Among the experiments in progress which are designed to distinguish between the above effects is the measurement of the sign of the electric field gradient at the ^{119}Sn nucleus. In the case of an electric field gradient produced by the back donation of electrons into the vacant orbitals of tin, there is an excess of charge along the Sn-substituent bond direction whilst for the ionic charge transfer mechanism there is charge density missing along this bond direction and accordingly the sign of the electric field gradient is different in the two cases.

Acknowledgements—It is a pleasure to thank Professor P. B. Moon, F.R.S. for his continued interest in this research and both the Science Research Council and I.C.I., Ltd. for financial support.

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J. inorg. nucl. Chem. 1967, Vol. 29, pp. 1180 to 1182. Pergamon Press Ltd. Printed in Northern Ireland

Kinetics of oxidation of tellurium

(*Received* 7 *November* 1966)

In the extraction of gold from telluride ores it is usual to roast the ore prior to the cyanidation stage. In some cases cyanidation of roasted ores leads to incomplete recovery of gold.(1) The reason for this is not clear, but is probably related to the mechanism and extent of the oxidation of the ores under the various conditions obtaining. The present Note reports some results on the oxidation of tellurium on heating in air or oxygen, a reaction which contributes to the overall oxidation of gold telluride.

The only stable oxide of tellurium appears to be the dioxide. Reports of the existence of suboxides(2) have not received subsequent confirmation,(3) and no reaction or mutual solubility has been found between tellurium and its dioxide in either the liquid or solid state below 800°C.(4)

EXPERIMENTAL

The kinetics of the oxidation were conveniently studied using a quartz spring microbalance in the usual type of apparatus.(5) Within the section of the furnace containing both the specimen and the measuring thermocouple the temperature was constant to $\pm 2°$. Polycrystalline specimens were prepared from crushed "Semiconductor" grade tellurium (Mining and Chemical Products Ltd.) by pressing at 48,000 psi in a rectangular die. Each specimen weighed about 1 g and was about 90 per cent of theoretical density. Platinum wire 0·1 mm in dia. was used to suspend the specimen from the spring. The reaction was started by lowering the specimen into the furnace at temperature and with the required gas flow. Because of the time taken by the specimen to attain the temperature of the furnace, the first 5–10 min of each run were neglected. So that changes in surface area could be ignored, overall reaction was restricted to less than 2 per cent.(5)

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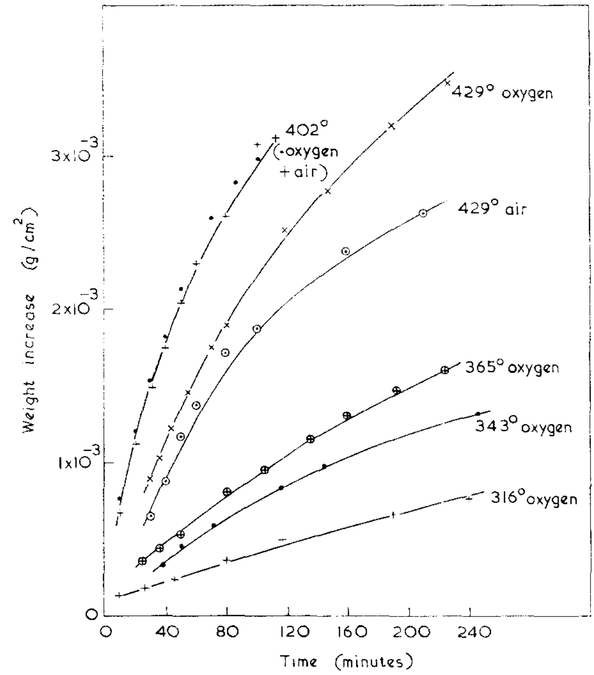

FIG. 1.—Some typical curves of wt. gain vs. time for different temperatures.

RESULTS AND DISCUSSION

X-ray powder diffraction patterns of a partially-oxidized specimen showed the presence of tellurium and tellurium dioxide only.

Some typical curves of wt. gain vs. time are shown in Fig. 1. In general these curves show the parabolic growth rate usually associated with oxidation occurring in the presence of a thick coherent pore-free layer of oxide, where diffusion through the oxide is the rate-controlling factor.(6) It is noticeable that, while oxygen concentration is a controlling factor at 429°C, this is not so at 402°C (or below). After oxidation in air at 429°C a deposit of oxide was seen on the walls of the furnace tube. At this temperature the vapour pressure of tellurium dioxide is $<10^{-6}$ mm(7), so direct volatilization of the dioxide may be neglected. It thus appears that at 429°C tellurium diffuses through the oxide film more rapidly than the surface oxidation occurs. Since some tellurium escapes

TABLE 1.—RATE DATA FOR OXIDATION OF TELLURIUM AT 402°C AND BELOW

Temp. (°C)	Oxidizing gas	Gas flow	Rate [(g/cm²)²/min]
316	Oxygen	3 l./hr	1.09×10^{-9}
343	Oxygen	3 l./hr	3.31×10^{-9}
	Air	3 l./hr	3.12×10^{-9}
365	Oxygen	3 l./hr	8.84×10^{-9}
402	Oxygen	3 l./hr	8.60×10^{-8}
	Air	3 l./hr	7.80×10^{-8}

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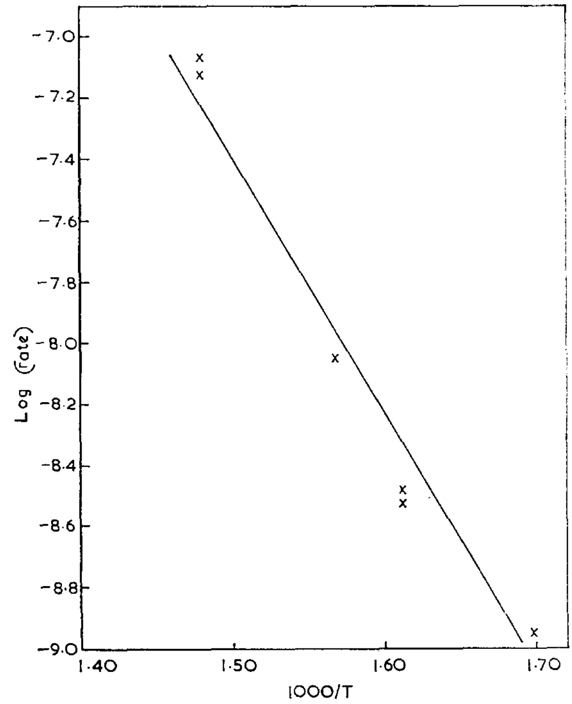

FIG. 2.—Arrhenius plot for reaction at 402°C and below.

from the surface of the specimen, the recorded wt. gain is less than that representing the actual extent of the reaction, so that in Fig. 1 the curves for 429°C lie below those for 402°C.

Reaction rates given in Table 1 were obtained from the slopes of the straight line relation between a and t/a where a is the wt. gain/cm^2 of apparent surface (related to the true surface area by a roughness coefficient assumed to be constant).(6) Reaction rates for duplicate runs were within 15 per cent of each other.

An Arrhenius plot of log (rate) against $1/T$ for 402°C and below (Fig. 2) gives a value of ~37·3 kcal/mole for the activation energy for diffusion through the dioxide. Owing to the narrow temperature range over which measurements were made, this value is not very accurate, but it is of the same order as values for thorium diffusing through its predominantly ionic dioxide.(8)

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