Heat Capacity and Heat of Dissociation of Methane Hydrates

The objective of this study was to determine the heat capacity and heat of dissociation of methane hydrates. A technique has been devised which circumvents the two major problems encountered in measuring gas hydrate heat capacity: the need to impose a mechanical pressure during the measurement and the need to have an absolutely pure hydrate sample. The technique was shown to be successful utilizing high-pressure, constant-volume cells in a differential scanning calorimeter.

Roger M. Rueff
Amoco Oil Company
Naperville, IL 60566

E. Dendy Sloan,
Victor F. Yesavage
Colorado School of Mines
Golden, CO 80401

Introduction

Natural gas hydrates are clathrate inclusion compounds. They are nonstoichiometric solid solutions in which gas molecules are trapped inside of cages formed from water molecules. The gas molecules are called the "guest" species, and the water molecules form the "host" lattice.

Gas hydrates may form in either of two solid structures. Both structures are based on the *pentagonal dodecahedron.* This is a cage of 12 pentagonal faces with a water molecule oxygen atom at each vertex of each pentagon. There are 20 water molecules in this fundamental cage structure.

Pure methane, the basic component of natural gas, forms structure I hydrates. This hydrate structure consists not only of pentagonal dodecahedra but also of tetradecahedra (14-faced cages, two faces of which are hexagonal). Some pure components of natural gas (e.g., propane) form structure II hydrates. This structure contains both pentagonal dodecahedra and hexadecahedra (16-faced cages, four faces of which are hexagonal). Natural gas mixtures may form either structure I or structure II hydrates, depending on the composition of the gas and the hydrate formation conditions.

In recent years, researchers have discovered that gas hydrates exist in nature in quantities large enough to constitute a major energy resource potential. (Makogon, 1981; Judge, 1982; Bily and Dick, 1974; Weaver and Stewart, 1982; Makogon, 1982). They exist not only in Arctic permafrost regions of the world but in ocean bottom sediment near the equator as well. Consequently, much of the recent gas hydrate research has been directed toward determining economic production schemes for natural gas from the solid hydrate deposits. (Makogon, 1982; McGuire, 1981; McGuire, 1982).

Fundamentally, all scenarios for producing gas from naturally occurring hydrates depend on disturbing the natural equilibrium in the hydrate deposit. This means changing the pressure of the deposit, injecting an inhibitor, or heating the deposit to break the lattice and free the gas. To realistically model either scheme it is necessary (but not sufficient) to know the heat capacity of the hydrate mass, the heat of hydrate dissociation, and the pressure-temperature relationship governing hydrate equilibrium. Many measurements have been made of the conditions of pressure and temperature required for gas hydrate stability. Actual measurements of hydrate heat capacity and heat of dissociation, on the other hand, are scarce. The only measurements that exist, in fact, for the heat of dissociation of high-pressure gas hydrates are those of Cherskii et al. (1982), Stackelburg (1949), Villard (1897), and Nagayev et al. (1979). The heat of gas hydrate dissociation is usually obtained by inference from hydrate vapor pressure data. This method utilizes modified forms of the Clausius-Clapeyron equation. It has been used by many researchers to determine the ratio of water molecules to gas molecules in hydrates formed from different types of gases (Deaton and Frost, 1946; Deaton and Frost, 1947; Harris, 1943; Holder et al., 1980; Sortland and Robinson, 1964; Saito et al., 1964).

Measurements of gas hydrate heat capacity are also rare. Several researchers have measured the constant pressure heat capacity of hydrates formed from cyclic eithers (e.g., tetrahydrofuran, ethylene oxide, trimethylene oxide) (Leaist et al., 1982; Callanan and Sloan, 1982; Rueff, 1983). These substances are miscible with water and form hydrates easily at conditions not far removed from ambient temperature and pressure. Hydrates formed from them have a very low vapor pressure. The only heat capacity data that exists for hydrates with significant vapor pressure, however, are those of Cherskii et al. (1983) who report the dependence of gas hydrate heat capacity on tempera-

---

Correspondence concerning this paper should be directed to R. M. Rueff.

ture at 9 MPa. They also report the heat capacity pressure dependence of the same hydrate at 243 K. The hydrates used in their experiments were formed from natural gas produced from the Mastakh field in Yakutia, USSR.

It is the goal of this work to present new methods of experimentally determining gas hydrate heat capacity and heat of dissociation. These data will eventually be useful in modelling gas hydrate recovery scenarios.

Major Problems in Determining Hydrate Heat Capacity

There are two major problems which must be overcome to measure the heat capacity of natural gas hydrates by conventional calorimetry methods.

The first problem is that the vapor pressure of natural gas hydrate increases greatly with temperature. Unless the pressure of the hydrate sample mass is maintained above its vapor pressure mechanically, some of the hydrate mass will dissociate as the sample temperature increases. The heat required to dissociate the hydrate will render the apparent heat capacity of the hydrate much higher than the actual heat capacity.

The second problem is that the sample mass must be composed *entirely* of pure gas hydrate. If the sample contains excess ice, for instance, the apparent heat capacity of the sample will contain contributions from both the ice and the hydrate mass. This is a particularly severe problem above the ice point where water, rather than ice, can coexist with the hydrates. The heat capacity of water is about twice that of ice, and any excess water in the sample mass will greatly inflate the apparent heat capacity of the hydrate.

This study presents a new method for determining the heat capacity of gas hydrates. The procedure circumvents both of the major problems listed above. It requires only that:

1. The calorimetry experiments be performed in vessels of constant volume.
2. It be possible to determine the composition and size of the sample when the experiment is complete.

