Low temperature calorimetry for weakly interacting molecular systems*

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With development of small-sample calorimeters and their computer control, adiabatic low temperature calorimetry, an established source of chemical thermodynamic properties, has now become one of the diverse experimental methods for studying more general low temperature properties of matter. A device to increase the efficiency of the calorimetric experiment is described. Calorimetric studies of deuterium-induced phase transitions for which recent development of the experimental technique was essential are reviewed. Substances discussed are ammonium hexachlorometallates, rubidium hydrogen selenate, 5-bromo-9-hydroxyphenalenone and their deuterated analogues.

INTRODUCTION

Low temperature calorimetry has a long history of development starting at the beginning of this century. It provided one of the key experimental facts leading to birth of quantum theory. Low temperature behavior of the heat capacity of a solid could be understood on the quantum assumption. The Einstein and Debye theories of the low temperature heat capacity of solids are direct consequences of the basic notion that the energy is quantized. The third law of thermodynamics was established by Nernst on calorimetric experiments at low temperatures and its general validity could be rationalized by quantum theory[1].

As these fundamental issues settled, chemical thermodynamics provided a motivation for the research activities in low temperature calorimetry[2,3]. Low temperature calorimetry determines the absolute entropy of a chemical substance. This quantity, combined with the enthalpy referred to zero kelvin, gives the Gibbs energy needed for all the chemical equilibrium calculations. As an increasingly large number of organic and inorganic substances were synthesized for various scientific and technological purposes, low temperature calorimetry was established as the source of their free energy data.

Although the role of low temperature calorimetry in the chemical thermodynamics proper continues to be unique and cannot be replaced by other techniques, there has been another development in calorimetry that it is used as one of diverse experimental techniques (such as spectroscopy and diffraction) for studying low temperature properties of matter. Calorimetry contributes to solid state physical chemistry thanks to the very accurate temperature and energy measurement developed for chemical thermodynamics purposes. Temperature resolution better than 1mK is routinely attained in adiabatic calorimetry but is exceptional in most of other low temperature experiments. Careful distinction between equilibrium and non-equilibrium states practiced in chemical thermodynamics is another feature of a calorimetric experiment that makes it distinguished among the diverse experimental methods. Because of these characteristics, low temperature calorimetry is particularly suitable for studying phase transitions involving subtle intermolecular effects. This report is concerned with the calorimetric method applied to the studies of low temperature properties of matter related to isotope effects involving weak intermolecular interactions in solid state.

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SMALL-SAMPLE CALORIMETERS

As the low temperature calorimetry finds more and more applications in the study of various substances for their specific properties, the amount of substance available for the experiment becomes smaller. Previously when determination of the standard thermodynamic functions was the main objective of a calorimetric experiment, one could expect that samples were available in large quantities. However, substances of interest for their specific physico-chemical properties are usually prepared in smaller quantities than industrially important materials. For this reason, small sample calorimeters have been a much needed development[4-6], though a sample size of 20 to 50 cm3 is still found desirable for ultimate accuracy or for studying thermal phenomena involving very small energy density[7,8]. The volume of the sample cells of the small-sample calorimeters so far developed is a few cm^3 to less than one cm^3. This is a reduction of the sample amount by a factor of ten or more from what was previously normal. One of the factors contributing to reduction of the sample size is small-size resistance thermometers now available (3 mm in diameter and 20 mm long). For further reduction of the sample size, a calorimeter was constructed using thermocouples not only for the temperature control of adiabatic shields but also for the measurement of the sample temperature[9,10]. It is also true that thermometry and energy measurement have become accurate recently so that a cell heat capacity representing as large as, e.g., 80 % of the gross heat capacity may be acceptable because it can be subtracted accurately.

Introduction of microcomputers to operate low temperature calorimeters has increased the efficiency of the experiment. This has had a rather important effect on the types of experiment that can be done by calorimetry. Previously it took a few weeks to collect a full set (10 - 320K) of heat capacity data on a sample. With a computer-controlled calorimeter, this can be done in less than a week. Thus one may use calorimetry to study, e.g., a solid solution system for which several samples of different compositions need be examined. Such an experiment takes a discouragingly long time to perform with a manually operated calorimeter, if it may not be entirely impractical . Efficiency in the experiment has an effect on the human side of research: with less time needed for one experiment, more samples of probable calorimetric interest can be studied in joint projects with other laboratories. Samples may be sent to the laboratory for the measurement or visitors may stay in the laboratory for a week to do the experiment. This would have been impractical if it took a month to complete a measurement.

