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Enthalpies of Decomposition and Heat Capacities of Ethylene Oxide and Tetrahydrofuran Hydrates[†]

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Heat capacities at temperatures between 120 and 260 K and enthalpies of congruent melting have been determined for clathrate hydrates of ethylene oxide and tetrahydrofuran (von Stackelberg's structures I and II, respectively). A Tian-Calvet differential heat conduction calorimeter was used. Enthalpies of decomposition and estimates of the heat capacities of the hydrate lattices and enclathrated guests are reported.

Introduction

Clathrate hydrates are nonstoichiometric solids formed from mixtures of water and low molecular weight gases or liquids.¹⁻⁴ The hydrate structure contains cavities enclosed by a lattice of hydrogen-bonded water molecules. Within the cavities are held loosely bound "guest" molecules which stabilize the "host" framework of water molecules.

The p - T conditions necessary for hydrate stability have been extensively studied.⁵⁻⁷ From measurements of hydrate decomposition pressures at different temperatures,

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other thermodynamic properties may be estimated by use of a suitable potential energy function for the guest–host interaction together with the ideal solution model developed by van der Waals and Platteeuw.⁸

Calorimetric studies on clathrate hydrates would also be useful. Heat capacity data, for example, would provide information about the motion of encaged guests and would allow a more sensitive test than has been possible so far of the ideal solution model as applied to clathrate hydrates. Furthermore, enthalpy data are required for the correct evaluation of schemes proposed for the eventual recovery of natural gas found in hydrate deposits in the Arctic permafrost regions and beneath the oceans.^{9–11}

In this note we report enthalpy of decomposition and heat capacity data for ethylene oxide (EO) and tetrahydrofuran (THF) hydrates (von Stackelberg's structures I and II, respectively).^{12,13} These hydrates were chosen for several reasons. Because both EO and THF are water soluble, ice-free samples of their hydrates are easily prepared by freezing the appropriate aqueous solution. The low decomposition pressure of these hydrates is another convenient feature. Also, EO and THF hydrates have essentially fixed compositions over a wide temperature range. And finally, the heat capacity data should be of interest to those workers investigating the unusual thermal conductances of the hydrates.^{14–16}

Experimental Section

Calorimeter. A Tian–Calvet differential heat conduction calorimeter, Model BT, built by Setaram of Lyon, France was used in this work. Such a calorimeter incorporates a massive heat sink and is generally used isothermally as a reaction calorimeter. In this type of calorimetry the total heat flux to the sample cell relative to the heat flux to the reference cell is measured from the output of a differential thermopile.¹⁷ The twin cell configuration permits operation in slow temperature scan to obtain heat capacities and enthalpies of phase changes and transitions. Temperature scan is obtained by resistive heating of the heat sink, the entire system being contained in a liquid nitrogen cooled enclosure. As described in detail elsewhere,^{18,19} the calorimeter was operated with a direct digital control and data acquisition system and was extensively calibrated with electrical Joule heating calibration, enthalpy increment calibration obtained by using NBS standard sapphire rods (NBS: SRM 720) and by measuring several well-established enthalpies of fusion.

The same pair of matched stainless steel cells with Viton O-ring sealed closures were employed for all the hydrate measurements and most of the calibration procedures

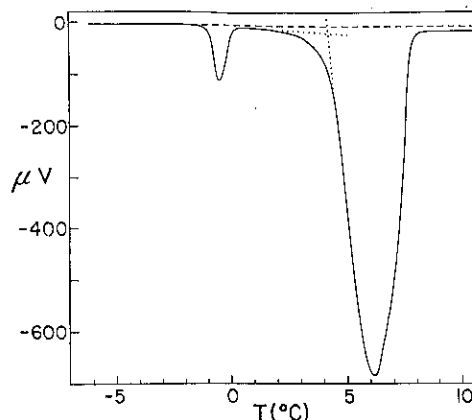


Figure 1. Thermopile output against temperature for the melting of THF hydrate. This particular sample exhibited the highest proportion of eutectic (4%) observed in these measurements. The dotted lines illustrate the technique used to obtain the reported melting point. The dashed extension of the initial baseline illustrates the baseline shift on melting. The ramp rate for this output was 3 °C h⁻¹.

described above. Each cell had a volumetric capacity of about 15 cm³. For heat capacity measurements the reference cell was empty and the sample cell contained about 10 g of the hydrate. Measurements were made at scan rates of 6 and 10 K h⁻¹. The effects of minor C_p differences between the sample and reference cells were corrected for by making measurements under the same scan conditions with both cells empty. For measurements of the enthalpies of melting, samples of 0.6–1.0 g of the hydrate were placed into the sample cell and a quantity of methanol or alumina powder having approximately the same heat capacity as the hydrate was placed in the reference cell to establish optimum baseline behavior. The calorimeter temperature was then increased at a fixed rate between 0.5 and 3 K h⁻¹ through the expected melting temperature. As a final system and calibration check, the enthalpy of melting and the heat capacities of ice were determined under the same conditions.

