The thermodynamic properties of norbornane, the bicyclo[2,2,1] system and the application to solar energy.[a,b]

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Short title: PROPERTIES OF NORBORNANE

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ABSTRACT

Measurements leading to the calculation of the standard thermodynamic properties for norbornane (bicylo[2,2,1]heptane) (Chemical Abstracts registry number [279-23-2]) via adiabatic heat-capacity calorimetry measurements are reported. Standard molar entropies, standard molar enthalpies, and standard molar Gibbs free energies are reported at selected temperatures between 10 K and 380 K. Discussion of ab Initio calculations and the problems with values determined by Density Functional Theory follows. Comments are made on the possibility of the bicylo[2,2,1]heptane system forming the foundation of a cheap solar energy system in the Developing World.

Keywords: bicylo[2,2,1]heptane, heat capacity, condensed thermodynamic properties, enthalpy of fusion, triple-point temperature, phase transition

1. INTRODUCTION

Fossil fuels continue to supply greater than 85 percent of the energy needs of the United States, and their combustion accounts for greater than 90 percent of the greenhouse gas (GHG) emissions in the contiguous 48 states [i]. In a recent article in Environmental Progress, Klara and Srivastava [ii] note, “The Energy Information Administration within the U.S. Department of Energy (DOE) projects U.S. consumption of coal, oil, and natural gas to increase by 40 percent and carbon emissions to rise by 33 percent over the next 20 years.” If these projections are correct, carbon sequestration then becomes very important, if GHG emissions are to be contained. One can visualize some means of carbon sequestration when considering reduction of CO_2(g) emissions from power plants and other industrial entities. Klara and Srivastava [ii] list five such technologies (separation and capture; geological sequestration; terrestrial sequestration; oceanic sequestration; and novel sequestration systems) that are being pursued within the DOE’s Office of Fossil Energy’s (FE) carbon sequestration effort. However, when total U.S. carbon emission sources are considered, 33 percent of the total arises from transportation. It is difficult to envision any of the five technologies listed above resulting in significant carbon sequestration in the transportation sector. Implementation of technologies resulting in capture of the CO_2(g) would, in turn, lower fuel efficiency with the excess weight of the capture system accounting for most of the decrease.

Decreasing the GHG emissions in the transportation sector can be accomplished by increased engine efficiency, lighter materials for vehicle construction, etc., and by fuel changes. This series of papers of which this is Part 1 considers the latter. Modern gasolines have aromatic contents in the range of 25 to 35 volume percent. Diesel fuels have similar aromatic contents made up of one, two, and even three-ring systems (alkylbenzenes, alkylnapththalenes and alkylphenanthrenes). Increasing the content of napthenes (saturated rings) in these fuels via hydrogenation of the aromatic systems would result in products with an increased energy of combustion: “Designer Gasoline” and “Designer Diesel Fuel.” These “designer” fuels would have increased miles per unit of CO_2(g) production. In addition studies by CARB (California Air Resources Board) [iii] have shown that reduction of aromatics in gasoline engines leads to a cooler-burning engine with less benzene and NO_x formation and engine deposits. Similarly, reducing diesel aromatics from 30 percent to 10 percent reduces NO_x formation by greater than 5 percent. Reductions in polyaromatic hydrocarbon (PAH) content results in significant decreases in particulate (soot) content. Also, toxic PAH emissions in the exhaust are directly related to the amount of PAH in the fuel [iv].

This series of papers details thermodynamic property measurements on molecular entities that form the foundation from which the corresponding properties can be derived for other

structurally related compounds present in an existing or hypothetical fuel. For example, this paper reports properties for norbornane [bicyclo(2,2,1)heptane) see Figure 1, and a “structurally related compound” would be any containing the cyclopentyl substructure. To expand the example further, the reported experimental heat capacities could be used in combination with any of the estimation techniques listed in Chapter 3 of reference v (The Properties of Gases and Liquids) to derive a correction factor for five-membered-rings and/or bridged-ring systems for that particular scheme. At a higher level, the improved estimation technique may then be used to develop pseudo-heat capacities for naphthenic fractions containing cyclopentyl and bridged-ring entities. As most petroleum naphthenic fractions are comprised extensively of compounds constructed of 5- and 6-membered ring systems, the importance of the cyclopentyl group is clear.

