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Stability of KAg_4I_5 and K_2AgI_3

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Abstract. The thermal stability of KAg_4I_5 and K_2AgI_3 was studied using single crystals as starting materials and by means of thermal analysis, X-ray powder diffraction and impedance measurements. Some discrepancies of the present results with earlier works, mainly concerning the stability temperature range of these compounds, are found and they are attributed to the presence of small traces of AgI and KI or to slight deviations from stoichiometric compositions in the earlier samples whish were prepared by solid state reactions.

Resumen. La estabilidad térmica de KAg_4I_5 y K_2AgI_3 fue estudiada partiendo de monocristales como materiales de estudio y por medio de análisis térmico, difracción policristalina de rayos-X y medidas de impedancia. Se encuentran algunas discrepancias de los resultados actuales con los trabajos anteriores, especialmente relacionados con el rango de temperatura de la estabilidad de estos compuestos, las que se atribuyen a la presencia de pequeñas trazas de AgI y KI o a pequeñas desviaciones de las composiciones estequiométricas en las muestras originales las que fueron preparadas por reacciones de estado sólido.

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1. Introduction

From previous works on the formation of double salts of the KI·AgI system either by solid state reactions [1,2] or by crystallizing them from solutions [3], it has become apparent that at least two intermediate compounds, KAg_4I_5 and K_2AgI_3, can be obtained. KAg_4I_5 has been the most largely investigated because of its high-conducting solid phase at room temperature. However, these solid compounds are not thermodynamically stables. It has been found [1] that KAg_4I_5 is unstable below 36° C where the reaction

$$7/2\,\mathrm{AgI} + 1/2\,\mathrm{K_2AgI_3} \leftrightarrows \mathrm{KAg_4I_5} \tag{1}$$

is in equilibrium. In addition, Topol and Owens [2] found that K_2AgI_3 samples obtained by solid state reactions exhibited two thermal transformations at 136° C and 160° C, respectively: the DTA trace showed thermal halts at these points on heating but none on subsequent cooling. In an earlier work, Bradley and Green [1] attributed the 136° C thermal arrest to the dissociation of K_2AgI_3 at this temperature where the reaction

$$\mathrm{K_2AgI_3} \leftrightarrows 1/4\,\mathrm{KAg_4I_5} + 7/4\,\mathrm{KI} \tag{2}$$

is in equilibrium, but the 160° C transformation has not been identified so far. Such a common discrepancies for these type of materials most probably due to small deviations from stoichiometric compositions of the samples caused by different preparation conditions. One purpose of the present study is to look carefully at the two solid state disproportionated reactions (1) and (2), using single crystals of KAg_4I_5 and K_2AgI_3, grown from solutions, as starting materials and involving the use differential scanning calorimetry, X-ray analysis and electrical conductivity measurements as experimental techniques.

Single crystals studies offered two major advantages. Firstly, recrystallization from solution results in a further purification of the starting materials. This point is especially important because of elimination of possible effects caused by deviation from stoichiometric compositions as it is the usual case for those samples prepared by solid state reactions of the binary components AgI and KI. Secondly, sample qualities can easily be monitored by optical inspection, mainly for those cases in which the samples undergo decomposition or any other chemical reaction.

2. Experimental

KAg_4I_5 single crystals were grown by the solution-evaporation technique at a temperature of 40° C in a dry atmosphere and a solution as described in Ref. 3. Accordingly, the following starting materials were used: KI, Merck, suprapure grade; AgI, Fluke, purissimum grade; HI, Fluke 65% in water, purissimum grade. The three possibly crystallizing phases at the growing temperature are: β-AgI, α-KAg_4I_5 and K_2AgI_3. Each of these solids have a well defined shape which can be immediately used for finding the growth conditions of KAg_4I_5 which crystallizes in yellowish octahedra. K_2AgI_3 crystallizes in transparent, colourless meddles and β-AgI forms yellow hexagonal prisms topped by hexagonal pyramids.

K_2AgI_3 single crystal were grown at room temperature by the slow evaporation of a 4 molar aqueous KI solution saturated with AgI.

