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DEVELOPMENT DIVISION

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CRYSTAL DENSITIES OF URANIUM CHLORIDES

ABSTRACT

Using xylene as the densimetric solvent, the crystal densities have been determined by the pycnometric method for the following chlorides, UCl_3 , UCl_4 , $\text{UCl}_6 \cdot \text{UCl}_4$, UCl_6 and UO_2Cl_2 .

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CRYSTAL DENSITIES OF URANIUM CHLORIDES

INTRODUCTION

The work in this laboratory on the fundamental chemistry of uranium compounds has led to the determination of the approximate crystal densities of UCl_3 , UCl_4 , so-called UCl_5 , UCl_6 , and UO_2Cl_2 . The crystal density is often needed in determinations of molecular properties and constants. For example, the approximate molecular radius of a compound can be determined by means of the Clausius-Mosotti relationship when the index of refraction and the crystal density are known. An attempt will be made in this laboratory to determine the molecular radius of UCl_4 , apparent UCl_5 , and UCl_6 by this method for the purpose of substantiating the spectrophotometric evidence (see document No. E-8.385.11) that so-called UCl_5 is actually a double compound of the formula $\text{UCl}_6 \cdot \text{UCl}_4$.

However, the crystal densities of the above-named chlorides have been collected here for convenience.

THEORY

The crystal density of a substance is the density in gms./cc of a single crystal, and thus can be regarded as a fundamental constant, whereas the bulk density can vary with samples of the same substance, and can depend upon the method of preparation. Crystal densities can be determined by the displacement of a liquid by a crystalline powder, when precautions are taken to remove trapped air from the liquid and the powder. This method was used for the values reported here, and is described below.

718'-2

It may be well to note that errors can be introduced into these determinations by the occlusion of mother liquor by the crystals, by air adhering to the crystals, by the hygroscopic nature of some crystals, and by the presence of small amounts of impurities in the substance.

EXPERIMENTAL PROCEDURE

The crystal densities were determined by the pycnometric method, using xylene as the standard liquid, all of the above-named chlorides being insoluble in this solvent. The conical pycnometer used had a volume of 25 ml, and was connected to a thermometer through a ground glass joint. A sketch of this pycnometer has been enclosed. The crystal density was determined by permitting the crystalline powder to displace xylene in the pycnometer and was calculated by the formula: $D = \frac{ad}{b-ca}$

where a = weight of solid

b = weight of pycnometer full of std. liquid

c = weight of bottle containing solid and std. liquid

d = density of std. liquid.

Since the crystal density is the density in gms./cc. of a single crystal of the substance, precautions must be taken to remove all occluded and trapped air from the crystalline powder. These precautions were observed by using the apparatus shown in the enclosed sketch.

The volume of the pycnometer in cc. was determined by filling it with water. The dissolved air was first removed from the water by placing it in the separatory funnel, S, and subjecting it to vacuum evacuation for approximately twenty minutes; then the water was led into the pycnometer inside the evacuated desiccator, D. The density of the xylene was then

715-3

determined by removing the dissolved air and filling the pycnometer in the same manner as with water.

The density of the crystalline powder was obtained by placing the compound in the pycnometer and removing the occluded and trapped air from the powder by evacuation within the dessicator. The degassed xylene was then introduced from the separatory funnel, and the pycnometer was removed and weighed. All weighings were made at approximately 30°C, but the temperature of the pycnometer was not controlled by a thermostat.

The compounds used in these determinations were analyzed by C. D. Susano and associates, and the results were reported as follows:

UCl_3	UCl_4	$UCl_4 \cdot UCl_6$ (UCl_5)	UCl_6	UO_2Cl_2
%U = 66.4	%U = 62.3	%U = 56.6	%U = 52.7	%U = 67.1
%Cl = 29.7	%Cl = 37.3	%Cl = 42.0	%Cl = 47.6	%Cl = 18.0
Cl/U = 3.00	Cl/U = 4.04	Cl/U = 4.99	Cl/U = 5.94	Cl/U = 1.8

RESULTS

Two determinations of the crystal density were made on each compound and the values obtained in gms./cc. are shown in Table I.

TABLE I

<u>Compound</u>	<u>1st. Det.</u>	<u>2nd. Det.</u>	<u>gms./cc. Aver. D</u>
UCl_3	5.026	5.008	5.017 $\pm$.009
UCl_4	4.793	4.655	4.724 $\pm$.069
$UCl_5 \cdot UCl_6$	3.565	3.699	3.632 $\pm$.067
UCl_6	3.271	3.246	3.258 $\pm$.013
UO_2Cl_2	4.300	4.135	4.217 $\pm$.082

715-4

CONCLUSIONS

According to recognized authorities on the subject of crystal densities, the values obtained can be made accurate to the fourth or fifth place, but that this sort of accuracy is obtained only when numerous precautions are observed. Some of these precautions consist of:

1. Performing all the weighings at exactly the same temperature. This involves placing the pycnometer in a controlled temperature bath before weighing as well as having a means of controlling the temperature of the balance case.
2. Insuring the extreme purity of the compound by various methods such as fractional distillation, freezing, etc. The accuracy of the pycnometric method is so great that it is sensibly affected by even small amounts of impurities.
3. Drying hygroscopic crystals in a stream of air before admitting them to the pycnometer.

The proposed use of the crystal densities in this laboratory did not warrant the extreme accuracy obtainable only through strict observance of the above precautions, and hence only practical precautionary measures were taken throughout these determinations. All weighings, however, were made at approximately 30°C , and the variation from this temperature was rarely more than $\pm 1^{\circ}\text{C}$.

The values reported in Table I, then, are to be considered as approximate, but sufficient for many types of calculation wherein the other variables are known only to the same degree of accuracy.

715-5

CCS/ap

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SKETCH OF PYKNOMETER

715-7

SKETCH OF CRYSTAL DENSITY APPARATUS