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The Enthalpies of Binary Mixtures of Chalcogen Elements

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The enthalpies of binary mixtures among chalcogen elements were measured by means of calorimetry. In the system of sulfur+selenium, the positive enthalpy increment suggests the formation of a co-ring and a co-chain on mixing. In the selenium+tellurium and sulfur+tellurium systems, some local ordered structures were deduced from the minimum points of the enthalpy at the compositions of Te_3Se_2 and Te_3S. In the latter system, the entropy of mixing was calculated from the reported phase diagram and the present enthalpy values. The entropy diagram also suggests that the local order is present.

The chalcogen elements (sulfur, selenium, and tellurium) have been studied extensively in both the solid and liquid states. However, the study of mixtures of these elements has drawn little attention. Recently, we have measured the enthalpies of mixing of metal+chalcogen systems using a high-temperature calorimeter and observed interesting behavior in the enthalpies as functions of the compositions.[1] These results motivated us to measure the enthalpies of mixing among chalcogen elements and to compare the results with the characteristic properties of these elements, for instance, the electronegativity and the molecular structure.

Experimental

The calorimeter employed in this experiment was a twin construction of the Calvet type. The details of the calorimeter and the experimental procedure were the same as have been described in a previous paper.[1] In sulfur+selenium, the temperature dependence of the enthalpies of mixing was examined. The purity of S, Se, and Te are as follows, as claimed by the makers, S>99.9999% (Wako Pure Chem. Co.), Se>99.999% (Wako Pure Chem. Co.), and Te>99.99% (Nippon Mining Co.). These were used without further purification.

Results and Discussion

The experimental results are shown in Tables 1, 2, and 3 and are plotted in Figs. 1, 2, 3, and 5.[2] In the figures, we have also plotted the interaction parameter defined by Wagner,[3] $\xi = \Delta H^M / X(1-X)$, where X is an atomic fraction of one of the components. When both components are considered to mix randomly, the interaction parameter should be proportional to the interchange energy, $E_{ab} - (E_{aa} + E_{bb})/2$, where E_{aa}, E_{bb}, and E_{ab} refer to the bond energies of the a-a, b-b, and a-b pairs respectively. In the present systems ξ comes from a covalent intramolecular bond energy as well as an intermolecular van der Waals energy. An ionic contribution must be taken into account when there is an appreciable electronegativity difference between the component elements. The electronegativity values and single covalent bond energies of each element are as follows;[4]

S	4.11	S–S	50.9 kcal mol^{-1}
Se	4.25	Se–Se	44.0
Te	3.62	Te–Te	(34)

One may note that the experimental values of the three systems at, for example, an equiatomic mixture are consistent with this view. The fact that ξ changes with the composition in sulfur+tellurium and selenium+tellurium calls for further consideration. Below, several comments will be made on the individual systems.

Sulfur+Selenium. In this system, the enthalpy is positive throughout the composition range and is symmetric with respect to the compositions. In this system, high viscosity of the melt prevented the effective stirring of the melt. Further, at the lower temperatures, the reaction of the ring opening and the chain scission to form co-polymers and co-rings of sulfur with selenium are slow. The scatter in the results seems to be the result of those two factors. The vapor pressure of sulfur is high at the experimental temperature. We examined these effects by comparing the values observed when sulfur was charged in an inner, smaller ampoule with those when it was charged in an outer ampoule. However, no systematic difference was observed between the two sets of data. Further, the temperature dependence of the enthalpies of mixing was

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[1] T. Maekawa, T. Yokokawa, and K. Niwa, *J. Chem. Thermodynamics*, **3**, 143 (1971); **3**, 707 (1971); **4**, 153 (1972).

[2] Throughout this paper 1 cal = 4.184 J.

[3] C. Wagner, "Thermodynamics of Alloys," Addison-Wesley, Cambridge, (1952).

[4] R. T. Sanderson, "Chemical Periodicity," Reinhold, New York, (1960); "Inorganic Chemistry," Reinhold, New York, (1967).