A small contrivance described below shortens the experimental time in an essential way and probably increases the accuracy of the data at the same time. This device can be implemented easily in any computer-controlled adiabatic calorimeter by small addition of hardware and modification of the computer program. In adiabatic heat capacity calorimetry, a large part of the experimental time is spent in heating the sample at a constant power. Obviously, the time necessary to heat a sample by a given temperature increment is shorter with a larger heating power. However, the heating power cannot be increased to an arbitrarily large value because of the requirement that the adiabatic shield should not overshoot when the heater is turned off. Homogeneity of the temperature over the cell surface is also important and should be taken care of in the design of the cell (particularly, distribution of the heating wire). The overheating occurs as the temperature of the cell decreases in the course of equilibration. The sample, which has been lagging behind in temperature during the heating, receives heat from the cell, thus decreasing the temperature of the latter. The adiabatic shield can be controlled when the temperature is increasing or stationary but not when the temperature decreases rapidly. Therefore, at a large heating power, the adiabatic shield tends to overheat because of the decrease of the temperature of the cell when the heater is turned off. This can be avoided by decreasing the heating power for a certain time at the end of the heating interval. During this time heat is transferred from the cell to the sample thus homogenizing the temperature, while the (reduced) heating power still keeps the temperature of the cell stationary or slightly

increasing. When the heater is fully turned off finally, the temperature in the cell is sufficiently even, so that the adiabatic shield can follow its temperature without overshooting. Thus a high heating power and undisturbed adiabatic shield control are made compatible both in the heating and equilibrium intervals as well as in the transition period between them. How effective this contrivance is depends on the design of the cell and properties of the sample it contains. In our experience the heating interval could be reduced by a factor of two, which is a rather large increase of the experimental efficiency. This device should also increase the precision of the heat capacity data obtained, because shorter extrapolation in time is involved now in determining the temperature increment. As a further improvement on the present contrivance, the heating power may be reduced in more than two steps. This will further increase the highest heating power that can be employed without causing overheating of the shield.

DEUTERIUM-INDUCED PHASE TRANSITIONS

It is generally believed that properties of molecular and ionic molecular crystals are ultimately understood on the basis of intermolecular forces. This approach, realized in the lattice energy calculation and molecular dynamics simulation, has been successful in predicting crystal structures, lattice vibrations, enthalpies of sublimation and other properties of molecular crystals[11]. In this approach nuclear masses enter only in a secondary way since the intermolecular forces do not depend on them. However, ordinary ice melts at 273.15 K and D_2O ice at 276.97 K, while the melting point of heavy oxygen ice $H_2{}^{18}O$ is 273.46 K[12]. Small shifts of the melting temperature have also been found in lithium salts of which those enriched with ^6Li and ^7Li have been studied[13]. These examples show that bulk properties do depend on the nuclear mass. However, the effect is rather minor, and even though no conclusive explanation appears to have been given, several possibilities can be pointed out; difference in vibrational frequencies due to the mass difference may modify the relative stability of the phases, or bond lengths and other molecular geometries may depend (for an unknown reason) on the nuclear mass, which in effect changes the intermolecular force.

