Formation and Transformation of $3TeO_2{\cdot}Nb_2O_5$

Osamu Yamaguchi,* Takahiro Shirai, Yasumichi Mukaida, and Kiyoshi Shimizu
Department of Applied Chemistry, Faculty of Engineering, Doshisha University, Kyoto 602, Japan

A compound so far denoted as $4TeO_2{\cdot}Nb_2O_5$ has been determined to be a metastable modification of $3TeO_2{\cdot}Nb_2O_5$. At a heating rate of 10 °C min^{-1} the metastable modification crystallizes at 530—550 °C from an amorphous material prepared by the simultaneous hydrolysis of tellurium tetrachloride and niobium isopropoxide. It has a tetragonal unit cell with a = 1.2308 and c = 0.9924 nm. The structure consists of the Te_3O_8 unit, built up of two TeO_3 groups and a TeO_4 group. The tetragonal-to-orthorhombic phase transformation occurs at 620—655 °C.

Few investigations[1–4] have been reported on the formation of tellurium niobium oxides in the TeO_2 rich region. Guillaume[1] first described the presence of $4TeO_2{\cdot}Nb_2O_5$ and $2TeO_2{\cdot}Nb_2O_5$. Galy and Lindqvist[2] synthesized a single crystal of $3TeO_2{\cdot}Nb_2O_5$ from a melt of starting composition $2TeO_2{:}1Nb_2O_5$ in a sealed gold tube and suggested that the *X*-ray powder diffraction data were the same as those from $2TeO_2{\cdot}Nb_2O_5$. Bart and co-workers[3,4] studied the reaction between TeO_2 and Nb_2O_5 over a long period of time at 500—800 °C and reported the presence of $4TeO_2{\cdot}Nb_2O_5$ and $3TeO_2{\cdot}Nb_2O_5$. They also pointed out that the $2TeO_2{\cdot}Nb_2O_5$ described by Guillaume[1] was a compound corresponding to $3TeO_2{\cdot}Nb_2O_5$. Thus it is certain that $2TeO_2{\cdot}Nb_2O_5$ is absent in the TeO_2–Nb_2O_5 system.

In the present study, a compound so far denoted as $4TeO_2{\cdot}Nb_2O_5$ was found to be a metastable modification of $3TeO_2{\cdot}Nb_2O_5$, by using an amorphous material prepared by the simultaneous hydrolysis of tellurium tetrachloride and niobium isopropoxide. The present paper deals with the formation and transformation of $3TeO_2{\cdot}Nb_2O_5$.

Experimental

Materials and Procedure.—Tellurium tetrachloride $TeCl_4$ (>99% pure) and niobium isopropoxide $Nb(OC_3H_7)_5$ (99.999% pure) were used as received; they were dissolved in propan-2-ol. The mixed solutions (A, $3Te^{4+}{:}2Nb^{5+}$ and B, $2Te^{4+}{:}Nb^{5+}$) were refluxed for 3 h and then hydrolyzed by adding distilled water at room temperature. The temperature was slowly increased to 75 °C while the resulting suspensions were stirred. The hydrolysis products were separated from the suspensions by filtration, washed 20 times in hot water, and dried at 120 °C under reduced pressure. The powders obtained are termed 'starting powders'.

Measurements.—The starting powders for electron microscopic observation were dispersed in amyl acetate by an ultrasonic treatment for 5 min. The dispersed drops were dried on carbon film, and observed under a 35-keV (*ca.* 5.6×10^{-15} J) beam. Thermal analyses (t.g.a, d.t.a.) were carried out in air at a heating rate of 10 °C min^{-1}; α-alumina was used as the reference for the d.t.a. The starting powders and specimens, obtained from the d.t.a. studies and then quenched, were examined by *X*-ray diffraction analysis using nickel-filtered Cu-K_α radiation. The goniometer scanning speed of 0.25° min^{-1} was selected so as to achieve accurate *d* spacings. Lattice parameters were determined using an internal standard of silicon. Infrared spectroscopy was performed on a dispersion in potassium bromide using the pressed-disc technique.

