KINETICS OF PHASE GROWTH IN SILVER NITRATE CRYSTALS

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THESIS

SUBMITTED FOR THE DEGREE OF MASTER OF SCIENCE IN

THE UNIVERSITY OF ADELAIDE

DEPARTMENT OF PHYSICAL AND INORGANIC CHEMISTRY

MAY 1962

C O N T E N T S

S U M M A R Y

Growth kinetics of the $AgNO_3$ phase transition were investigated by heating the crystals in a microfurnace, placed on the stage of a polarizing microscope, photographing the transition with a moving-camera, and determining the rate of change graphically.

Linear growth rates, on flat plate single crystals (001) of roughly uniform size (0.5 x 0.5 x 0.05 mm.), were measured in a temperature range of over 200°C. Crystals of bigger and smaller size were used to determine the influence of crystal size on transformation rates. The influence of varied annealing conditions, purity, and decomposition were also checked. Isothermal rates along different crystallographic directions in the same crystal were measured, as well as rates in crystals containing up to 0.3% of $Cd(NO_3)_2$ as impurity. $AgNO_3$ whiskers were grown and their transition rates and properties studied; the bending of whiskers during transition was observed in a few cases. Striations were seen in many crystals during transformation; the presence of strains was verified by X-rays.

The orthorhombic room temperature form could be superheated by about fifteen degrees (actual rates measured up to 11°C superheating), while the trigonal high temperature form was supercooled to any desired temperature by fast cooling. On superheating the crystals nucleated spontaneously, while on supercooling they were nucleated artificially with a room temperature form $AgNO_3$ crystal. The rates

were, on the whole, constant with time, but rose exponentially with temperature on superheating, while on supercooling they rose at first, reaching a maximum, (0.394 mm./sec. at ΔT = 58.5 deg.) then fell exponentially to zero (at about -30°C).

Linear growth rate equations for solid reaction were applied to the experimental results; and as found by other workers the equations gave a reasonable value for the activation energy far away from the transition point (21.1 kcal./mole) but changed to negative values near the transition on supercooling; on superheating a varying activation energy, decreasing with increasing superheating was obtained. The experimental rates were also much faster than predicted by most of these equations.

Since the presence of strains was observed experimentally Turnbull's growth rate equation, which is derived from the absolute reaction rate theory, was modified by adding a strain energy factor to the free nergy term; this correction resulted in a single valued activation energy throughout the whole temperature range for both transitions. On supercooling close agreement between theoretical and experimental growth rates was obtained. The merits and deficiencies of the various growth rate equations are discussed in the light of the experimental values obtained.

DECLARATION

This thesis describes my own work, carried out by me between February 1960 and December 1961. It contains no material previously published, or submitted for a degree, by me or any other person, except where due reference is given.

ACKNOWLEDGEMENTS

The author wishes to thank Dr. S.W. Kennedy for constant guidance and advice, and J.H. Patterson for practical help and useful discussions. Thanks are also due to the Colonial Sugar Refining Co. for providing a research studentship for the year 1960, and to Mr. A.W.G. Wittle, then of Australian Mineral Development Laboratories, and Dr. A.W. Kleeman, of the Zoology Department, University of Adelaide, who in turn lent the microscopes with which this work was carried out.