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SHORT COMMUNICATION

On the preparation of condensed ScO

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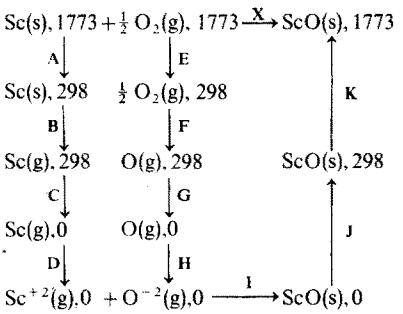
The reported[1] reduction of Sc_2O_3 to condensed ScO under relatively mild reducing conditions is surprising in view of the questionable existence of the solid monoxide at high temperatures. Accordingly, this investigation was undertaken to study the thermodynamic feasibility of the reaction and to re-examine the data cited by Dufek *et al.* as evidence for the existence of ScO under the specified conditions.

Condensed scandium monoxide has reportedly been prepared by reducing the sesquioxide with silicon powder at 1500°C in a 10^{-3} Torr vacuum according to reaction (1):

$$Sc_2O_3(s) + Si(l) = 2ScO(s) + SiO(g) \quad (1)$$

That this reaction actually occurs under the given conditions is suspect for two reasons: (1) an estimation of $\Delta G^\circ_{f,ScO(s)}$ at 1500°C indicates that the monoxide is unstable with respect to disproportionation to the sesquioxide and elemental scandium, and (2) ΔG_{1773} for reaction (1) is very positive for reasonable pressures of SiO(g).

First, a value for $\Delta G^\circ_{f,1773,ScO}$ was obtained by making independent estimates of $\Delta H^\circ_{f,1773}$ and $\Delta S^\circ_{f,1773}$. The $\Delta H^\circ_{f,1773}$ was estimated as shown in Fig. 1, while



Reaction (RCN)	ΔH_{RNC} *(kcal/mole)*	*Reference*
A	− 12.5	3
B	91.2	12
C	− 1.5	
D	449	13
E	− 6.0	2
F	59.55	2
G	− 1.6	2
H, I	−730	14
J	2	
K	19.7∓1.3	5*
X	−130	

* Values reported for 9 monoxides (BaO, CaO, CoO, MgO, NiO, SrO, TiO, VO) were averaged.

Fig. 1. Scheme and values used to calculate $\Delta H^\circ_{f,1773}$ for ScO(s).

$\Delta S^\circ_{f,1773}$ was estimated by use of reported S°_{1773} values for O_2^2 and Sc[3], an estimate of $S^\circ_{298,ScO}$ obtained by use of Latimer's[4] scheme, and an average of $S^\circ_{1773} - S^\circ_{298}$ values for 9 other monoxides[5] (see Fig. 1) for $(S^\circ_{1773} - S^\circ_{298})_{ScO}$. These estimations yielded for ScO(s) at 1500°C, $\Delta H^\circ_f = -130$ kcal/gfw, $\Delta S^\circ_f = -20.3$ eu, and $\Delta G^\circ_f = -94$ kcal/gfw. Combination of this latter value with $\Delta G^\circ_{f,1773,Sc_2O_3}$[3] gave $\Delta G^\circ_{1773} = -51$ kcal/gfw for disproportionation reaction(2):

$$3ScO(s) = Sc(s) + Sc_2O_3(s) \qquad (2)$$

This value indicates clearly the instability of condensed ScO at this temperature.

Second, reaction (1) was analyzed with respect to its thermodynamic feasibility on the assumptions that SiO is an ideal gas and that equilibrium conditions existed in the reaction chamber. Values of ΔG_{RCN} for several P_{SiO} values were calculated through use of published data for Sc_2O_3[3] and SiO[6], and by setting $\Delta G^\circ_{f,1773,ScO}$ equal to the variable, Y. The results are given in Table I. If $\Delta G^\circ_{f,1773,ScO} \simeq -94$ kcal/mole, as was estimated above, then $P(SiO)$ must be less than 10^{-11} atm in order for reaction (1) to occur spontaneously, and the earlier assumption that the system was in equilibrium is justified. That Dufek *et al.* were able to detect condensed SiO on the Mo shields during a 5 h heating indicates that the SiO(g) pressure must have been much higher than 10^{-11} atm, and is indicative of a positive ΔG for reaction (1).