This paper includes details of the measurements leading to the determination of the standard thermodynamic properties for norbornane in the condensed state. An earlier paper [vi] reported measurements made by rotating-bomb combustion calorimetry. No detailed heat capacity measurements were found in the literature for comparison with those reported here.

2. EXPERIMENTAL

MATERIALS

The sample of norbornane was synthesized as part of the American Petroleum Institute Research Project 58 at Carnegie-Mellon University. Prior to loading into the measurement cell, the sample was degassed through a series of freeze-pump-thaw cycles. The mole-fraction purity (x = 0.9985) of the sample was determined by fractional melting as part of the adiabatic heat-capacity calorimetric studies reported here. The sample used in this research is the same batch as that used in the determination of the enthalpy of combustion published previously by Steele [vi].

PHYSICAL CONSTANTS AND STANDARDS

Molar values are reported in terms of M = 96.1718 $g \cdot mol^{-1}$ norbornane, and the gas constant R = 8.314472 $J \cdot K^{-1} \cdot mol^{-1}$ adopted in 1998 by CODATA [vii]. The platinum resistance thermometers used in these measurements were calibrated by comparison with standard thermometers whose constants were determined at the National Bureau of Standards (NBS), now the National Institute of Standards and Technology (NIST). Temperatures were measured in terms of IPTS-48 for temperatures between T = 90 K and T = 400 K and in terms of a provisional scale of the National Bureau of Standards between 11 K and 90 K[viii], and were converted approximately to ITPS-68 [ix] with published temperature increments. Further conversion to ITS-90 was not justified because of the uncertainties involved. Measurements of mass, time, electrical

resistance, and potential difference were made in terms of standards traceable to calibrations at NIST.

APPARATUS AND PROCEDURES

Heat-capacity and enthalpy measurements were made with an adiabatic calorimetric system described previously [x]. The calorimeter characteristics and sealing conditions are given in table 1. The energy increments to the filled platinum calorimeter were corrected for enthalpy changes in the empty calorimeter vessel, for the helium exchange gas, and for vaporization of the sample into the free space of the sealed vessel. The maximum correction to the measured energy for the helium exchange gas was 0.07 percent near 11.5 K. The sizes of the other two corrections are indicated in table 1.

3. RESULTS

ADIABATIC HEAT-CAPACITY CALORIMETRY

Crystallization and Melting Studies. Crystallization of norbornane was initiated by slow cooling (approximately 2 $mK \cdot s^{-1}$) of the liquid sample. After initial crystallization, the sample was reheated and maintained under adiabatic conditions in the partially melting state (5 percent to 10 percent liquid) for approximately 2 hours, followed by cooling at an effective rate of 2 $mK \cdot s^{-1}$ to crystallize the remaining liquid. All of the solid-phase measurements were performed upon crystals pre-treated in this manner.

The triple-point temperature T_{tp} and the mole fraction purity x were determined by measurement of the equilibrium melting temperatures T(F) as a function of fraction F of the sample in the liquid state [xi]. The sample was allowed to equilibrate for 8 to 16 hours between heats. The observed temperatures at the end of the equilibration period are listed in table 2 with the corresponding fractions melted. No evidence for the presence of solid-soluble impurities was found. Published procedures [xi] were used to derive the mole fraction purity x and T_{tp}. The results are summarized in table 2.