A number of small single crystals of KAg_4I_5 and K_2AgI_3 were chosen as representative specimens for crystallographic identification. These were ground to a powder. X-ray diffraction powder data were taken at room temperature for each sample with a Philips PW-1130 diffractometer using $CuK\alpha_1$ radiation. The lines in the diffraction profile for α-KAg_4I_5 powder could be indexed assuming a cubic unit cell with a lattice constant of 11.13 Å as previously reported [4]. Similarly, the diffraction pattern for K_2AgI_3 could be indexed on the basis of an orthorhombic unit cell with dimensions: $a = 19.52$ Å, $b = 9.98$ Å and $c = 4.74$ Å, as determined by Brink and Kroese [5]. A few samples of K_2AgI_3 were also studied in a high-temperature X-ray powder camera for phase identification.

The ionic conductivity of the materials was determined by means of impedance measurements in the frequency range 100 Hz–100 kHz using a HP-4274 LCR meter. The measurements were performed in air on samples obtained by grinding small single crystals of the materials and then cold pressed (20 ton/cm^2) into pellets (cylindrical disk: $\phi = 10$ mm and $l = 2.5$-5 mm). Diffused silver electrodes were applied to the samples by using finely ground silver powder and silver paint and then producing a large temperature gradient between the electrodes and the sample with a transient heating pulse applied to the electrodes. The sample resistance, R, was taken for $\theta = 0$, were θ is the phase angle between R and the sample impedance Z as given by a complex impedance analysis [6]. No significant variation of the operating frequency (approximately 10 kHz, for which $\theta = 0$) as a function of temperature was observed for the type of nonblocking electrodes used in these measurements.

Differential scanning calorimeter traces were obtained using a Rigaku DSC/DTA Instrument for samples of KAg_4I_5 and K_2AgI_3 in sealed aluminum pans and at heating and cooling rates of approximately 5 K/min.

3. Analysis and Discussion

It was verified that single crystals of KAg_4I_5 grown above $T =$ 36° C were thermodynamically stable up to its melting point at 253° C. However, if the crystal were cooled to a temperature below 36° C and retained there for many hours in a damp atmosphere, a peak in the DSC trace was shown at 140° C on heating but none on subsequent cooling or reheating (the reheating was done from a temperature above 36° C when the sample was quenched above 140° C). This results shows, then, that effectively the reaction (1) has a tendency to go to the left when cooling a sample of KAg_4I_5 below 36° C, but the reaction proceeds at a very slow rate in an inert atmosphere in such a way that, at temperature T, the concentration of KAg_4I_5 molecules is constant when the equilibrium is reached after several hours (as indicated by the constant value of the sample electrical resistance as a function of time).

When the products of the above disproportionate reaction were reheated, the complete regeneration of KAg_4I_5 took place only at a temperature above 140° C. In other works, the reaction (1) only goes to completion when it proceeds from left to right at 140° C, immediately after the reactants absorb certain amount of heat and where the final product is only KAg_4I_5 (of course, for a starting stoichiometric concentration of AgI and K_2AgI_3, according to the unimolecular regeneration of KAg_4I_5 given by the Eq. (1)). An example of the DSC traces of starting KAg_4I_5 sample is presented in Fig. 1.