Results and Discussion

Characterization of Starting Powders.—Figure 1 shows the electron micrographs of the starting powders; their average particle size was *ca.* 0.2 μm. The starting powder A was amorphous. On the other hand, a small amount of crystalline TeO_2 (tetragonal) was present in B. The i.r. spectra for the starting powders are shown in Figure 2 and compared with that of the $3TeO_2{\cdot}Nb_2O_5$ glass;[5] these are very similar in shape, except that a shoulder at 770 cm^{-1} is present in the starting powders. Although characteristic bands derived from the structure of TeO_2 (tetragonal), built up of TeO_4 groups, are located at 780, 714, 675, and 635 cm^{-1},[5,6] these were not clearly detected in the spectrum of B. Dimitriev *et al.*[5] suggested that because the i.r. spectrum of the $3TeO_2{\cdot}Nb_2O_5$ glass is similar to that of the crystalline phase, the structure of the glass may be the same as that of the crystal consisting of the Te_3O_8 unit, built up of two TeO_3 groups and a TeO_4 group. The bands corresponding to 770 cm^{-1} in the starting powders, as will be described in a later section, were observed at 795 cm^{-1} in the spectrum of $3TeO_2{\cdot}Nb_2O_5$. Thus the starting powder A and the amorphous phase in B, as well as in the glass, may be characterized by the Te_3O_8 unit.

Thermal Analysis.—Figure 3 shows the t.g.a. curves for the starting powders. In A weight losses of 9.51% to 340 °C and 64.41% at 790—1 215 °C were observed. On the other hand, the data for B showed weight losses of 8.63% to 310 °C and 70.71% at 740—1 220 °C. The first weight loss in both starting powders can be attributed to the release of absorbed water, hydrated water, and organic residues from the parent alcohol.[7] The second weight loss at high temperatures corresponds to the loss due to the volatilization of the TeO_2 component from the melt; in fact, these weight losses are in agreement with the theoretical values of 64.30% for A and 70.60% for B.

The d.t.a. curves reveal two exothermic and one endothermic peaks for A and two exothermic and two endothermic peaks for B (Figure 4). The sharp exothermic peaks at 530—550 °C for A and 535—555 °C for B, as will be described, were found to result from the crystallization of tetragonal $3TeO_2{\cdot}Nb_2O_5$. The small exothermic peaks at 620—655 °C for A and 635—670 °C for B were confirmed to be due to the tetragonal-to-orthorhombic phase transformation. The small endothermic peak at 730 °C for B is the result of melting of free TeO_2; this melting temperature is in agreement with that reported.[3,4] The sharp endothermic peaks at 823 °C in both starting powders are due to the melting of $3TeO_2{\cdot}Nb_2O_5$. As soon as TeO_2 and $3TeO_2{\cdot}Nb_2O_5$ melted, the volatilization occurred as can be seen from the t.g.a. data. No peaks in both starting powders were detected in the cooling process below 700 °C.