In this work, the procedure outlined above was used to determine the heat capacity at constant volume of pure methane hydrate. The results of this study indicate that this method represents a valid approach to obtaining gas hydrate heat capacity. Since this procedure circumvents the two major problems associated with hydrate heat capacity measurements, it represents the best method available for such measurements. This paper also presents a technique by which to measure the average internal energy of hydrate dissociation above the ice point by differential scanning calorimetry.

Theory

Consider a closed system of constant volume which is filled with a pure material. The rate of change of specific entropy of the system with respect to temperature may be expressed as,

$$\left(\frac{\partial s_{sys}}{\partial T}\right)_V = v_{sys}\left(\frac{\partial^2 p}{\partial T^2}\right)_V - \left(\frac{\partial^2 \mu}{\partial T^2}\right)_V \tag{1}$$

where the subscript V indicates that the derivatives are taken with respect to constant total system volume. The heat capacity of the system at constant volume is, therefore,

$$c_{V,sys} = v_{sys} T\left(\frac{\partial^2 p}{\partial T^2}\right)_V - T\left(\frac{\partial^2 \mu}{\partial T^2}\right)_V \tag{2}$$

If the system is in the two-phase region, then it has only one degree of freedom. The differentials in Eq. 2 are ordinary in that case, and it becomes possible to write Eq 2. as

$$c_{V,sys}(T) = k_1(T)v_{sys} + k_2(T) \tag{3}$$

where,

$$k_1(T) = T\left(\frac{d^2 p}{dT^2}\right)_V \tag{4}$$

and

$$k_2(T) = -T\left(\frac{d^2 \mu}{dT^2}\right)_V \tag{5}$$

The change in internal energy of the system from T_1 to T_2 is,

$$\Delta u = A + Bv_{sys} \tag{6}$$

where the constants A and B are simply the integrated forms of Eqs. 4 and 5. This can, of course, be put in terms of average heat capacity for the system by dividing Eq. 6 by ΔT, the difference between T_2 and T_1.

Equation 2 has been used by Yang and Yang (1964) in their investigations concerning the critical point in liquid-gas transitions. It has also been used by Rice and Chang (1972) and by Goodwin and Weber (1969).

Rueff (1985) has shown that a similar analysis may be applied to natural gas hydrate systems. The starting point for such a derivation is the Gibbs-Duhem equation applied to a multiphase system. That is,

$$S_{sys}dT - V_{sys}dp + \Sigma n_i d\mu_i = 0 \tag{7}$$

The resulting equation for the rate of change of specific entropy of the system is,

$$\left(\frac{\partial s_{sys}}{\partial T}\right)_V = v_{sys}\left(\frac{\partial^2 p}{\partial T^2}\right)_V - \sum x_i\left(\frac{\partial^2 \mu_i}{\partial T^2}\right)_V \tag{8}$$

And $c_{V,sys}$ is, simply,

$$c_{V,sys} = v_{sys} T\left(\frac{\partial^2 p}{\partial T^2}\right)_V - T\sum x_i\left(\frac{\partial^2 \mu_i}{\partial T^2}\right)_V \tag{9}$$

If the closed, constant volume system is in the three-phase region and the hydrate is formed from a pure gas (e.g., pure methane), then the system is univariant, just as the two-phase, pure component system is univariant. In that case the differentials in Eq. 9 are ordinary, and the change in internal energy of the system from T_1 to T_2 is,

$$\Delta u = K_o v_{sys} + \Sigma K_i x_i \tag{10}$$

where,

$$K_0 = \int_{T_1}^{T_2} T\left(\frac{d^2p}{dT^2}\right)_V dT \tag{11}$$

and

$$K_i = -\int_{T_1}^{T_2} T\left(\frac{d^2\mu_i}{dT^2}\right)_V dT \tag{12}$$

Finally, since the system contains only two components,

$$\Delta u = A + Bv_{\text{sys}} + Cx_1 \tag{14}$$

where,

$$A = K_2 \tag{15}$$

$$B = K_0 \tag{16}$$

$$C = K_1 - K_2 \tag{17}$$

Since the numbering of the two components is arbitrary, we can allow component 1 to be water so that,

$$\Delta u = A + Bv_{\text{sys}} + Cx_{\text{wat}} \tag{18}$$

This again can be put in terms of average heat capacity by dividing both sides by ΔT. The resulting equation forms the theoretical basis for this work.

To understand the utility of this theory to actual heat capacity measurements, it is best to work in terms of system heat capacity. Formally, for the two-phase system at any given temperature, this means,

$$c_{V,\text{sys}(2)} = a + bv_{\text{sys}} \tag{19}$$

For the three-phase, gas hydrate system, the relevant expression is,

$$c_{V,\text{sys}(3)} = a + bv_{\text{sys}} + cx_{\text{wat}} \tag{20}$$

It is important to remember that in each of these equations, the specific heat capacity of the *system* refers to the amount of energy required to raise the temperature of the system divided by the *total number of moles of all chemical species in the system.*

Equation 19 may be extrapolated to the conditions under which the system is almost entirely composed of saturated liquid by simply using the specific volume of the saturated liquid in the equation. The resulting value for $c_{V,\text{sys}}$ is neither the saturation heat capacity of the liquid, nor is it the constant-volume heat capacity of the liquid. It is, rather, only the heat capacity of the system when it is filled with a saturated liquid. However, $c_{V,\text{sys}}$ may be adjusted to obtain each of the other heat capacities. For instance, the saturation heat capacity may be obtained from,

$$c_{\sigma,1} = c_{V,\text{sys}(1)} + T\left(\frac{dp}{dT}\right)_\sigma\left(\frac{dv_1}{dT}\right)_\sigma \tag{21}$$

Likewise, the constant volume heat capacity may be calculated from,

$$c_{V,1} = c_{V,\text{sys}(1)} + T\left(\frac{dv_1}{dT}\right)_\sigma^2\left(\frac{\partial p}{\partial v_1}\right)_T \tag{22}$$

In both cases, $c_{V,\text{sys}(1)}$ is the value of $c_{V,\text{sys}}$, calculated from Eq. 19 by extrapolating it to the specific volume of the saturated liquid.

