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THE THERMAL BEHAVIOUR OF SOLID PHASES IN THE Te–Se–O_2 SYSTEM

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ABSTRACT

A comparative study is made of the thermoanalytical stabilities of various tellurium and selenium mixed oxides ($TeSeO_4$, Te_2SeO_6, Te_3SeO_8, Te_4SeO_{10} and Te_8SeO_{18}). The observed stabilities are then approximately correlated with data given by a kinetic analysis of the thermal decomposition processes in the non-isothermal regime obtained from TG and DSC by using two calculation methods (Freeman and Carroll and modified Freeman and Carroll).

INTRODUCTION

A new series of compounds in the Te–Se–O_2 system has recently been obtained by solid-state chemical reactions [1]. These compounds can be represented by the general formula $Te_xSeO_{2(x+1)}$ and have been characterised by various experimental techniques [2]. One important aspect of the reactivity of new inorganic materials, which is often little investigated, is their thermoanalytical study from which other physico-chemical properties, in particular structural data, can be obtained. Previous studies somewhat related to this work, although with a purely phenomenological and qualitative emphasis, give information on the SeO_2–TeO_2 phase diagram [3] and on the formation of the glasses in selenite systems [4]. Of more relevance, the thermal decomposition processes of materials of fixed compositions, formulated as mixed oxides Te_3SeO_8 and $TeSeO_4$, were published by the present authors [5].

This paper reports details of a comparative study carried out on the thermoanalytical stabilities of mixed oxides of the Te–Se–O_2 system. The observed stabilities are then approximately correlated with the data given by a kinetic analysis of the thermal decomposition processes in the non-isother-

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mal regime obtained from TG and DSC by using two calculation methods (Freeman and Carroll and modified Freeman and Carroll).

EXPERIMENTAL

The starting materials are oxycompounds of tellurium and selenium of composition $TeSeO_4$, Te_2SeO_6, Te_3SeO_8, Te_4SeO_{10} and Te_8SeO_{18} which can be represented as members of the series $Te_xSeO_{2(x+1)}$ where $x = 1, 2, 3, 4$ or 8.

The thermogravimetric (TG) and differential scanning calorimetric curves (DSC) were obtained with a Mettler thermal analyser model TA 3000. The experiments were carried out in air using 25-mg samples with a cooling rate of between 2 and 5°C min^{-1}.

RESULTS AND DISCUSSION

Table 1 shows the data deduced from TG for the compounds studied; all are stable in air below 300°C, above which the decomposition of $TeSeO_4$ starts. The temperature interval in which the samples transform is very variable and is relatively high for Te_8SeO_{18}, therefore this oxide could not be studied by DSC since the higher temperature limit to the reaction exceeded the detection limit (600°C) of the cell used. The residue of all the decomposi-

TABLE 1

Thermal analysis data on the decomposition of $Te_xSeO_{2(x+1)}$ oxides obtained by TG

$Te_xSeO_{2(x+1)}$	Temperature interval (°C)	ΔP (%)$_{exp}$	ΔP (%)$_{calc}$
$TeSeO_4$	320–400	41.25	41.01
Te_2SeO_6	400–475	25.7	25.79
Te_3SeO_8	440–480	18.7	18.81
Te_4SeO_{10}	410–510	14.6	14.81
Te_8SeO_{18}	390–700	7.91	7.99

TABLE 2

Thermal analysis data on the decomposition of $Te_xSeO_{2(x+1)}$ oxides obtained by DSC

$Te_xSeO_{2(x+1)}$	Temperature interval (°C)	ΔH_{endo} (kJ mol^{-1})
$TeSeO_4$	370–415	97.1
Te_2SeO_6	420–490	87.3
Te_3SeO_8	440–490	120.9
Te_4SeO_{10}	400–450	40.5

tion processes is TeO_2 (tetragonal) which indicates that all the selenium contained in the starting oxides was eliminated in the form of SeO_2 gas (sublimation temperature at atmospheric pressure is 315°C). The losses in weight, expressed as ΔP (%) are in good agreement with this supposition.

Table 2 shows the temperature intervals in which these transformations are shown in DSC for the first four terms in the series together with the values deduced for their associated enthalpies.

The curves registered show only one endothermic effect which corresponds to the gradual loss of weight observed in TG which suggests that the elimination of SeO_2 takes place in only one well-defined step. As an example, Figs. 1 and 2 show the graphs of TG, DTG and DSC of Te_2SeO_6 and Te_4SeO_{10}, respectively.