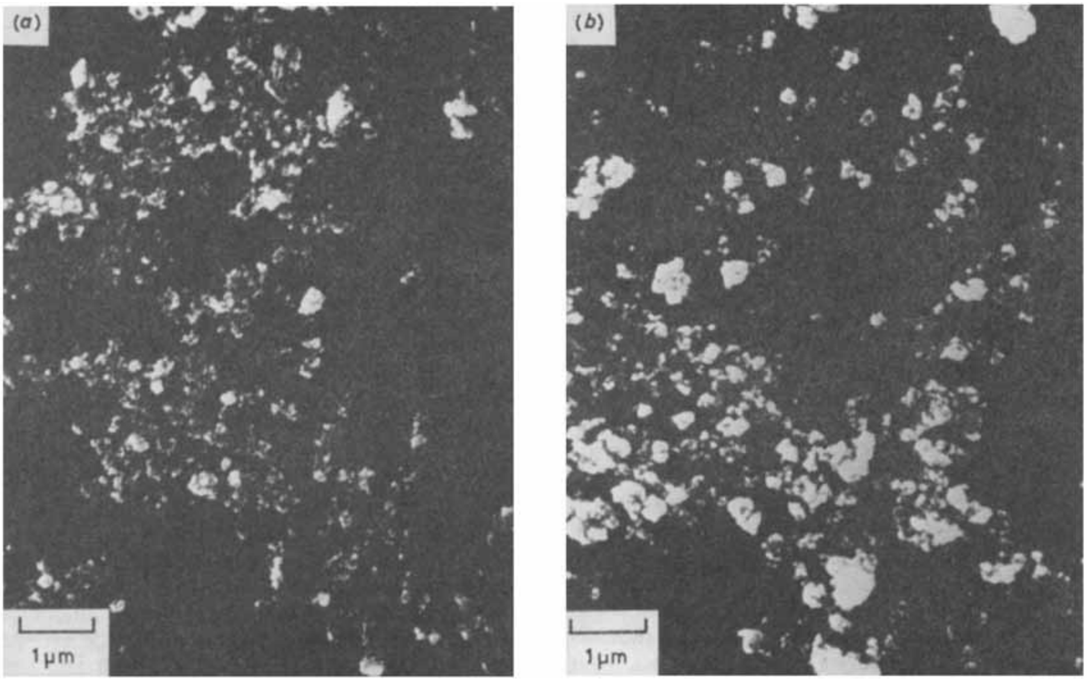

Figure 1. Electron micrographs for (*a*) starting powder A and (*b*) starting powder B

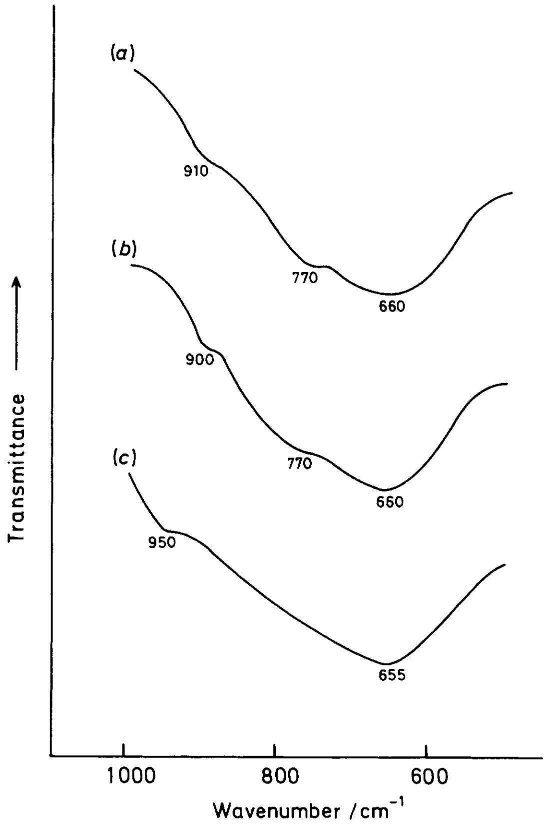

Figure 2. I.r. spectra for (*a*) starting powder A, (*b*) starting powder B, and (*c*) $3TeO_2{\cdot}Nb_2O_5$ glass (ref. 5)

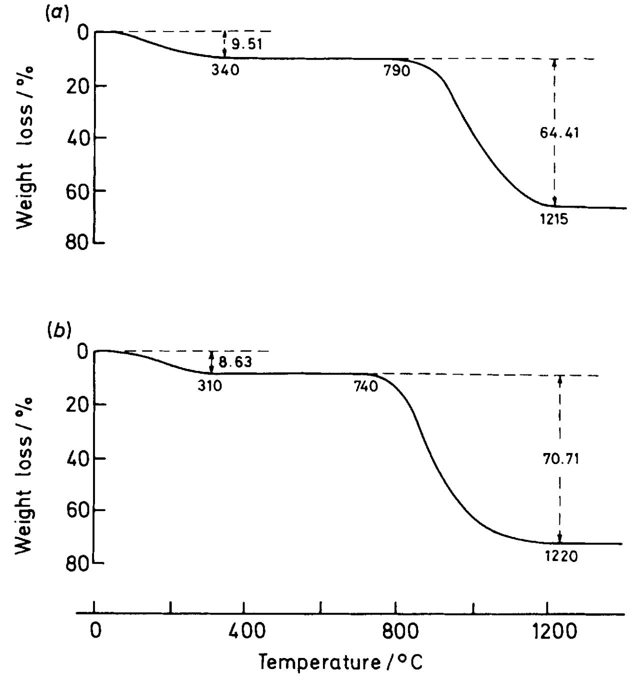

Figure 3. Thermogravimetric analysis curves for (*a*) starting powder A and (*b*) starting powder B