It is interesting to note that while the saturation heat capacity of the liquid differs very little numerically from $c_{V,\text{sys}(1)}$, $c_{V,1}$ differs substantially. Equation 19 may, of course, be extrapolated to the condition of the system containing only saturated vapor by simply using the specific volume of saturated vapor in Eq. 19. In that case,

$$c_{\sigma,v} = c_{v,\text{sys}(v)} + T\left(\frac{dp}{dT}\right)_\sigma\left(\frac{dv_v}{dT}\right)_\sigma \tag{23}$$

and

$$c_{V,v} = c_{V,\text{sys}(v)} + T\left(\frac{dv_v}{dT}\right)_\sigma^2\left(\frac{\partial p}{\partial v_v}\right)_T \tag{24}$$

The second term on the right side of Eq. 23 is so large and negative that it frequently causes the saturation heat capacity of the vapor to be negative.

In a similar manner, the constant volume heat capacity of hydrates formed from a pure gas may be obtained by,

$$c_{V,h} = c_{v,\text{sys}(3\text{-}h)} + T\left(\frac{dv_h}{dT}\right)_\sigma^2\left(\frac{\partial p}{\partial v_h}\right)_T \tag{25}$$

where $c_{V,\text{sys}(3\text{-}h)}$ refers to the heat capacity of the three-phase hydrate system extrapolated to the specific volume and mole fraction of water characteristic of the pure hydrate mass.

The equations above form the basis of a general experiment principle for determining the constant volume heat capacity of pure liquids and of hydrates formed from a pure gas. Formally, the principle is as follows:

Two-phase pure-component system

1. Perform experiments to determine the heat capacity of systems of various specific volumes.
2. Regress the heat capacity data, $c_{V,\text{sys}}$, on the system specific volume to estimate the coefficients of Eq. 19.
3. Extrapolate the $c_{V,\text{sys}}$ line to the specific volume of the saturated liquid to obtain $c_{V,\text{sys}(1)}$.
4. Adjust $c_{V,\text{sys}(1)}$ according to Eqs. 21 and 22 to obtain the saturation heat capacity and the constant volume heat capacity of the pure liquid.

Three-phase hydrate system

1. Perform experiments to determine the heat capacity of systems of various specific volumes and total water mole fractions.
2. Regress the heat capacity data, $c_{V,\text{sys}}$, on the system specific volume, v_{sys}, and the total mole fraction of water in the system, x_{wat}, to estimate the coefficients of Eq. 20.

3. Extrapolate the $c_{V,sys}$ plane to the specific volume of pure hydrate and to the total mole fraction of water in pure hydrate to obtain $c_{V,sys(3\text{-}h)}$.

4. Adjust $c_{V,sys(3\text{-}h)}$ according to Eq. 25 to obtain $c_{V,h}$, the heat capacity of pure one-phase hydrate.

Experiment

Apparatus

All of the experiments were performed using a Perkin-Elmer model DSC-2 differential scanning calorimeter which was interfaced to an Apple II Plus microcomputer. The interfacing set-up is described in detail by Rueff (1983). Subambient temperatures were achieved by filling the DSC-2 fluid bath with a mixture of ethanol and dry ice. Extra-dry nitrogen was used to purge the DSC head during the experiments.

Because of the pressures generated by carbon dioxide and by methane hydrates at and below ambient temperature, it was necessary to use Perkin-Elmer high-pressure stainless steel DSC capsules for these measurements. It was necessary, in all of these experiments, to replace the copper gaskets that Perkin-Elmer sells with the capsules with indium gaskets and indium disks of our own construction. Samples sealed using the indium seals easily contained pressures in excess of 2,000 psia (14MPa).

Each of the samples were weighed on a Cahn 4700 electrobalance, which had a precision of 0.01 mg. The carbon dioxide samples were weighed both before and after the experiments to insure that no loss of mass occurred during the DSC scan. This same procedure could not be applied to the methane hydrate samples because, once dissociated, the hydrates were not easily formed again.

Procedure: sample cell volume

The total internal volumes of the sample capsules were determined by observing the temperature at which the DSC thermogram took a sudden and dramatic drop when each capsule was filled with carbon dioxide. Each of the carbon dioxide scans exhibited such behavior. The thermogram drop temperature represents the point at which the system makes the transition from a two-phase system to a one-phase system. For systems which have a total density less than the critical density of carbon dioxide, this is the point at which the last droplet of liquid evaporates. For systems which have a total density greater than the critical density of carbon dioxide, this is the point at which the system becomes entirely liquid. In either case, the density of the saturated phase at this temperature may be obtained from a good equation of state. Since the total system mass is known, it is a simple matter to calculate the total volume of the high-pressure capsules. The total volume of the capsule used for the carbon dioxide experiments, as determined by this procedure, was 23.51 μL with a standard deviation of 0.535 μL. The total volume of the capsule used in the methane hydrate experiments was 23.54 μL with a standard deviation for six samples of 0.212 μL. The carbon dioxide system densities were calculated from a 32 parameter equation of state computer program for carbon dioxide which was developed and coded by Dr. James F. Ely at the National Bureau of Standards in Boulder, Colorado. The program is called "PROPS."

