

CHEMISTRY

Adsorption of Krypton and Xenon on Evaporated Metal Films

Time (min)	Growth rate (cm s ⁻¹) × 10 ⁴
0	0.2
34	0.1
34 touched surface inside capillary with glass spike	
34½	11.9
40	4.6
45	2.1
50	0.9

The above growth rates were determined from the slope of the displacement/time curve.

20×10^{-5} cm s⁻¹. Growth measurements were then begun at a time when the rate had already fallen to a very low figure.

Most of the experiments were carried out in tubes of diameter 1.5 mm or less. In one experiment, however, the (010) (the slowest growing) face of a salol crystal was allowed to grow into a much wider tube of 0.8 cm internal diameter at an under-cooling of 2.2°C: the effect was similar although the retardation was somewhat less, the results being as follows.

Time (h)	Displacement (cm)	Rate (cm s ⁻¹) × 10 ³
0	0	
1	0.04	6.7
½	0.087	
1½	0.382	8.2

The crystal which had hitherto been free growing now entered the 0.8 cm diameter tube

2½	0.480	1.6
20	1.498	
67	2.886	0.18
96	3.074	
122	3.159	0.09
146	3.198	
		0.045

(The rates given are the average rates over the times indicated by the brackets)

Several different types of experiment were carried out with salol which convinced us that the observed retardation is not due to accumulation of impurities in the melt in advance of the growing face. No altogether satisfactory explanation of the observation has yet been found; but tentatively two alternative lines of approach are suggested. If growth layers were normally nucleated at the edges of faces, it seems possible that when the crystal grows into, and fills, a glass tube this nucleation process would be hindered or eliminated; this would explain the retardation on entering the tube. But it would also be necessary to assume that scratching the crystal surface with a glass spike would temporarily set up defects in the surface which would enable new layers to be nucleated at those defects, until such time as the defects are healed over or grow out to the walls.

Alternatively, growth layers may always be initiated at defects in the surface (which may be screw dislocations, groups of screw dislocations, or major defects such as grain boundaries). Then it would be necessary to assume that when growing in a tube these defects either grow out to the walls or are healed over. At the same time it would be necessary to assume that fresh defects are less easily formed in a crystal that is confined in a tube than in a free-growing crystal.

When growing in capillaries at under-coolings of greater than about 6°C the advancing faces were no longer plane, the crystals were no longer transparent and appeared to be polycrystalline; under these conditions the slowing up of growth was not observed.

The results presented here suggest that the measurement of growth rates in capillary tubes, on which much reliance has been placed in the past, is no guide to the behaviour of free-growing crystals.

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BRENNAN *et al.*¹ quoted our earlier communication² in connexion with the determination of the effective cross-sectional areas of adsorbed xenon molecules, $\sigma(\text{Xe})$. However, a numerical error appears in their article. The values 13.8 and 17.2 Å² were not given in our communication and the value $\sigma(\text{Kr}) = 19.5$ Å² was not used as a reference value. Our communication indicated that we found from the measurements of xenon adsorption on evaporated nickel films at 78° K that $\sigma(\text{Xe}) = 19.3$ Å², and from measurements at 90° K that $\sigma(\text{Xe}) = 21.8$ Å². Moreover, $\sigma(\text{Kr}) = 21$ Å² was used as the reference value. The adsorbed amounts of xenon and krypton were always estimated by the same volumetric method and evaluated by means of the Brunauer-Emmett-Teller theory.

The value of the ratio $\sigma(\text{Xe})/\sigma(\text{Kr})$ (xenon and krypton adsorption was measured at 78° K) was 0.92 in our communication, which is in good agreement with the value 0.95, which Brennan *et al.* calculated from their experimental data for the same system.

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¹ Brennan, D., Graham, M. J., and Hayes, F. H., *Nature*, **199**, 1152 (1963).
² Ponec, V., and Knor, Z., *Coll. Czech. Chem. Comm.*, **27**, 1091 (1962).

Catalysed Reaction of Xenon with Fluorine

NICKEL reaction vessels have been used in the past for the preparation of xenon fluorides because of the good resistance of this metal to attack by fluorine¹⁻³. However, despite the apparent ease with which these compounds form, the possibility that nickel may be acting as a catalyst has apparently been overlooked. To test this possibility we have carried out the following experiments.

Xenon (99–100 per cent, balance krypton) and fluorine (at its vapour pressure at -196°C) were mixed in a fused silica vessel. A nickel filament (0.020 cm diam.) was heated electrically in the gas mixture and its temperature monitored by following the resistance. Pressure changes in the vessel were followed with an all-metal bellows manometer. The results shown in Fig. 1 were obtained with the walls of the vessel cooled to -78°C. The number of molecules that reacted was determined from the pressure changes observed when the nickel wire was heated in the range 180–400°C. The reaction is of zero order until about half the initial material has reacted, then slows down, and has almost stopped when two-thirds has reacted. The product condenses in the form of a fine white powder on the cooled walls of the reaction vessel. The composition of the gas phase at the end of an experiment was determined by freezing the xenon in liquid nitrogen and pumping the excess fluorine away.

The ratio of fluorine to xenon (F_2/Xe) reacted was reproducibly 1.2 and was independent of the temperature of reaction over the range examined and independent of the initial F_2/Xe ratio in the range 0.8–2.0. The product, on standing at room temperature in the evacuated vessel, decomposed over about one hour to give a total pressure corresponding to the amounts of xenon and fluorine reacted.

The Arrhenius plot of the reaction rates is shown in Fig. 2. From this is derived an activation energy of 10.4 kcal mole⁻¹ and a pre-exponential factor of $\sim 10^{21}$ molecules sec⁻¹ cm⁻². This last-mentioned value is comparable with the collision frequency of xenon with the nickel wire.