amount of the short-lived volatile fission materials ^{132}Te–^{132}I and ^{133}I, and therefore after the samples had been fused with sodium carbonate they were dissolved in nitric acid. The sample solution was then analysed by a TTA–xylene extraction method[2] and the purified radiozirconium sample submitted to γ-spectrometric measurement.

Fig. 1 shows the measured activity ratio of ^{97}Zr : ^{95}Zr (open circles) plotted as a function of time 2–7 days after the explosion, together with an assumed line (solid line) of the time variation in the ^{97}Zr : ^{95}Zr ratio. The line is plotted against time on the assumption that cumulative fission yields of ^{97}Zr and ^{95}Zr are 5·9 and 6·2, respectively[3]. The single particle used for these measurements was spherical in shape, 16μ in diameter, reddish brown in colour and had a total β-activity of $2{\cdot}1 \times 10^5$ pc. at 1300 h, May 11. As can be seen from the figure, most of the results seem to lie along the assumed line. Thus it would seem that no enrichment of ^{97}Zr relative to ^{95}Zr occurred in the particle. As a result, it was possible to calculate an age for it, without making any corrections for fractionation, by comparing a measured activity ratio of the two isotopes with a corresponding value on the assumed line. The results obtained are given in Table 1. It can be seen that most of the estimated ages agree with the values calculated from the known time of explosion for the May 9 nuclear test; they do so especially well within 5 days of the explosion. Thus it would seem possible that when two nuclear explosions are conducted with a time interval of more than 10 h between them, particles released from them can be distinguished by measuring their activity ratio of ^{97}Zr : ^{95}Zr for up to a week after their formation.

Table 1. CALCULATED AND ESTIMATED AGES AT DIFFERENT TIMES OF A SINGLE FALL-OUT PARTICLE OF KNOWN ORIGIN

Date of measurement	Age since the formation Calculated* (h)	Estimated (h)
1000 h, May 11, 1966	41	41
1000 h, ,, 12 ,,	65	66
1100 h, ,, 13 ,,	90	91
1800 h, ,, 14 ,,	121	116
1300 h, ,, 15 ,,	140	138
1300 h, ,, 16 ,,	164	172

* These figures were calculated on the basis of the time of explosion—1700 h, May 9, 1966 (Japanese time)—given by the responsible Chinese agency.

Table 2. ACTIVITY RATIO OF ^{97}Zr TO ^{95}Zr AND ESTIMATED AGE OF FRESH NUCLEAR DEBRIS PARTICLES COLLECTED ON DECEMBER 30, 1966

Date of measurement	Activity ratio	Estimated age (h)
2300 h, Dec. 30, 1966	9·0	56 (1500)*
1100 h, ,, 31 ,,	5·3	69 (1400)
2100 h, ,, 31 ,,	3·7	77 (1600)
1400 h, Jan. 1, 1967	1·7	97 (1500)
1700 h, ,, 2 ,,	0·67	120 (1700)
1400 h, ,, 3 ,,	0·24	145 (1500)
1400 h, ,, 4 ,,	0·09	170 (1200)

* The figures in parentheses refer to assumed times of explosion on December 28, 1966, calculated from each of the respective ages estimated.

In order to test this method of age determination, we estimated the age of hot fall-out particles collected on December 30, 1966, at Niigata. As the radiozirconium content in a single particle collected on December 30 was too small to determine the activity ratio of ^{97}Zr : ^{95}Zr with a sufficient accuracy—less than one-two-hundredth that of the May 9, 1966, test—a composite sample of fifty-five particles was used for measurement. The ratios were determined at different times after collection using a chemically purified sample of radiozirconium. Table 2 shows the activity ratios of ^{97}Zr : ^{95}Zr measured during the period December 30, 1966–January 5, 1967 (solid circles in Fig. 1), and the estimated ages at different times of the composite sample. They were also evaluated by a comparison of their ^{97}Zr : ^{95}Zr ratios with the corresponding values on the assumed line (Fig. 1). From the ages thus obtained, we conclude that the explosion from which these hot particles originated was probably between 1200 and 1700 h (Japanese time), December 28, 1966.