It is surprising, in the light of these experimental knowledges, that there are several compounds in which deuterium substitution causes new crystalline phases to appear at low temperatures where there is none in the hydrogenous compounds. There are also a few inverse cases where a crystalline phase stable in a certain temperature interval for a hydrogenous compound does not appear when the hydrogen atom is replaced by deuterium. These isotope-related phase changes occur in such diverse substances as
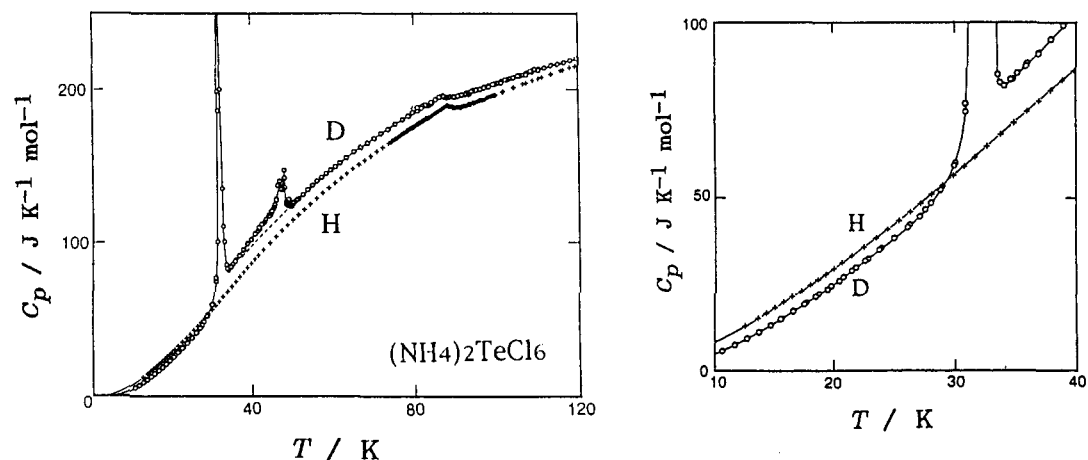

Fig. 1 (left) Heat capacities of $(NH_4)_2TeCl_6$ and $(ND_4)_2TeCl_6$ [21].
Fig. 2 (right) The same as above. Low temperature region [21].

ammonium compounds, inorganic acidic salts, a hydroxide, an aromatic organic compound and a hydrogen halide.

AMMONIUM HEXACHLOROMETALLATES   In 1984 Prager and others studied ammonium hexachloropalladate $(NH_4)_2[PdCl_6]$ by neutron scattering[14]. This compound was of interest to study by the neutron spectroscopic method because of the low barrier to rotation of the ammonium ion. For the sake of comparison they studied the deuterated ammonium salt $(ND_4)_2[PdCl_6]$ and found a neutron spectrum totally unrelated to that of the hydrogenous compound.   This was explained by a phase transition of the deuterated compound at 34 K.   For some time this unexpected results did not attract attention but in 1992 Callanan, Weir and Westrum measured the heat capacity of the two ammonium salts and found a first order transition at 30.2 K for the deuterated analogue[15]. Prior to this, they studied an isomorphous platinum compound $(NH_4)_2[PtCl_6][16,17]$.   This compound, when deuterated, undergoes a phase transition at 27.2 K.   Barrier to rotation of ammonium ions are low in these crystals (2.5-2.8kJ mol^{-1}[18]).

Isotope dependent properties of ammonium hexachlorotellurate was first suspected in ^{35}Cl nuclear quadrupole resonance experiments[19,20].   Figure 1 shows the heat capacities of ammonium hexachlorotellurate and its deuterated analogue[10,21]. Both of them undergo a gradual transition at 86-88 K. For the deuterated ammonium salt, there are two more peaks at 46-48 K and 31.9 K where there is none for the hydrogenous salt. The entropy of transition determined by integration of the excess heat capacity was 20 J $K^{-1}mol^{-1}$.   The large entropy of transition indicates that the transitions are of an order-disorder type. By contrast the lambda transitions at 86-88 may be displacive type related to rotation of the octahedral cation.   A calorimetric experiment was independently performed by Callanan, Weir and Westrum[22,23], the two results being essentially in agreement. Large entropy changes have been found also at the transition points of the palladate and platinate complexes[15-17]. Structural aspects of the deuterium induced transition have been investigated by a high resolution powder diffraction method using a pulsed neutron beam[21,24].   It showed a sequence of crystal phases of cubic, rhombohedral, monoclinic and tetragonal symmetries in the decreasing order of temperature.   The molar volumes of the low temperature phases are of interest in relation to the transition entropy: the molar volume of the phase that appears at lower temperature is larger. Thus in this crystal the decrease of the entropy is accompanied by increase of the volume both at the rhombohedral-monoclinic transition and at the monoclinic-tetragonal transition. Volume expansion accompanied by decrease of the entropy is associated with presence of strongly directional forces in the intermolecular potential as in the freezing of ice or beta-gamma transition of ammonium bromide.   This may well be the case in the present compound.