Phase Transformations and Enthalpy Measurements. Two solid-to-solid phase transitions were detected in addition to the crystal-to-liquid transition. Figure 1 shows the complete heat-capacity results obtained in this research including all phase transitions. Experimental molar enthalpy results are summarized in table 3. The table includes both transition enthalpies and single-phase measurements, which serve as checks on the integration of the heat-capacity results. All phase transition enthalpies showed good repeatability. Cooling rates used for phase conversion ranged between approximately 0.05 and 0.1 $mK \cdot s^{-1}$. Corrections for premelting caused by impurities were made in these evaluations. Results with the same series number in tables 3 and 4 were taken without interruption of adiabatic conditions.

Equilibrium was reached in less than 1 h for all measurements in the liquid phase and for measurements in the solid phase not in the vicinity of the phase-transition temperatures. As the triple-point temperature (T_{tp} = 360.502 K) was approached, the equilibration times increased gradually from less than 1 h near 300 K to approximately 12 h near 360 K. This increase in equilibration times as the triple-point temperature is approached is typical for organic compounds of high purity.

Measurements in the region of the cr(II) to cr(I) transition are shown in figure 1. Equilibration times increased dramatically to several days in the transition region. The maximum value shown on the Figure 1 ($C_{sat,m}/R \approx 30.5$ in measurement series 16) was used to estimate T_{trs}. = 306.07 K. The very long equilibration times involved in series 16 made corrections for heat leaks very uncertain. Consequently, results from this series were not averaged with the value of the enthalpy of transition determined using series 1 and 17.

Measurements in the region of the cr(III) to cr(II) transition are also shown in figure 1. Equilibration times increased to approximately 12 h near the estimated transition temperature T_{trs} = (131.487) K. Again, the very long equilibration times involved in series 7 and 14 made corrections for heat leaks very uncertain. However, results from these series were consistent and hence, were averaged with the value of the enthalpy of transition determined using the single heat in series 15.

The experimental molar heat capacities under vapor saturation pressure $C_{sat,m}$ are listed in table 4. Values in table 4 were corrected for effects of sample vaporization into the free space of the calorimeter vessel. The maximum vaporization correction was only $0.015 \cdot C_{sat,m}$, as indicated in table 1. The temperature increments were small enough to obviate the need for corrections for nonlinear variation of $C_{sat,m}$ with temperature except near the transition temperatures. The estimated uncertainties in the heat-capacity measurements range from approximately 5 percent at 5 K, to 0.5 percent at 10 K, and improve gradually to better than 0.1 percent above 30 K. Heat capacities were extrapolated to T_0 with a Debye function fitted by least squares to heat capacities below T = 20 K. The Debye characteristic temperature and the number of degrees of freedom were adjusted in the fit.

Condensed-phase molar entropies and molar enthalpies relative to that of the crystals at $T \rightarrow 0$ for the solid and liquid phases under vapor saturation pressure are listed in table 5. These were derived by integration of the smoothed molar heat capacities, corrected for pre-melting, together with the molar entropy and molar enthalpy of fusion. The molar heat capacities were smoothed with cubic-spline functions by least-squares fits to six points at a time and by requiring continuity in value, slope, and curvature at the junction of successive cubic functions. Due to limitations in the spline-function procedure, some acceptable values from table 4 were not included in the fit, while in other regions graphical values were introduced to ensure that the

second derivative of the heat capacity with respect to temperature was a smooth function of temperature. Pre-melting corrections were made using standard methods [xi] for solid-insoluble impurities and the mole-fraction impurity value shown in table 1.

4. DISCUSSION

A search of the literature located few significant thermochemical or thermophysical property measurements on norbornane. Most reports were limited to measurement of a boiling temperature at reduced pressure obtained during synthesis or purification of the compound or a density value at a single temperature for the liquid phase. An enthalpy of formation study by Verevkin and Emel'yanenko (xii) noted that their sample of norbornane did not undergo the phase transition at 305.9 K observed by Steele (vi) in his earlier study. Please note that the transition corresponds to that reported in this research as occurring at 306.07 K (see table 3).