Sample Preparation. Reagent grade THF and EO were purified by distillation. Aqueous solutions were prepared by weight from deaerated, distilled water. The calorimeter cell was loaded with solution then sealed by means of the Viton O-ring sealed cap. The filled cell was cooled, followed by conditioning of the resulting hydrate sample for at least 3 days at 263–273 K. The sample cell containing the hydrate was transferred to the calorimeter which had been precooled to 255 K. For C_p measurements the calorimeter was subsequently cooled to ~90–100 K over 8–12 h. All samples were of composition EO·6.89H₂O (as suggested by Glew²⁰) or THF·16.9H₂O.

Results and Discussion

Enthalpies of Decomposition. In heat conduction calorimetry, enthalpies are obtained as the product of the calibrated sensitivity and the area obtained by integration over time of the thermopile output during the phase change relative to the baseline output established before and after the phase change. A typical thermopile output during hydrate melting is shown in Figure 1. A baseline shift through the melting event is clearly evident; such a shift is a function of the ΔC_p of the event and the temperature scan rate, and, in this case, is due to the relatively large ΔC_p for hydrate melting. Error from this source is less than 0.5% when the baseline is appropriately averaged. Reproducibility in the decomposition or melting enthalpies

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TABLE I: Enthalpies of Decomposition

	T/K	$\Delta H/(\text{kJ mol}^{-1})$
EO·6.89H ₂ O		
h → l (congruent melting)	283	48 (±1)
h → H ₂ O(l) + EO(l)	283	54 (±2)
h → H ₂ O(l) + EO(g)	283	79 (±2)
h → H ₂ O(l) + EO(g)	273	75 (±2)
h → H ₂ O(s) + EO(g)	273	34 (±2)
THF·16.9H ₂ O		
h → l (congruent melting)	277	98 (±2)
h → H ₂ O(l) + THF(l)	277	110 (±4)
h → H ₂ O(l) + THF(g)	277	142 (±4)
h → H ₂ O(l) + THF(g)	273	139 (±4)
h → H ₂ O(s) + THF(g)	273	37 (±4)

was about ±1% and accuracy is estimated at ±2%, the major error sources being calibration and baseline uncertainties. Minor sample inhomogeneities and traces of dissolved air are probably responsible for the broadness of the output curves as well as for the minor variations in their shapes observed from sample to sample.

EO and THF hydrates melted at 283.2 ± 0.4 and 277.4 ± 0.4 K with enthalpy changes of congruent melting (h → l) of 48 ± 1 kJ mol⁻¹ (286 ± 6 J g⁻¹) and 98 ± 2 kJ mol⁻¹ (260 ± 5 J g⁻¹), respectively. (We define 1 mol of hydrate of composition M·nH₂O as 1 mol of M plus n mol of H₂O.) The reported enthalpy changes include minor heat contributions (generally <1% but on one occasion 4% (Figure 1)) from eutectic melting observed at 270.2 ± 0.3 and 270.7 ± 0.3 K for EO and THF hydrates, respectively. The reported temperatures of melting were obtained by interpolation as illustrated in Figure 1. Enthalpies of decomposition based on these and other data^{21,22} are listed in Table I. The value obtained for the enthalpy of melting of THF hydrate is in good agreement with the value of 101 ± 5 kJ mol⁻¹ obtained in a recent study.¹⁸ The melting temperature of the THF hydrate, which was about 1 K lower than that observed for the air-saturated hydrate,²² suggests that the hydrate samples studied here were relatively air-free. Measurements made on several samples of ice gave a melting temperature of 273.1 ± 0.2 K and an enthalpy of fusion of 336 ± 3 J g⁻¹ (accepted value 334 J g⁻¹ (ref 23)).

Effect of Hydrate Decomposition. Although the vapor pressures of EO and THF over their hydrates are both low, there is a small amount of hydrate decomposition with rising calorimeter temperature. Sample decomposition, which absorbs heat, acts to increase the measured heat capacity of the hydrates as they are warmed. This source of error is larger for EO hydrate because of its higher volatility. The magnitude of the error in the measured heat capacity due to decomposition was estimated by use of the vapor pressure data for the EO-water system.²¹ Calculations based on a sample size of ~10 g, a calorimeter headspace of ~5 cm³, and a heat of decomposition of ~30 kJ mol⁻¹ indicated the errors would amount to only ~0.3% of C_p at 270 K, and was much smaller at lower temperatures. Similar calculations indicated vaporization of EO would increase the measured heat of melting of EO hydrate by only ~0.2%. Since these error estimates were well within the precision of the measurements, the data were not corrected for sample decomposition.