Figure 2 shows the heat capacities of the hydrogenous and deuterated ammonium hexachlorotellurate in the lowest temperature region. One sees that the heat capacity of the deuterated analogue is lower than that of the hydrogenous compound. The opposite is normally found, and is explained by more densely distributed energy levels in the deuterated crystal chiefly coming from the rotational lattice vibration of ammonium ions.   The low heat capacity found in the present deuterated ammonium salt can be understood by assuming that the deuterated ammonium ions are rotationally strongly restricted in the environment of the lowest temperature tetragonal phase, while in the hydrogenous analogue the cation is relatively free to rotate in the rhombohedral phase.   A phase transition induced by deuterium substitution was also found in ammonium hexachloroplumbate[25].   In figure 3, one sees the heat capacity peak due to a first order transition at 34.8 K.   Interestingly, also in this compound, the heat capacity of the deuterated analogue is smaller than that of the normal compound in the low temperature phase.   The same was found again in the pair of ammonium - deuterated ammonium hexachloroselenates[26].
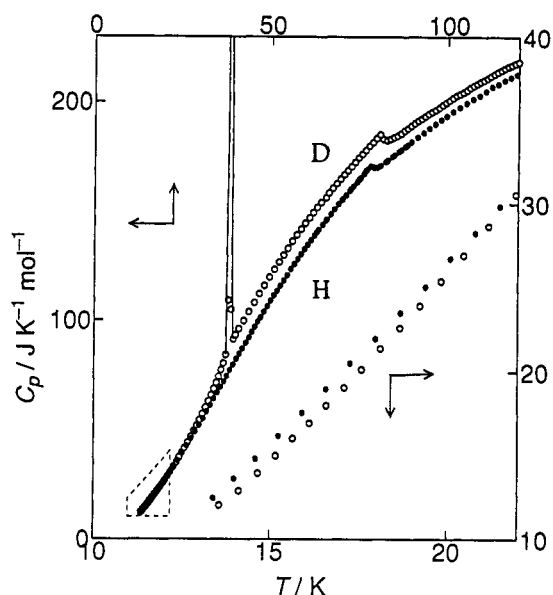
Fig. 3 Heat capacities of $(NH_4)_2PbCl_6$ and $(ND_4)_2PbCl_6$ [25].

This inverse isotope effect in the low temperature heat capacities may be a general consequence of the third law of thermodynamics. Suppose ammonium and deuterated ammonium ions are orientationally disordered in a similar way in the high temperature phase. At a low temperature the deuterated ammonium becomes ordered while the normal ammonium salts remains in a disordered state. The high heat capacity of the hydrogenous ammonium salts allows the crystal to lose its entropy faster than the deuterated analogue. Thus, at the lowest temperature, they are both in the ordered state in agreement with the third law. Molecular mechanisms by which this occurs has yet to be understood.

TRIALKALI HYDROGEN SULFATE AND SELENATE   Acidic salts of alkali sulfate and selenate undergo phase transitions when the hydrogen atoms are replaced by deuterium. Figure 4 shows the heat capacities of tri-rubidium hydrogen selenate $Rb_3H(SeO_4)_2$ and its deuterated analogue, $Rb_3D(SeO_4)_2$[27,28]. The heat capacity of the hydrogenous comppound is smooth at all temperatures down to 2 K. In the deuterated compound a lambda anomaly due a gradual transition occurs at 95 K. A similar lambda transition occur at 78.5 K in tri-rubidium deuterium sulfate[29]. In these crystals, the sulfate and selenate anions form dimers connected by a hydrogen bond[30]. The trivalent dimers and the three rubidium ions form a normal ionic crystal lattice. It is most likely that the phase transitions are related to ordering of the deuterium atoms on the hydrogen bonds, although structural studies have not been conclusive in this respect. The effect of deuterium substitution is particularly striking when the two compounds are compared in terms of the molar mass: the low temperature phase appears as a result of difference by one unit in the molar mass of 543.