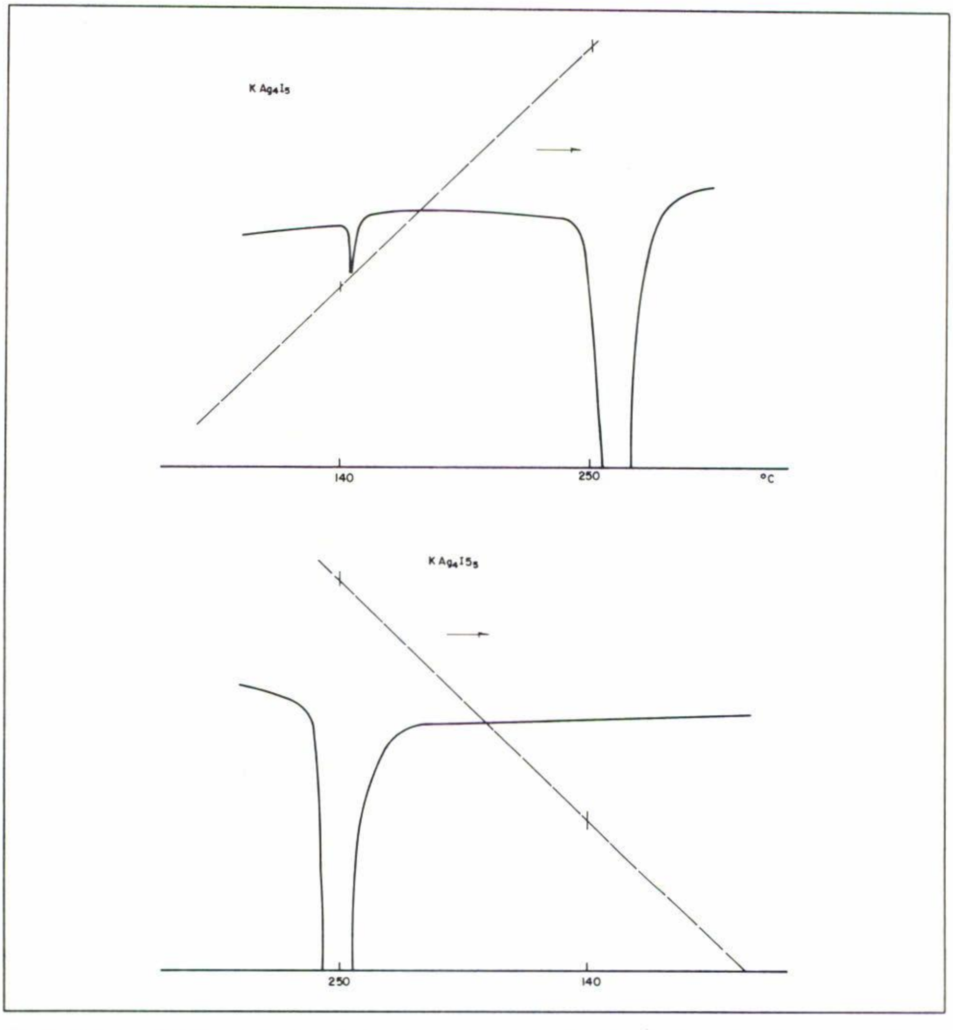

FIGURE 1. DSC traces for KAg_4I_5, grown at 40° C: a) First heating cycle from below 36° C to its melting point at 253° C. b) On subsequent cooling down the sample to room temperature.

On the other hand, if a single crystal of K_2AgI_3, grown at room temperature, were used as starting material, it was found, by DSC, X-ray and resistance analysis, that it was thermodynamically stable up to 160° C, where a very slow dissociation into KAg_4I_5 and KI took place after absorbing certain amount of heat: a thermal arrest was shown in its DSC trace on heating but none on subsequent cooling. Samples, quenched above 160° C, showed no halts on reheating unless they were brought to room temperature and kept there for several days. In other words, it was found that the reaction (2) proceeds to the right only at 160° C instead of at 136° C as previously reported [1,2], and this is done at a very slow rate up to the point at which certain concentration of the reactant (K_2AgI_3) and products (KI and KAg_4I_5) is reached above 160° C. If the substances of the previous reaction were cooled from a temperature above 160° C, the reaction (2) proceeded from right to left and it went to completion only at 36° C where the final product is K_2AgI_3 (of course, as before, for an initial stoichiometric concentration of KI and KAg_4I_5 which corresponds to the unimolecular regeneration of K_2AgI_3, according to Eq. (2)). An example of the DSC traces (on heating and cooling) for a starting K_2AgI_3 sample is presented in Fig. 2.

