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PHASE TRANSFORMATIONS STUDY OF THE POTASSIUM NITRATE-DIVISION AND PRESSURE EFFECTS

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ABSTRACT

A calorimetric analysis of potassium nitrate held inside a porous material shows, in the case of atmospheric pressure, an increase of the transition temperature during heating and a decrease during cooling. At higher pressure, the phase diagrams of bulk and divided material are obtained up to 500 MPa.

INTRODUCTION

It is now well established that the division of a compound into sufficiently small particles, as it occurs for example during capillary condensation, changes the temperature of the liquid ⇄ solid phase transition (1) as well as the temperature of a solid ⇄ solid transformation (2,3).

This study performed on potassium nitrate held inside a porous material shows that these results can be extended to the solid ⇄ solid transitions of an ionic salt under pressure.

PHASE TRANSFORMATIONS OF POTASSIUM NITRATE

Under atmospheric pressure potassium nitrate is usually orthorhombic (S_{II}) or hexagonal (S_I) (4).

The differential calorimetric analysis of porous samples saturated with potassium nitrate shows that the liquid → solid I and solid I → solid II transformation points are shifted as indicated on figure 1. Three fundamental remarks are to be noted :

1 - the important decrease of the $L \rightleftarrows S_I$ ans $S_I \rightarrow S_{II}$ transformation temperatures.

The free energy of the liquid phase held inside a pore is lowered by the effect of surface tension, therefore the liquid ⇄ solid equilibrium temperature

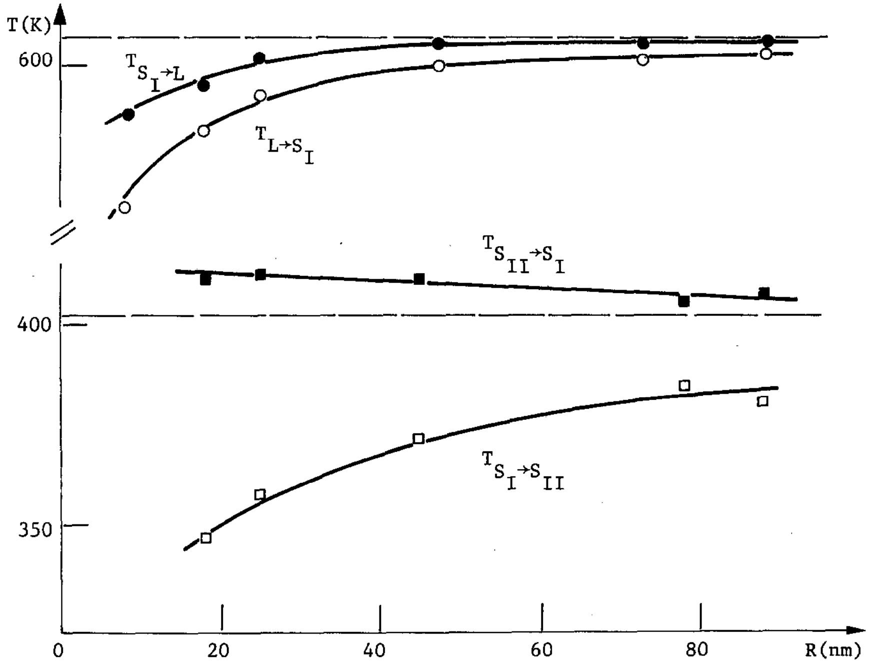


Figure 1

is decreased proportionally to this tension. According to the LAPLACE equation, this diminution is a function of the reciprocal of the pore radius. The coefficient of proportionality is 224 K.nm indicating a high sensitivity of the phenomenon. Potassium nitrate can therefore be used successfully as a capillary condensate for the study of very large pores by thermoporometry (5).

2 - the decrease of the $S_I \rightarrow S_{II}$ and the increase of the $S_{II} \rightarrow S_I$ transformation temperatures.