X-Ray Analysis.—The starting powder A, being amorphous, showed that no significant change in structure was observed up to the temperature of the sharp exothermic peak. After the peak, the specimen heated at 550 °C gave *X*-ray diffraction lines corresponding to $4TeO_2{\cdot}Nb_2O_5$. The characteristic pattern was obtained by heating for 30 min at 550 °C; only this phase was observed up to 615 °C. The lines of $3TeO_2{\cdot}Nb_2O_5$ (orthorhombic) began to appear at 625 °C, and the intensity of their lines increased rapidly up to 655 °C in inverse proportion to that of $4TeO_2{\cdot}Nb_2O_5$. Orthorhombic $3TeO_2{\cdot}Nb_2O_5$ was formed as a single phase after heating for 30 min at 655 °C; the specimens heated up to 790 °C showed the pattern of only this phase. After $3TeO_2{\cdot}Nb_2O_5$ melted, the specimen became amorphous. However the lines of γ-Nb_2O_5 (orthorhombic)

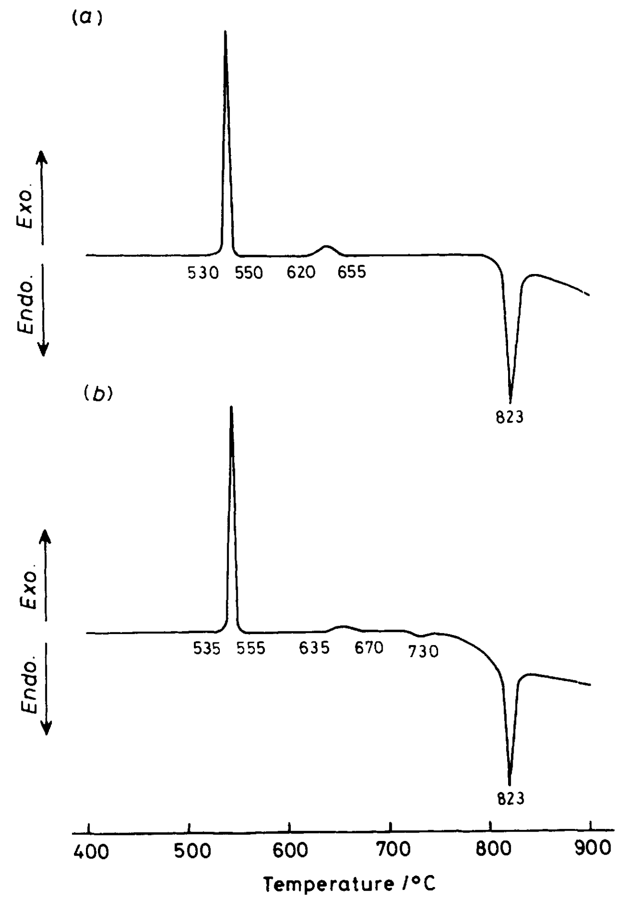

Figure 4. Differential thermal analysis curves for (*a*) starting powder A and (*b*) starting powder B

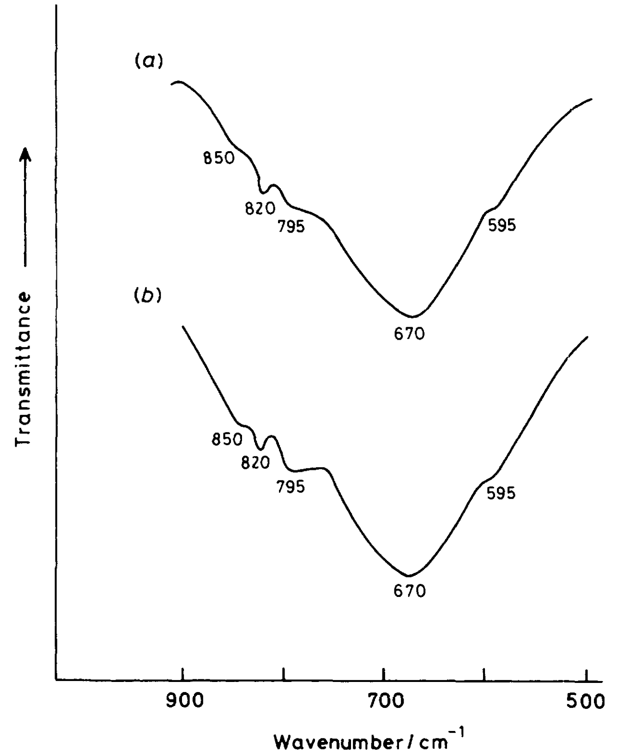

Figure 5. I.r. spectra for (*a*) tetragonal and (*b*) orthorhombic modifications of $3TeO_2{\cdot}Nb_2O_5$

