# Formation and Decomposition of Oxygen Clathrate Hydrate as seen by Two-step Differential Scanning Calorimetry; Novel Method for Investigating Reactions Accompanied by Gas Release

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Using differential scanning calorimetry, a two-step procedure is described whereby gas release from a sample is made observable; its utility is demonstrated with regard to $O_2$ clathrate hydrate and its decomposition which occurs in two distinct steps.

In a differential scanning calorimeter (DSC), evolution of gas of thermal conductivity significantly lower than that of the purge gas produces artefacts which have the appearance of exothermic peaks.[1] This is because DSCs require for proper operation a well defined heat flow from the sample and the reference to their environments, and this heat flow is accomplished largely *via* convection by the purge gas.[2] Therefore dilution of the purge gas by a gas of lower thermal conductivity, which is given off from a sample during heating, leads to reduced heat transfer from the sample to its environment, and this is observed as a diminution of power input. This artefact can be used to advantage to relate in a two-step procedure the various thermal processes during heating of a sample with the parallel evolution of gas. This is demonstrated for the decomposition of $O_2$ clathrate hydrate which has been prepared from vapour-deposited amorphous solid water (ASW).[3]

ASW was prepared as described before.[4,5] After formation of an ASW deposit of $\approx 1$ mm thickness, the apparatus was pressurized with $O_2$ (99.995%) and the deposit warmed to $\approx 120$ K. This procedure causes the ASW to sinter and to enclose considerable amounts of $O_2$ which cannot be pumped off *in vacuo*.[6,7] A differential scanning calorimeter (Perkin-Elmer DSC-4) with a computerized data acquisition system was used. The baseline obtained with empty sample pans was subtracted during each scan. High-pressure cells for the DSC-4 instrument were filled with 13—17 mg of sample under liquid $N_2$, and transferred into the precooled instrument.

Figure 1 shows DSC scans of two samples prepared as described above, one with He (a) and the other with $N_2$ as purge gas (b), recorded from 113 to 293 K at a rate of 10 K min$^{-1}$. The intense endotherms due to melting of ice are not shown, but their areas were used to determine the sample mass.[8] Temperatures reported in the following are for the peak maximum and minimum, respectively. Curve b contains only features from exothermic or endothermic processes of the sample because the thermal conductivity of the purge gas is very similar to that of evolved $O_2$. Curve a contains three additional peaks which are superimposed on those of curve b, with minima at 249, 220, and 160 K. These peaks are due to $O_2$ released from the sample and have the appearance of exotherms because now the purge gas has a much higher thermal conductivity than $O_2$ (thermal conductivity at 273 K and 1.013 bar: $N_2$ 24.3, $O_2$ 24.6, He 140.5 J m$^{-1}$ s$^{-1}$ K$^{-1}$ $\times$ $10^3$). The additional peaks of curve a at 220 and 249 K agree remarkably well with the endothermic peaks of curve b at $\approx 222$ and 246 K. They are therefore assigned to $O_2$ evolved during decomposition of oxygen clathrate hydrate in the two temperature regions. (The peak at 220 K could alternatively also be partly due to $O_2$ evolved during the phase transition of cubic to hexagonal ice which is expected to occur in the same temperature region.) The third additional peak of curve a, at 160 K, is partly due to $O_2$ evolved during crystallization of ASW to cubic ice. The exotherm at 201 K is due to formation of oxygen clathrate hydrate. The set of exothermic peaks from

$\approx 160$ to 180 K, which is due to stepwise crystallization of ASW to cubic ice, had been reported before.[4] We have confirmed these assignments by parallel investigation of the $X$-ray diffractograms. Earlier studies of release of trapped gas during heating of ASW by Ghormley[7] and others[6,9,10] had related maxima in the release of gas mainly with phase transitions of ASW to cubic ice, and of cubic to hexagonal ice.

Integration of band areas, with limits as indicated in the curves by broken lines, gave $-7.7$ and $-8.9$ J (g $H_2O)^{-1}$, respectively, for the exotherm of curves a and b at 201 K, and 17 J (g $H_2O)^{-1}$ for the sum of the areas of the two endotherms of curve b at $\approx 222$ and 246 K. According to the $X$-ray diffractograms about 15% of ASW and/or crystalline ice were
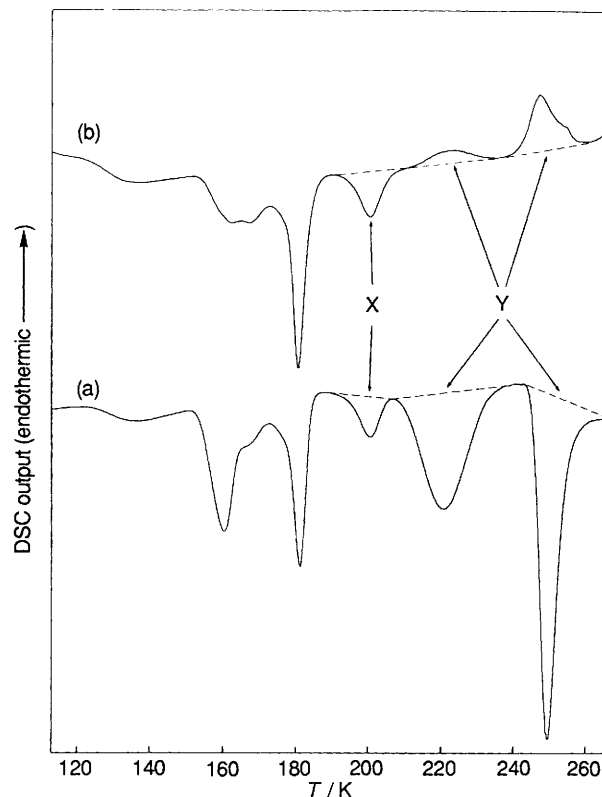


**Figure 1.** DSC heating curves of two samples of ASW treated with $O_2$ as described in the text: curve a, using He; curve b, with $N_2$ as purge gas (both at 3.5 bar). The samples were filled under liquid $N_2$ in high-pressure cells, with the lid closed only loosely to allow release of gas. Weight of the water fraction was 16.9 mg for curve a and 13.0 mg for curve b. Heating rate was 10 K min$^{-1}$. The curves are normalized with respect to the sample's weight and drawn on the same scale. Broken lines indicate the limits of integration. X formation and Y decomposition of oxygen clathrate hydrate.

converted to oxygen clathrate hydrate.[3] If we assume a composition of $O_2 \cdot 6H_2O$, which is about the value for a type II clathrate hydrate with nearly all cages filled,[11] then we obtain an estimate for the enthalpy of formation of $-6.9$ and $-8.0$ kJ (mol $O_2 \cdot 6H_2O)^{-1}$ (from curves a and b), and for its decomposition of $\approx 15$ kJ (mol $O_2 \cdot 6H_2O)^{-1}$ (from curve b). The latter value is of the order of magnitude expected for decomposition of oxygen clathrate hydrate.[12—14] However it is obvious that because of overlap of bands in curves a and b the limits of integration could be chosen quite differently.

Dissociation of oxygen clathrate hydrate occurs in two distinct steps, with peaks at $\approx 222$ and $\approx 246$ K. It is likely that this is related to two different types of pores which differ in wall strength of the enclosing ice layers. Had we used only He as purge gas, which is the gas recommended by the manufacturer for work at subambient temperatures, it would have been very difficult to understand the features of curve a.

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