The resistance measurements of K_2AgI_3 also confirmed the previous DSC results. When the sample was heated by first time, its resistance decreased very rapidly at 160° C. When the reaction has reached equilibrium at this temperature (as shown by the stable resistance value after several hours), the resistance of the final product decreased as the temperature increased following an Arrhenius behavior whose activation energy corresponded approximately to that of KAg_4I_5 ($E = 0.17$ eV). But, when the resistance of the products of the previous reaction, quenched above 160° C, was monitored as a function of the decreased temperature no appreciable change in the activation energy could be detected down to room temperature. An example of the electrical resistance measurements for an original K_2AgI_3 sample (on heating and cooling) is presented in Fig. 3.

In Fig. 4, the X-ray powder profile of a K_2AgI_3 sample taken at 250° C, after 2 or 3 hours of being heated by first time from

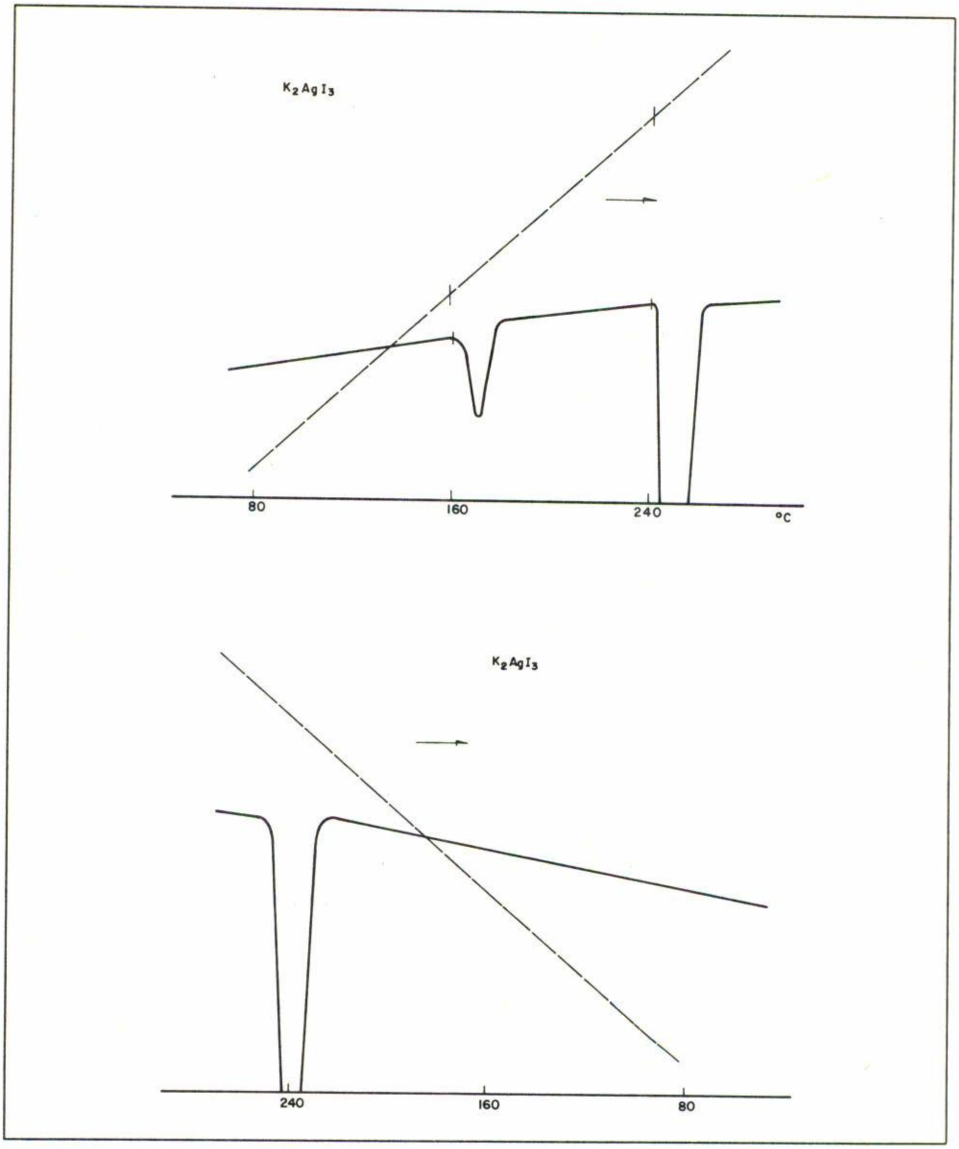

FIGURE 2. DSC traces for K_2AgI_3,grown at room temperature: a) First heating cycle. The 238° C peak corresponds to the eutectic point of the $KAg_4I_5 + K_2AgI_3$ components [1,2]. b) On subsequent cooling down the sample to room temperature.

