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THERMAL BEHAVIOURS OF SULPHUR-SELENIUM MIXTURES

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The thermal behaviours of sulphur, selenium and their mixtures have been studied over the range 40 – 450°. It has been shown that the polymerization threshold temperature of sulphur, $T_{\emptyset}$, decreases with increasing selenium content and follows the equilibrium copolymerization model proposed by Tobolsky and Owen. The formation of octa-atomic species $Se_{8-x}S_x$, where $8 > x > 4$, takes place only after sulphur is in the liquid state. The rate of polymerization is enhanced by the addition of increasing amounts of selenium and this is reflected in the higher polymerization peak temperatures. The X-ray powder diffractograms show that all the sulphur-selenium melts belong to the same phase as that of SeS, though the constituent atoms are randomly distributed.

Sulphur and selenium are known to undergo polymerization on application of heat. Tobolsky and coworkers have proposed a model for the homopolymerization of sulphur [1] and selenium [2], and have shown the utility of such models in explaining the experimental results obtained in the copolymerization of sulphur-selenium mixtures [3]. The central theme of their work is the decrease of the polymerization threshold temperature $T_{\emptyset}$ of sulphur on progressive addition of selenium, and in the development of a relationship between the temperature-dependent number-average chain length, and monomer concentration and the equilibrium constants for the initiation and propagation reactions. Ward and Meyers [4] found a marked decrease in the $T_{\emptyset}$ of sulphur with increasing selenium content (up to 15 atomic percent), which is not predicted by the Tobolsky – Owen treatment [3]. This decrease was attributed to the formation of species of the type Se_xS_{8-x}, where $8 > x > 4$, in the sulphur-selenium melt.

In view of our successful synthesis of Se_4S_4 under thermal conditions [5], we thought it worthwhile to explore the thermal behaviours of sulphur selenium mixtures over the entire range of composition from 100% sulphur to 100% selenium. Differential thermal analysis (DTA) followed by X-ray powder diffraction were the main techniques used, and the experimental conditions maintained were similar to those adopted for the synthesis of Se_4S_4.

Experimental

Twice sublimed sulphur was used. Selenium was of 99.99% purity and was supplied by the Bhabha Atomic Energy Establishment, Bombay.

The DTA apparatus used was locally fabricated [6]. Pyrex glass tubes sealed at one end were used as sample holders. A small groove made at the sealed end of the tube served for the housing of the thermocouples. Weighed amounts of the pure components or the mixtures were intimately mixed in an agate mortar, filled into the glass tubes, evacuated to 10^{-2} torr and sealed. Calcined Al_2O_3 was taken as the reference material and subjected to the same conditions as for the samples. The sealed glass tubes containing samples/Al_2O_3 (0.950 g) had the following dimensions: length = 60 mm, internal diameter = 8.75 mm, and external diameter = = 9.5 mm. The apparatus was standardized using KNO_3 and $Na_2WO_4 \cdot 2\,H_2O$. A heating rate of 6–7° min was maintained and the DTA patterns were recorded over the temperature range 40–450°.

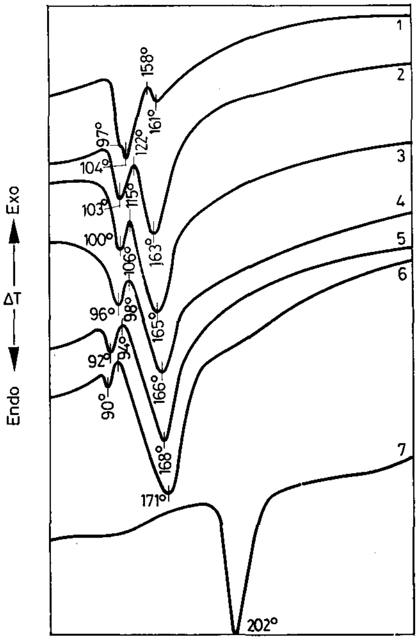

Fig. 1. Heating curves of sulphur–selenium mixtures. (1) 100% S, (2) 75% S + 25% Se, (3) 66.67% S + 33.33% Se, (4) 50% S + 50% Se, (5) 33.33% S + 66.67% Se, (6) 25% S + + 75% Se, and (7) 100% Se

The heating curves are given in Fig. 1. The samples were allowed to cool in the furnace itself. After one day, reheating was performed (Fig. 2) and the material then cooled. Finally the samples were recovered and, after grinding, the X-ray