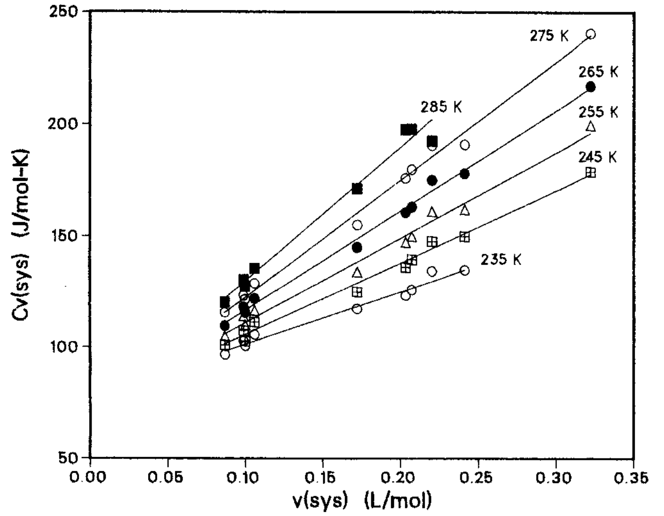

Figure 1. Carbon dioxide two-phase system heat capacity.

Heat capacity measurements

The carbon dioxide samples were scanned across 10 K intervals from 230 to 290 K at 5 K/min.

Two types of experiments were performed on the hydrate samples. One type of experiment was designed to yield the hydrate heat capacity; the other was designed to measure the internal energy of hydrate dissociation.

All of the methane hydrate samples were scanned across 10 K intervals from 230 to 260 K at a scan rate of 2.5 K/min. The heat capacity of the samples was calculated by both the enthalpy method (for average heat capacities) and the scanning method (for heat capacities at individual temperatures) as outlined by Mraw (1986). The next step in the procedures involved scanning the interval from 270 K to the end of the ice/water phase transition peak at 1.25 K/min. This peak indicated how much ice was in the sample before any hydrate dissociation occurred above the ice point.

Heat of dissociation

To determine the internal energy of dissociation of the hydrate, a 20 K temperature interval was scanned, beginning at the end of the ice/water phase transition, at a scan rate of 2.5 K/min. To calculate the heat capacity above the ice point, on the other hand, 5 K intervals from 280 K to the temperature at which hydrate dissociation ceased were scanned using a scan rate of 1.25 K/min. The endpoint of hydrate dissociation produced an effect on the DSC thermogram which was similar in form to the thermogram drop accompanying the two-phase/one-phase transition of the carbon dioxide samples.

The amount of water in each hydrate sample was determined

Table 1. Slopes and Confidence Intervals of Eq. 19

T Avg. (K)	PROPS	Slope Regression (J/L · K)	95% Regression Confidence Intervals
235	244.17	235.93	41.15
245	298.54	323.09	33.15
255	359.47	382.80	40.87
265	428.40	447.58	31.91
275	508.25	526.94	42.63
285	610.68	599.41	98.66

Table 2. Intercepts and Confidence Intervals of Eq. 19

T Avg. (K)	PROPS	Intercept Regression (J/mol · K)	95% Regression Confidence Intervals
235	75.460	77.907	6.962
245	73.370	73.558	6.297
255	72.577	72.753	7.772
265	72.005	71.956	6.067
275	71.754	69.839	8.098
285	71.129	70.082	15.582

by chilling the sample to liquid nitrogen temperatures and venting the capsule. The chilling step froze the system water and minimized the amount of water that might leave the cell in the vented methane vapor. The capsule was closed, brought to ambient temperature, then rechilled and vented. By performing this chill-and-vent step three times and weighing the cell after each time, it was possible to determine the amount of water, and, hence, the amount of methane in the original sample. Since the total volume of the cell was known, it was possible to divide by the total number of moles of both chemical species in the sample to obtain the system specific volume.

Results and Discussion

Carbon dioxide heat capacity

Equation 19 describes the relationship between specific volume and heat capacity for a closed, constant-volume, two-phase, pure component system. A pure material, encapsulated in a high-pressure DSC capsule, represents such a system as long as the sample is in the two-phase region. The experiments on samples of carbon dioxide were designed to test the ability of the DSC to discern the relationship in Eq. 19 and to test the general experiment principle for two-phase systems. For carbon dioxide, the temperature range from 217 to 304 K constitutes the liquid-vapor two-phase region.

The raw carbon dioxide data are presented graphically in Figure 1. This figure also shows the lines resulting from simple linear regression of each data set. Tables 1 and 2 give the slopes and intercepts of the regression lines, their respective 95% confidence intervals, and a comparison to the slopes and intercepts predicted by the PROPS equation of state computer program.

The great utility of Eq. 20 is that manifested in Eq. 25. That is, in order for Eq. 20 to be useful, it must be extrapolated to the properties of the condensed hydrate phase. By analogy, the most important application of Eq. 19 is that given in Eq. 21 and 22. To test the accuracy of the general experiment principle, it was necessary to extrapolate the carbon dioxide data to the condensed phase (liquid) specific volume and to make the adjustments indicated in Eqs. 21 and 22. Table 3 shows the value of $c_{V,\mathrm{sys}}$ that results when the regression models and the PROPS prediction lines are each extrapolated to the specific volume of the saturated liquid at the interval midpoint temperature. Table 3 also shows 95% prediction intervals on the extrapolated value of $c_{V,\mathrm{sys}}$ at v_l.