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CHEMISTRY

Irradiation and the Subsequent Solid State Thermal Decomposition of Silver Nitrite

WE have examined the thermal decomposition of solid silver nitrite at 50° C after it has been exposed to γ-radiation from a cobalt-60 source (dose rate at the sample = $1{\cdot}5 \times 10^4$ r./h). The kinetics were followed gravimetrically *in vacuo* using collections of many well formed single crystals (sample size about 10 mg). The results are shown in Fig. 1. In contrast with results found in decomposition studies of other solids, which have shown either an enhancement of rate or negligible effect following irradiation[1], with silver nitrite there is a marked inhibition in the rate of decomposition with the dose of γ-rays. There was no significant loss in weight of the sample during irradiation. The irradiation was performed *in vacuo*. If the irradiation was carried out in a poor vacuum or at 1 atm. there was no effect on the subsequent thermal decomposition. This finding is of considerable importance because it may apply to the study of radiation damage in other reversible solid state decomposition reactions of the type $A_{(s)} \rightarrow B_{(s)} + C_{(g)}$.

The kinetics of the thermal decomposition of unirradiated silver nitrite have been examined from 35° C to 90° C. The decomposition of both irradiated and unirradiated silver nitrite continues to completion (100 ± 3 per cent), that is, $AgNO_{2(s)} \rightarrow Ag_{(s)} + NO_{2(g)}$, if the nitrogen dioxide is continually removed during a run. It was found that the rate constants determined from the slope of the extensive linear region (15–45 per cent) in the decomposition curves (Fig. 1) for runs at temperatures above 60° C fell below the extrapolated Arrhenius plot as determined from data at lower temperatures. This fall-off is believed to result mainly from inhibition by gaseous

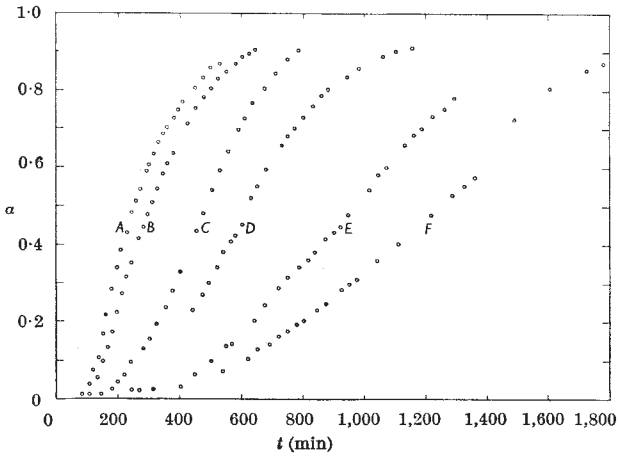

Fig. 1. Fraction decomposed, α, versus time plots for the decomposition of irradiated silver nitrite at 50° C. Exposure time in hours: *A*, 0; *B*, 1; *C*, 2·5; *D*, 5; *E*, 10; *F*, 20 (dose rate $1{\cdot}5 \times 10^4$ r. h^{-1}).

products, that is, even with direct evacuation the gases are evolved too rapidly to be removed. For this reason most effort has been concentrated on slow runs, at temperatures below 60° C; this, of course, also minimizes any errors arising from self-cooling. It should be noted that the lowest temperature at which this reaction previously appears to have been studied is 72° C (ref. 2).

Boldyrev and Eroshkin[3] have recently observed similar behaviour when silver nitrite is irradiated wiht X-rays before decomposition (80° C). Their results show an inversion effect, that is, at higher doses the rate increases relative to lower doses. This behaviour was not observed in our work. Their inversion effect occurs at a relatively low level of inhibition when compared with the more marked inhibitory effects observed in the present data. Because this reaction is sensitive to the presence of gaseous products both during the irradiation and the subsequent thermal decomposition, we suggest that the inversion which they observed is an experimental artefact and may result from inhibition by gaseous products.

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Solubility of Cupric Oxide in Pure Water at Temperatures up to 550° C

WE report here work in progress on the measurement of the solubility of metals and metal oxides in pure water, in the temperature range 50°–550° C and at pressures up to 400 bars. The isobaric solubility of cupric oxide at 310 bars is reported here and compared with the 300 bar isobar for silica (quartz).

