Moreover, if the results of this paper are accepted, the experimental peaks observed by Clark and Duane cannot have been produced by the reflection of characteristic cesium and iodine radiation from planes of these crystals.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

A HYDROGEN LIQUEFYING CYCLE AND CRYOSTAT FOR THE MAINTENANCE OF LOW TEMPERATURES

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A combined hydrogen liquefier and cryostat of simple design has been developed in this Laboratory for carrying out such experiments as the measurements of specific heat, coefficients of expansion and electrical resistance at the temperatures of liquid and solid hydrogen. A brief description of the apparatus with the auxiliary liquefying system will be given in this paper.

When liquid hydrogen is used as a cooling agent by submerging an object in the liquid, the available cooling is due entirely to the heat of vaporization of the hydrogen. If, however, advantage is taken of the low heat content of the hydrogen evaporating from the liquid by passing this gas over the coils of the hydrogen liquefier, the effective cooling may be increased by the production of a larger amount of liquid hydrogen. The increased cooling which may be obtained amounts to the difference in temperature, 85–20°, multiplied by the average specific heat, 6 cal. per degree, or about 390 cal. per mole. The heat of vaporization of hydrogen is 240 cal. per mole, and the effective cooling is thus increased from 240 to 630 cal. For this reason it is advantageous when possible to build a small liquefier in connection with the object to be cooled. Such a system also obviates the necessity of storing liquid hydrogen and the losses which occur in transferring the liquid from the container to other vessels. It is such a combination[2] of liquefier and cryostat that is to be described.

Preparation and Purification of Hydrogen

The source of the greatest difficulties in the liquefaction of hydrogen is the maintenance of a supply of hydrogen free from small amounts of oxygen and nitrogen. The purity required depends upon the size of the valve orifice and the rate of flow of the high-pressure gas, but in general it has been our experience that with impurities in excess of 0.05% it is difficult to avoid plugging the orifice with solids. We have been unable to purchase pure hydrogen, due mainly to the fact that the commercial hydrogen obtainable in this locality is used for oxy-hydrogen torches and is mixed with coal gas to

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[2] A similar combination of somewhat different design is described by Nernst, *Z. Elektrochem.*, **17**, 735 (1911).

give a luminous flame. We have therefore generated the hydrogen from two Burdette oxygen-hydrogen cells of 400 amp. capacity. The surface of these cells is covered with a viscous oil which decreases materially the rate of solution of air into the electrolyte. The gas coming from the generators contains 1–1.5% of oxygen, due to diffusion from the positive side of the cells. The hydrogen under a head of a few cc. of water passes first over concd. sulfuric acid to cut down the alkali spray and then through a tube containing a nickel catalyst to remove the oxygen. This catalyst is prepared by saturating pieces of porous brick of about 10-mesh size with nickel nitrate which is then decomposed to the oxide by heating, and later reduced to nickel in the catalyst tube. This tube, of approximately 2000cc. capacity, is heated in a roughly constructed electric furnace. The reduction of the nickel oxide by the hydrogen is carried out at 425°. At a rate of flow of 0.4 cu. m. per hour and a temperature of 325°, the nickel catalyst removes the oxygen to less than 0.01%. The low-pressure hydrogen is then stored in a floating gas holder of 3 cu. m. capacity which contains heavy oil[3] as a sealing medium.

Analysis for Oxygen

In order to determine the efficiency of the catalyst and to test for the presence of air-leaks into the low-pressure system, which occur on the instrokes of the compressor, it was necessary to devise a rapid, semi-quantitative procedure for the detection of about 0.01% of oxygen in hydrogen. A very satisfactory procedure was worked out, based on a quantitative method proposed by Binder and Weinland,[4] which appears to have received less attention from analysts than it deserves.

The method depends on the fact that pyrocatechol forms a compound with ferrous iron which is stable against oxidation in acid solution, but which in alkaline solution is rapidly oxidized to an intensely red ferric compound by oxygen even in concentrations as low as 0.01% in hydrogen.

This reaction is carried out in a 70cc. test-tube with a closely fitting 3-hole rubber stopper which carries inlet and outlet tubes and a dropping funnel. The inlet, which reaches nearly to the bottom of the reaction tube, delivers hydrogen in small bubbles through several small holes at the end. The outlet tube, which reaches barely through the stopper is provided with a stopcock to regulate the flow of gas, and to protect the system from air when no gas is flowing. The dropping funnel, which extends 1 cm. below the stopper, is used to admit alkali. A leveling bulb containing water is used to draw hydrogen from the low-pressure line into the sampling bulb through one leg of a two-way stopcock, and to force it out through the other leg to the inlet of the reaction tube. Successful

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[3] Since this was written, an article by Kanolt and Cook [*Ind. Eng. Chem.*, **17**, 183 (1925)] has appeared in which the advantages of glycerol for this use have been pointed out. The oil which we are using is apparently much more viscous than that which Kanolt employed, and this factor is very important in cutting down the rate of solution. It might also be noted that the nickel catalyst has an advantage over the platinum metals, not only from the standpoint of cost, but also, due to the inactivity of the nickel at lower temperatures, in enabling the line to be swept free from impure hydrogen without danger of an explosion.

