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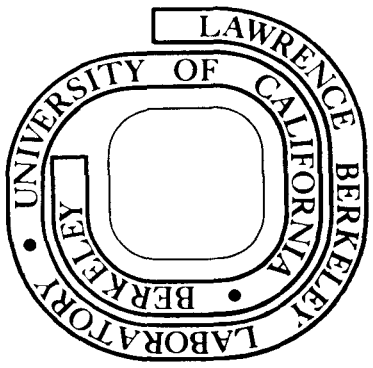

DISCLAIMER

SPIN SPECIES CONVERSION AND THE HEAT CAPACITY OF SOLID METHANE NEAR 1°K

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In order to further explore[1] the energy levels and interconversion properties of the various nuclear-spin species of methane, we have measured the heat capacity of samples containing controlled amounts of a spin conversion catalyst, oxygen. With approximately 0.8% O_2, the spin-species conversion is fast enough to allow measurements of the equilibrium heat capacity. Our results, which start at 0.4°K, are shown in Figure 1. An anomalous peak near 1°K is apparent. The time to reach thermal equilibrium after each introduction of heat ranged from 20 to 40 min and was longest near 0.8°K. These long equilibration times reduce the accuracy, of course, but there is no doubt about the essential character of the results.

It was impractical to measure the heat capacity of pure methane below about 2.2°K. The time to reach spin-species equilibrium was impossibly long, but the heat release from conversion caused a rapid temperature drift. Above 2.2°K we were able to measure the non-equilibrium heat capacity for methane with no change in spin-species composition; these results are generally similar to those of earlier investigators.[2]

Our results for the equilibrium heat capacity above 5.5°K agree satisfactorily with those of Colwell, Gill, and Morrison[2c]

Kataoka, Okada, and Yamamoto[3] have recently proposed a model for CH_4 (below 20°K) which appears to be consistent with our results. This model assumes the 8-sublattice antiferro-rotational structure with three quarters of the molecules in sites of symmetry D_{2d} and one fourth in sites of O_h symmetry. The lowest energy levels of spin species A, T, and E in O_h sites are so widely separated that conversion to the A species is practically complete below 2°K. Kataoka, et al, suggest that the energy separations for the D_{2d} sites for T and E molecules are 1.9° and 2.8°K, respectively, above that for A molecules. The respective degeneracies of these lowest levels are 5, 9, and 2 for A, T, and E species.

Our equilibrium heat capacities through 1.5°K are fitted quite well by this pattern with three-fourths of the molecules in a set of levels with separations of 1.951 and 2.89°K and the degeneracies stated above and with a small correction for the heat capacity of oxygen. If all of the molecules had access to such a set of energy states the heat capacity would be four-thirds as large — a definite conflict with our data. This provides confirmation of that aspect of the structure placing three quarters of the molecules in a set of sites with smaller energy separations.

Since the oxygen molecules are presumably in cavities of approximately cubic or octahedral symmetry, their rotation and spin energy-level pattern is estimated to be approximately the

same as in the gas. The heat capacity of oxygen calculated on this basis was subtracted from the experimental values to obtain equilibrium heat capacities of methane.

Recent experiments of other types have been interpreted on the basis of energy separations of 1.69° and 2.05° for the level-crossing method, Glättli, et al,[4] and 1.66° and 2.51°K for neutron scattering, Press and Kollmar.[5] Our results are definitely in disagreement with an energy separation as small as 1.7°K for all nine T states (above the A level). Among possibilities for resolution of this discrepancy are more complex models involving the splitting of the group of nine T states.

Our measurements were made with calorimetric techniques similar to those described by Finegold and Phillips.[6] Helium-3 was used for cooling below 1°K. A full report of our measurements will be given later together with a discussion of various calculations and interpretation.

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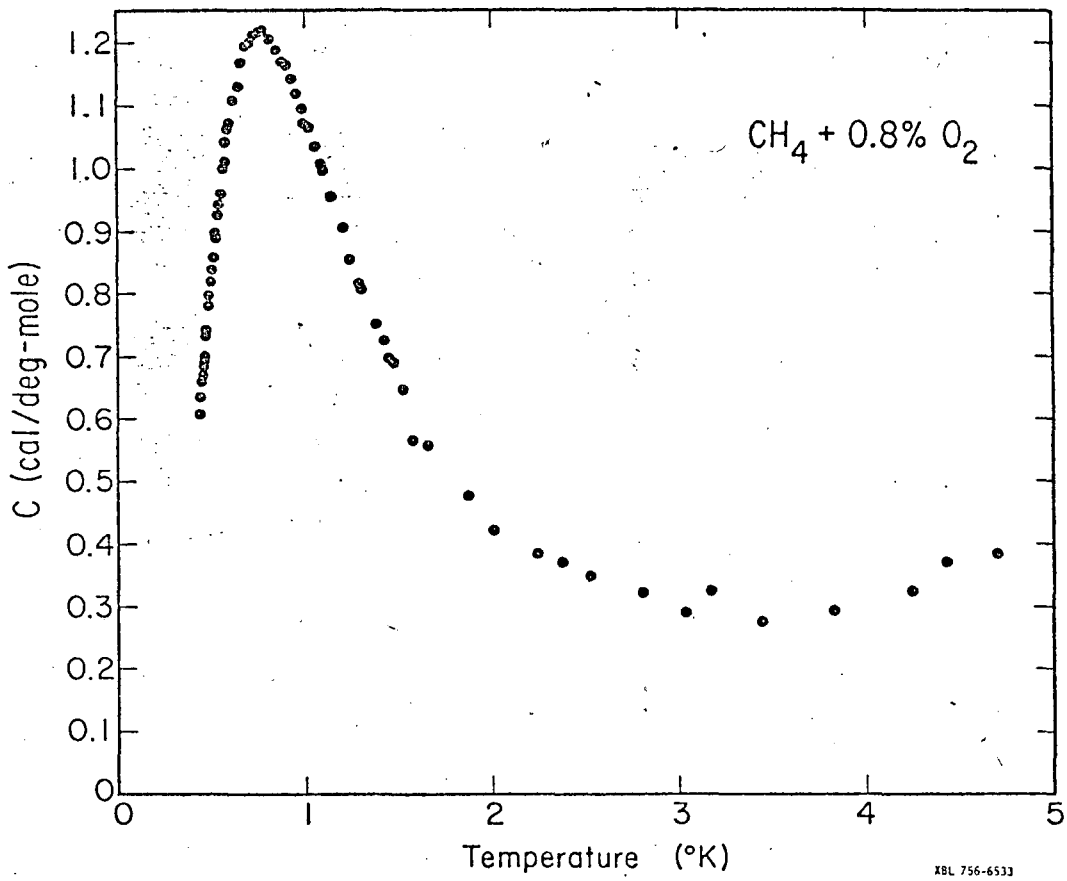

Figure 1. The heat capacity of methane catalyzed for spin-species conversion.

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