Effect of Air Impurity. It is well-known that hydrates (especially structure II) grown in air enclathrate significant

TABLE II: Specific Heats of the Hydrates of Tetrahydrofuran, Ethylene Oxide, and Water

T/K	specific heats/(J g ⁻¹ K ⁻¹)			
	water		THF	EO
	ref 26	this work	hydrate	hydrate
120	1.030	1.041	1.066	1.118
130	1.098	1.093	1.109	1.115
140	1.160	1.154	1.152	1.203
150	1.223	1.213	1.195	1.247
160	1.289	1.270	1.244	1.289
170	1.358	1.331	1.284	1.329
180	1.427	1.392	1.333	1.374
190	1.496	1.453	1.383	1.428
200	1.566	1.521	1.439	1.488
210	1.643	1.581	1.494	1.540
220	1.717	1.653	1.564	1.602
230	1.789	1.726	1.637	1.667
240	1.861	1.802	1.716	1.739
250	1.934	1.874	1.798	1.804
260	2.007	1.957	1.893	1.898
270	2.081	2.052		

amounts of oxygen and nitrogen.^{22,24,25} Air impurity would increase both the apparent heat of melting and heat capacity of a hydrate sample. Under the experimental conditions, the hydrates were exposed only to the air in the calorimeter cell headspace present during sample loading. On the basis of a molar specific heat of enclathrated air of ~30 J K⁻¹ mol⁻¹ and an enthalpy of enclathration of ~20 kJ mol⁻¹, it was calculated that the enclathration of *all* the air in the calorimeter headspace would increase the heat capacity and enthalpy of melting by at most only 0.1 and 0.5%, respectively. Corrections for air impurity were therefore neglected.

Heat Capacities. Heat capacities, in J K⁻¹ mol⁻¹, were determined at 5-K intervals from the calorimeter scans with the equation

$$C_p = (O_S - O_R)M/SWR \quad (1)$$

where O_S is the instantaneous thermopile output at temperature T , O_R is the output at the same temperature T and scan rate for the reference condition (both cells empty), M is the molecular weight, W is the sample weight, R is the scan rate, and S is the calorimetric sensitivity (which is a function of T). The digital control and acquisition system permitted the precise linearity, reproduction, and measurement of the ramp rate which is necessary in this technique. Accurate determination of S over the measurement range in a variety of separate calibrations experiments, and the calorimetric construction which ensures that the thermopile output is a measurement of virtually all the heat flux, ensures the accuracy of the measurements. Analysis of the various calibrations indicate that the results should be accurate to ±2%, with an instrument measurement precision of ±1% or better.

Specific heats of the hydrates and ice are given at 10-K intervals in Table II. For any one sample with various scan rates, the data were reproducible to ±1% or better. The sample-to-sample reproducibility was about ±1.5%. The ice data may be compared (Table II) with the results of Giauque and Stout²⁶ obtained by adiabatic calorimetry; the agreement is within 1% for $110 < T < 155$ and $260 < T < 270$, whereas in the region $155 < T < 260$, the values measured are as much as 4% below those reported by

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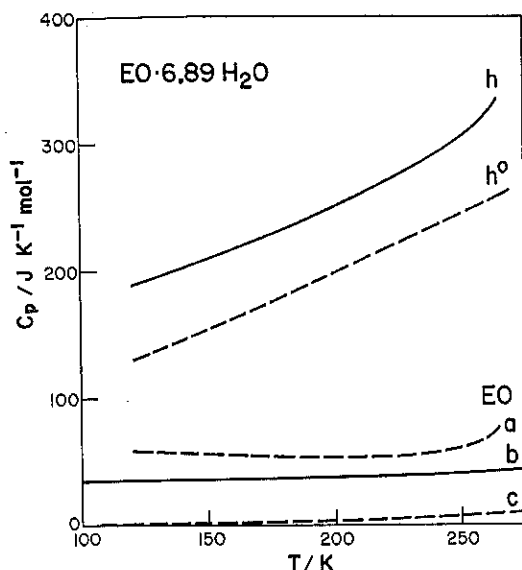


Figure 2. Molar heat capacities plotted against temperature for EO hydrate (h); hydrate lattice (h^0); EO guest (a); EO ideal gas (b); and EO intramolecular vibrations (c).

Giauque and Stout. This is probably a difference in samples since in the present study the ice was cooled relatively rapidly to ~ 90 K to start the measurements, and such rapid cooling is known to "freeze-in" strains in ice. As might have been anticipated, the heat contents per gram of the hydrates and ice are very similar over the range of temperature investigated, essentially doubling over the temperature range 100–270 K.