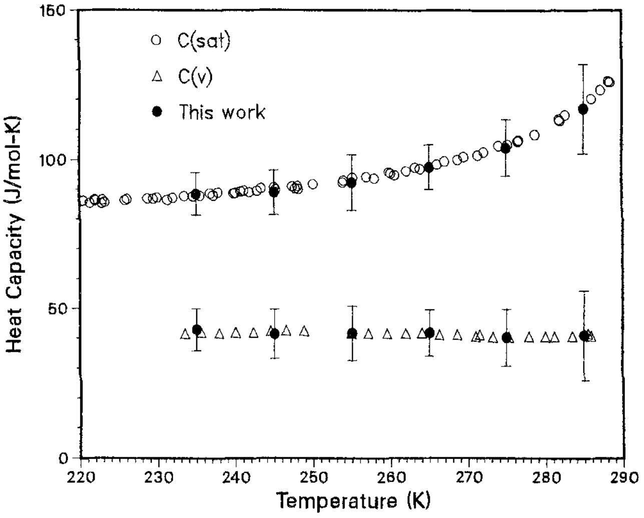

Figure 2. Carbon dioxide liquid heat capacity: saturation and constant volume.

Figure 2 illustrates how the calculated values of $c_{\sigma,l}$ and $c_{V,l}$ compare to the measurements of Magee and Ely (1985).

Hydrate heat capacity

Table 4 shows the raw data for average heat capacity experiments involving methane hydrate systems. This table gives the data for average $c_{V,\mathrm{sys}}$ across 10 K temperature intervals from 240 to 250 K and from 250 to 260 K. Table 5 presents similar data obtained by the DSC scanning method at four individual temperatures. The two-dimensional sample space map for these data is shown in Figure 3. Tables 6 and 7 present the results of multiple regression analysis on the average heat capacity values. Table 8 shows the results of extrapolating the $c_{V,\mathrm{sys}}$ regression planes to the pure hydrate properties. This table also shows 95% prediction intervals for each extrapolated value of $c_{V,\mathrm{sys}}$. Table 9 lists the value of $c_{V,h}$, the heat capacity for the pure one-phase hydrate, when the values of Table 8 are adjusted according to Eq 25. Finally, Figure 4 illustrates how these data compare to the low-pressure heat capacity data for structure I cyclopropane hydrate reported by Callanan and Sloan (1982).

Table 3. Condensed-Phase Extrapolation to $c_{V,\mathrm{sys(l)}}$

T Avg. (K)	Specific Volume (L/mol)	$c_{V\mathrm{sys(l)}}$ (J/mol · K) PROPS	Regression	± 95% Interval*
235	0.03971	85.16	87.28	7.44
245	0.04214	86.04	86.88	7.70
255	0.04303	88.05	89.26	9.46
265	0.04520	91.37	92.19	7.35
275	0.04800	96.15	95.13	9.77
285	0.05192	102.84	101.20	15.05

*Prediction Interval

Table 4. Methane Hydrate: Average Heat Capacity

Sample	v_{sys}	x_{wat}	$c_{V,\mathrm{sys}}$ (J/mol · K) 245 K	255 K
A	0.05898	0.9123	42.10	46.98
B	0.03725	0.9020	35.89	37.70
C	0.04562	0.9261	39.75	43.14
D	0.05236	0.8679	38.28	40.48
E	0.04170	0.8849	—	39.31
F	0.05690	0.9350	43.01	—
G	0.04076	0.9361	39.69	41.48

Table 5. Hydrate System: Heat Capacity vs. Temperature*

Sample*	$c_{V,sys}$ (J/mol · K) 255 K	256 K	257 K	259 K
A	42.45	42.90	43.57	45.31
B	36.59	37.59	37.44	37.70
C	40.53	41.27	41.48	42.53
D	37.68	38.54	38.73	39.44
E	36.53	37.49	37.71	38.46
G	39.28	39.50	39.29	40.04

*See Table 4 for sample composition and specific volume.

Heat of hydrate dissociation

Table 10 shows the results of the internal energy of dissociation calculations and the enthalpy of hydrate dissociation for each of six samples. The adjustment from internal energy to enthalpy is based on an average temperature of hydrate dissociation of 285 K. This results in a value for $P\Delta v_{dis}$ of 13.28 J/g.

Discussion

Of primary interest in the carbon dioxide experiments are the slopes and intercepts of the regression lines given in Tables 1 and 2. It is apparent from these results that the DSC is capable of discerning the relationship of Eq. 19 for high-pressure liquid-vapor systems. The slopes and intercepts of the regression lines are very close to those predicted by the PROPS computer program. Furthermore, for each temperature interval, the statistical hypothesis that the regression slope is actually equal to the PROPS prediction slope cannot be rejected at a 95% level of significance. The same is true of the regression intercepts. Of these two statements, however, the one regarding the slopes is the more significant. This is due to the fact that the slope of Eq. 19 is related only to the vapor pressure of the pure material in the system. Accurately predicting carbon dioxide vapor pressure is one of the simpler tasks that PROPS performs.

Of more practical importance, however, is the ability of the general experiment principle to produce accurate saturation and one-phase heat capacities for the condensed phase from DSC data. This requires that the regression lines be extrapolated to the specific volume of pure, saturated liquid carbon dioxide at each interval midpoint temperature. Table 3 indicates that the data regression compares extremely well with the PROPS program when each is extrapolated to the specific volume of the liquid phase. With the exception of the value at 235 K, the data regression extrapolation agrees with the PROPS program values to within about 1.6%. Figure 2 indicates that the general experiment principle is workable for liquid-vapor systems with a differential scanning calorimeter. The DSC data compare very well with the experimental data of Magee and Ely (1985).