At the lowest temperature, the heat capacity of the hydrogenous compound is larger than that of the deuterated analogue as figure 5 shows for the selenate compounds. Thus the inverse isotope effect discussed above is also found here. The excess heat capacity of the hydrogenous compound was reproduced well by the Schottky levels centered at 61 K above the ground state and distributed in a gaussian with a width of 28K. It is interesting that in the neutron inelastic scattering spectrum[31] a peak occurs at the same energy as the calorimetric Schottky levels. The neutron inelastic peak does not occur for the deuterated compound. The calorimetric data shows that there is a set of isolated energy levels in the hydrogenous compound where there is none in the deuterated analogue. The neutron data alone might be interpreted simply as a matter of difference in the scattering cross section. It is tempting to discuss the extra energy levels as arising from tunneling motion of the proton in the double

minimum potential provided by the hydrogen bond between two selenate ions.   The O-O distance 0.249 nm[30] is appropriate for this interpretation. However, the neutron peak intensity does not conform to this model in its temperature dependence.   A comprehensive model encompassing the excess heat capacity of the hydrogenous compound on the one hand and the occurrence of the phase transition in the deuterated analogue on the other is still to be constructed.
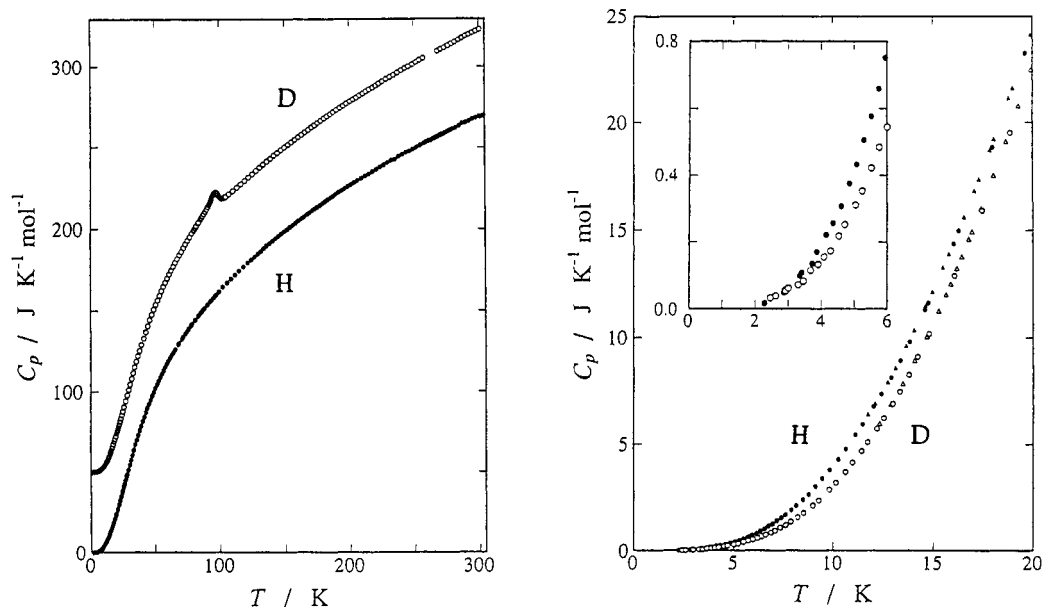

Fig. 4 (left)   Heat capacities of $Rb_3H(SeO_4)_2$ and $Rb_3D(SeO_4)_2$ [27,28].
Fig. 5 (right)   The same as above. Low temperature region [27,28].

