rising temperature from 20 to 100° the pressure increases more rapidly above 70° than for an ideal gas. The final pressure after cooling is greater than the initial pressure. At no stage does a pressure drop occur as would be required for the reaction

$$SF_4 + FNO_3 \longrightarrow SF_5ONO_2$$

The products of reaction include SF_6, NO_2F, SOF_2, NO_2, O_2, and SiF_4 but apparently not SF_5ONO_2.

The reaction between sulfur tetrafluoride and fluorine nitrate in a quartz and glass system under irradiation by ultraviolet light gives SF_4O, NO_2, O_2, SO_2F_2, and SiF_4. These probably result from the known decomposition of fluorine nitrate into NO_2F and O_2 followed by reaction of decomposition products with sulfur tetrafluoride. The reaction under ultraviolet light of sulfur tetrafluoride with a mixture of oxygen and nitrogen dioxide to give SF_4O is known[8] and probably accounts for the formation of SF_4O, a product not found in the thermal reaction.

Fluorine nitrate reacts with tetrafluorohydrazine at room temperature to form NF_3, NO_2, NOF, and NO_2F.

Experimental

Fluorine nitrate was prepared by a method similar to that of Skiens and Cady.[9] Adequate precautions were taken against harm by explosions. The addition of fluorine nitrate to a second reactant can initiate an explosive reaction which propagates back through the connecting tubes and causes an explosion in the fluorine nitrate reservoir. This was avoided by expanding the fluorine nitrate into a third, small evacuated chamber and isolating the reservoir. The small quantity of fluorine nitrate was then expanded into the second reactant held in another vessel at lower pressure.

Fluorine nitrate contained in a 1-l. Pyrex glass vessel at a pressure of 12.5 cm. was admitted to a second 1-l. vessel containing tetrafluoroethylene at a pressure of 5 cm. The final pressure was 8.4 cm. If no change in the total number of molecules had occurred, the pressure would have been 8.1 cm. The product was separated by low-temperature fractional codistillation.[10] The more volatile of the two principal fractions had strong infrared absorptions at 775, 965, 1230, and 1910 $cm.^{-1}$ corresponding to carbonyl fluoride.[11] The less volatile principal fraction had strong infrared absorptions at 750, 860, 1150, 1300, and 1620 $cm.^{-1}$ corresponding to CF_3NO_2.[12] Mass spectra of these fractions also corresponded to COF_2 and CF_3NO_2. Small amounts of SiF_4 and NO_2 were also present in the product.

Fluorine nitrate at 22 cm. pressure in a 1-l. Pyrex vessel was admitted to ethylene in a 2-l. vessel at 6 cm. pressure diluted by nitrogen at 4 cm. The pressure after mixing was 14 cm., corresponding to no combination. After 45 min. the pressure was 12 cm. and after 90 min. it was 11 cm. The final pressure was 10 cm., the total reduction being the same as the pressure initially due to NO_3F. The product was removed from the reaction vessel and was separated by bulb to bulb distillation at low pressure.

Fluorine nitrate at 10.2 cm. in a 1-l. vessel was mixed with tetrafluorohydrazine at 7.0 cm. in a 1-l. glass vessel. The final pressure in the 2-l. system was 8.1 cm. The expected pressure assuming no change in number of molecules was 8.6 cm. The products were separated by low-temperature codistillation and identified by infrared spectroscopy to be NF_3, NO_2F, and NOF. A material having the properties of $(NO_2)_2SiF_6$ was also observed. When the reaction of fluorine nitrate with tetrafluorohydrazine occurred in a nickel vessel no nitryl fluorosilicate was found; otherwise the observed products were the same.

Equimolar amounts of SF_4 and fluorine nitrate were introduced into a 5-l. flask to a total pressure of above 5 cm. Irradiation was accomplished by using a mercury vapor lamp. After irradiation for 5 hr. the products were removed, separated by low-temperature codistillation, and identified by infrared spectroscopy.

