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Vapour Pressure Measurements in the Copper-Selenium System

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Se_2 dissociation pressures in the Cu–Se system were measured by different methods. The results agree with the phase diagram published by Heyding (*1*). Some thermodynamic data for the phases in equilibrium were calculated.

1. Introduction

The copper-selenium system (Fig. 1) has been studied in recent times by Heyding (*1*) who established the selenium-rich part of the phase diagram, the copper-rich part being already well known (*2*). G. Gattow and A. Schneider (*3*) measured the heats of formation of the compounds in the system by reaction of the elements in a calorimeter, but the results did not agree well with the DTA peaks which Heyding (*1*) observed during his studies. Considerable uncertainty therefore exists as to the thermodynamic data of the compounds.

The present study reports measurements of the Se_2 dissociation pressures of $Cu_{2-x}Se$, CuSe and $CuSe_2$. These together with measurements of the pressure in equilibrium with $Cu_{2-x}Se$ and a melt confirm the phase diagram of Heyding (*1*). Some thermodynamic data are calculated from the results.

2. Measurements and Calculations of Thermodynamic Data

2.1. Se_2 Pressure in Equilibrium with Cu + $Cu_{2-x}Se$

According to the phase diagram the $Cu_{2-x}Se$ phase in equilibrium with copper has a composition near $x = 0$. A powder of Cu_2Se with additional copper (30 at.% Se) was mixed with Al_2O_3 and poured into the apparatus shown in Fig. 2. At constant temperatures (560–1000°C) purified hydrogen was passed over the solid, removing selenium and forming a H_2Se/H_2 mixture. Variations in the gas flow velocity (0.8–1.8 liter/h) produced no effect, so that equilibrium according to the equation

$$Cu_2Se + H_2 = 2Cu + H_2Se$$

was established completely. The gas mixture leaving the furnace was burned with oxygen to form H_2O and SeO_2. The SeO_2 was titrated (*4*) with 1/100 $Na_2S_2O_3$ in a solution containing KI, HCl and starch. From the result of the titration and the total amount of hydrogen that had passed over the solid the partial pressure of Se_2 was calculated using the known constants for the formation equilibrium of H_2Se (*4*). The measured values are represented (see also Fig. 3) by equation

$$\log(p_{Se_2}) = -12970/T + 2.945 \text{ (atm)}.$$

According to Kubaschewski and Evans (*5*), the heat capacity of β-Cu_2Se at 383–500°K is 20.2 cal/°K mole and can be estimated at about 21.75 cal/°K mole at its melting point (1115°C). From these values and the known data for Se_2 (*6*), (*7*) and Cu (*5*) the standard heat of formation and the standard entropy of Cu_2Se are calculated to be:

$$\Delta H_{298}(\beta\text{-}Cu_2Se) = -15.00 \text{ kcal/mole};$$

$$S_{298}(\beta\text{-}Cu_2Se) = 38.8 \text{ cal/°K mole}$$

with a statistical error of 160 cal/mole. The total error, including the uncertainties as to temperature (± 3°K), analysis (± 3%) and the thermodynamic data of Se_2 (*6*), (*7*), is about ± 1.0 kcal/mole for the heat of formation and about ± 1.0 cal/°K mole for the standard entropy. The entropy of α-Cu_2Se can be estimated (*5*) at about 37.6 cal/°K mole. Since the entropy of the β-modification should be somewhat higher, the value deduced from the measurements appears to be reliable.

2.2 The Se_2 Pressure in Equilibrium with Mixtures of $Cu_{2-x}Se$ and CuSe (40 at.% Se) or of CuSe and $CuSe_2$ (60 at.% Se)

These selenium pressures were measured by the transportation method, using argon as the carrier gas. The experimental arrangement has already been described (*4*). The Se_2 partial pressures were calculated from the amounts of selenium transported