In principle, the partial molar heat capacity due to the engaged guest is obtainable from the variation of the heat capacity of the clathrate with composition. Unfortunately, the range of composition over which hydrates are stable is very narrow. As a result, the guest contribution to the heat capacity cannot be directly measured for clathrate hydrates. Instead, we have estimated the molar guest heat capacity, $C_p(\text{guest})$, by subtracting from the molar hydrate heat capacity, $C_p(h)$, the "empty" lattice heat capacity, $C_p(h^0)$, calculated for gas hydrates from decomposition pressure data by use of the ideal solution model^{15,7}

$$C_p(h^0, \text{structure I}) \approx nC_p(\text{ice}) + n[0.565 + 0.002(T - 273 \text{ K})] \text{ J K}^{-1} \text{ mol}^{-1} \quad (2)$$

$$C_p(h^0, \text{structure II}) \approx nC_p(\text{ice}) \quad (3)$$

The results are plotted against the temperature in Figure 2 and 3; over the range of temperature investigated the temperature dependence of the hydrate heat capacities is due almost entirely to the temperature dependence of the lattice heat capacity.

It is customary to analyze the heat capacity of the enclathrated guest in terms of intramolecular vibrational, rattling (motion of the center of mass within the cage), and rotational contributions.^{27,28} For EO hydrate, the heat capacity of the guest due to intramolecular vibrations may be calculated by use of the harmonic oscillator approximation together with the observed intramolecular vibrational frequencies of enclathrated EO.²⁹ The heat capacity of enclathrated EO due to internal vibrations obtained in this manner (plotted against the temperature in Figure 2) lies between 0 and about $1.2R$ over the range of temper-

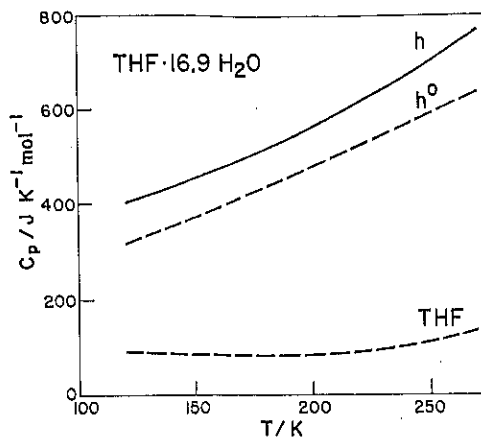


Figure 3. Molar heat capacities plotted against temperature for THF hydrate (h); hydrate lattice (h^0); and THF guest.

ature investigated (100–270 K). Because guest–host interaction potentials are not available for EO and THF hydrates, the rattling and rotational heat capacities of the guests cannot be calculated. However, contributions made by these two sources are probably each less than about $3R$ (the value $3R$ corresponds to the heat capacity of a three-dimensional harmonic oscillator). On the basis of these considerations, values of the heat capacity of enclathrated EO between $7R$ and $8R$ depicted in Figure 2 are slightly higher than expected, though not unreasonable. For comparison, the heat capacity of ideal, gaseous EO³⁰ is also shown in Figure 2. The higher heat capacity of the enclathrated molecules arises from additional degrees of freedom associated with rattling and hindered rotation within the cage over those associated with translation and free rotation in the gas phase.

It is noteworthy that above 220 K the apparent heat capacities of both EO and THF guests increase as the melting temperatures are approached. Although an actual increase in the guest heat capacity could be responsible for this behavior, a small increase in the lattice heat capacity (representing a departure from the ideal solution model) is a more plausible explanation. Near the melting point ($T > 260$ K) premelting likely contributes to the increase in the apparent guest heat capacities.

It should be emphasized that, whereas the separation of lattice and guest heat capacities may be justifiable in the case of monatomic and diatomic guests, the separation may not be entirely correct for polar, polyatomic guests like EO and THF. (X-ray studies, for example, suggest that the lattice dimensions of EO hydrate vary with the degree of cage occupancy.³¹) Further, the procedure we have used to resolve the lattice and guest contributions to the hydrate heat capacity involves the direct transfer of enthalpy data of the hydrate lattices of gas hydrates with relatively simple, nonpolar guests to more complex systems containing EO and THF. For these reasons, the lattice and guest heat capacities reported here are only approximations to the real situation. Although the experiments would be more difficult, it would be of interest to obtain heat capacity data for a series of gas hydrates for which the guest–host interaction potentials are accurately known. It would then be possible to compare the results with detailed statistical mechanical calculations and thereby add to our understanding of clathrate hydrate thermodynamics.

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