Table 1. *X*-Ray diffraction data for metastable modification of $3TeO_2{\cdot}Nb_2O_5$ and for $4TeO_2{\cdot}Nb_2O_5$

Metastable modification of $3TeO_2{\cdot}Nb_2O_5$ *				$4TeO_2{\cdot}Nb_2O_5$ (ref. 3)	
$d_{obs.}$/nm	$d_{calc.}$/nm	I/I_0	*hkl*	$d_{obs.}$/nm	I/I_0
0.386	0.386	30	202	0.378	20
0.360	0.362	60	311	0.358	100
0.341	0.341	3	320	0.339	13
0.332	0.331	5	003	0.335	18
0.328	0.327	100	222	0.328	88
0.319	0.319	25	103	0.320	38
0.316	0.316	25	302	0.314	29
0.309	0.309	3	113	0.309	4
0.306	0.306	3	312	0.306	3
0.2988	0.2985	3	410	0.2979	5
				0.2947	3
				0.2870	6
0.2835	0.2835	20	213	0.2843	22
0.2812	0.2812	20	322	0.2804	18
				0.2780	3
				0.2662	1
0.2615	0.2615	5	402	0.2597	2
0.2500	0.2504	25	332	0.2510	3
				0.2448	6
0.2430	0.2432	25	104	0.2444	71
0.2414	0.2414	3	510	0.2419	35
				0.2386	3
				0.2335	3
0.2262	0.2262	5	214	0.2268	2
				0.2248	1
				0.2229	1
0.2155	0.2155	5	224	0.2151	8
0.2092	0.2092	5	314	0.2098	3
				0.2081	3
				0.2055	1
				0.2027	2
				0.1949	1
0.1922		15	540	0.1927	8
0.1894	0.1922	25	062	0.1893	13
0.1890	0.1896	25	205	0.1889	11
0.1867	0.1889	10	215	0.1860	7
0.1843	0.1867	5	424	0.1856	6
	0.1843				

* Tetragonal: a = 1.2308, c = 0.9924 nm.

were recognized at 850—1 000 °C. The specimen heated at 1 100 °C contained a mixture of γ- and α-NbO_5 (monoclinic). Well-formed α-Nb_2O_5 was obtained at 1 220 °C. It is clear that the results represent the volatilization of the TeO_2 component from the melt. No other ternary or binary phases were observed throughout the heating process up to 790 °C. Therefore the above mentioned results suggest that the compound so far denoted as $4TeO_2{\cdot}Nb_2O_5$ is a new modification of $3TeO_2{\cdot}Nb_2O_5$. High-temperature *X*-ray diffraction analysis showed that during cooling, the orthorhombic modification did not transform to the new modification. Clearly, the new modification must be metastable. The diffraction data for the metastable modification are shown in Table 1 and compared with those denoted tentatively as $4TeO_2{\cdot}Nb_2O_5$;[3] they are consistent with each other, although some weak lines are absent in the present study. No crystal structure for $4TeO_2{\cdot}Nb_2O_5$ has been described. The diffraction lines for the metastable modification of $3TeO_2{\cdot}Nb_2O_5$ were indexed as a tetragonal unit cell with a = 1.2308 nm and c = 0.9924 nm. Table 2 shows the diffraction data for the orthorhombic modification. Although some additional lines, compared with the data reported by Galy and Lindqvist (Table 2),[2] were observed, all diffraction lines were reasonably indexed by a unit cell with a = 0.7693, b = 1.5698, and c = 0.3977 nm.

The starting powder B, containing a small amount of TeO_2, proceeded in the same heating process as with A; the tetragonal modification of $3TeO_2{\cdot}Nb_2O_5$ crystallized at 535—555 °C and the tetragonal-to-orthorhombic phase transformation occurred at 635—670 °C. Free TeO_2 was recognized up to the melting temperature at 730 °C. From the above mentioned results, it was confirmed that no compound corresponding to $4TeO_2{\cdot}Nb_2O_5$ exists in the TeO_2–Nb_2O_5 system.