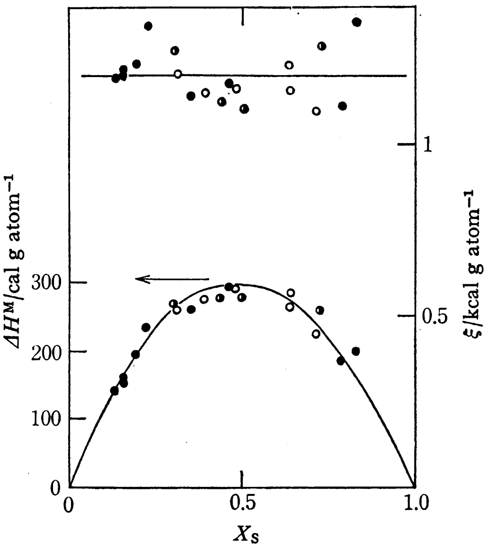

Fig. 1. Enthalpies of mixing of sulfur + selenium.
○: 345 °C, sulfur (inner ampoule)*
●: 460 °C, sulfur (inner ampoule)
◑: 460 °C, sulfur (outer ampoule)
* See text for charging method.

Table 1. Enthalpies of mixing and interaction parameters of sulfur + selenium

Mole fraction X(S)	Total moles	ΔH^M cal/g atom	$\xi^M = \dfrac{\Delta H}{X(1-X)}$ cal/g atom
	345 °C		
	Sulfur: inner ampoule		
0.314	0.0420	260	1210
0.392	0.0429	275	1150
0.485	0.0435	291	1170
0.636	0.0419	285	1240
0.639	0.0425	266	1150
0.714	0.0460	224	1100
	460 °C		
	Sulfur; inner ampoule		
0.138	0.0513	142	1190
0.157	0.0290	159	1200
0.158	0.0561	153	1230
0.196	0.0340	195	1240
0.224	0.0319	234	1350
0.355	0.0246	262	1140
0.462	0.0416	294	1180
0.788	0.0401	185	1110
0.824	0.0465	198	1370
	Sulfur; outer ampoule		
0.303	0.0319	269	1270
0.349	0.0321	277	1130
0.504	0.0432	277	1110
0.725	0.0426	258	1290

not observed within the range of experimental scattering. The ξ-function of this system is almost constant over the entire composition range. In view of the small difference in the electronegativity values of sulfur and selenium, the enthalpies seem to be attributable to the transformation of the covalent bonding, that is, to

$$\text{-S-S-} + \text{-Se-Se-} \longrightarrow 2\,\text{-S-Se-}$$

in rings or chains, and to minor effects from the change in the van der Waals interaction among the rings and chains of various chain compositions. Although the equilibria between ring and chain molecules of various lengths will shift on mixing, the heat effects due to this transformation can not be estimated at the present stage of knowledge.

Sulfur + Tellurium. In this system, the enthalpy of mixing is positive on the sulfur- and tellurium-rich sides, but negative in the intermediate composition ranges. The composition at which the minimum appears is about 0.25, by the suflur atomic fraction. The ξ-function of this system was divided conveniently into three straight lines. The least-squares method leads to the following results:

$$0 \leq X_s \lesssim 0.25:\ \xi = 2880 - 19890X_s,$$

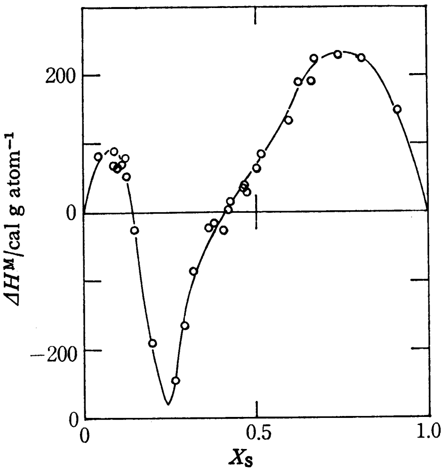

Fig. 2. Enthalpies of mixing of sulfur + tellurium at 468 °C.

