A Study of the Reaction between Germanium Dioxide and Concentrated Sulfuric Acid. A New Spectrophotometric Method for the Determination of the Stability Complexes of the Form AB_n and AD_p in Mixture

GUNNAR NORHEIM*

Chemical Institute A, University of Oslo, Blindern, Oslo 3, Norway

The reaction in concentrated sulfuric acid between germanium(IV) and 1,1'-dianthrimide has been described in two earlier papers.^{1,2} The conditional constant of the 1:1 complex found present was determined. In these previous studies the solvation reaction of germanium dioxide was not considered since the concentration of the sulfuric acid and the hydrogen sulfate ion were maintained constant.

In the present paper the reaction between germanium(IV) and hydrogen sulfate is studied. The hydrogen sulfate ion concentration in concentrated sulfuric acid can be varied by varying the water content, and this possibility was utilized to determine the stability constants of the two germanium(IV) complexes with 1,1'-dianthrimide or hydrogen sulfate. A new spectrophotometric method for the simultaneous determination of the two stability constants is described.

Experimental. Standard solutions of germanium dioxide and 1,1'-dianthrimide in concentrated sulfuric acid were prepared as described in a previous paper.² The reaction mixtures were heated for 16 h at 70°C before the extinctions were measured in a Zeiss PMQII spectrophotometer at 660 nm. The conditional constant for the germanium(IV)-1,1'-dianthrimide complex was determined from the spectrophotometric data for five different concentrations of the hydrogen sulfate ion. The Lang method^{3,4} was used and optimum conditions⁵ were chosen.

Theory. When a central atom A forms complexes with two different ligands B and D, the reactions are

and the stability constants are

$$K_1 = c_1/(a - c_1 - c_2)(b - nc_1)^n \quad (3)$$

$$K_2 = c_2/(a - c_1 - c_2)(d - pc_2)^p \quad (4)$$

where a , b , and d are the initial concentrations of A, B, and D, and c_1 and c_2 are the actual concentrations of the complexes AB_n and AD_p , respectively. The conditional constant for the AB_n complex is calculated from the following formula

$$K_{cal} = c_1/(a - c_1)(b - nc_1)^n \quad (5)$$

When D represents the solvent, D is in great excess. By introducing $(d - pc_2)^p \approx d^p$ in eqn. (4), the following relation can be set up

$$1/K_{cal} = K_2 d^p / K_1 + 1/K_1 \quad (6)$$

By determining K_{cal} for different concentrations of D, eqn. (6) gives a basis for the determination of K_1 and K_2 . Eqn. (6) can be represented graphically with $1/K_{cal}$ as ordinate and d^p as abscissa, this giving a straight line.

The composition of the complex AB_n can be determined independent of the complex AD_p , if the latter is not too stable and c_1/a not too small. The composition of the complex AD_p can be determined from eqn. (6), because the curve representing this equation will be a straight line only for the correct value of p .

To demonstrate that the new method, represented by eqn. (6), gives correct values for K_1 , K_2 , and p it was tested with values for a , b , d , c_1 , and c_2 calculated from eqns. (3) and (4) for given values of K_1 and K_2 . These data were obtained in the following way.

Eqns. (7) and (8) can be rearranged to:

$$\left(1 - \frac{c_1}{a} - \frac{c_2}{a}\right) \left(\frac{b}{a} - n \frac{c_1}{a}\right)^n - \frac{c_1/a}{K_1 a^n} = 0 \quad (7)$$

$$\left(1 - \frac{c_1}{a} - \frac{c_2}{a}\right) \left(\frac{d}{a} - p \frac{c_2}{a}\right)^p - \frac{c_2/a}{K_2 a^p} = 0 \quad (8)$$

For $y_1 = c_1/a$, $y_2 = c_2/a$, $x_1 = b/a$, $x_2 = d/a$, $W_1 = 1/K_1 a^n$ and $W_2 = 1/K_2 a^p$ the eqns. (7) and (8) become

$$(1 - y_1 - y_2)(x_1 - ny_1)^n - y_1 W_1 = 0 \quad (9)$$

$$(1 - y_1 - y_2)(x_2 - py_2)^p - y_2 W_2 = 0 \quad (10)$$

For any given value of W_1 , W_2 , x_1 and x_2 , y_1 and y_2 can be calculated.

These data were then used to calculate K_{cal} . In the calculations a was kept constant. Using eqn. (6) and the calculated values for K_{cal} , K_1 and K_2 were determined. The new method was tested on a series of combinations between K_1 , K_2 , n and p . These calculations gave a satisfactory result and the curves drawn were straight lines only for the correct value of p .

Results and discussion. When arsenic trioxide and selenium dioxide are dissolved in sulfuric acid, the ions AsO^+ and SeO_2H^+ are formed, respectively. These ions are in equilibria with hydrogen sulfate.^{6,7}

At concentrations similar to those used for germanium dioxide in the present study, arsenic trioxide and selenium dioxide form very little polymeric ions.

In Table 1 the results of the determinations of the conditional constants for the germanium-

* Present address: Institute of Forensic Medicine, University of Oslo, Rikshospitalet, Oslo 1, Norway.

Table 1. The conditional constant for the germanium(IV)-1,1'-dianthrimide complex calculated for different mol concentrations of the hydrogen sulfate ion in concentrated sulfuric acid.