Table 1

X-ray powder data ('d' spacings in Å) on sulphur-selenium melts*

Pure S	75% S + + 25% Se	66.67% S + 33.33% Se	50% S + + 50% Se	SeS	Pure Se
	4.41 (35)	4.44 (35)	4.44 (25)	4.42 (50)	
4.06 (15)					
3.85 (100)	3.77 (100)	3.79 (100)	3.79 (100)	3.77 (100)	3.78 (40)
	3.70 (65)	3.73 (55)	3.73 (55)	3.70 (50)	3.63 (25)
3.58 (8)	3.53 (30)	3.56 (30)	3.57 (30)	3.54 (50)	
3.45 (37)					
3.34 (20)	3.36 (10)			3.34 (10)	
3.22 (46)	3.21 (50)	3.23 (40)	3.24 (35)	3.22 (60)	
3.11 (25)	3.11 (25)	3.14 (25)	3.15 (25)	3.13 (40)	
3.09 (10)	3.05 (10)	3.08 (10)	3.09 (15)	3.06 (30)	
2.85 (20)		2.98 (6)			3.01 (100)
2.78 (15)	2.78 (15)		2.79 (10)	2.78 (10)	
	2.63 (15)	2.64 (10)		2.63 (20)	
2.50 (8)	2.51 (15)	2.53 (10)	2.55 (10)	2.52 (40)	
2.43 (15)					
2.38 (10)					
2.29 (10)	2.24 (15)	2.25 (10)		2.24 (20)	
2.11 (10)					
	2.01 (10)			2.01 (20)	
1.91 (10)					
1.78 (15)	1.79 (15)			1.78 (30)	

* Figures in paranthesis indicate relative intensity.

powder diffractograms were taken on a Phillips PW 1051 X-ray diffractometer using Ni-filtered Cu K_α ($\lambda = 1.5418$ Å) radiation. The observed '*d*' spacings are listed in Table 1 along with the relative intensities, and compared with those reported for SeS.

Results and discussion

The heating and the reheating curves of pure sulphur are essentially the same. The transition of rhombic to monoclinic sulphur at 97° and the melting at 104° were seen as endotherms. The polymerization of liquid sulphur has been located at the centre of the broad endotherm at 161°, the polymerization threshold temperature T_{ϕ} being at 158°. The fact that liquid sulphur, even after polymerization and heating up to 450°, returns to the rhombic variety on cooling is clearly seen from the X-ray powder diffractogram [7]. In contrast to the thermal behaviour of pure sulphur, the heating and reheating curves of selenium are different. An endotherm at 202° was observed in the heating curve of selenium, while an exotherm at 110°, in addition to an endotherm at 204°, were seen in the reheating curve. The reheated sample gave a weak X-ray diffractogram which corresponds to the trigonal modification of selenium [8]. The melting of this modification is seen as an endotherm at 204°. The presence of the exotherm at 110° would indicate that there is also a vitreous variety of selenium along with the trigonal form under the conditions employed in these experiments. No polymerization of selenium in the liquid state is observed from the DTA results, indicating that the selenium is already present in the form of Se_n chains.

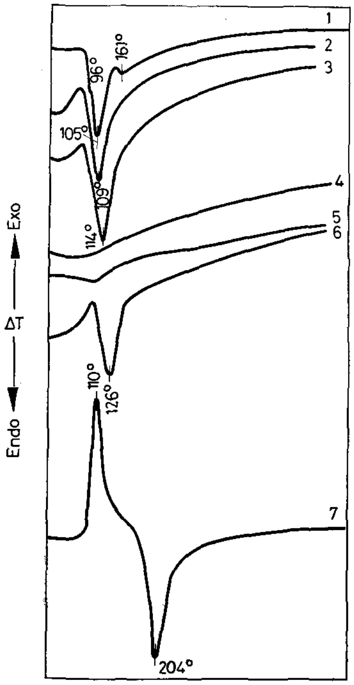

Fig. 2. Reheating curves of sulphur–selenium mixtures. (1) 100% S, (2) 75% S + 25% Se, (3) 66.67% S + 33.33% Se, (4) 50% S + 50% Se, (5) 33.33% S + 66.67% Se, (6) 25% S + + 75% Se, and (7) 100% Se

The heating curves of sulphur-selenium mixtures exhibit two endotherms, around 93 – 103° and 160 – 171°. The former corresponds to the melting of sulphur, the melting point decreasing with increasing selenium content. This can be explained as due to the effect of selenium, which can be regarded as an impurity in sulphur. The observed decrease in area under the endotherm with increasing selenium content can be attributed to the decrease in the sulphur content of the mixtures.