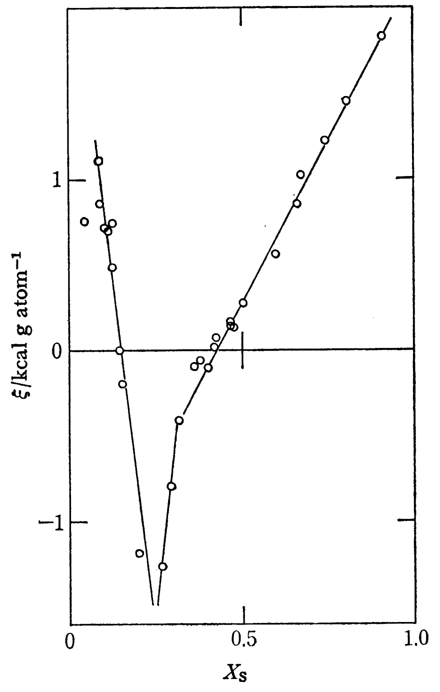

Fig. 3. ξ-functions of sulfur + tellurium. Experimental points and the straight lines by the least squares method.

Table 2. Enthalpies of mixing and interaction parameters of sulfur+tellurium at 468 °C

Mole fraction X(S)	Total moles	ΔH^{M} cal/g atom	$\xi^{\mathrm{M}}=\dfrac{\Delta H}{X(1-X)}$
	Sulfur; inner ampoule		
0.045	0.0438	83	755
0.090	0.0510	70	855
0.090	0.0416	91	1110
0.102	0.0403	65	724
0.115	0.0415	72	707
0.125	0.0422	83	755
0.126	0.0481	54	489
0.150	0.0481	−25	−196
0.200	0.0412	−190	−1190
0.263	0.0494	−244	−1260
0.291	0.0229	−164	−794
0.315	0.0343	−88	−406
0.362	0.0389	−23	−100
0.380	0.0433	−14	−59
0.404	0.0593	−27	−112
0.419	0.0376	3	12
0.424	0.0453	17	70
0.464	0.0440	36	145
0.466	0.0455	40	161
0.474	0.0386	32	128
0.503	0.0436	63	272
0.512	0.0375	85	340
0.597	0.0421	133	553
0.624	0.0481	192	818
0.660	0.0350	191	851
0.670	0.0330	224	1010
0.742	0.0253	231	1200
0.807	0.0256	224	1440
0.912	0.0246	147	1830

$$0.25 \lesssim X_s \lesssim 0.30:\ \xi = -5500 + 16160X_s,$$

and:

$$0.30 \lesssim X_s \lesssim 1.0:\ \xi = -1620 + 3825X_s,$$

where X_S is the atomic fraction of sulfur.

The above equations are helpful in calculating the partial molar enthalpies of mixing. The forms of the ξ-functions is similar to that of binary systems in which the associated species are formed on mixing, for example, in the $MgCl_2$+KCl system studied by Kleppa.[5] The activity of each component can be calculated from the equilibrium-phase diagram.[6] With the data of the heat of fusion and the melting point of tellurium,[7] and on the assumption that the solid solution of sulfur in tellurium is ideal with respect to the tellurium solvent, the activity of tellurium on the liquidus temperature was derived. Further, the present enthalpy data permitted us to calculate the change in activity with the temperature. The acitivity of tellurium and that of sulfur derived from the former by means of the Gibbs-Duhem relation were combined with the present enthalpy values in order to evaluate the entropy of mixing. The free energy from the activities and the entropy are shown in Fig. 4, together with the enthalpy values. Although the free energy curve is smooth, the entropy value is less than that of the ideal solution and shows a minimum at $X_S=0.25$. These curves are similar to those of mixtures which generate the associated complex on mixing. From the trends of the entropy as well as from the enthalpy, some sorts of orderings can be suspected in the mixture around $X_S=0.25$. In order to interpret this entropy, let us consider for a moment a pseudo-binary mixture consisting of Te_3S and excess tellurium or sulfur, like thallium+tellurium.[8] The configurational entropies of the pseudo-binary mixture can be calculated on the basis of the quasi-crystalline lattice model. When $X_S>$ 0.25, the mixture consists of Te_3S and S and the entropy of mixing is given by:

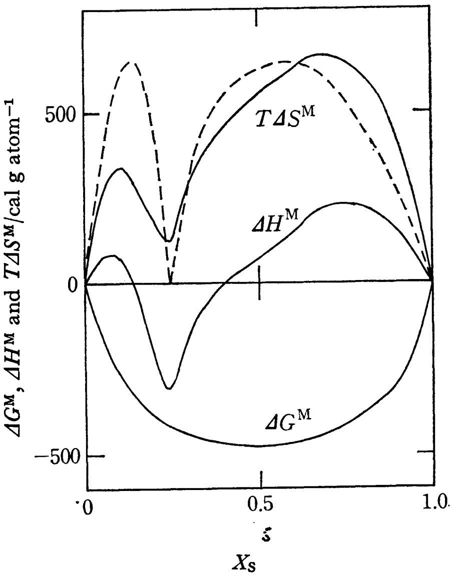

Fig. 4. The thermodynamic fuctions of sulfur + tellurium. The broken line; calculated values at 468 °C.

$$-\Delta S^{\mathrm{M}}/R = X_s[(1-X_2)\ln\phi_1+X_2\ln\phi_2]$$

in which

$$X_2 = (1-X_s)/3X_s$$

and

$$\phi_2 = 1 - \phi_1 = rX_2/[(1-X_2)+rX_2]\quad (r=4 \text{ in this case})$$

and for Te_3S+Te ($X_S<0.25$) by:

$$-\Delta S^{\mathrm{M}}/R = (1-3X_s)[(1-X_2)\ln\phi_1+X_2\ln\phi_2]$$

in which

$$X_2 = X_s/(1-X_s).$$

The entropies based upon above model are shown in Fig. 4 as a broken line. The agreement between the experimental and calculated values is satisfactory. One may note, however, that this does not necessarily mean that any molecule like Te_3S is present in the mixture. Considering the small enthalpy of mixing, the idea of the compound formation is far from reality. Rather,

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[5] O. J. Kleppa and F. G. McCarty, *J. Phys. Chem.*, **70**, 1249 (1966).

[6] M. Hansen and K. Anderko, "Constitution of Binary Alloys," McGraw-Hill, New York, (1958).

[7] O. Kubaschewski, E. LL. Evans and C. B. Alcock, "Metallurgical Thermochemistry," Chap. 5, Pergamon Press, Oxford (1967).

[8] Y. Nakamura and M. Shimoji, *Trans. Faraday Soc.*, **67**, 1270 (1971).

the sulfur atoms seem to be preferably surrounded by three tellurium atoms when $X_S<0.25$. The positive enthalpies of mixing on the two sides of the composition may be attributable to positive heats effects, such as the difference in size between sulfur and tellurium.

Selenium+Tellurium. In this system, the enthalpy is negative throughout the composition range. The minimum of the enthalpies of mixing appears at the composition of 0.4, by the atomic fraction of selenium. The electronegativity difference between selenium and tellurium is the largest among the three combinations. Therefore, the enthalpies of mixing of this system are expected to be the most exothermic, in agreement with the experimental results. The ξ-function of this system can also be divided into two portions. Though there are no thermodynamic functions available except the present enthalpy data, the ordered structure may be constructed in the same manner as in the sulfur+tellurium system.

As has been shown by many authors, liquid sulfur has the so-called transition temperature, above which long chains with various chain lengths are formed in addition to the S_8 ring.[9] Liquid selenium can also be understood similarly, though the transition temperature lies below its melting point.[10] Since the experimental temperatures of the present work are higher than the transition temperatures, we must consider the presence of these species. In contrast to sulfur and selenium, liquid tellurium has only a short chain structure at low temperatures. However, it has recently been shown that liquid tellurium has a three-dimensional network structure. This idea is proposed on the basis of the experimental evidence that the numbers of the nearest neighbors in liquid tellurium are not two but three, even as high as above the temperature of 950 °C, as determined by the neutron diffraction measurement.[11] Therefore, the mixing process of these elements involve ring opening, chain scission, and the formation of co-ring and co-polymer chains.[12] The observed enthalpies of mixing are related to these processes. Therefore, the mixture cannot be simply treated like a usual metallic solution. A further aspect to be noted is the fact that the present enthalpy-composition curves are similar to those of metal+chalcogen systems. In the binary mixture of tellurium with sulfur or selenium, tellurium perhaps functions as a metal-like component. The theoretical evaluation of the thermodynamic functions depends on a certain structural model of the mixture. Unfortunately, such information is not available at the present time and a quantitative discussion was not attempted in this work. At the end of this paper, it may be noted that, in the selenium+tellurium system, the mixture is conventionally divided into two distinct portions, according to recent NMR studies.[13]