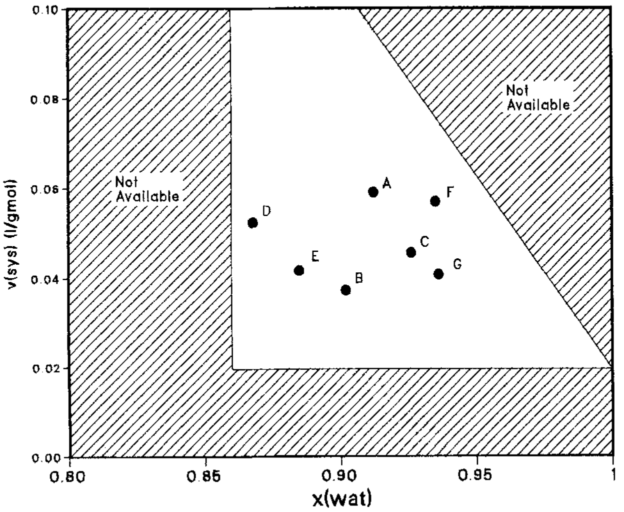

Figure 3. Allowable sample space: methane hydrate experiments.

Table 6. Statistical Analysis of Average Heat Capacity Data at 245 K

Coeff.	Value	Std. Dev.	t-ratio	±95% Confidence Interval
a	−26.551	6.822	−3.89	33.128
b	245.07	21.36	11.48	103.69
c	59.585	7.292	8.17	35.41

Standard Deviation about the regression line = 0.4204 J/mol · K.

It was much more difficult to measure the heat capacity of the three-phase, methane hydrate systems than it was the two-phase carbon dioxide systems. This is due largely to the differences in the physical properties of each type of sample. Still, the methane hydrate experiments established that the technique presented here is workable as a method of determining the heat capacity of pure gas hydrates.

Tables 6 and 7 indicate that the two "slope" coefficients of Eq. 20 are statistically significant at a 95% level of significance. The constant, *a*, in Eq. 20, is significant at about a 90% level of significance for both temperature intervals. Furthermore, the coefficient, *b*, calculated from the slope of the methane hydrate vapor pressure curve, compares reasonably well with the value obtained from regression of the heat capacity data. At 245 K, the coefficients differ by about 17.6%. At 255 K, this difference is about 4.6%. In both cases, however, the statistical hypothesis that the regression coefficient is actually equal to the coefficient calculated from the vapor pressure data cannot be rejected at a 95% level of significance.

The heat capacity data obtained by the scanning method at four individual temperatures in the region from 250 to 260 K were far more scattered than the average heat capacity data. This implies that the hydrate sample may have lagged the DSC-indicated temperature slightly throughout the scan. Only the beginning and ending temperatures and the total heat input is important to the average heat capacity, but for individual heat capacity values, it is essential that the sample temperature be

Table 7. Statistical Analysis of Average Heat Capacity Data at 255 K*

Coeff.	Value	Std. Dev.	*t* ratio	±95% Confidence Interval
a	−42.21	11.95	−3.53	58.029
b	366.67	39.67	9.24	192.64
c	73.84	12.66	5.83	61.48

*Standard Deviation about the regression line = 0.7089J/mol · K.

Table 8. Extrapolated System Heat Capacities and 95% Prediction Intervals

Temp. (K)	$c_{V,sys}$ (J/mol · K)	±95% Interval
245	29.47*	2.82
255	28.44*	4.78
255	29.43**	2.23
256	30.98**	3.71
257	30.27**	4.76
258	29.29**	5.74

*Average $c_{V,sys}$ at 10 K interval midpoint.
**$c_{V,sys}$ at individual temperatures.

known. Nevertheless, all except one of the b and c coefficients were statistically significant for the heat capacity planes at each of these temperatures.

For the purposes of extrapolating the heat capacity plane, it is important to keep in mind that the specific volume is in terms of liters per *total number of molecules in the system.* It is not in terms of liters per mole of hydrate. The nature of Eq. 20 demands this distinction.

Aside from the data of Comper et al. (1983) the data in Figure 4 are the only other data that exist for the heat capacity of structure I hydrates. Unfortunately, it is impossible to compare the results of that study to this one in this temperature range.

The prediction intervals of this study bracket the regression line for the data of Callanan and Sloan, with the exception of $c_{V,h}$ calculated by the scanning method at 255 K. At 245 K, in fact, the data points of each study are quite close.

A 95% prediction interval for the structure I cyclopropane hydrate data of Callanan and Sloan, extrapolated to 5 K below the lowest temperature data point in their study, serves as a means of error comparison to the results of this study. This interval and extrapolation point is shown in Figure 4. The size of such a prediction interval is on the same order as the prediction intervals of this study. This is particularly significant because their data is the result of straightforward low-pressure DSC heat capacity measurements. The results of this work, on the other hand, come from the general experiment principle applied to high-pressure differential scanning calorimetry. The confidence intervals around individual data points are about the same in each study.

Figure 5 shows the heat capacity of hydrates formed from several different types of guest molecules. Of these data, only Cherskii et al. (1982) and this study report the heat capacity of high-pressure gas hydrates. The composition of the gas used to form the hydrates of that study suggests that theirs was a structure II hydrate. The relationship reported by Cherskii, et al. is so much higher than the other hydrate data that it may be suspect. They may have hydrate had dissociation occurred during the sample heat capacity measurements.