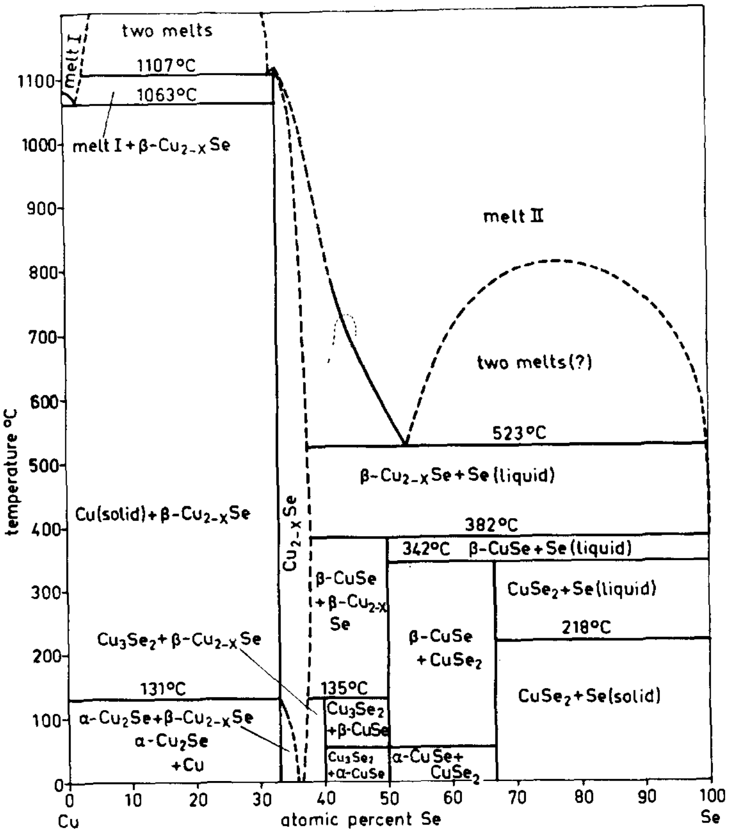

FIG. 1 Phase diagram of the Cu–Se system after Heyding (*1*) and Hansen (*2*).

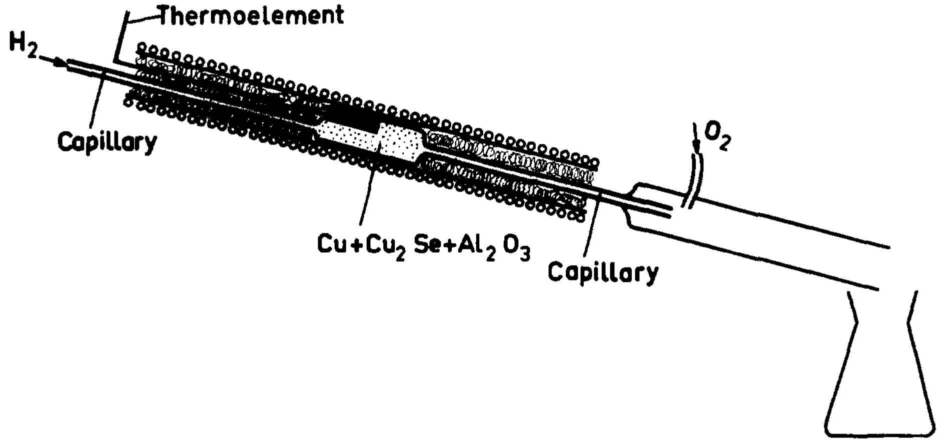

FIG. 2 Quartz apparatus used for the determination of the Se_2 pressure in contact with a Cu/Cu_{2-x} Se mixture.

with the flowing argon, the mass action equations published by one of us (*6*) being used for this purpose. As can be seen from Fig. 3, the peritectic temperatures, i.e., the temperatures at which the selenium pressure above the respective mixtures equals that of liquid selenium, are exactly the same as given by Heyding (*1*). The measured pressures are represented by the following equations:

$$\beta\text{-}Cu_{2-x}Se + \beta\text{-}CuSe:$$

$$\log(p_{Se_2}) = -9917/T + 11.634 \text{ (atm)},$$

$$\beta\text{-}CuSe + CuSe_2:$$

$$\log(p_{Se_2}) = -7922/T + 8.747 \text{ (atm)}.$$

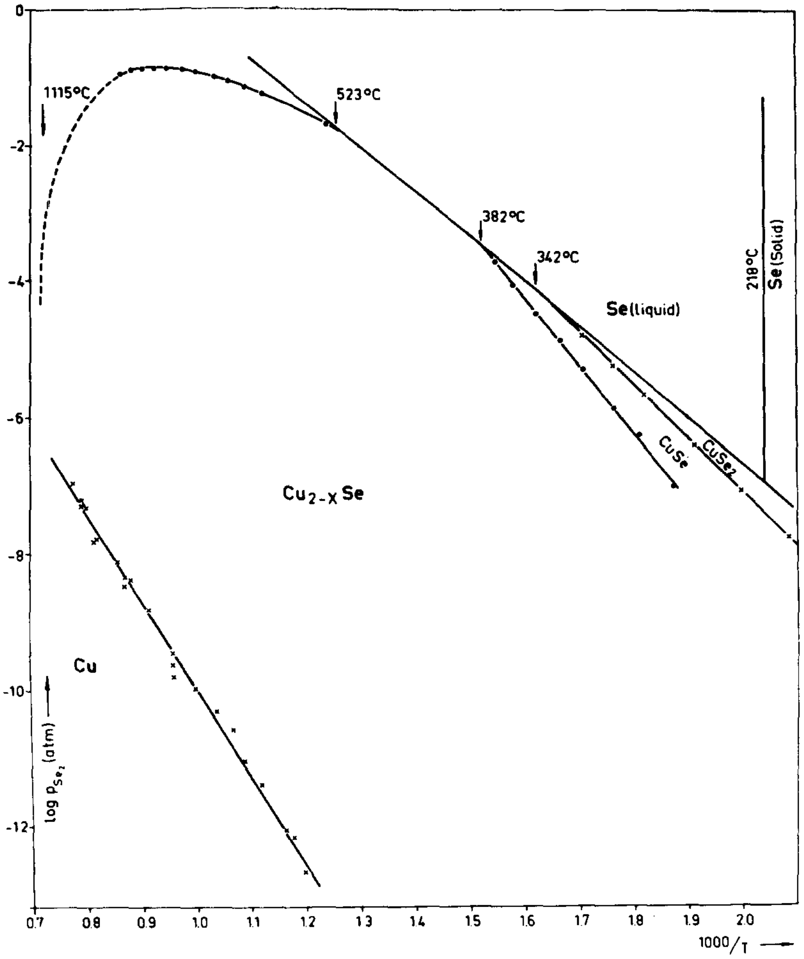

FIG. 3 Se_2 partial pressures in the Cu–Se system (in atm).

The composition of the $Cu_{2-x}Se$ phase in equilibrium with β-CuSe at temperatures above 135°C (see Fig. 1) is not known. If the defect structure of this phase is similar to that of the digenite phase ($Cu_{2-x}S$) (*8*), the composition of the phase may be near to Cu_7Se_4. Furthermore, it may be assumed that as in the case of digenite the heat of formation and the entropy per atom are very flat functions of the composition and may be nearly equal at both boundaries of the homogeneity range at a given temperature. On the basis of this assumption [which is also supported by the measurements of Gattow and Schneider (*3*)] the heat of formation and standard entropy of Cu_7Se_4 can be estimated as

$$\Delta H_{298}(Cu_7Se_4) = -55.0 \text{ kcal/mole};$$

$$S_{298}(Cu_7Se_4) = 142.2 \text{ cal/°K mole}.$$

With these values and estimated heat capacities (*5*) (6.25 cal/°K atom at room temperature and 7.25 cal/°K atom at the peritectic point) the following thermodynamic data were calculated:

$$\Delta H_{298}(\beta\text{-CuSe}) = -10.5 \text{ kcal/mole};$$

$$S_{298}(\beta\text{-CuSe}) = 20.6 \text{ cal/°K mole},$$

$$\Delta H_{298}(CuSe_2) = -11.7 \text{ kcal/mole};$$

$$S_{298}(CuSe_2) = 28.8 \text{ cal/°K mole}.$$

No measurements could be performed in equilibrium with solid Cu_3Se_2 because of the latter's low peritectoid temperature.

All the heats of formation measured are higher than those given by Gattow and Schneider (*3*), who used direct calorimetry. These differences may be caused by insufficient formation of the compounds from the elements in the calorimeter. The corrections applied by Gattow and Schneider for this factor appear not to be large enough.

2.3. Se_2 Equilibrium Pressures above a Mixture of $Cu_{2-x}Se$ and Melt

These measurements were effected on a mixture containing about 38.0 at.% of selenium with a quartz spiral manometer. Se_2 partial pressures, calculated from the total pressures measured originally (*6*), are shown also in Fig. 3. The monotectic temperature is the same as that found by Heyding (*1*).

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