[4] Binder and Weinland, *Ber.*, **46**, 255 (1913).

operation of the method depends entirely on the completeness with which air is removed from the acid ferrous-pyrocatechol solution and the sampling tube. This is best accomplished by bubbling hydrogen from the high-pressure storage tank through the solution and also through the water in the leveling bulb. It is necessary to carry out this removal of air from the apparatus after the latter has been set up for the analysis, as a solution in contact with air dissolves enough oxygen in a few seconds to ruin an analysis.

Procedure.—The reaction tube and fittings are rinsed with 0.04 *N* sulfuric acid. Pyrocatechol, 0.4 g., and c. p. ferrous ammonium sulfate, 0.3 g., are dissolved in 50 cc. of 0.04 *N* sulfuric acid in the reaction tube, which is then put in place. Oxygen is removed from the solution and also from the water of the sampling bulb by bubbling with hydrogen. A 2-liter sample of hydrogen for analysis is now drawn into the sampling bulb, 5 cc. of concd. sodium hydroxide solution run into the ferrous-pyrocatechol solution from the dropping funnel, and the sample then forced slowly through the solution. The initial color of the alkaline solution should not be deeper than a very faint red. By comparing the final color with that obtained from known mixtures of oxygen and hydrogen, the concentration of oxygen may be estimated to within 0.01–0.02%, when the concentration of oxygen is under 0.1%. Permanent standards for comparison may be made up from known concentrations of ferric salt. The time required for an analysis is about 15 minutes.

Liquefying Cycle

The compressor operates directly from the large, floating gas holder. The high-pressure hydrogen after leaving the compressor passes through a coil cooled by ammonia refrigeration in order to remove moisture and any oil that may be carried over from the compressor. The temperature of the bath of kerosene which surrounds the condensing coil and the coil of the ammonia cycle is maintained between —30° and —40°. The trap a, Fig. 1, which collects the condensed material, is blown out between runs. The trap b, containing fused calcium chloride, serves as a protection for the line when blowing out Trap a, and also when hydrogen from the high-pressure storage is used to flush out the liquefier. The side tube c is packed with cloth to prevent the passage of solid particles.

The hydrogen then enters the pre-interchanger d where it is cooled to approximately liquid-air temperature by the low-pressure hydrogen returning from the liquefier. This interchanger employs the Nelson[5] principle of flattened and twisted tubes. Three strands of 6 meters each, made from 4mm. copper tubing, are wound in parallel upon a thin steel tube and covered with a close-fitting sheath of monel metal. The cold,

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[5] Bichowsky, *J. Ind. Eng. Chem.*, **14**, 62 (1922).

low-pressure hydrogen enters at the bottom and passes up over these twisted coils which carry the high-pressure hydrogen flowing in the opposite direction. The high-pressure hydrogen leaves the pre-interchanger through the inner member of the double tube e; the high-pressure tube being placed inside the larger tube carrying the low-pressure hydrogen. These tubes run down the center of the pre-interchanger and are insulated from it by a packing of silk floss. This interchanger is easy to construct and is extremely efficient. A silvered Dewar tube fits closely about the interchanger for heat insulation, and the tube e is insulated by wool wrappings.

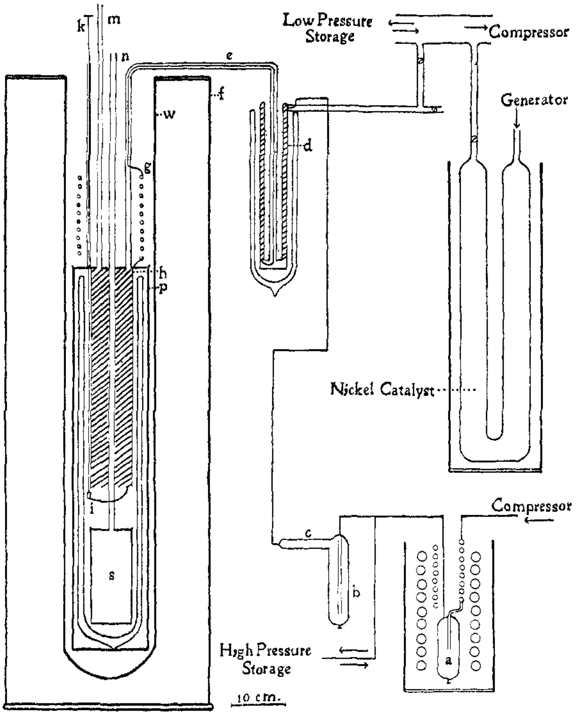

Fig. 1.