Infrared Spectrum.—Figure 5 shows the i.r. spectra for both modifications; these have the same spectral pattern as $3TeO_2{\cdot}Nb_2O_5$.[6] It has been shown that $3TeO_2{\cdot}Nb_2O_5$ contains Te_3O_8 groups by *X*-ray measurements.[2] Arnaudov *et al.*[6] interpreted the i.r. spectral data for a series of inorganic tellurites and indicated that the structure of $3TeO_2{\cdot}Nb_2O_5$ is formed by the Te_3O_8 unit, built up of two TeO_3 groups and a TeO_4 group, and the characteristic bands are located at 800 [$\nu(TeO_3) + \nu(TeO_4)$], 655 [$\nu(TeO_3) + \nu(TeO_4)$], and 580 cm^{-1} [$\nu(TeO_4)$]. In the present study, these bands correspond to 795, 670, and 595 cm^{-1}. It can therefore be concluded that the tetragonal modification is also characterized by the Te_3O_8 unit.

Table 2. *X*-Ray diffraction data for orthorhombic modification of $3TeO_2{\cdot}Nb_2O_5$

This work[a]				Ref. 2[b]	
$d_{obs.}$/nm	$d_{calc.}$/nm	I/I_0	*hkl*	$d_{obs.}$/nm	I/I_0
0.691	0.691	5	110	0.690	7
0.433	0.433	15	130	0.433	25
0.398	0.398	40	001	0.398	65
0.385	0.385	25	200	0.3853	30
0.373	0.374	70	210	0.3735	90
0.353	0.353	40	101	0.3534	50
0.349	0.350	90	140	0.3497	100
0.345	0.345	100	111	0.3453	90
0.322	0.322	55	121	0.3222	65
0.316	0.317	60	031	0.3166	70
0.310	0.310	10	230	0.3097	7
0.2928	0.2928	70	131	0.2928	60
0.2910	0.2907	80	150	0.2908	60
0.2793	0.2793	10	041	0.2794	10
0.2721	0.2723	25	211	0.2722	20
0.2625	0.2626	25	141		
0.2607	0.2608	55	221	0.2609	45
0.2527	0.2531	10	310		
0.2477	0.2477	30	160	0.2479	20
0.2438	0.2438	15	320	0.2439	10
0.2432	0.2432	15	250		
0.2347	0.2347	10	151	0.2348	7
0.2301	0.2303	15	330	0.2302	7
0.2186	0.2186	5	061		
0.2156	0.2155	15	301		
0.2149	0.2147	15	340		
0.2134	0.2135	10	311		
0.2103	0.2103	10	161		
0.2075	0.2075	35	251	0.2076	20
0.1989	0.1989	45	002	0.1990	20
0.1986	0.1986	50	350		
0.1953	0.1953	25	071	0.1955	15
0.1937	0.1937	10	270		
0.1908	0.1909	35	410	0.1910	15
0.1889	0.1889	50	341	0.1889	30
0.1868	0.1868	25	420	0.1870	7
0.1859	0.1859	25	032	0.1860	7

[a] Orthorhombic: a = 0.7693, b = 1.5698, and c = 0.3977 nm. [b] Orthorhombic: a = 0.7700, b = 1.5700, and c = 0.3980 nm.

References

1 G. Guillaume, Thesis, No. 808, University of Bordeaux, France, 1970.
2 J. Galy and O. Lindqvist, *J. Solid State Chem.*, 1979, **27**, 279.
3 J. C. J. Bart and G. Petrini, *Z. Anorg. Allg. Chem.*, 1980, **466**, 81.
4 F. Garbassi, J. C. J. Bart, and G. Petrini, *J. Electron Spectrosc. Relat. Phenom.*, 1981, **22**, 95.
5 Y. Dimitriev, V. Dimitrov, and M. Arnaudov, *J. Mater. Sci.*, 1983, **18**, 1353.
6 M. Arnaudov, V. Dimitrov, Y. Dimitriev, and L. Markova, *Mater. Res. Bull.*, 1982, **17**, 1121.
7 O. Yamaguchi, K. Sugiura, A. Mitsui, and K. Shimizu, *J. Am. Ceram. Soc.*, 1985, **68**, C44.

Received 28th September 1987; Paper 7/1731