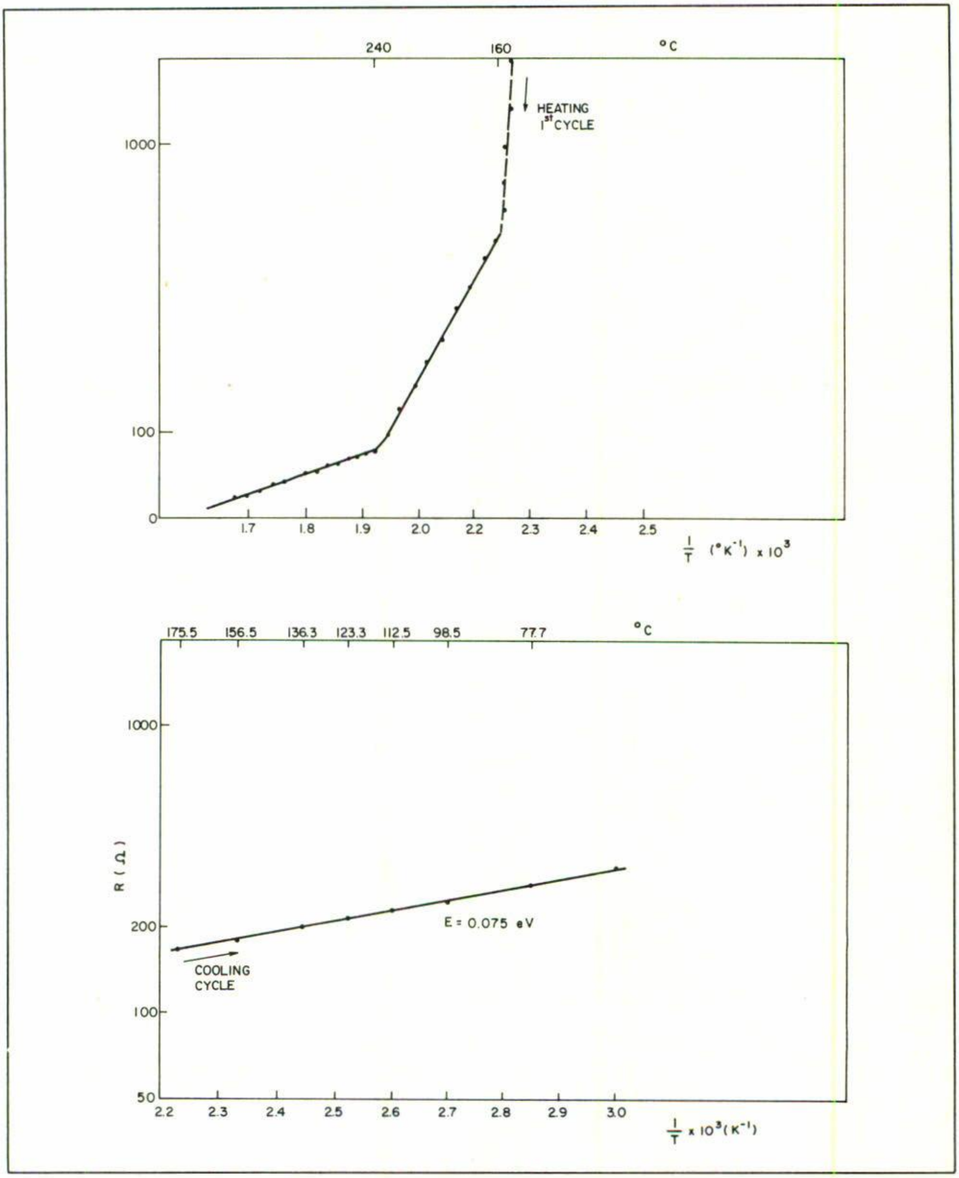

FIGURE 3. DC electrical resistance of a starting pure K_2AgI_3 sample in the log R vs. $1/T$ representation: a) First heating cycle. b) On subsequent cooling down the sample from 176° C.