The second endotherm occurs around the polymerization temperature of sulphur. The polymerization threshold temperature T_{ϕ} has earlier been defined [1] as the point where a small amount of polymer is already present with a high degree of polymerization, and in the calorimetric experiments as the starting point or the most rapid ascent of the C_p *vs.* T curve [4]. It is reasonable to presume that in DTA measurements $T_\emptyset$ is represented as the temperature immediately preceding the endotherm from which there is a rapid descent. Using this criterion, the $T_\emptyset$'s for the different compositions of sulphur and selenium were plotted against the selenium content of the mixtures (Fig. 3). It immediately became obvious that, in the range 25 to 75 atomic percent of selenium, the decrease in $T_\emptyset$ is in good agreement with that predicted by Tobolsky and Owen.

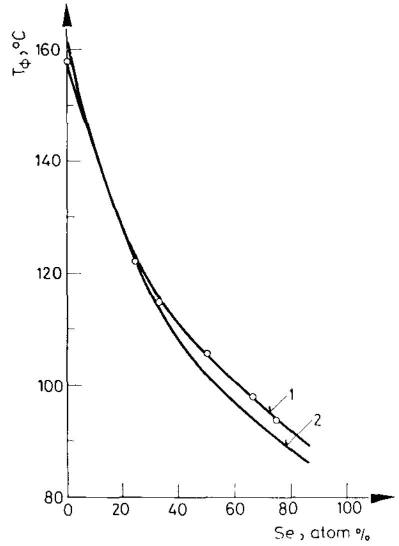

Fig. 3. Variation of polymerization threshold temperature (T) in the S – Se system: (1) present experimental DTA results, and (2) as predicted by the Tobolsky – Owen model

The decrease in $T_\emptyset$ as a function of increasing amount of selenium is reasonable in view of the lower bond energy of Se – Se (41 kcal/mole) compared to that of S – S (54 kcal/mole), which would mean a lower enthalpy of propagation for selenium than for sulphur. However, if, as shown by Ward [4], the addition of selenium to sulphur leads to the formation of selenosulphides before the polymerization threshold temperature, then the decrease in $T_\emptyset$ arises from two factors: (a) the formation of Se_xS_{8-x} would essentially decrease the initial monomer concentration of S_8 and, due to the higher bond energy of S – S compared to that of either Se – Se or Se – S, the enthalpy of propagation would be lower; (b) although all the selenium will now be present as S_xSe_{8-x}, the enthalpy of propagation is still likely to be that of Se_8, since it is decided by the strength of the weakest bond, i.e. the Se – Se bond, in the selenosulphides.

These two factors contribute to the marked decrease in $T_{\emptyset}$ on the addition of Se (up to 15 atomic percent) as observed by Ward [4]. However, for mixtures having a large selenium content the decrease in $T_{\emptyset}$ will predominantly be due to factor (a). The effect of factor (b) will be negligible, because the increase in selenium content will mean that the mixed rings will have more Se – Se bonds. However, since the enthalpy of propagation is determined by the strength of the weakest bond, it is not likely to be different for species having more than one Se – Se bond. Consequently, for mixtures of large selenium content (above 15 atomic percent) the decrease in $T_{\emptyset}$ should be slower. The observed results are in accordance with the above reasoning.

It is interesting to note that the polymerization peak temperature increases as the selenium content increases. This can be attributed to the fact that as the selenium content increases the ease with which polymerization takes place also increases, since selenium has a greater tendency to be in the polymeric form than sulphur.

The actual polymerization peak temperature is related to the rate of heat absorption as

$$\Delta T_{\max} = \left(\frac{\partial H}{\partial t}\right)_{\max} \times \left(\frac{M}{gk}\right)$$

where M = mass of the sample, g = geometrical shape of the container, and k = thermal conductivity of the sample. Under the experimental conditions the second term is almost constant, and hence any change in $\Delta T_{\max}$ is mainly dictated by the first term. Thus, if more reaction is taking place in the same interval of time, the increased rate of polymerization will lead to an increase in $\Delta T_{\max}$.

