Density of Single Crystals of Cupric Acetate Monohydrate

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Lennard-Jones $\phi_1=\left(\frac{51}{r^9}-\frac{1.78}{r^6}\right)10^{-11}$ erg.

$\phi_2=\left(\frac{116}{r^{10}}-\frac{1.42}{r^6}\right)10^{-11}$ erg.

$\phi_3=\left(\frac{649}{r^{12}}-\frac{1.05}{r^6}\right)10^{-11}$ erg.

Bijl $\phi_4=\left(113e^{-3.87r}-\frac{1.30}{r^6}\right)10^{-11}$ erg.

Wohl $\phi_5=\left(\frac{29.1}{r^9}-\frac{1.22}{r^6}\right)10^{-11}$ erg.

(r in A)

As may be seen in Fig. 4, ϕ_1 and ϕ_2 are not very different from each other, and actually yield about the same agreement for the energy and volume of solid H_2 and D_2. The agreement using ϕ_3 is not particularly good. All three of these are, of course, based on experimental data for H_2. Bijl's expression, ϕ_4, is based on a theoretical calculation of the r^{-6} term and the use of the mentioned analogy with He for the repulsive term. Wohl's function, ϕ_5, was determined by using the London expression for the numerator of the attractive term. This term is too small as is to be expected since the London expression gives, if only the r^{-6} term is considered, too small a value for the attraction. In view of this one might anticipate that the repulsion in ϕ_4, and ϕ_5 is assumed too small, since it has to compensate for too small an attraction. Accordingly ϕ_4 and ϕ_5 give only very poor agreement with experiment. ϕ_1 is so closely related to the experimental observation as to inspire confidence in its use. The use of the same Lennard-Jones equation for D_2, H_2 and HD may be open to some objections, as for example those suggested theoretically by Beth and Uhlenbeck.[15] However, it is felt that the results obtained are in such close agreement with experiment that one may consider the above procedure as justified for H_2 and as a reasonable approach for HD and D_2.*

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[15] R. Beth and G. Uhlenbeck, Physica **3**, 729 (1936).

* In this connection see the reports by K. Schafer (Naturwiss. **24**, 539 (1936); Zeits. f. physik. Chemie **B36**, 85 (1937); **B38**, 187 (1937)) on the second virial coefficients of H_2 and D_2.

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Densities of single crystals of cupric acetate monohydrate have been determined by the pycnometer method for temperatures 21.0°C, 23.5°C and 25.0°C, and are 1.907±0.001, 1.891±0.004 and 1.880±0.003 g cm^{-3}, respectively. The first one compares favorably with the value (1.906 g cm^{-3}) calculated at about 21.0°C from accurately determined lattice parameters of the unit cell and the number of molecules per unit cell. It is considerably higher, however, than the value (1.882 g cm^{-3}) given in the *International Critical Tables*.

I. INTRODUCTION

FROM accurately determined values of the lattice parameters[1] of the unit cell of copper acetate monohydrate, the volume of the elementary cell was found to be $1379\pm0.04\times10^{-24}$ cc. Taking the value of density for this substance from the *International Critical Tables*[2] as 1.882 g cm^{-3}, the number of molecules per unit cell was calculated as 7.90. This value, though sufficiently close to indicate that there are eight molecules per unit cell, gave a discrepancy which was too large for an experimental error in the

[1] R. B. Hull, Thesis for the degree of Doctor of Philosophy, University of Pittsburgh, 1938.

[2] *Int. Crit. Tab.* (McGraw-Hill, New York), Vol. 1, p. 123.

determination of the lattice parameters. Therefore, it was decided to determine experimentally the value of the density of single crystals of copper acetate monohydrate similar to those used for the x-ray study.

Growth of the crystals from dilute solution

The crystals were grown from a dilute solution of Mallinckrodt analytic reagent grade copper acetate. The solution was filtered three times, poured into a clean porcelain dish with free acetic acid and allowed to evaporate slowly on a steam radiator at a temperature of approximately 33°C. In about fifteen hours good sized, dark, blue-green crystals were taken out of the dish. An attempt was also made to grow single crystals from saturated solutions of copper acetate, but the crystals thus obtained were too small and were considered unsatisfactory for this work.

II. Experimental Procedure

Determination of specific gravity was made by the pycnometer method. The crystals were well dried and polished with lens paper before weighing. Small pycnometers were chosen to eliminate the buoyancy effect due to the net volume of air displaced. The outer volume of the pycnometer including the plug was 14.0 cc; and the volume of the weights used varied from 1.5 to 2.0 cc. The buoyancy effect of the air displaced (12.0 to 12.5 cc) was well within the experimental error.

In determining the weight of the pycnometer filled with the crystals and oil, the crystals were well shaken when immersed, to eliminate any air bubbles adhering to them. The pycnometer was kept in an ice bath for 45 minutes before transferring to a constant temperature calorimeter bath. The temperature of the latter was higher than that of the ice bath; hence, the oil on expansion expelled any air which might have been present in the capillary of the pycnometer plug. Similar procedure was followed in obtaining weights of pycnometer filled with oil and filled with water alone. White Russian mineral oil (specific gravity 0.861 at 21.0°C) was found to be a convenient nonsolvent for these determinations.

The temperature of the calorimeter bath was regulated at 21.0°C and 23.5°C and 25.0°C, and measured by a thermometer that was calibrated from one, certified by the National Bureau of Standards. The room temperature was kept practically the same as that of the calorimeter bath.

Table I. *Density of single crystals of copper acetate monohydrate.*

Temperature °C	Specific Gravity	Density g cm^{-3}
21.0	1.911±0.001	1.907±0.001
23.5	1.896±0.004	1.891±0.004
25.0	1.886±0.003	1.880±0.003

III. Results

In Table I are given the values of specific gravity and the corresponding values of density. The final values together with mean deviations presented here were obtained from the average of three readings taken at each temperature.

The diffraction patterns of single crystals from which the lattice parameters were obtained were made at about 21.0°C. Using 1.907 grams per cc as the density and Hull's value of $1379\pm0.04\times10^{-24}$ cc as the volume of the elementary cell, the number of molecules per unit cell has been calculated as follows:

$$\text{Mass per cell} = 1.907\ \text{g/cm}^3\times1379\times10^{-24}\ \text{cm}^3$$
$$= 2630\times10^{-24}\ \text{g}.$$

$$\text{Mass per molecule} = \frac{\text{Mole wt. of copper acetate}\times\text{mass of H atom}}{\text{Mole wt. of hydrogen}}$$
$$= \frac{199.632\times1.659\times10^{-24}\ \text{g}}{1.0078}$$
$$= 328.6\times10^{-24}\ \text{g}.$$

$$\text{No. molecules per cell} = \frac{\text{mass per cell}}{\text{mass per molecule}} = 8.00.$$

This value agrees very well with the actual value of 8. The value of the density used in this calculation compares favorably with the value of 1.906 g cm^{-3} calculated at 21.0°C. It is higher, however, than the two other values obtained here, and also the value given in *The International Critical Tables*.[2]