The solid - solid transformation inside the pores proceeds from a nucleus in which the internal pressure is higher than the pressure of the bulk material. During cooling the pressure of the nucleus of solid II is higher than the pressure of solid I. The temperature of formation of solid II is then decreased in the same way as the temperature of crystallisation of the liquid condensate. When the temperature is increased the nucleus of solid I is formed inside solid II. The curvature of the interface and therefore the pressure difference between the two phases are reversed. The result is a shift of the transformation temperature above the equilibrium point. It is interesting to note that the observation of two phases in equilibrium (metastable ?) above their normal transition point is very uncommon.

The dissymmetry which is observed for a same size of pore between the heating and the cooling of the sample is to be related to an elastic stress due to the change of the specific volume of the material. This stress favours or opposes the transformation according to the way it occurs.

3 - the disappearance of the transformation $S_I \rightleftarrows S_{II}$ under a certain size of pores (18 nm).

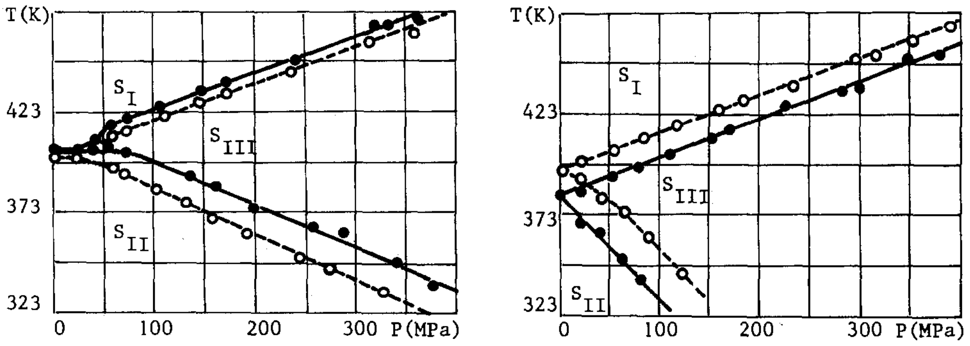
This observation made previously for other condensates (3,6,8) is to be related to a change of the thermodynamic parameters involved in the variation of the transition point : surface tension and volumic entropy of fusion.

EFFECT OF THE PRESSURE ON THE PHASE TRANSFORMATIONS OF POTASSIUM NITRATE

Above atmospheric pressure the transition $S_I \rightleftarrows S_{II}$ takes place through the formation of a new phase S_{III}.

The differential enthalpic analysis of a porous sample (radius 78 nm) saturated with potassium nitrate has been performed in a resistance calorimeter enclosed inside an autoclave whose temperature can be programmed from 300 to 725 K at pressures up to 500 MPa.

The thermograms obtained during the heating up show four peaks corresponding to each of the transitions taking place inside the pores and inside the condensate in excess. (figure 2)



INCREASING TEMPERATURE —— DIVIDED
---- BULK

DECREASING TEMPERATURE —— DIVIDED
--- BULK

Figure 2

Above the triple point (p=25 MPa, T=503 K) all the transition temperature versus pressure curves for the capillary condensate follow the same pattern as the corresponding curves for the condensate in excess. Even for these new solid-solid transformations, the transition temperatures for the capillary condensate are still higher than the corresponding temperatures for the bulk phase. For example above 40 MPa the difference is 16 K for $S_{II} \rightarrow S_{III}$ and 6 K for $S_{III} \rightarrow S_I$.

For the highest pressures, the S_{IV} phase observed by BRIDGMAN has not been detected even for the condensate in excess. On the contrary the $S_{II} \rightarrow S_{III}$ still takes place.

During cooling the four peaks are observed only for pressures under 120 MPa. Above this pressure the $S_{III} \rightarrow S_{II}$ transformation is delayed so that its observation is difficult. In order to observe the transition $S_{II} - S_{III}$ during heating up it is necessary to go back to atmospheric pressure to form the phase S_{III}.

The equilibrium diagrams obtained by cooling are situated under the diagrams obtained by increasing the temperature which show also an hysteresis phenomenon which is particularly important in the case of the transition $S_{II} \rightleftarrows S_{III}$.

Moreover, whatever the pressure applied, in the range under study, the effect of division is approximately the same which shows that the compression energy has only a secondary effect in comparison with the effect of capillary energy even for transformations involving a variation of the size of the unit cell.

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