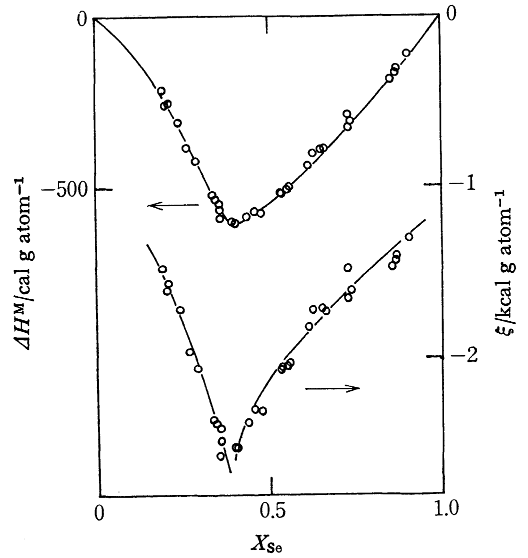

Fig. 5. The enthalpies of mixing of selenium + tellurium at 460°C.

TABLE 3. ENTHALPIES OF MIXING AND INTERACTION PARAMETERS OF SELENIUM+TELLURIUM AT 460 °C

Mole fraction X(Se)	Total moles	ΔH^M cal/g atom	$\xi^M=\frac{\Delta H}{X(1-X)}$ cal/g atom
0.193	0.0464	−229	−1470
0.206	0.0480	−263	−1610
0.209	0.0344	−257	−1550
0.239	0.0447	−312	−1720
0.265	0.0465	−382	−1960
0.290	0.0495	−424	−2060
0.333	0.0294	−524	−2360
0.342	0.0508	−536	−2380
0.357	0.0412	−550	−2400
0.357	0.0312	−569	−2480
0.358	0.0326	−592	−2580
0.394	0.0347	−599	−2510
0.403	0.0340	−607	−2520
0.438	0.0356	−584	−2370
0.454	0.0484	−571	−2300
0.474	0.0349	−576	−2310
0.532	0.0417	−515	−2070
0.537	0.0403	−517	−2060
0.552	0.0424	−509	−2060
0.554	0.0512	−499	−2020
0.611	0.0380	−433	−1820
0.624	0.0438	−403	−1710
0.651	0.0408	−390	−1720
0.660	0.0456	−389	−1730
0.726	0.0378	−292	−1470
0.729	0.0492	−329	−1670
0.735	0.0392	−313	−1610
0.853	0.0430	−184	−1470
0.864	0.0418	−168	−1430
0.866	0.0436	−163	−1400
0.900	0.0493	−117	−1300

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9) V. Tobolsky and E. Eisenberg, *J. Amer. Chem. Soc.*, **81**, 871 (1959).

10) A. Eisenberg and V. Tobolsky, *J. Polym. Sci.*, **46**, 19 (1960).

11) B. Cabane and J. Friedel, *J. Phys.*, (Paris), **32**, 73 (1971).

12) R. Cooper and J. V. Culka, *J. Inorg. Nuclear Chem.*, **29**, 1217 (1967); **29** ,1877 (1967); **31**, 685 (1969).

13) E. F. W. Seymour and D. Brown, The Second International Conference on the Properties of Liquid Metals, Tokyo, Japan, September, 1972.

In the region in which the compositions of tellurium are higher than 70 at. per cent, the mixture behaves in a metallic manner. On the other hand, in the lower composition range, the valence electrons are localized in the chain molecules. Although the composition of the minimum ΔH observation is slightly different from the above boundary, our opinions that an ordered structure is present and that the system is divided into two portions in the mixture are consistent with this view.