It is noticed that, even for a mixture with a selenium content as high as 75 atomic percent, no endotherm corresponding to the melting of selenium is observed. This suggests that sulphur and selenium will copolymerize in the melt, irrespective of the nature of the composition of the melt. Further, the decrease in $T_{\emptyset}$ is accompanied by a decrease in the melting point of sulphur, indicating that the selenium substitution into the S_8 rings takes place only after sulphur is in the liquid state.

The reheating curves (Fig. 2) show only an endotherm around 105 – 126°, with no peak corresponding to polymerization as observed in the heating patterns (Fig. 1). The endotherm has been ascribed to the melting of the sulphur-selenium melt. This gains support from the finding that the temperature increases with increasing content of the higher-melting selenium in the mixtures. The retainment of the polymeric nature of the melt is clearly seen from the absence of a peak corresponding to the polymerization in the reheating curves. The reason for the absence of an endotherm in mixtures containing 50 and 66 atomic percent selenium is not very clear.

The crystallinity of the melts is seen only up to a composition of 50 atomic percent of selenium. A further increase in the amount of selenium leads to the formation of amorphous materials. The observed '*d*' spacings of the melts are in good agreement with those reported for SeS [9]. This suggests that all the sulphur-selenium melts belong to the same phase as that of SeS. It is observed that there is a progressive decrease in the relative intensities of some of the lines in going from melts containing 25 to 50 atomic percent selenium. This relative decrease can be attributed to random distribution of sulphur and selenium atoms in the melt. Addition of increasing amounts of selenium beyond 50 atomic percent would enhance randomization of sulphur and selenium atoms, and the higher scattering power of the heavier selenium would destructively reduce the intensities of the lines, leading to amorphous materials.

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Résumé — Le comportement thermique du soufre, du sélénium et de leur mélanges a été étudié dans l'intervalle de températures compris entre 40 et 450°. On a montré que la valeur de seuil de la température de polymérisation du soufre T_ϕ diminue avec l'augmentation de la quantité de sélénium et suit le modèle de copolymérisation d'équilibre proposé par Tobolsky et Owen. La formation d'espèces octa-atomiques $Se_{8-x}S_x$, où $8 > x > 4$, n'a lieu que quand le soufre est à l'état liquide. L'addition de quantités croissantes de sélénium accélère la vitesse de la polymérisation, ce qui se reflète par des températures du pic de polymérisation plus élevées. Les diffractogrammes de rayons X sur poudre montrent que tous les produits fondus soufre-sélénium appartiennent à la même phase que celle de SeS, bien que les atomes constituants soient distribués au hasard.

Zusammenfassung — Das thermische verhalten von Schwefel, Selen und ihren Gemischen wurde im Temperaturbereich von 40 bis 450° studiert. Es wurde gezeigt, daß die Polymerisations-Schwellentemperatur von Schwefel T_ϕ mit steigender Selenmenge abnimmt und dem von Tobolsky und Owen vorgeschlagenen Gleichgewichts-Kopolymerisations-modell folgt. Die Bildung okta-atomarer Species $Se_{8-x}S_x$, wobei $8 > x > 4$ ist, erfolgt nur nachdem der Schwefel in den flüssigen Zustand übergegangen ist. Die Polymerisationsgeschwindigkeit wird durch Zusatz zunehmender Selenmengen beschleunigt und dies wird in den höheren Polymerisations-Peaktemperaturen widergespiegelt. Die Röntgen-Pulverdiffraktogramme zeigen, daß alle Schwefel-Selen Schmelzen zu derselben Phase wie SeS gehören, obwohl die beteiligten Atome zufallsbestimmt verteilt sind.

Резюме — Было изучено термическое поведение серы, селена и их смесей в области температур 40 – 450°. Показано, что температурный порог полимеризации серы *T* уменьшается с увеличением количества селена и соответствует равновесной кополимеризационной модели, предложенной Тобольски и Оуэном. Образование окта-атомных частиц $Se_{8-x}S_x$ где 8 >x> 4, имеет место только после перехода серы в жидкое состояние. Скорость полимеризации увеличивается при добавлении все больших количеств селена и это отражается во все более высоких температурных пиках полимеризации. Порошковые рентгенодифрактограммы показали, что все селен-сера расплавы относятся к той же самой фазе, что и SeS, хотя состояные атомы распределены произвольно.