Thus, the general transformation scheme can be represented as

$$\mathrm{Te}_x\mathrm{SeO}_{2(x+1)}(\text{solid}) \rightarrow x\mathrm{TeO}_2(\text{solid}) + \mathrm{SeO}_2(\text{gas})\ \Delta H_{\mathrm{d}} > 0$$

Instead of separately analysing the significance of each of the enthalpy values involved in these processes (see Table 2) it is more constructive to study comparatively the relative thermodynamic stabilities of the compounds in terms of their formation enthalpies based on certain experimental magnitudes. Thus, a thermodynamic cycle can be established from the elements concerned so as to arrive at the formation of the mixed oxide as indicated in Scheme 1.

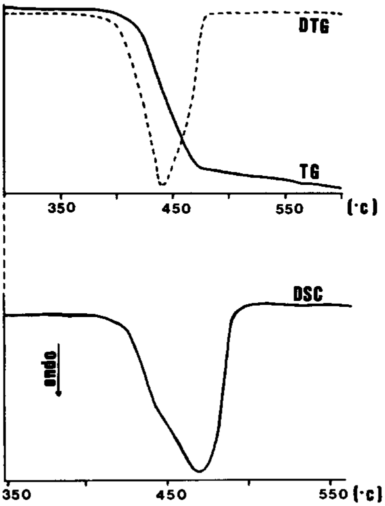


Fig. 1. TG, DTG and DSC curves for Te_2SeO_6.

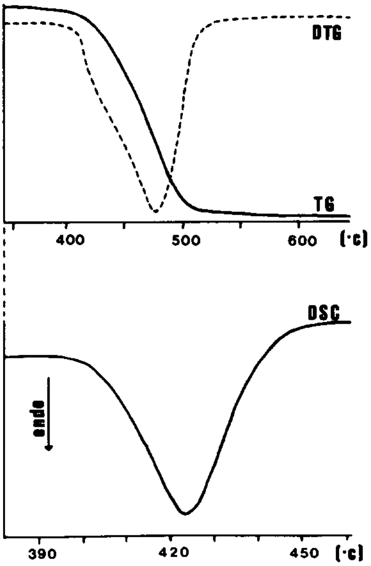
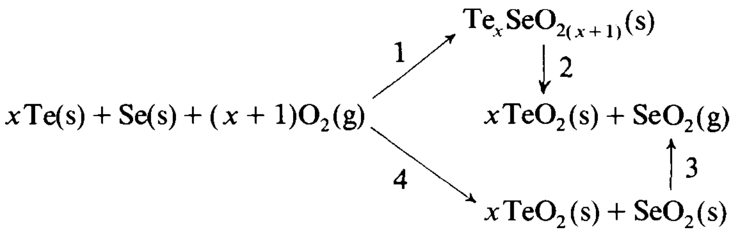


Fig. 2. TG, DTG and DSC curves for Te_4SeO_{10}.



Scheme 1. Thermodynamic quantities involved in the formation of the $Te_xSeO_{2(x+1)}$ oxides. (1) $\Delta H_f(MO)$, formation enthalpy of the mixed oxide; (2) ΔH_d, decomposition enthalpy of the oxide; (3) $\Delta H_s(SeO_2)$, sublimation enthalpy of SeO_2; (4) $x\Delta H_f(TeO_2) + \Delta H_f(SeO_2)$, sum of the molar enthalpies of formation of tellurium and selenium dioxides.

From these expressions it can thus be deduced that

$$\Delta H_f(MO) = x\Delta H_f(TeO_2) + \Delta H_f(SeO_2) + \Delta H_s(SeO_2) - \Delta H_d \qquad (1)$$

The ΔH_d term of eqn. (1) can be correlated with the experimentally obtained value, ΔH_{endo}, which appears in Table 2 for each compound. Although the literature data on the standard formation enthalpies of tellurium and selenium dioxide are not strictly applicable since, in the temperature conditions under which the reaction takes place, the system is not in the standard state, they are, however, useful data for establishing a means of comparing the thermodynamic stability of mixed oxides. That is, their relative influence will be approximately the same for all processes taking place in similar temperature intervals.

Since the $\Delta H_f(SeO_2)$ and $\Delta H_s(SeO_2)$ terms in eqn. (1) are the same throughout the $Te_xSeO_{2(x+1)}$ series the contribution of the remaining terms, which vary for each oxide, to the stability can be estimated. The results are shown in Table 3 where the column $\Delta H_{relative}$ gives the algebraic sum $\Delta H_{relative} = x\Delta H_f(TeO_2) - \Delta H_d$.