The solubility measurements were made by passing demineralized, distilled and de-aerated water, at the required temperature and pressure, through a packed bed of solute particles contained in an autoclave. To prevent carry-over of particulate material, the solution leaving the autoclave was filtered through a stainless steel frit (1 μm pore diameter). It was then cooled at pressure to reduce deposition in the cooling system and passed through a back-pressure regulator to be collected for analysis. The high pressure water circuit was constructed from 'Nimonic' 80*A* and 90 alloys. For the cupric oxide–water system the samples of solution were collected in dilute hydrochloric acid and were analysed for copper by the solvent extraction–colorimetric method described by Wilson[1]. The random error of the solubility values reported is about ± 5 per cent, but this excludes the systematic error resulting from the deposition of copper in the sampling system. It has been shown, however, that deposition was only significant at the highest solubility values, above 400 μg copper/kg. No dependence of solubility on the rate of flow through the autoclave was found at rates from 1–12 kg water per hour, indicating that solutions leaving the autoclave were saturated.

Pocock and Stewart[2] have also measured the solubility of copper, cuprous and cupric oxides in water in the temperature range 480°–620° C, but their results are almost an order of magnitude lower than those presented here. It is suggested that this discrepancy may result from: (*a*) incomplete acid cleaning of their sampling system; (*b*) insufficient equilibration time in the solubility autoclave; (*c*) interaction with the high concentrations of iron in the water, which resulted from their use of stainless steel equipment; (*d*) interaction with the hydrogen evolved during the corrosion of the stainless steel system.

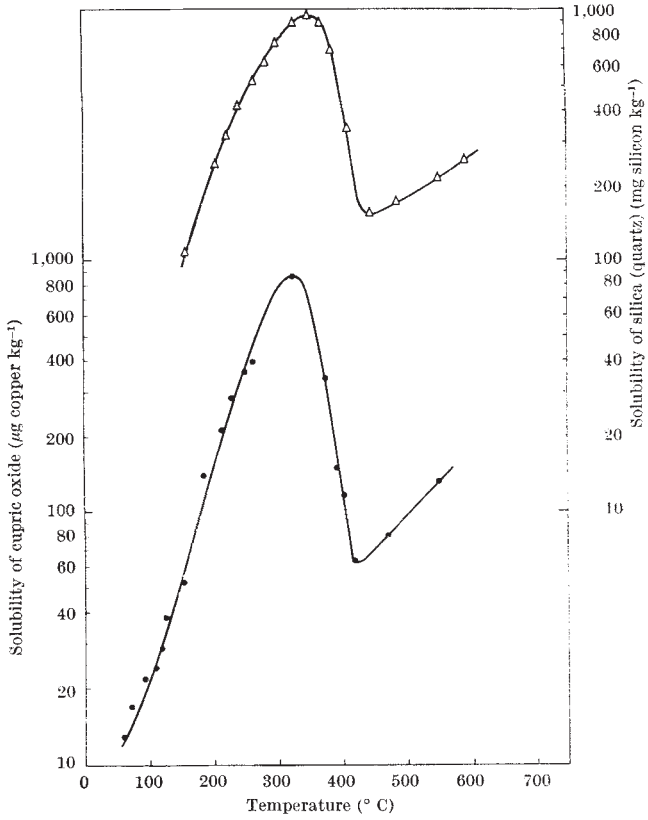

Fig. 1. Isobaric solubility of cupric oxide and silica in water. ●, Present results with cupric oxide at 310 bars; △, Heitmann's results[3] with silica at 300 bars.

The isobaric solubility of cupric oxide in water (*p*H 7·5) at 310 bars obtained in the present work is shown in Fig. 1, which also shows the 300 bar isobar for the silica (quartz) water system[3]. The two curves show a markedly similar variation of solubility with temperature, with the silica solubilities about three orders of magnitude greater than those of cupric oxide. This similarity suggests that the nature of the solvent determines the isobaric temperature coefficient of solubility for systems of this type, while the nature of the solute determines the absolute solubility level. It follows therefore that a generalized solubility equation based on the physical properties of the solvent is feasible. Attempts to formulate such an equation, for example by Martynova[4], have included only the specific volume of the solvent and have not successfully correlated the experimental data for any given system. Work is in progress in this laboratory on an empirical equation which includes further physical properties of water.

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