The liquefying coil and cryostat are submerged in a bath of liquid air contained in the large Pyrex glass tube w. This tube is contained in a case f packed with silk floss.[6] The high-pressure hydrogen first passes through the coil g, which completes the cooling of the gas to the temperature of liquid air. The gas then enters the liquefying coil h. This coil fits snugly into a silvered vacuum tube of Pyrex glass, and this in turn is enclosed in a monel metal case p. The liquefying interchanger contains a single strand, 60 meters long, of copper tubing of 3mm. outside diameter, and is wound in a succession of spirals in the ordinary manner. A thin

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[6] We now have the Pyrex glass to construct a Dewar tube to replace this case.

sheet of monel metal is wrapped about the interchanger and soldered to the top of the case p in order to compel the returning hydrogen to flow directly through the spirals. The flow of hydrogen is controlled by the rod k operating the valve i. The cryostat chamber s is constructed of brass and may be evacuated through the thin steel tube n. The tops of both the monel metal case p and the brass case s fit snugly, and the joints are made gas-tight by soldering. It requires only a few minutes by this method either to put together or to take apart a joint of moderate size. When constructed on a large scale a device similar to that used by Gibson and Giauque[7] may be employed.

The first step in the procedure is to cool the liquefying coil by introducing liquid air through the tube m. The excess of liquid is removed by evaporation under reduced pressure aided by a heating coil placed in the bottom of the inside Dewar vessel. The air in the tube is then flushed out by a stream of hydrogen from the low-pressure storage. These operations require about an hour. The tube w is then filled with liquid air, and the ammonia machine started in order to cool the trap s. The compressor is then started, and the valve i regulated until the pressure of hydrogen entering the liquefier is about 133 atmospheres (2000 pounds per sq. in.). With a compressor delivering 0.2 cu. m. per minute, about an hour is required to cool the cryostat and fill the Dewar tube with liquid hydrogen up to the bottom of the liquefying coil. When this point is reached further liquefication ceases, as the liquid is blown up onto the warmer parts of the coil. This is indicated by the level of the large storage tank ceasing to fall.

The rate of evaporation of liquid air from the tube w is about 1 liter per hour. During the liquefaction process this increases to 3 or 4 liters. This rate of evaporation could be decreased by passing the cold, evaporated air through an additional interchanger to meet the incoming hydrogen. It has not seemed worth while to make such conservations, however, as the capacity of our liquid-air plant is 25 liters per hour, and additional interchangers are a source of further complications.

When a supply of pure, high-pressure hydrogen in cylinders is available, it is possible to cool the cryostat without using a compressor simply, by employing a battery of cylinders and utilizing the pressure down to about 80 atmospheres. Our first experiments were carried out with such a battery of cylinders but without pure hydrogen. The difficulties of purifying a rapidly-flowing stream of high-pressure gas are too great to make the operation feasible. The compressor in use at present is a 20 hp., four-stage Norwalk machine which unfortunately was built for air compression and is not well adapted for a hydrogen cycle. The compressor readily delivers 0.8 cu. m. per minute of air at 200 atmospheres, but only with

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[7] Gibson and Giauque, THIS JOURNAL, **45**, 93 (1923).

difficulty are we able to make it deliver 0.22 cu. m. (8 cu. ft.) of hydrogen at 133 atmospheres. It has been necessary to build an extra stuffing box with an oil seal over the piston rod of the low pressure cylinder to prevent the suction of air into the line on the in-stroke.

The size of the liquefying coil may be reduced by using the Nelson interchanger constructed along the same lines as the pre-interchanger. For certain types of experiment such a coil is very convenient. One is now in use on an apparatus for measuring coefficients of expansion by the interference method, where it is desirable to reduce the distance from the cryostat to the outside.

The quantity of liquid hydrogen produced at one time is sufficient to maintain a temperature of 20°K. for more than 12 hours. If a longer period of time is desired an additional quantity of hydrogen may be liquefied. In order to cool the cryostat still further, the liquid hydrogen may be evaporated under reduced pressure. The triple point of hydrogen, 13.97°K., may easily be obtained with a pump of moderate capacity. The temperature of an object within the case s is controlled by suspending it from a large block of lead wound with a heating coil, this block being in turn suspended from the top of the case. Heat insulation from the wall is secured by evacuating the chamber. In order to maintain a high vacuum it is necessary to fill the cryostat with extremely pure hydrogen while cooling. The presence of solid oxygen and nitrogen constitute a very annoying source of gas which makes it impossible to hold a vacuum as the apparatus is slowly warmed. A more complete description of the temperature control will be given in an article on the entropy of bromine, to be published shortly.

Summary

The preparation of pure hydrogen has been discussed, and the feasibility of the ferrous-pyrocatechol analysis for small percentages of oxygen has been pointed out.

A simple cycle for the maintenance of low temperatures by liquid and solid hydrogen has been described.

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