As can be seen the values of ΔH_d in the series do not seem to follow a regular and thus significant trend in relation to the stoichiometry of the compound. On the other hand, these values combined with the contribution from the enthalpy of formation of TeO_2 (giving $\Delta H_{relative}$), do increase as the tellurium oxide content increases.

These findings suggest that the thermodynamic stability of the mixed

TABLE 3

Some thermodynamic data for the $Te_xSeO_{2(x+1)}$ series (kJ mol^{-1})

$Te_xSeO_{2(x+1)}$	$x\Delta H_f(TeO_2)$	ΔH_d	$\Delta H_{relative}$
$TeSeO_4$	−322.2	97.1	−419.3
Te_2SeO_6	−644.4	87.3	−731.7
Te_3SeO_8	−966.6	120.9	−1086.6
Te_4SeO_{10}	−1288.8	40.5	−1329.3

TABLE 4

Kinetic parameters for the decomposition reactions of the $Te_xSeO_{2(x+1)}$ mixed oxides obtained by the Freeman and Carroll method

$Te_xSeO_{2(x+1)}$	TG		DSC	
	n	E^* (kJ mol^{-1})	*n*	E^* (kJ mol^{-1})
$TeSeO_4$	1.31	154.05	0.03	143.47
Te_2SeO_6	0.52	213.13	0.95	289.44
Te_3SeO_8	1.00	272.10	0.74	291.75
Te_4SeO_{10}	0.76	130.05	1.34	525.65

oxide increases with tellurium content which is compatible with the structural and chemical characteristics of this element with respect to selenium. However this increase in stability is not apparently reflected in the temperature at which the thermal decomposition starts nor in the values of ΔH_{endo} determined by DSC.

The kinetic analysis of these thermal decomposition processes has been carried out by the classical method of Freeman and Carroll [6] (FC) and by the so-called modified Freeman and Caroll (MFC) treatment proposed by Jerez [7]. Both methods are based on the assumptions that the kinetics of the process studied can be described by an equation of order *n*. The calculated values of *n* both from the FC method (Table 4) and from the MFC method (Table 5) do not have any significance in the majority of cases. This suggests that the operative decomposition mechanism does not conform to the starting hypothesis. This seems to be due to the different factors which influence the overall transformation and which affect the quantities registered by different amounts.

However, although the values of *n* in the kinetic equation are considered irrelevant in these cases, the magnitudes of the respective activation energies should be reliable. In addition, in cases such as the present, both the FC and MFC methods often give acceptable values of E^*. However, before discussing the variation of the E^* values in the series, some comments on the factors influencing them are necessary.

TABLE 5

Kinetic paramaters for the decomposition reactions of the $Te_xSeO_{2(x+1)}$ mixed oxides obtained by the modified Freeman and Carroll method

$Te_xSeO_{2(x+1)}$	TG		DSC	
	n	E^* (kJ mol^{-1})	*n*	E^* (kJ mol^{-1})
$TeSeO_4$	1.04	128.50	0.42	156.24
Te_2SeO_6	0.57	219.30	0.96	294.49
Te_3SeO_8	1.22	341.49	1.03	329.13
Te_4SeO_{10}	1.19	178.22	1.09	452.65

As stated earlier, the decomposition of the mixed oxides of tellurium and selenium consists in: (a) the formation of the respective dioxides; and (b) the elimination of SeO_2 in the form of a gas which is concommitant with and after step (a).

On analysing the process by TG, the data relevant to step (b) are registered with a certain independence of the previous step when the overall process is essentially controlled by the diffusion of the gaseous component. On the other hand, the variation of enthalpy measured by DSC implies that the decomposition of the starting material and the vaporisation of the eliminated dioxide occur simultaneously, both contributions being endothermic.

The values of E^* deduced from TG follow an approximately similar trend to those of the reaction enthalpy (DSC) although the two calculation methods give different values. (In addition in some cases they differ from the values previously found [5] which seems to invalidate any conjecture regarding their interpretation.)

However, appreciable coincidences are observed between the activation energies calculated from DSC by using both methods and a certain pattern in their magnitude is observed on descending the mixed oxide series. This is consistent with the increase in stabilities found (cf. Tables 3 and 5). Additionally, the fact that the values of n obtained by the MFC method correspond appreciably with kinetic equations of order 0.5 for the first term in the oxide series and of order for the remaining terms may be significant.

These results will acquire significance on comparison with those determined by isothermal methods which are in progress.

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