5-BROMO-9-HYDROXYPHENALENONE   One of the reasons for which we are interested in this type of hydrogen bonded crystals is that they are closely related to a more general type of ferro- and antiferroelectrics represented by potassium dihydrogen phosphate, KH_2PO_4.   This compound has long been studied extensively by a great variety of experimental and theoretical methods.   There is still no conclusive explanation for, e. g., the large shift of the transition temperature on deuteration or for the value of the transition entropy.   One of the difficulties is that in this crystal the hydrogen bonds form a network extending all through the entire three dimensional lattice. It has been hoped that the isolated hydrogen bonds in the sulfate and selenate will simplify the discussion of the correlation between the positions of neighboring hydrogen atoms. This expectation has been partially fulfilled by the identification of the extra energy levels associated by the presence of the hydrogen atoms.   The same argument lead to a study of intramolecularly hydrogen bonded organic molecular crystals.   5-bromo-9-hydroxyphenalenone (BHP) was prepared for the first time by Mochida et al. and studied by dielectric measurement.   Figure 6 shows the heat capacities of the hydrogenous and deuterated (BDP) 5-bromo-9-hydroxyphenalenone. In the latter only the hydroxyl part was deuterated. The molecular formula is given in the figure. The heat capacity curve of the deuterated analogue has two peaks at 21.5 K and 33.9 K, whereas the heat capacity of the hydrogenous crystal is smooth down to 2 K, in agreement with the dielectric data.   The entropy associated with the excess heat capacity is 3J $K^{-1}mol^{-1}$, considerably smaller than $R\ln 2$ expected from the positional disorder of the deuterium atoms on the hydrogen bonds. Analysis of the data using lattice and molecular vibrations will   allow more detailed interpretation of the extra entropy. For the BHP and BDP pair, the inverse isotope effect in the heat capacity occurs at higher temperatures than the transition points.   The argument based on the mass effect on the frequency of a harmonic oscillator is also applicable here.   Thus
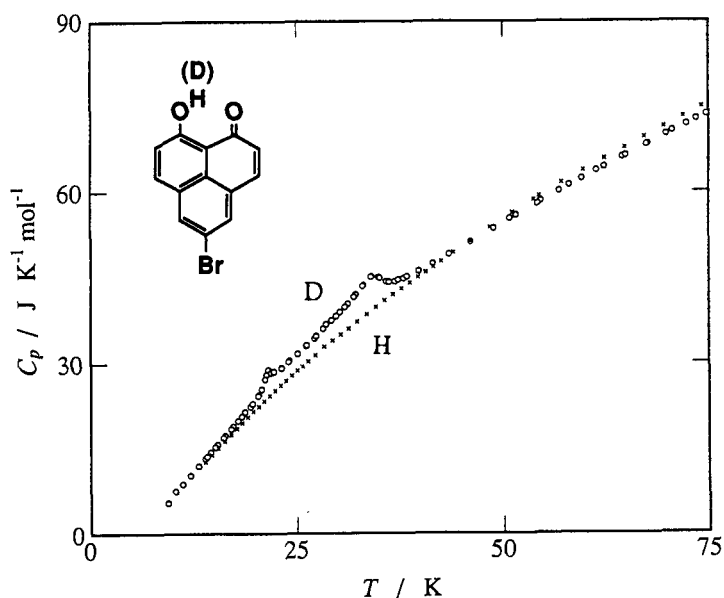
Fig. 6 Heat capacities of 5
-bromo-9-hydroxyphena-
lenone and ts deuterated
analogue [33].

there is an isolated group of energy levels associated with the hydrogen atoms on the hydrogen bonds but not with the deuterium atoms. This may be identified with intramolecular tunnelling mode.

OTHER SYSTEMS   In TlH_2PO_4 a phase transition occurring at 230 K shifts to 356 K when the crystal is deuterated[34-37].   In addition there appear two other transitions at 45 K[38] and 130 K[34,35]. These are subtle changes involving only small transition entropies.   Deuterium induced transitions have been also reported in NaOD[39] and an organic molecular crystals[40].

In all of the compounds discussed above hydrogen atoms are situated at sites where they are relatively free to move in a certain extent of space without experiencing much increase of the potential energy. This will smear their distribution in the space. This in turn will weaken the interaction between neighboring hydrogen atoms, decreasing the driving force of the phase transition. The smeared distribution is essentially a quantum effect. For the deuterated analogues the classical picture is more or less appropriate because of the larger mass. Thus, The phase transition discussed here may be better described as ones suppressed when deuterium is replaced by hydrogen. Finally it should be added that in hydrogen bromide[41] and ammoniated ammonium iodide[42], deuteration reduces the number of phases that occur. These are another aspect of the isotope effect which has to studied.

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