Interest in norbornane compounds has been maintained lying in their potential use as energy storage systems. The norbornadiene – quadricyclane system in particular continues to be studied as a solar energy container. Norbornadiene can be converted, even in cold climes such as the Artic to its high-energy isomer quadricyclane by the ultraviolet component of sunlight. It can then be stored and regenerated into norbornadiene by flowing over a suitable catalyst with the evolution of heat [greater than 100 kJ.mol-1 (vi)]. The cycle can be repeated indefinitely, see review in reference [xiiI].

"One of the most attractive features of contemporary molecular orbital calculations is the ease with which one can compute fundamental thermodynamic properties that are difficult or impossible to obtain by classical experimental means." – the opening quote in a paper by Rogers and McLafferty [xiii] on the norbornadiene cycle in 1999. However, the various methods and levels of theory given by Rogers and McLafferty and by Verevkin and Emel'yanenko (xii) do not give one a cozy felling that such calculations are of sufficient accuracy to be reliable in equilibria calculations. Maybe, the thermodynamic properties for norbornane given in this paper can be used to iron out some of the problems with the computational methods. Derivation of the ideal gas entropies and comparison with values determined via computation of the fundamental frequencies (an example of which is given in our last publication on dimethylquinolines [xiv]) may aid in solving the problems clearly present.

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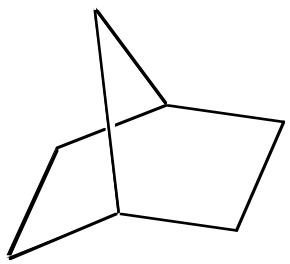
TABLE 1. Calorimeter and sample characteristics for adiabatic heat-capacity calorimetry studies: m is the sample mass; V_i is the internal volume of the calorimeter; T_{cal} is the temperature of the calorimeter when sealed; p_{cal} is the pressure of the helium and sample when sealed; $r(T_{max})$ is the ratio of the heat capacity of the full calorimeter to that of the empty at the highest temperature of the measurements; r_{min} is the lowest observed value for the ratio of the heat capacity of the full calorimeter to that of the empty; $(\delta C/C)_{max}$ is the maximum vaporization correction; and x_{pre} is the mole-fraction impurity used for premelting corrections.

Norbornane, Bicyclo[2,2,1]heptane



m / g	43.363
V_i(298.15 K) / cm^3	59.86
T_{cal} / K	295
p_{cal} / kPa	45.0
$r(T_{max})$	4.5
r_{min}	2.8
$10^2 \cdot (\delta C/C)_{max}$	0.015
x_{pre}	0.0015

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TABLE 2. Melting-study summaries for norbornane: F is the fraction melted at observed temperature T(F); T_{tp} is the triple-point temperature; x is the mole-fraction impurity

F	T(F)/K
0.1550	359.3
0.2877	359.643
0.5274	359.894
0.7221	360.008
0.9164	360.113

T_{tp} = 360.50 K
x = 0.0015

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TABLE 3. Molar enthalpy measurements for norbornane

N [a]	h [b]	T_i / K	T_f / K	T_{trs} / K	$\Delta_{tot}U_m$ [c] / R.T	$\Delta_{trs}H_m$ [d] / R.T
			Single-phase measurements in cr (III)			
15	1	91.952	108.315	-	117.73	0.005
			cr(III) to cr (II)			
7	5	121.625	139.406	131.487	676.95	497.19
14	8	122.870	136.877		637.38	498.52
15	1	108.315	138.595		772.23	496.99
					Average:	497.09
			Single-phase measurements in cr (II)			
15	1	138.483	292.832	-	2077.90	0.41
			cr(II) to cr (I)			
16	6	296.026	308.88	306.070	225.59	9.13 [e]
3	2	297.970	315.708		311.91	10.01 [e]
1	2	295.926	312.224		285.01	9.68
17	3	296.478	312.100		273.77	9.70
					Average:	9.68
			cr(I) to liquid			
2	4	329.076	365.155	360.502	1256.55	549.54
5	6	337.362	364.110		1079.69	549.44
19	1	341.692	364.124		997.96	549.04
					Average:	549.34

[a] Adiabatic series number.