% H ₂ SO ₄	86.4	89.8	93.2	95.8	97.2
$C_{\text{HSO}_4^-}$	11.4	9.4	6.8	4.3	2.8
K_{cal}	144	174	221	336	432

(IV)-1,1'-dianthrimide complex are presented. Curves were drawn from the data in Table 1 with $(C_{\text{HSO}_4^-})^p$ as ordinate and $1/K_{\text{cal}}$ as abscissa for $p=1$ and $p=2$. For $p=1$ the curve is a straight line, for $p=2$ the line is curved. This shows that one mol of hydrogen sulfate reacts with one mol of germanium dioxide. Using linear least squares analysis the two stability constants were calculated from the intercept on the ordinate axis and the slope of the line. The following reaction may be suggested:

As may be expected the stability constant for the reaction between germanium dioxide and hydrogen sulfate is less than the corresponding constants for arsenic trioxide and selenium dioxide. The 1:1 complex between selenium dioxide and 1,1'-dianthrimide has been studied both in concentrated sulfuric acid and in solid form.⁸ This complex did not contain sulfur. The present study indicates a similar reaction for the germanium(IV) complex:

Attempts to isolate the solid germanium(IV)-1,1'-dianthrimide complex failed.

1. Skaar, O. B. and Langmyhr, F. J. *Anal. Chim. Acta* 21 (1959) 370.
2. Langmyhr, F. J. and Norheim, G. *Anal. Chim. Acta* 41 (1968) 341.
3. Lang, R. P. *J. Amer. Chem. Soc.* 84 (1962) 1185.
4. Norheim, G. *Acta Chem. Scand.* 25 (1971) 987.
5. Norheim, G. *Acta Chem. Scand.* 23 (1969) 2808.
6. Gillespie, R. J. and Robinson, E. A. *Can. J. Chem.* 41 (1963) 450.
7. Flowers, R. H., Gillespie, R. J. and Robinson, E. A. *J. Inorg. Nucl. Chem.* 9 (1959) 155.
8. Langmyhr, F. J. and Myhrstad, J. A. *Anal. Chim. Acta* 35 (1966) 212.

Received October 12, 1973.

Über Kupferselenocyanate

ERIK SÖDERBÄCK

Chemisches Institut der Universität Uppsala,
Box 531, S-751 21 Uppsala 1, Schweden

CuSeCN. Das CuSeCN ist von V. F. Toropova¹ dargestellt worden und zwar durch Einwirkung von KSeCN in Wasser auf Cu₂SO₄ oder Cu₂S₂O₃. Bevor diese Untersuchung mir bekannt war, hatte ich CuSeCN durch Reaktion von KSeCN mit einer Mischung von CuSO₄ und Na₂S₂O₃ dargestellt. Es bildet sich der Komplex NaCuS₂O₃, welcher dann anschliessend mit KSeCN reagiert. Um gute Ausbeuten zu erhalten, ist es notwendig, dass bei Reaktionsende kein Thiosulfat übrig ist. Es wurde deshalb das CuSO₄ mit nur einem Mol Na₂S₂O₃ versetzt. Die Bruttoreaktion ist:

Das CuSeCN wurde in etwa quantitativer Ausbeute erhalten und war von gräulich weisser Farbe. Es ist dem CuSCN äusserlich sehr ähnlich und wie dieses sehr schwerlöslich in Wasser. Es kann mit diesem ohne Selenabscheidung zum Kochen erhitzt werden. Wie von Toropova beobachtet, löst sich CuSeCN in konzentrierten wässrigen Lösungen von KSeCN. Die Lösungen sind nicht stabil, sondern scheiden bald rotes Selen aus. Die Lösungen in KSCN sind jedoch, wie ich gefunden habe, stabiler.

Cu(SeCN)₂. Eine sehr alte Untersuchung über Cu(SeCN)₂ geht auf Sir William Crookes² zurück.* Mischt man eine Cu²⁺-Lösung mit einer Lösung von KSeCN, entsteht nach diesem Autor zunächst ein brauner Niederschlag von Cu(SeCN)₂, der bald in schwarzes CuSe übergeht. Analytische Belege fehlen. Bei Wiederholen des Versuches von Crookes wurde eine Lösung von Cu²⁺-Nitrat in Wasser zu einer solchen von KSeCN in äquivalenter Mengen getropft. Jeder Tropfen erzeugte einen hellbraunen Niederschlag, der sich beim Umschütteln mit der Mutterlange in einen ziegelroten verwandelte. Allmählich wurde die Farbe dunkler und war bei Reaktionsende dunkelbraun. Beim Stehen unter gelegentlichem Umschütteln wurde die Farbe schwarz. Nach etwa 12 Stunden Stehens in der Kälte wurde der feinkristalline Niederschlag abfiltriert, mehrmals mit Wasser gewaschen und im Vakuum über H₂SO₄ getrocknet. Sowohl qualitative wie quantitative Analysen zeigten, dass das schwarze Produkt nicht aus CuSe, sondern aus Cu(SeCN)₂ bestand. Das Salz ist in Wasser schwerlöslich und geht bei der Behandlung mit wässrigem Chlor oder Brom glatt in Lösung,

* Später ausgeführte Versuche von Bergstrom³ und von Watkins und Schütt⁴ führten zu nicht einheitlichen Produkten.