Equimolar amounts of fluorine nitrate and sulfur tetrafluoride were introduced into a 1.4-l. nickel reactor to a total pressure of 12.5 cm. This mixture was heated to 98° over a period of 2 hr. with pressure readings taken by means of a Booth Cromer pressure transmitter every 5 min. After cooling to room temperature the products were separated by low-temperature codistillation and the fractions identified by infrared spectroscopy. Oxygen was identified by its volatility at low temperature and its density.

Acknowledgment.—The work was performed in part under contract with the Office of Naval Research.

---

(8) W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 3838 (1960).

(9) W. E. Skiens and G. H. Cady, *ibid.*, **80**, 5640 (1958).

(10) G. H. Cady and D. P. Siegwarth, *Anal. Chem.*, **31**, 618 (1959).

(11) J. Overend and J. C. Evans, *Trans. Faraday Soc.*, **55**, 1817 (1959).

(12) J. Mason and J. Dunderdale, *J. Chem. Soc.*, 759 (1956).

CONTRIBUTION NO. 1601 FROM THE INSTITUTE FOR ATOMIC
RESEARCH AND THE DEPARTMENT OF CHEMISTRY,
IOWA STATE UNIVERSITY, AMES, IOWA

The Scandium Trichloride–Scandium System and the Question of the Existence of Solid, Lower Chlorides of Scandium[1]

BY JOHN D. CORBETT AND BOB N. RAMSEY

Received September 28, 1964

The $ScCl_3$–Sc system might be expected to show a substantial amount of reduction of the molten trichloride by metal and even the formation of a reduced, solid phase. The reasons for this are (1) the expectation that, as in other transition metal groups, the stability of the M^{2+} ion $ns^2np^6nd^1$ should increase from La^{2+} to Sc^{2+}, the former being a reasonable interpretation[2] of the solution of up to 9 mole % La in liquid $LaCl_3$,[3] and (2) the prediction from Born–Haber cycle calculations[4] that $ScCl_2$ should be on the borderline of stability. To this point, Polyachenok and Novikov[5] have recently reported thermal analysis data for the $ScCl_3$–Sc system that were interpreted as indicating the formation of the solid phases $ScCl_2$ and $2ScCl_3 \cdot ScCl_2$ ($ScCl_{2.67}$). However, their results are in almost complete disagreement with those reported here, which deny the existence of any lower chloride.

Experimental

Materials.—Scandium metal that was used for reduction of $ScCl_3$ had been vacuum-distilled in tantalum and contained, in p.p.m., O, 750–950; H, 10; Fe, 100; Si, 30; Ca, <25; Ta, 1300; Y, 100; Er, <100; Tm, Yb, Lu, <50 as impurities. The $ScCl_3$ was prepared as before[6] except that commercial HCl

---

(1) Work was performed in the Ames Laboratory of the U. S. Atomic Energy Commission.

(2) A. S. Dworkin, H. R. Bronstein, and M. A. Bredig, *Discussions Faraday Soc.*, **32**, 188 (1961).

(3) F. J. Keneshea and D. Cubicciotti, *J. Chem. Eng. Data*, **6**, 507 (1961).

(4) M. Barber, J. W. Linnett, and N. H. Taylor, *J. Chem. Soc.*, 3323 (1961).

(5) O. G. Polyachenok and G. I. Novikov, *Zh. Neorgan. Khim.*, **8**, 2819 (1963); USAEC Translation IS-2.

(6) L. F. Druding and J. D. Corbett, *J. Am. Chem. Soc.*, **83**, 2462 (1961).