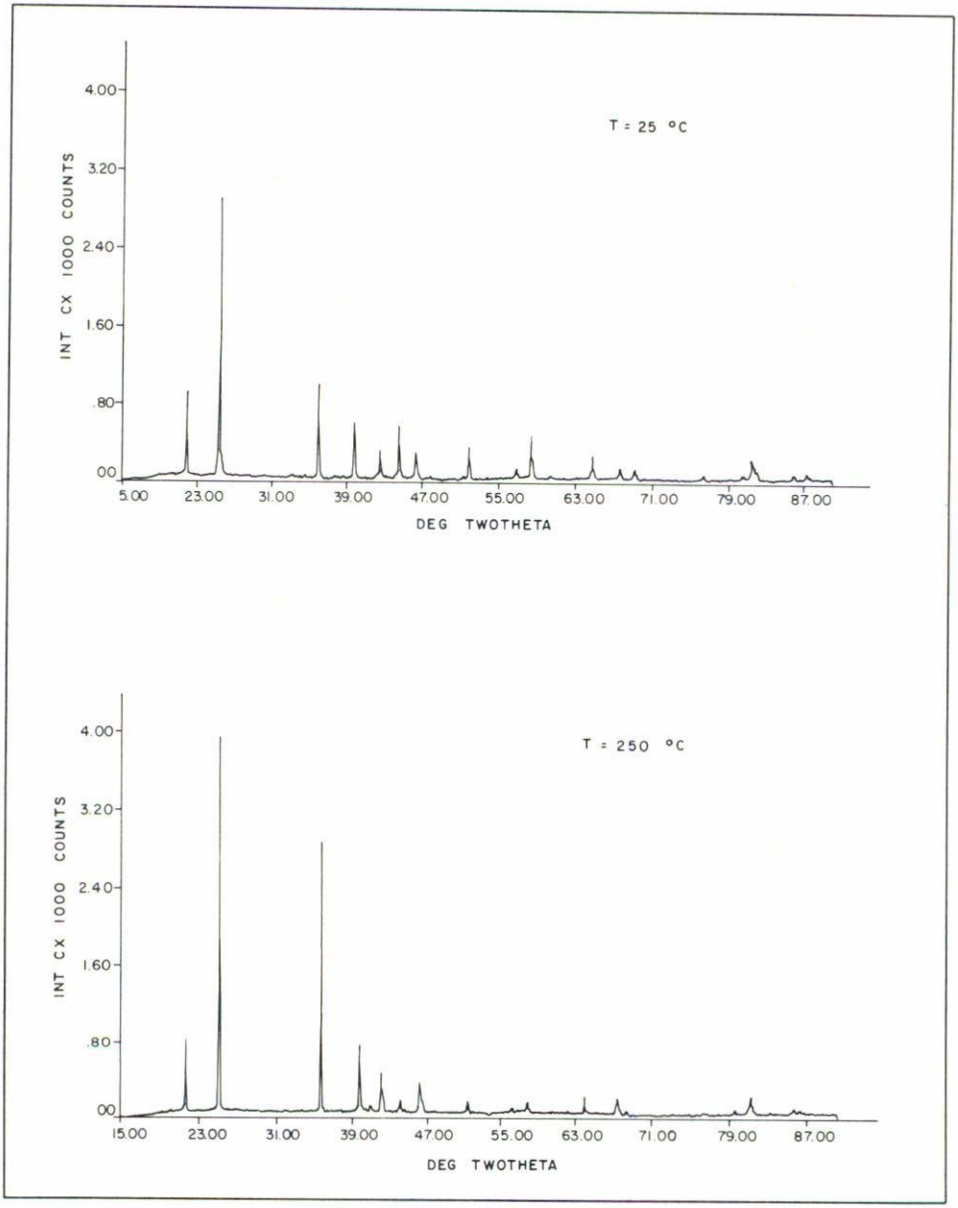

FIGURE 4. Diffractograms from an K_2AgI_3 powder sample, made at a) room temperature; b) 250° C.

