CARBON TETRACHLORIDE HYDRATE

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INTRODUCTION

Hydrates of halogenated hydrocarbons are crystalline compounds which are stable near 0°C. They have been known for over 60 years. Chancel and Parmentier (1885) initially announced the hydrate of chloroform. Villard (1897) published data on two groups of hydrates; the first group was stable at atmospheric pressure, while the others were listed as being stable only under higher pressure. Carbon tetrachloride hydrate was described in the latter division as decomposing at 14°C under 45 atmospheres of nitrogen, and reforming readily under 60 atmospheres of nitrogen. No other references to carbon tetrachloride hydrate have been found in literature.

Recent investigations on hydrates at the University of Oklahoma have been concerned with halogenated methane derivatives. Decomposition temperatures at atmospheric pressure are listed in the literature (Anonymous 1926, Villard 1897) for hydrates of all the chlorine derivatives except carbon tetrachloride. As a result of the present work, carbon tetrachloride hydrate has been found to be stable at atmospheric pressure, and the series has thus been completed.

EXPERIMENTAL

The determinations were conducted with the aid of a refrigerated bath thermostatted just above 0°C. The hydrates were formed in 500-ml wide-mouth glass jars. Electrical stirrers, equipped with glass stirring rods, were used to agitate the mixtures. Baker's c. p. carbon tetrachloride with boiling range from 76° to 78°C was used in preparing the hydrates.

The hydrate was first made by seeding a cold mixture of 25 ml of carbon tetrachloride and 200 ml of distilled water with crystals of chloroform hydrate. (To reduce contamination, subsequent samples were seeded with carbon tetrachloride hydrate.) In spite of seeding the hydrate formed only after a prolonged period of vigorous stirring. The early stages of formation of the hydrate were the most difficult. After a small amount of hydrate was formed the reaction proceeded fairly rapidly. Possibly the original hydrate acts as a surface-active agent in stabilizing an emulsion of the carbon tetrachloride and water. A stable emulsion would provide more surface and result in more rapid reaction. Three to four hours of vigorous stirring are necessary to convert completely 25 ml of carbon tetrachloride to hydrate.

Efforts to determine the exact decomposition temperature from heating curves gave results varying from 1.40° to 1.49°C. The first determinations were made in a wide-mouth Dewar flask, fitted with a stirrer and Beckman thermometer, calibrated at the ice point. Typical heating curves of hydrates were then obtained by allowing the flask and contents to absorb heat at room temperature. As stirring was started the temperature of the hydrate rose rapidly to approximately 1.5°C then slowly fell off to a plateau in the range of 1.40° to 1.44°C, depending on the rate of stirring. As long as the stirring rate was not changed plateaus constant to within 0.01°C were held for several hours. It was noted that while the lowest plateaus were obtained with the most-vigorous stirring, a decrease in stirring rate would show a sudden fall in temperature followed by a rise to a value higher than the first plateau. The temperature drop varied from 0.02° to 0.06°C. When the original stirring rate was resumed the temperature returned to the original plateau. The rate of stirring had no effect on the temperature of a mixture of ice and water. The temperature of a mixture of ice, water, and carbon tetrachloride was also checked and found to be independent of stirring rate.

In order to determine the approximate heat effect of stirring, the glass reaction jar containing 250 ml of cold water was placed in the cooling bath. It was found that on vigorous stirring the temperature of the water in the reaction jar could be raised approximately 0.2°C above the temperature of the bath before the heat lost balanced the heat due to friction.

Inconsistent temperatures obtained during hydrate formation in a bath regulated just above 0°C had indicated the unsuitability of cooling curves. However, an effort was made to obtain a more-consistent formation temperature by cooling with a smaller temperature difference between hydrate and bath. A seeded mixture of carbon tetrachloride and water was placed in a bath maintained at a temperature a few tenths of a degree below the assumed formation temperature. Under these conditions of low heat transfer, an inappreciable amount of hydrate was formed and the attempt was considered unsuccessful.

A third method, involving heating with a small temperature difference between hydrate and bath, was tried. A sample of hydrate was prepared and left in the reaction jar. The mixture was stirred while slowly raising the bath temperature. The assumption was made that the heat effect of stirring would be great enough to start decomposition of the hydrate after the bath temperature was raised to a value just under that of the decomposition temperature of the hydrate. The temperature of the hydrate mixture should then remain constant as the bath temperature was increased. The bath temperature was varied from 1.0° to 1.7°C by 0.1°C increments. It was found that as the bath temperature was raised to 1.13°C the temperature of the hydrate mixture changed rapidly and reached a maximum average temperature of around 1.43°C. As the bath temperature was increased from 1.3°C to 1.7°C, the temperature of the hydrate increased to the average value of 1.49°C. In this range the effect of stirring rate was not as noticeable as in previous tests. The decomposition range thus obtained agreed well with that of the first method. This was to be expected as the methods differed only in rate of heat exchange with the surroundings.

A previous paper presented before this Academy (Blankenship 1945) reported that the hydrate of chloroform dissolved and decomposed in chloroform. This conclusion was reached as a result of the failure to form or preserve hydrate in the presence of any but small amounts of chloroform during preliminary trials. The present work has shown that carbon tetrachloride hydrate is stable in the presence of carbon tetrachloride, and that the hydrate can be formed from mixtures having a large excess of the nonaqueous component. The same is true of chloroform hydrate prepared with Baker's c. p. chloroform.

SUMMARY

While a temperature range of decomposition has been fairly well established, it has not been possible, thus far, to obtain a true invariant temperature. The decomposition temperature of carbon tetrachloride hydrate lies in the range from 1.40° to 1.49°C at atmospheric pressure.

The rate of stirring can shift the apparent temperature of decomposition over a range of 0.09°C, depending on the experimental conditions.

The decomposition temperature is not appreciably affected by the ratio of water and carbon tetrachloride used in preparation of the sample, and the hydrate is stable in either component.

LITERATURE CITED

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