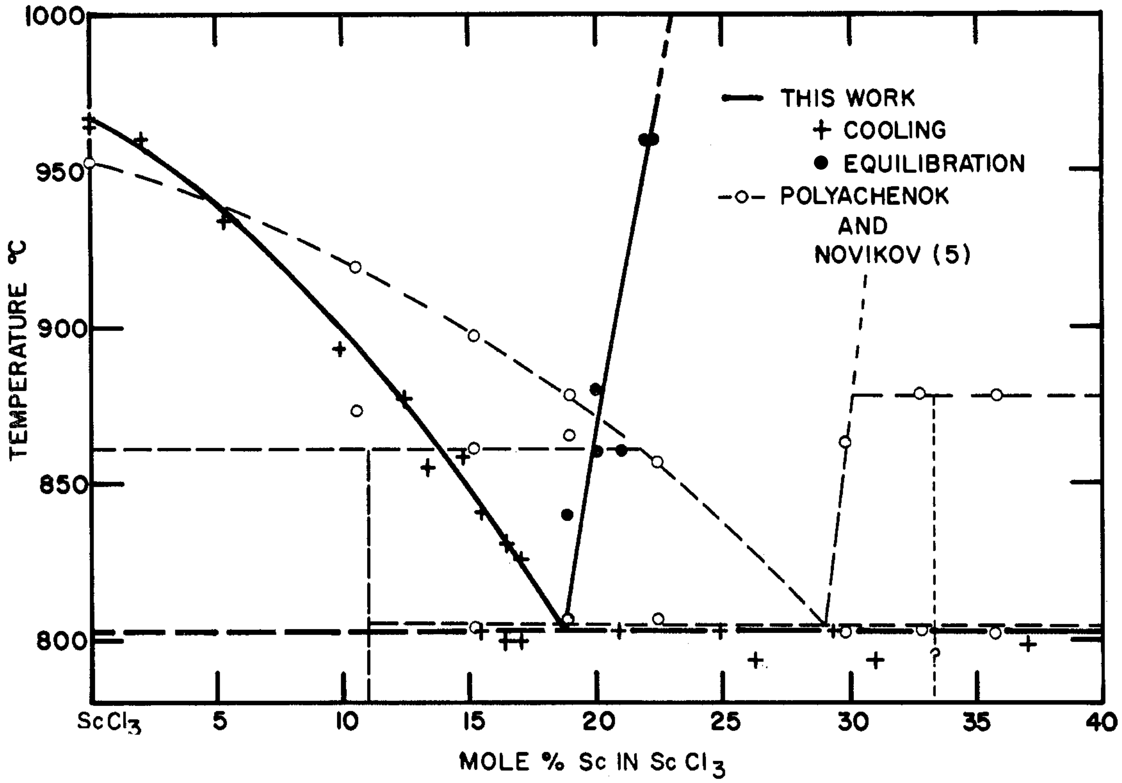

Figure 1.—The salt-rich portion of the $ScCl_3$–Sc system. This work: solid curves with +, thermal analysis on cooling; ●, equilibration with excess metal. Polyachenok and Novikov[5]: dashed curves, with O, thermal analysis. The vertical dashed line at 33.3% was added to their figure to mark the reported $ScCl_2$.

and metal direct from the Ca reduction of ScF_3 were used since the additional impurities, principally nonmetallic, were removed by a subsequent sublimation of the product under vacuum at 800°. Analyses[7] of the sublimed salt gave $Cl/Sc = 2.99 \pm 0.01$, with $100.0 \pm 0.2\%$ material balance.

Phase Studies.—Thermal analysis and DTA data were obtained as recently described.[8] Because of the volatility of $ScCl_3$ at the temperatures encountered, each sample was sealed into a 0.75-in. diameter × 2-in. high tantalum crucible equipped with a 0.125-in. diameter thermocouple well and a 0.25-in. diameter addition port welded through the lid and closed at the inner and outer ends, respectively. Subsequent additions of metal were made through the latter by cutting off the sealed tip in a drybox and then rewelding it after the weighed metal had been added. Final analyses agreed with the material added to within 0.2 mole %, with $100.0 \pm 0.3\%$ recovery as Sc + Cl.

For equilibrations,[8] excess metal was first melted into the closed end of a 0.25-in. tantalum tube, salt added, and the tube welded and briefly heated to 975–980° to melt the salt. The upper part of the tube was then crimped flat so as to reduce the free volume as much as possible. Erratic results were obtained without the last step, evidently because distillation of the salt into the otherwise accessible upper part resulted in the suspension of finely divided metal throughout the salt. With this precaution good reproducibility of the saturation limit was obtained with from 0.5 to 2 hr. equilibration at temperature.