[b] Number of heating increments.

[c] $\Delta_{tot}U_m$ is the molar energy input from the initial temperature T_i to the final temperature T_f.

[d] $\Delta_{trs}H_m$ is the net molar enthalpy of transition (or melting) at the transition temperature T_{trs} or the excess enthalpy relative to the heat-capacity curve described in the text for single-phase measurements.

[e] This determination involved long equilibration times resulting in relatively large uncertainties

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TABLE 4. Experimental molar heat capacities for norbornane at vapor-saturation pressure (R = 8.314472 $J \cdot K^{-1} \cdot mol^{-1}$)

N [a]	<T>/K	ΔT/K	$C_{sat,m}/R$ [b]	N [a]	<T>/K	ΔT/K	$C_{sat,m}/R$ [b]
			cr(III)				
12	13.38	0.996	0.632	11	58.34	4.705	5.300
13	13.46	0.971	0.646	11	63.50	5.605	5.570
12	14.58	1.356	0.776	11	69.45	6.285	5.861
13	14.77	1.575	0.801	11	75.93	6.672	6.154
12	16.12	1.719	0.978	11	82.39	6.249	6.423
13	16.40	1.639	1.021	6	87.08	5.554	6.604
12	17.92	1.891	1.233	11	88.86	6.681	6.688
13	18.14	1.833	1.270	6	93.16	6.604	6.872
12	19.87	2.009	1.519	6	99.60	6.290	7.163
13	20.04	1.966	1.545	10	105.72	5.210	7.442
12	22.02	2.296	1.829	6	105.76	6.019	7.454
13	22.31	2.550	1.874	10	110.84	5.028	7.701
12	24.39	2.442	2.168	6	112.09	6.643	7.775
13	24.89	2.613	2.239	14	112.55	7.114	7.774
12	26.90	2.575	2.507	6	118.58	6.343	8.161
13	27.67	2.941	2.609	14	119.49	6.776	8.188
12	29.72	3.066	2.865	7	124.63	6.015	8.703
13	30.79	3.316	2.995	14	126.01	6.278	9.056
13	34.23	3.553	3.385	7	128.92	2.550	27.438
13	38.18	4.343	3.787	14	129.80	1.324	62.295
13	42.70	4.713	4.199	7	130.52	0.661	120.840
13	47.56	4.989	4.582	14	130.72	0.532	162.990
13	52.66	5.207	4.945	14	131.13	0.350	250.600
11	54.15	3.686	5.047	14	131.43	0.329	266.230
			cr(II)				
14	131.78	0.353	248.540	8	240.38	8.854	13.912
14	132.40	0.913	92.572	8	249.13	8.665	14.268
7	132.73	3.754	111.140	9	257.69	8.447	14.620
14	134.86	4.043	16.662	9	266.05	8.265	15.022
7	137.01	4.800	12.104	9	274.23	8.094	15.419
14	139.33	5.065	12.074	3	276.08	8.245	15.440
7	142.18	5.595	12.132	9	283.03	9.499	15.852
7	148.95	7.932	12.093	3	283.78	9.634	15.857
7	156.84	7.859	12.100	3	293.28	9.382	16.378
7	164.66	7.779	12.140	16	299.28	6.501	16.700
7	172.40	7.699	12.201	1	299.76	7.669	16.698
8	180.15	7.973	12.274	17	300.51	8.065	16.739
8	188.09	7.862	12.410	3	302.34	8.744	17.982
8	196.38	8.729	12.573	16	303.47	1.888	16.924
8	205.03	8.583	12.767	16	304.92	1.005	16.921
8	213.49	8.467	12.968	17	305.20	1.315	22.098
8	222.33	9.207	13.266	16	305.75	0.640	30.504
8	231.44	9.028	13.576				
			cr(I)				
1	307.91	8.629	18.205	4	326.68	7.152	18.084
16	306.54	0.939	17.851	4	333.76	7.015	18.502
16	307.95	1.876	16.984	2	334.03	9.902	18.446
17	308.99	6.226	17.576	1	334.64	9.845	18.557
3	311.21	9.000	17.198	18	338.73	7.332	18.811
1	316.65	8.858	17.485	2	343.10	8.257	19.055
4	319.45	7.303	17.624	18	345.99	7.179	19.237
18	323.61	22.910	17.897	2	351.22	7.989	19.582
1	325.40	8.646	18.008				

