

---

## CHLOROFORM HYDRATE

FORREST BLANKENSHIP, University of Oklahoma, Norman

Hydrates of natural gas have received considerable attention recently because their formation in pipelines creates a difficult and important problem. For purposes of comparison, it was of interest to investigate the formation of hydrates of hydrocarbon derivatives. There was also the hope that more easily studied hydrates might be found. Accordingly, hydrocarbon derivatives which are liquid at room conditions were selected for further attention.

The literature revealed that a few investigators (Villard 1897), especially in France, had hydrated various liquids and gases during the last half of the 19th century.

The case of chloroform hydrate was typical. It was first announced by Chancel and Parmentier (1885). These investigators were engaged in a determination of the solubility of chloroform in water when they detected the existence of a solid snowlike substance, not ice, which formed at the interface between the two liquids at temperatures near freezing.

The only information which Chancel and Parmentier revealed on their method of formation was that it was necessary "to leave water and chloroform together for a sufficiently long time in some melting ice, taking care to agitate frequently." They reported that often it was quite difficult to make the hydrate form, but offered assurance that seeding with a crystal of hydrate was all that was necessary to give a good yield.

Villard (1897) claimed to have formed the hydrate and briefly commented to the effect that he had confirmed the work of Chancel and Parmentier except with respect to the formula.

Gibby and Hall (1931) published a study of the system of water-chloroform. With reference to chloroform hydrate, they stated that they had not encountered it. They added that they had made 36 separate attempts to prepare it, and had used chloroform from several sources in an effort to duplicate the findings of Chancel and Parmentier. This failure to obtain chloroform hydrate is mentioned by Seidell (1941: 13).

In the present work it was first attempted to prepare the hydrate from the two liquid phases by immersing them in a water bath at 0° C and agitating. The experiments were unsuccessful. Then chloroform vapor

was passed through almost-freezing water in a Milligan gas-washing apparatus, but no hydrate formed. Other attempts at formation gave negative results until it was found that the hydrate could be formed with certainty and ease if the following two simple points are observed.

First, the hydrate may be seeded with ice crystals. These may be added to the system or formed in it. Without them the hydrate has not been observed to form. Once hydrate formation has been initiated, the ice is removed by raising the temperature above  $0^{\circ}$  C but not above  $1.6^{\circ}$  C, the melting point of the hydrate.

Second, the hydrate dissolves and decomposes in chloroform. Thus it can be formed in quantity only in the presence of excess water. Apparently, it can form only at the water-chloroform interface. If agitation carries the compound into the water phase, it is stable. If a relatively large amount of chloroform is present, so that agitation serves to bathe the crystals with chloroform, they dissolve and decompose. It may be conjectured that this second factor is responsible for many of the failures reported by Gibby and Hall.

The formation of chloroform hydrate has been tried as an experiment in the Elementary Physical Chemistry Laboratory at Oklahoma University. It has the following advantages.

1. Its decomposition at  $1.6^{\circ}$  C furnishes an example of an arrested-temperature curve showing phase transition.
2. The materials involved are inexpensive and easily obtained. USP chloroform containing 0.75 percent of  $C_2H_5OH$  is satisfactory. Other halogenated hydrocarbons may be substituted for chloroform.
3. It illustrates the formation of a molecular compound in which the usual valence or coordination numbers are not operative.
4. The necessary techniques, involving the use of a Beckmann thermometer and stopwatch to obtain a heating curve, are simple, but fundamental.

A disadvantage lies in the fact that heating curves obtained by students have not shown a sharp lower break. This may likely be attributed to the presence of unreacted chloroform in the hydrate slush which causes "pre-melting." Vigorous agitation in a large excess of water is required to obtain smooth curves.

Work on hydrates of hydrocarbons and hydrocarbon derivatives is being continued in the Physical Chemistry Laboratory at the University of Oklahoma.

#### LITERATURE CITED

- Chancel, G., and F. Parmentier. 1835. Sur un hydrate de chloroform. *Compt. Rend.* 100: 27-30.
- Gibby, C. W., and J. Hall. 1931. The system water-chloroform. *J. Chem. Soc.* 134: 691-693.
- Seidell, A. 1941. Solubilities of organic compounds; a compilation of quantitative solubility data from the periodical literature. New York: D. Van Nostrand.
- Villard, M. P. 1897. Etude expérimentale des hydrates de gaz. *Ann. Chim. Phys.* 11: 289-394.