Results and Discussion

The salt-rich portion of the equilibrium diagram for $ScCl_3$–Sc is shown in Figure 1 (solid curves). The metal exhibits a very substantial solubility in the melt, 18.5% ($ScCl_{2.45}$) at the 803° eutectic, 22.2% at 960°, but no intermediate solid phase is formed.[9] The latter conclusion was supported in all respects by X-ray powder pattern data for the products, including the result of a reaction designed to maximize the formation of any new phase, heating with excess metal for 1 hr. at 980°, then 4 hr. at 830° and overnight at 780°. Up to six lines of the known pattern for Ta metal were found in such cases, however, the result of the substantial solution of this in the previously molten Sc, followed by solution of the latter in the salt.

A serious discrepancy exists between these results and those of Polyachenok and Novikov[5] (Figure 1, dashed curves) in the magnitude of the solution. In addition, our work gave absolutely no support for the formation of either the $ScCl_2$ or the $2ScCl_3 \cdot ScCl_2$ phase reported[5] to melt incongruently at 878 and 855°, respectively. The former transition was evidently not too clear, however, since they indicate that the very small effect of the 878° "monotectic" (peritectic?) tended to run together with that from the 805° eutectic. In addition, they gave no information whatsoever as to how these particular solid compositions were assigned. Other aspects of their work may be open to question as well, such as the purity of their unsublimed $ScCl_3$, melting at 953° *vs.* 967° here, and the problem of the

---

[7] J. S. Fritz, J. E. Abbink, and M. A. Payne, *Anal. Chem.*, **33**, 1381 (1961).

[8] J. E. Mee and J. D. Corbett, *Inorg. Chem.*, **4**, 88 (1965).

[9] A referee has pointed out that the absence of the eutectic halt with less than 15% Sc suggests the presence of significant solid solutions of the solute in $ScCl_3$. Although this seems a definite possibility, it is difficult to verify it from the initial freezing point depression because of the lack of good fusion data for $ScCl_3$. If the trichloride (BiI_3-type structure) is assumed to have an entropy of fusion of 8 e.u., similar to that measured for $ErCl_3$ and $HoCl_3$ ($AlCl_3$-type) [A. S. Dworkin and M. A. Bredig, *J. Phys. Chem.*, **67**, 2499 (1963)], a $ScCl_2$ solute should ideally yield about twice the initial depression observed. On the other hand, the use of 15 e.u. for ΔS_m, as estimated by L. Brewer, *et al.* ["The Chemistry and Metallurgy of Miscellaneous Matrials: Thermodynamics," L. L. Quill, Ed., NNES IV-19B, McGraw-Hill Book Co., New York, N. Y., 1950, p. 197] (or a ScCl solute) would just about eliminate the disparity.

volatilization of salt from the solutions at temperatures approaching its boiling point. However, the presence of a still more substantial error in the previous work would seem necessary to account for the false peritectic halts and larger apparent reaction of metal with the salt, 29% *vs.* 18.5% at the eutectic, for example. This may have been the failure of the Mo coating intended to protect the fused silica containers from the very reactive melt, since they noted that this coating ". . . adhered poorly to the quartz and on cooling came loose here and there . . . ." If so, the results pertain to a far more complex system containing silicide and oxide or oxychloride as well.

Disagreement with these workers has been noted before[10] in connection with the $PrCl_3$–Pr system. A later report of their work[11] does not help in that the alleged intermediate $PrCl_{2.5}$ is shown as separating from a eutectic melt of the same composition, and again there is no indication of the means by which its composition was established. In addition, the metal used contained 18% Nd, more than enough to stabilize the substituted $Pr(Nd)Cl_{2.32}$.[10]

---

[10] L. F. Druding, J. D. Corbett, and B. N. Ramsey, *Inorg. Chem.*, **2**, 869 (1963).

[11] G. I. Novikov and O. G. Polyachenok, *Zh. Neorgan. Khim.*, **8**, 1053 (1963).