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TABLE 4. Continued.

N [a]	<T>/K	$C_{sat,m}/R$ [b]	ΔT/K	N [a]	<T>/K	$C_{sat,m}/R$ [b]	ΔT/K
			liquid				
20	364.17	6.354	22.649	2	378.48	8.771	23.495
2	369.63	8.944	22.969	20	379.81	6.153	23.556
20	372.04	9.380	23.090				

a Adiabatic series number.

b Average heat capacity for a temperature increment of ΔT with a mean temperature <T>.

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TABLE 5. Molar thermodynamic functions at vapor-saturation pressure [a,b]

($R = 8.314472\ J \cdot K^{-1} \cdot mol^{-1}$)

$\frac{T}{K}$	$C_{sat,m}/R$	$\frac{\Delta_0^T H_m}{RT}$	$\frac{\Delta_0^T S_m}{R}$	$\frac{T}{K}$	$C_{sat,m}/R$	$\frac{\Delta_0^T H_m}{RT}$	$\frac{\Delta_0^T S_m}{R}$
			cr(III)				
10.00	0.282	0.071	0.095	80.00	6.325	3.481	6.100
20.00	1.538	0.465	0.639	90.00	6.736	3.820	6.868
30.00	2.899	1.057	1.529	100.00	7.181	4.133	7.601
40.00	3.959	1.656	2.516	110.00	7.668	4.432	8.308
50.00	4.761	2.200	3.489	120.00	8.155	4.722	8.996
60.00	5.390	2.682	4.415	130.00	8.688	5.006	9.669
70.00	5.887	3.105	5.284	131.49	8.770	5.048	9.768
			cr(II)				
131.49	12.139	8.832	13.553	220.00	13.182	10.259	19.902
140.00	12.095	9.032	14.312	240.00	13.898	10.531	21.079
150.00	12.092	9.236	15.147	260.00	14.736	10.822	22.224
160.00	12.113	9.415	15.927	280.00	15.702	11.136	23.351
180.00	12.275	9.722	17.362	300.00	16.739	11.474	24.469
200.00	12.652	9.995	18.674	306.07	17.057	11.582	24.808
			cr(I)				
306.07	16.885	11.613	24.839	340.00	18.887	12.238	26.716
310.00	17.115	11.681	25.056	350.00	19.459	12.436	27.272
320.00	17.681	11.860	25.608	360.00	20.029	12.639	27.828
330.00	18.279	12.045	26.161	360.50	20.053	12.649	27.856
			liquid				
360.50	22.414	14.173	29.380	380.00	23.568	14.626	30.591
370.00	22.992	14.392	29.971				

[a] To avoid round-off errors in subsequent calculations, property values listed in this table are reported with one digit more than is justified by the experimental uncertainty.

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Figure Captions

Figure 1. Structures of the compounds in the norbornane cycle.

Figure 2. Molar heat capacities at saturation pressure $C_{sat,m}$ for norbornane measured in this research.

