780 mm Hg the condensation temperature of nitrogen is 77.6°K. At this temperature the conversion factor for gaseous to liquid nitrogen is 1 ml of N_2 (STP) $\sim 15.486 \times 10^{-4}$ ml of liquid N_2.

Some Examples

In the following table some of our density measurements of nonporous substances are given:

	Density in liquid nitrogen (g/ml)	Density in methanol (g/ml)
Spheron-2700°	1.952	1.938
Sterling FT-2700°	2.151	2.150
Aerosil	2.289	2.253

The obtained results were reproducible up to 0.2%, but a higher precision is obtainable when more care is bestowed on the pressure and temperature measurements. Limiting factors are quality of the manometer, accuracy of temperature control, and end point determination.

Other applications might be density measurements with the aid of other very volatile, expensive, or poisonous fluids. The fluid has to be gaseous at room temperature. If a suitable refrigerant is available, density measurements with liquid NH_3 will be possible; this might be interesting because the molecule is rather small (3.08 Å). Measurements with neopentane (boiling point 9.5°C) will be rather easy with this measuring device, if the pycnometer is thermostated at a temperature between 0° and 9°C. The apparatus can also be used to carry out density measurements of liquids, if a gauged pycnometer is applied.

Acknowledgment

The author wishes to thank the Board of the National Defence Research Organization TNO for permission to publish this note.

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Received December 16, 1966

Homogeneous Hydrogenation Using Platinum-Tin Complexes

Complexes (*1*) prepared from chloroplatinic acid and stannous chloride in a molar ratio of 1:10 in methanol have been reported (*2*) to catalyze the homogeneous hydrogenation of ethylene at room temperature and atmospheric pressure. So far the