TABLE I

EQUILIBRIUM PRESSURE OF SiO(g) AS A FUNCTION OF $\Delta G^\circ_{f,1773,ScO}$ FOR REACTION (1) AT 1500°C

$P_{atm,SiO(g)}$	ΔG_{RCN} (*kcal/mole SiO*)	*Max. value of* Y $(\Delta G^\circ_{f,1773,ScO})$ *for* $\Delta G_{RCN} \leqslant 0$ (*kcal/mole*)
10^0	$274.12 + 2Y$	-137.06
10^{-3}	$249.78 + 2Y$	-124.89
10^{-6}	$225.45 + 2Y$	-112.72
10^{-9}	$201.11 + 2Y$	-100.55
10^{-12}	$176.78 + 2Y$	-88.39
10^{-15}	$152.44 + 2Y$	-76.22

Accordingly, we repeated the preparation reported for ScO. Our investigation did not reveal any condensed monoxide when equimolar amounts of Sc_2O_3 (reagent grade, 99.9% pure, Alfa Inorganics, Inc.) and Si (99+ % pure) were heated at 1600°C for 5 h at 10^{-3} Torr in a Mo effusion cell. Crucible interaction with the sample was evident. Furthermore, the heating of a 1:1.5 mole ratio mixture of Sc_2O_3–Si at 10^{-6} Torr and 1650°C (better reducing conditions) yielded only sesquioxide, there being considerable interaction between Si and the Mo crucible. The use of activated Sc_2O_3 (obtained by dissolving reagent grade sesquioxide in hydrochloric acid, precipitating the hydroxide, and firing at 600° for 4 h) yielded the same results.

In view of these results a different interpretation is suggested for the data presented by Dufek *et al.*, namely, the formation of a non-stoichiometric oxide–nitride. The reported structure of ScO (NaCl structure, $a_0 = 4.45$ Å) is very close to that reported for ScN[7,8] (NaCl structure, $a_0 = 4.44$ Å), with both structures in good agreement with the reported diffraction pattern (Table II). Scandium nitride is known to be non-stoichiometric[9], and it is reasonable that a ScO_xN_y species could give rise to the ob-

TABLE II

COMPARISON OF INTERPLANAR *d*-SPACINGS FOR ScN AND ScO

hkl	*Calculated for*		*Observed*[1] (Å)
	ScO ($a_0 = 4.45$ Å)[1] (Å)	*ScN* ($a_0 = 4.44$ Å)[7,8] (Å)	
111	2.569	2.563	2.556
200	2.225	2.220	2.220
220	1.573	1.570	1.573
311	1.342	1.339	1.345
222	1.285	1.282	1.285
400	1.112	1.110	1.111
331	1.021	1.019	1.021
420	0.995	0.993	0.996

served diffraction pattern. (One such NaCl-type scandium–oxide–nitride has been reported by Samsonov *et al.*, $a_0 = 4.503$ Å, and others may well exist). This possibility seems particularly likely in view of Felmlee and Eyring's study of a strikingly analogous samarium–oxygen–nitrogen system[10].

Although the condensation of gaseous SiO[1] is consistent with reaction (1), it does not confirm that this reaction occurred, as contended by the authors. Other reactions (*e.g.*, reaction 3) also predict the emanation of SiO(g):

$$Sc_2O_3(s) + Si(l) + yN_2(g) = 2ScO_xN_y(s) + SiO(g) + (1-x)O_2(g) \quad (3)$$

In our investigation, an amorphous condensate formed on the walls of the vacuum chamber above the effusion cell when an equimolar mixture of Si powder and the sesquioxide was heated at $\geqslant 1500°C$ for 4 h under 60 Torr of N_2. The diffraction pattern of the residue in the Mo crucible did not reveal the lines reported for ScO although lines corresponding to *d*-spacings of 1.355 Å and 1.298 Å were observed.

In any case, thermodynamic restrictions must be considered in determining which reactions are possible for a given set of experimental conditions. In this particular case, it seems clear from energy considerations that the condensed phase isolated by Dufek *et al.* must contain trivalent rather than divalent scandium if the reaction is to be energetically feasible and if the condensed product is to be thermodyamically stable. The additional energy required to produce the trivalent metal ion (572 kcal/mole) may be more than offset by the gain in the lattice energy[11]. Our belief that the reported ScO was actually a non-stoichiometric oxide–nitride of trivalent scandium stems from these energy considerations, the fact that the compound was prepared at 10^{-3} Torr, and the similarity between this system and the analogous samarium one[10].

Finally, the oxygen-absorption data of Dufek *et al.*, corresponding to a formula of $ScO_{0.98}$, must be regarded as credible evidence for the formation of ScO. The extent to which these data may agree with a formula ScO_xN_y depends on the accuracy of the oxygen-absorption measurements as well as the values of x and y. The possibility that oxidation of some scandium hydride contributed to the observed weight increase must also be considered carefully[10].

Through this investigation, the reported preparation of condensed ScO, with

scandium in the divalent state, is seen to be thermodynamically untenable. Although this discrepancy could result from inaccurate thermodynamic measurements and estimates, such an occurrence is unlikely in view of the magnitude of the Gibbs energies. Incorrect formalization of the preparative reaction and faulty product characterization seem more likely. In any case, the system merits further investigation, and an oxide–nitride reaction product appears to be a reasonable hypothesis at this time.

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