the growing solution at room temperature, is presented. The lines of this diffraction profile can also be indexed on the basis of an orthorhombic unit cell with the same dimensions as those of a sample at room temperature, which also shows that the decomposition of this compound at 160° C proceeds at a very slow rate.

It was also observed that the rate of decomposition of KAg_4I_5 into AgI and K_2AgI_3 below 36° C was increased by grinding the samples, and it was much faster in a damp atmosphere with no weight change of them. On the other hand, those single crystals of this compound which were exposed to air at room temperature for several weeks, turned opaque at the surface while maintaining their transparency in the bulk of the material. These results suggest that this material decomposition is a surface-related process. Surely, surface crystallography studies will reveal this process characteristics and, as a natural consequence, so much understanding of these materials their instabilities.

It was also observed that the rate of dissociation of KAg_4I_5 below 36° C was influenced by the excess of KI and AgI present. Fine mixtures containing KAg_4I_5 and minute amount of KI are much less stable at room temperature than pure KAg_4I_5. However, in presence of AgI, the stability of KAg_4I_5 increases in a remarkable way.

The previous observations can be readily explained or accounted for in terms of an equilibrium constant defined for each of the reactions (1) and (2), not only for the temperature at which they are supposed to be in equilibrium but also for any other temperature in which they proceed for one side to the other in such a low rate, after certain characteristic time, that a metastable equilibrium can be assumed. This constant, at a definite temperature T, is defined in terms of the concentration of the components of the reactions when the metastable equilibrium is reached, as follows:

$$K_1 = \frac{[\mathrm{AgI}]^{7/2}[\mathrm{K_2AgI_3}]^{1/2}}{[\mathrm{KAg_4I_5}]} \qquad (3)$$

for reaction (1), and

$$K_2 = \frac{[\mathrm{KAg_4I_5}]^{1/4}[\mathrm{KI}]^{7/4}}{[\mathrm{K_2AgI_3}]} \tag{4}$$

for reaction (2), and where [A] stands for molar concentration of component A (strictilly activity). Then, one can see why decomposition reaction of KAg_4I_5 and K_2AgI_3 do not go to completion in the range of temperature of metastable equilibrium, since otherwise K_1 or K_2 would be infinity; or why the KAg_4I_5 concentration at equilibrium can be increased by either adding AgI (by Eq. (3)) or subtracting KI (by Eq. (4)).

Moreover, it can be seen that, if K is related to the change in the Gibbs free energy, G, of a cell in which the reaction (1) is taken place, by

$$\Delta G = RT \ln K, \tag{5}$$

where R is the molar gas constant and T the temperature, then, using the values of G reported by Topol and Owens [2] by measuring the e.f.m. of a cell having this reaction as a function of temperature (25° C $\leq T \leq 138^\circ$ C), the reaction (1) follows a thermal activated process in this range of temperature according to the relation

$$K_1 = 83.91e^{-1369/T}, \tag{6}$$

with a low activation energy of 1369 K or 0.118 eV.

In summary, it was found that pure K_2AgI_3 dissociates into $KAg_4I_5 + KI$ at 160° C and not at 136° C as previously reported [1,2]. The 136° C thermal arrest is only shown if some traces of AgI are initially present in the sample which, by some kind of fast-diffusion controlled homogenization process taking place in the sample, the AgI is dissolved in the bulk of the material above 140° C. This seems to be so, since no trace of further free AgI is detected (no thermal arrest is shown on subsequent cooling or reheating the sample at 147° C where AgI undergoes the $\beta \rightarrow \alpha$ transformation with large latent heat [7]).

In thus would seem plausible that future stability studies on this type of materials should be correlated with sample composition and precise determination of their phase make-up.

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