Correspondence

The Indirect Assessment of a Catalytic Path

Sir:

In a study of the kinetics of formation of ZnL^{-2} from the reaction of NiL^{-2} with Zn^{+2} (L^{-4} = ethylenediaminetetraacetate) Margerum and Bydalek[1] have deduced that the reaction is catalyzed by Cu^{-2} according to the scheme

$$M'L + M'' \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} M''L + \mathrm{I}$$

$$M'L + M''' \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} M'''L + M' \qquad (2)$$

$$M'' + M'''L \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} M''L + M''' \qquad (3)$$

where M′ = Ni(II), M″ = Zn(II), and M‴ = Cu(II). The reaction of NiL^{-2} with Cu^{+2} is much faster than is the reaction with Zn^{+2} and the displacement of Cu^{+2} from CuL^{-2} by Zn^{+2} is also relatively fast. Thus, when Cu^{+2} is present an alternate means of forming ZnL^{-2} is provided.

Because the reaction was followed by spectrophotometrically observing the disappearance of NiL^{-2}, the procedure used by Margerum and Bydalek represents an indirect method of assessing the effect of the catalytic pathway. Catalytic paths analogous to the one proposed by these workers may be important in other systems: in general, the metal ions may be representative of any three competing species and L may represent any other ligand, an electron or reaction product resulting, say, from a condensation.

This indirect approach may be useful in cases where a direct measure of the reaction product is not feasible. Since this type of system is somewhat complicated and an intuitive feeling for the effects of the various parameters is not easily had, we have undertaken a numerical study of the NiL^{-2}–Cu^{+2}–Zn^{+2} system investigated by Margerum and Bydalek to determine what information regarding the catalytic path experiments such as this may furnish.

The integration was performed numerically using the fourth-order Runge–Kutta method.[2a,b] Simulated kinetic runs were made using the values of k_1 and k_2 and the equilibrium constants and concentrations pertaining to the experiments described in ref. 1 with various assumed values of k_3; see the legend of Figure 1 for details.

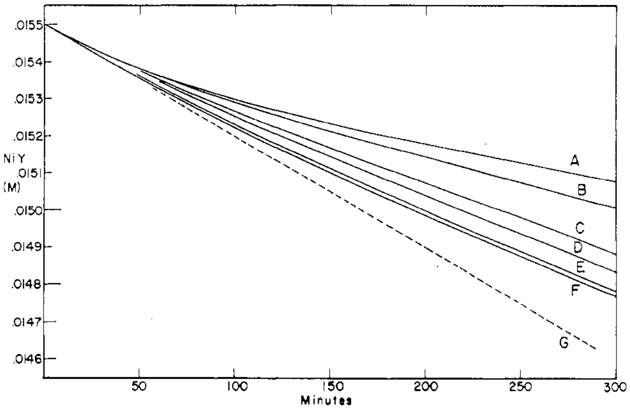

Figure 1.—The rate of disappearance of NiY^{-2}; conditions of ref. 1: $Ni_t = L_t = 0.01550$ *M;* $Zn_t = 0.3945$ *M;* $Cu_t = 0.000134$ *M;* $Q_{ZnL} = 3.2 \times 10^{16}$, $Q_{CuL} = 6.3 \times 10^{18}$, $Q_{NiL} = 4.0 \times 10^{18}$; $k_1 = 2.67 \times 10^{-6}$ l. mole^{-1} sec.$^{-1}$; $k_2 = 1.63 \times 10^{-2}$ l. mole^{-1} sec.$^{-1}$. Values of k_3 (l. mole^{-1} sec.$^{-1}$) $\times 10^4$ are: A, 0; B, 1.67; C, 8.33; D, 16.7; E, 83.3; F, 833, 1667; G, extrapolation of initial curves.

The constants for the back reactions were evaluated from the following relationships (Q_{ML} = the formation constant of ML^{-2}).

$$k_{-1} = k_1 Q_{NiL}/Q_{ZnL}$$

$$k_{-2} = k_2 Q_{NiL}/Q_{CuL}$$

$$k_{-3} = k_3 Q_{CuL}/Q_{ZnL}$$

The computed results are presented in Figures 1 and 2 for the first 300 min. of reaction. In Figure 1

---

[1] D. W. Margerum and T. J. Bydalek, *Inorg. Chem.*, **1**, 852 (1962).

[2] (a) F. B. Hildebrand, "Introduction to Numerical Analysis," McGraw-Hill Book Co., New York, N. Y., 1956, p. 237; (b) I. D. Gay, *J. Am. Chem. Soc.*, **86**, 2747 (1964).