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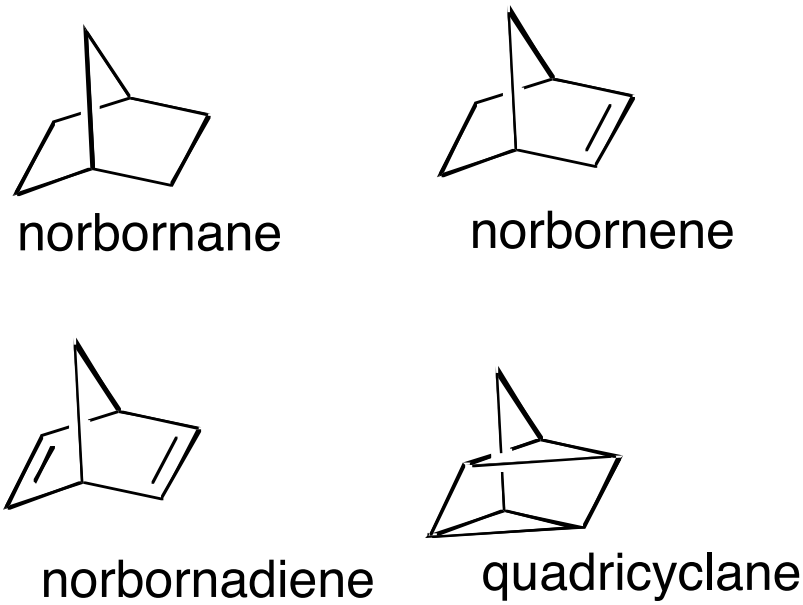

FIGURE 1

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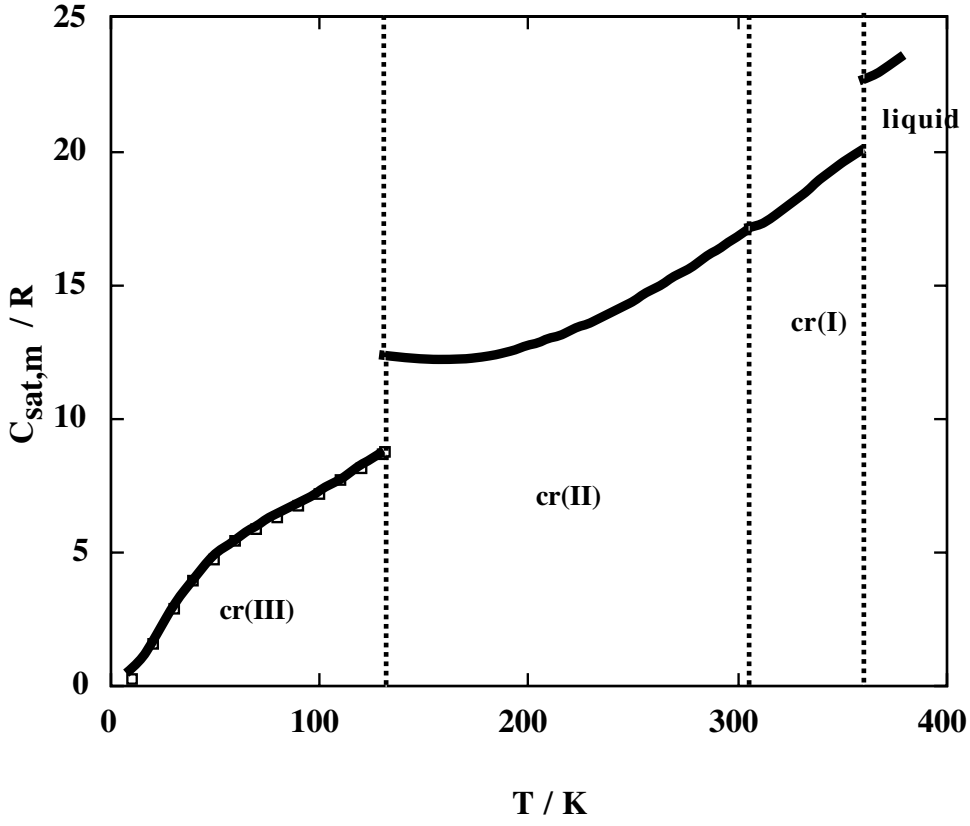

FIGURE 2

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