Table 9. Pure One-Phase Methane Hydrate Heat Capacity

Temp. (K)	$c_{V,h}$ (J/g · K)	±95% Prediction Interval
245	1.62	0.16
255	1.56	0.27
255	1.61	0.13
256	1.70	0.21
257	1.66	0.27
259	1.61	0.32

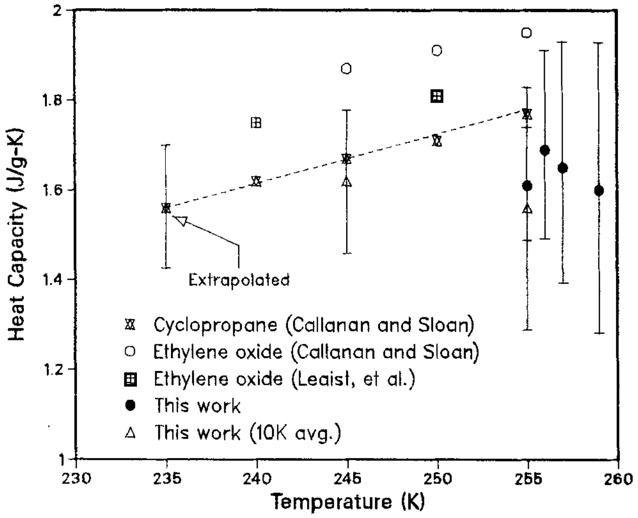

Figure 4. Structure I hydrate: heat capacity.

Finally, it must be noted that the methane hydrate data reported in this study represent $c_{V,h}$, the hydrate heat capacity at constant volume. All other data in Figure 5 are reported as c_p, the heat capacity at constant pressure. The solid hydrate mass is so incompressible, however, that the difference in $c_{p,h}$ and $c_{V,h}$ is on the order of one-tenth of one percent. The comparison of the results of this work to the rest of those in Figure 5 is, therefore, entirely justified.

Hydrate heat of dissociation

The average internal energy of hydrate dissociation above the ice point for the six samples shown in Table 10 is 416.38 J/g. The average enthalpy of dissociation is, therefore, 429.66 J/g. The standard deviation for six samples was 6.01 J/g.

The enthalpy of dissociation may be calculated from the Clausius-Clapeyron equation. If the slope of the vapor pressure curve (plotted as ln$p$ vs. $1/T$) is constant, then the enthalpy of hydrate dissociation varies linearly with the compressibility factor, Z. If we assume that the ratio of water to methane in the

Table 10. Heat of Hydrate Dissociation for Methane Hydrate and 95% Confidence Intervals

Sample	Δu_{diss} (J/g)	Δh_{diss} (J/g)
AA	418.25	431.53
BB	423.38	436.66
CC	422.28	435.56
DD	414.26	427.54
EE	412.17	425.45
FF	407.95	421.23
Avg.	416.38	429.66
Std. Dev.	6.01	6.01
±95% Interval	6.31	6.31

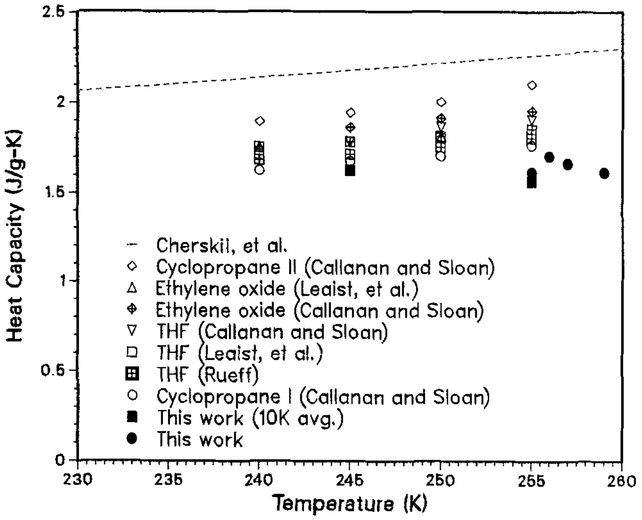

Figure 5. Hydrate heat capacity.

pure hydrate is 6.15:1, then the hydrate molecular weight is 126.81 g/mol. Furthermore, if we assume an average temperature of dissociation of 285 K and use the Peng-Robinson equation of state to calculate Z, then the Clausius-Clapeyron equation yields a value for the enthalpy of methane hydrate dissociation of 431.15 J/g. This differs from the average value determined by this study by only 0.35%.

Villard measured the heat of formation of carbon dioxide hydrate in 1897 and found it to be 63,000 J/mol. Carbon dioxide forms a structure I hydrate. If its molar ratio of water to guest molecules is the same as that for methane hydrate, then the molecular weight is 154.82 g/mol and the heat of formation is 406.92 J/g. Nagayev et al. (1979) measured the heat of dissociation of carbon dioxide hydrate and found it to be 57,980 J/mol (374.40 J/g) at 281 K and 53,100 J/mol (342.98 J/g) at 279 K.

Summary

Differential scanning calorimetry may be used, in conjunction with the principles set forth in this work, to determine both the heat capacity at constant volume and the heat of hydrate dissociation of pure gas hydrates. The method is quite sensitive to the accuracy of the system heat capacity measurements, however, and a more accurate calorimetry technique may provide very precise heat capacity values for pure gas hydrates of many kinds.

Acknowledgments

The authors gratefully acknowledge the U.S. Department of Energy for funding this research, which was performed at the Colorado School of Mines, under project DE-AC21-83MC20693. We also are grateful for the assistance of Dr. James F. Ely, who provided the PROPS computer program and shared his expertise in the thermodynamics of pure carbon dioxide systems.

