

Fig. 1

ideal gas state thermodynamic functions (entropy, heat capacity) for *n*-alkyl halides⁷.

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J. LIELMEZS
J. P. MORGAN

Department of Chemical Engineering,
University of British Columbia,
Vancouver 8.

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Ozone - Carbon Tetrachloride Double Hydrate

CLATHRATE compounds have been prepared for most of the known gases except ozone. Because of its extreme reactivity, it is unlikely that a stable clathrate compound could be formed between ozone and any organic compound, but a compound with water, of the gas-hydrate type, may be expected to exist. Experience with hydrates of the inert gases¹ has shown that the simple hydrates are difficult to prepare and that elevated pressures are usually required. In view of the difficulty of handling pure ozone gas even without compression, the use of high pressures is undesirable. The work with the inert gases did show, however, that the double hydrates with acetone, carbon tetrachloride or chloroform were relatively easy to prepare. Attempts to make a hydrate of ozone and carbon tetrachloride were therefore carried out, carbon tetrachloride being chosen since it is stable to ozone at low temperature and can, in fact, be used as an ozone solvent.

Pure ozone gas was prepared by condensing liquid ozone from ozonized oxygen and then reducing the pressure above the liquid ozone to remove dissolved oxygen. The liquid ozone was then carefully evaporated, allowing the gas to bubble through a mixture of carbon tetrachloride and water (1 : 3) cooled in an ice/salt bath to about -2°C . Up to this stage, the experimental work was carried out in a specially protected apparatus, due to the risk of explosion.

The carbon tetrachloride was saturated with ozone to give a deep blue solution. The mixture of cold water and ozone solution was then seeded with a crystal of carbon tetrachloride hydrate or, in later experiments, with some ozone-carbon tetrachloride hydrate. Vigorous stirring with a magnetic stirrer, keeping the temperature around 0°C , resulted in the formation of a white solid and in the

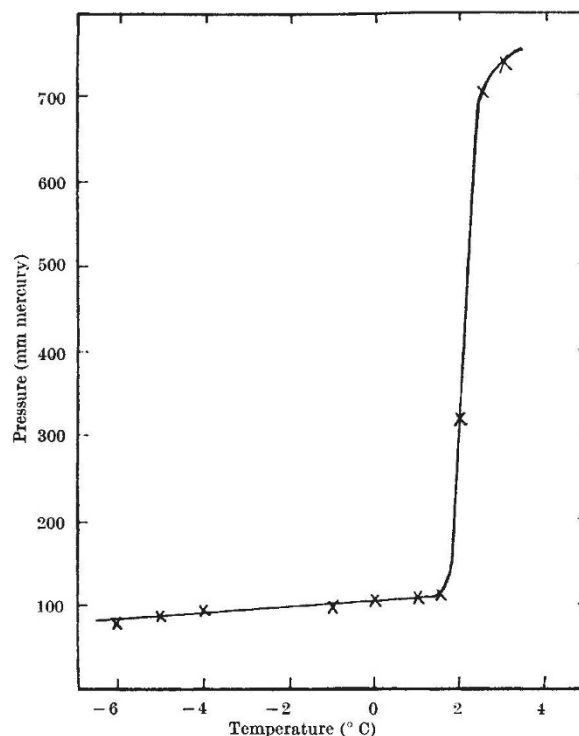


Fig. 1. Decomposition pressure of the double hydrate

removal of most of the blue colour from the carbon tetrachloride. The solid was recovered by filtration on a Buchner filter.

Some early samples were slightly blue in colour but this was probably due to traces of carbon tetrachloride containing dissolved ozone which remained. When the solid was retained on the filter for a longer time, it was isolated as a white microcrystalline solid. Examination by X-ray crystallography showed a diffraction pattern very similar to that of the double hydrate of argon and carbon tetrachloride, with roughly the same cell constant¹. It is to be expected that the hydrate has the limiting composition corresponding to $2\text{O}_3 \cdot \text{CCl}_4 \cdot 17\text{H}_2\text{O}$.

On warming, the material effervesces, ozone being evolved. Measurements of the decomposition pressure at different temperatures gave the results shown in Fig. 1. This curve is different in shape from the curves obtained for the inert gases, which gave a linear plot of $\log p$ versus $1/T$. It is felt that the different shape of the curve for the ozone compound may be due to the effect of solubility of the ozone in carbon tetrachloride and to some decomposition of the gaseous ozone in the presence of water. The results suggest that the hydrate could be stored at temperatures below 2°C without using a pressurized container.

The ozone content of the hydrate samples was determined by measuring the volume of gas evolved on warming. Ozone contents up to 30 ml. per gram of product were obtained, that is, up to about 30 per cent of the theoretical content for the formula $2\text{O}_3 \cdot \text{CCl}_4 \cdot 17\text{H}_2\text{O}$. This indicates that only about 30 per cent of the small cavities in the lattice are filled. To obtain higher ozone contents would probably necessitate the use of ozone under pressure.

This compound is the subject of a patent claim.

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G. MCTURK
J. G. WALLER

British Oxygen Co., Ltd.,
Deer Park Road, London, S.W.19.

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