Notation

$c_{V,h}$ = constant-volume heat capacity of pure hydrate
$c_{V,sys}$ = *constant-volume heat capacity of the system*
$c_{V,v}$ = constant-volume heat capacity of vapor
$c_{V,l}$ = constant-volume heat capacity of liquid
$c_{\sigma,v}$ = saturation heat capacity of vapor
$c_{\sigma,l}$ = saturation heat capacity of liquid
s_{sys} = specific entropy of the system
S_{sys} = total entropy of the system
v_{sys} = specific volume of the system
V_{sys} = total volume of the system
v_h = specific volume of pure hydrate
v_V = specific volume of vapor
x = mole fraction
Z = compressibility

Greek letters

σ = saturation condition
Δu = change in specific system internal energy
μ = chemical potential

Literature Cited

Bily, C., and J. W. L. Dick, "Naturally Occurring Gas Hydrates in the Mackenzie Delta, Northwest Territories," *Bull. Can. Petr. Geol.*, **22**, 340 (1974).

Callanan, J. E., and E. D. Sloan, Final Report, GRI Contract No. 5081-350-0487 (1982).

Cherskii, N. V., A. G. Groisman, L. M. Nikitina, and V. P.Tsarev, "Results of the First Experimental Determination of Heats of Decomposition of Natural Gas Hydrates," *Doklady Akademii Nauk SSSR*, **265**(1), 185 (1982).

Cherskii, N. V., A. G. Groisman, V. P. Tsarev, and L. M. Nikitina, "Thermophysical Properties of Hydrates of Natural Gases," *Dokl. Akad. Nauk SSSR (Geol.)*, **270**(4) 949 (1983).

Comper, J., A. Quesnel, C. A. Fyfe, and R. K. Boyd, "Experimental Study of the Structure I Clathrate Hydrate of Trimethylene Oxide by Adiabatic Calorimetry," *Can. J. Chem.*, **61**, 92 (1983).

Deaton, W. M., and E. M. Frost, "Gas Hydrates and Their Relation to the Operation of Natural Gas Pipelines," *Oil and Gas J.*, **45**(12), 170 (1947).

Deaton, W. M., and E. M. Frost, U.S. Bureau of Mines Monographs No. 8 (1946).

Goodwin, R. D., and L. A. Weber, "Specific Heats of Oxygen at Coexistence," *J. Res. of NBS A. Phys. and Chem.*, **73A**(1), (1969).

Harris, I., "Composition Of Cl Hydrate," *Nat.*, **141**, 309 (1943).

Holder, G. D., V. T. John, and S. Yen, "Geological Implications of Gas Production from *in-situ* Gas Hydrates Unconventional Gas Recovery Symposium," SPE/DOE 8929 (May, 1980).

Judge, A., *Proc. Can. Permafrost Conf.*, 320 (1982).

Leaist, D. G., J. J. Murray, M. L. Post, and D. W. Davidson, "Enthalpies of Decomposition and Heat Capacities of Ethylene Oxide and Tetrahydrofuran Hydrates," *J. Phys. Chem.*, **86**(21), 4175 (1982).

Magee, J., and J. Ely, "Specific Heats (Cv) of Saturated and Compressed Liquid and Vapor Carbon Dioxide," *Int. J. Thermophys.*, **7**, (6), 1163 (1986).

Makogon, Y., *Hydrates of Natural Gas*, Penwell Publishing, Tulsa, OK (1981).

———, *Proc. Can. Permafrost Conf.*, 299 (1982).

McGuire, P. L., "Methane Hydrate Gas Production: Evaluating and Exploiting the Solid Gas Resource," Int. Conf. on Alternative Energy Resources, Miami (1981).

———, "Methane Hydrate Gas Production by Thermal Stimulation," *Proc. Can. Permafrost Conf.* (1982).

Mraw, S., *Specific Heat in Solids*, A. Cezairliyan, ed., CINDAS, Purdue Univ. Press, West Lafayette, IN (1986).

Nagayev, V. B., A. I. Gritsenko, and V. I. Murin, All-Union Conf. on Calorimetry and Chemical Thermodynamics, Ivonovo, *Proc. 1-NOR*, 58 (1979).

Rice, O. K., and D. Chang, "Some Thermodynamic Relations at the Critical Point in Liquid-Vapor Systems," *Proc. Nat. Acad. Sci.*, **69** (11), 3436 (1972).

Rueff, R. M., "The Heat Capacity and Heat of Dissociation of Methane Hydrates: a New Approach," PhD Thesis T-2985, Colorado School of Mines (1985).

———, "The Effect of Sediment on Tetrahydrofuran Hydrate: a Study in Differential Scanning Calorimetry," MS PhD Thesis T-2693 Colorado School of Mines (1983).

Saito, S., D. R. Marshall, and R. Kobayashi, "Hydrates At High Pressure: Part II Applications Of Statistical Mechanics To The Study Of The Hydrates Of Methane, Argon, and Nitrogen," *AIChE J.*, **10**(5), 734, (Sept. 1964).

Sortland, L. D., and D. B. Robinson, "Hydrates Of CH_4 and SF_6," *Can. J. Chem.*, 38 (Feb., 1964).

Stackelburg, M., *Naturwiss*, **36**, 327, 359 (1949).

Weaver, J. S., and J. M. Stewart, *Proc. Can. Permafrost Conf.*, 312 (1982).

Yang, C. N., and C. P. Yang, "Critical Point In Liquid-Gas Transition," *Phys. Rev. Let.*, **13**(9), 303 (1964).

Manuscript received Feb. 24, 1987, and revision received Apr. 20, 1988.