composition of the mixture was decided by the equations

$$4AO + 6MoO_2 \longrightarrow A_4Mo_6O_{16} \quad (A = Mg^{++}, Zn^{++}, Co^{++}) \quad (1)$$

$$6Fe_2O_3 + 8Mo + 10MoO_3 \longrightarrow 3Fe_4Mo_6O_{16} \quad (2)$$

$$CaO + MoO_2 \longrightarrow CaMoO_3 \quad (3)$$

The use of a 50% excess of AO in reaction (1) did not affect the composition of the ternary oxide formed.

Chemical analysis of the calcium compound gave the following results. *Anal.* Calcd for $CaMoO_3$: Ca, 21.78; Mo, 52.14. Found: Ca, 21.54; Mo, 52.34. The X-ray powder diffraction pattern of this material can be indexed on the basis of a monoclinic unit cell with $a = c = 7.80 \pm 0.01$ Å., $b = 7.77 \pm 0.01$ Å. and $\beta = 91° 23' \pm 6'$. The observed density of 5.20 ± 0.05 g./cc. is in good agreement with the value of 5.17 g./cc. calculated for a unit cell containing 8 molecules of $CaMoO_3$. This compound apparently has a distorted perovskite structure similar to that of $YCrO_3$.[3]

The magnesium and zinc compounds can be obtained pure by washing the products of the solid phase reaction in dilute hydrochloric acid. The X-ray powder patterns of these compounds indicate that they are isomorphous with each other. The patterns can be indexed on the basis of a hexagonal unit cell with $a = 5.775 \pm 0.005$ Å. and $c = 9.915 \pm 0.010$ Å. for the zinc compound and $a = 5.761 \pm 0.005$ Å. and $c = 9.893 \pm 0.010$ Å. for the magnesium compound. The powder patterns of the cobalt and iron compounds are identical in nature to those of the magnesium and zinc compounds. Chemical analysis of the zinc compound coupled with density measurements and unit cell data for both the magnesium and zinc compounds clearly indicate that the general formula is $A_4Mo_6O_{16}$.

Anal. Calcd. for $Zn_4Mo_6O_{16}$: Zn, 23.92; Mo, 52.66. Found: Zn, 23.99; Mo, 52.89. Density: Calcd. for $Mg_4Mo_6O_{16}$: 5.43 g./cc. Found: 5.30 ± 0.06 g./cc. Calcd. for $Zn_4Mo_6O_{16}$: 6.33 g./cc. Found: 6.23 ± 0.06 g./cc.

Single crystals of the magnesium and zinc compounds have been grown which are suitable for X-ray analysis and structure determination is now in progress. Work is also being carried out in an attempt to extend this structure to other A and B cations.

This work has been supported by a contract between the Office of Naval Research and the University of Connecticut. Reproduction in whole or part is permitted for any purpose of the United States Government.

(3) L. Katz, *Acta Cryst.*, **8**, 121 (1955).

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RECEIVED MAY 4, 1956

A SIMPLE, RAPID METHOD FOR DETERMINATION OF METAL CHELATE STABILITY CONSTANTS

Sir:

A mercury electrode can be used as an indicator electrode for any metal ion in the presence of a chelating agent which forms a 1:1 complex with mercury(II) as well as with the metal ion in question. The potential is given by

$$E = E^{\circ}_{Hg^{++}} + \frac{RT}{2F} \ln \frac{[Me^{+\nu}][HgZ^{2-n}]K_{MeZ}}{[MeZ^{\nu-n}][K_{HgZ}} \quad (1)$$

So, in a solution, containing a metal ion, $Me^{+\nu}$, and constant concentrations of its chelate complex, $MeZ^{\nu-n}$, as well as of the mercury chelate complex, HgZ^{2-n}, the potential of a mercury electrode depends only on the $Me^{+\nu}$-ion concentration. However, pure logarithmic dependence is only warranted if the stability constant of the metal complex, $MeZ^{\nu-n}$, is several orders of magnitude smaller than that of the mercury complex, HgZ^{2-n}. On the other hand, *for various metal ions this potential depends linearly on the logarithm of the stability constant of the complex*, K_{MeZ}, and is, within a certain pH region, independent of pH. The stability constants, K_{MeZ}, therefore can be calculated by equation (1) using the observed potential of the mercury electrode, the concentrations occurring in (1) and the stability constant K_{HgZ}.[1]

The stability constant K_{HgZ} can be determined in a similar way. The potential of a mercury electrode in a solution containing mercury(II) chelate complex and excess chelating agent is

$$E = E^{\circ}_{Hg^{++}} + \frac{RT}{2F} \ln \frac{[HgZ^{2-n}]\phi}{[Z^{-n}]K_{HgZ}} \quad (2)$$

where

$$\phi = 1 + \frac{[H^+]}{K_n} + \frac{[H^+]^2}{K_nK_{n-1}} + \cdots + \frac{[H^+]^n}{\prod_{j=1}^{n} K_j}$$

K_j are the acidity constants of the complexing agent.

Equation (2) involves ϕ and hence the potential is pH dependent. In a solution containing equal amounts of mercury complex and free complexing agent, one simply measures the potential as a function of pH and calculates the stability constant, K_{HgZ}, from equation 2.

For a test of the method, the stability of the complexes of ethylenediaminetetraacetic acid (EDTA or Y) with several metal ions have been determined (Table I) and were found in excellent agreement with values obtained by other methods.

Potentials were measured as a function of pH, in solutions containing metal ion $Me^{+\nu}$, metal complex MeY^{--}, and mercury complex HgY^{--}, each 0.001 M, with the ionic strength kept at 0.1 by means of sodium perchlorate. For these definite concentrations, the potentials corresponding to various stability constants were calculated by means of equation (1) and plotted on a potential–pH diagram. The stability constants for a particular metal ion can then be directly read from the potential independent region of the experimental points.

In the case of the more stable complexes (Pb, Cu, Ni), the measurements were disturbed by the formation of white precipitates of mercurous mercury-

(1) G. Schwarzenbach, R. Gut, G. Anderegg, *Helv. Chim. Acta*, **37**, 937 (1954), G. Schwarzenbach, G. Anderegg, *ibid.*, **37**, 1289 (1954), have mentioned briefly the applicability of mercury electrodes for the determination of metal chelate stability constants although neither the principle of the method nor details of operation were described.

TABLE I
STABILITY CONSTANTS OF VARIOUS METAL-EDTA COMPLEXES

Metal ion	Log stability constant: Proposed method[a]	Log stability constant: Literature[b]
Ba^{++}	7.9	7.76[c]
Sr^{++}	8.7	8.63[c]
Mg^{++}	8.9	8.69[c]
Ca^{++}	10.7	10.59,[c] 10.70,[d] 10.96[d]
Mn^{++}	13.8	13.58,[d] 14.04,[d] 13.79[d]
Cd^{++}	16.4	16.59,[d] 16.46[d]
Zn^{++}	16.4	16.26,[d] 16.50[d]
Hg^{++}	22.1	21.80,[d] 22.15[e]

[a] 25.0°, in 0.1 *N* $NaClO_4$. [b] 20.0°, in 0.1 *N* KCl or KNO_3. [c] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1798 (1947). [d] G. Schwarzenbach, R. Gut and G. Anderegg, *ibid.*, **37**, 937 (1954). [e] J. Goffart, G. Michel and D. Duyckaerts, *Anal. Chim. Acta*, **9**, 184 (1953).

(II)-ethylenediaminetetraacetate. In order to avoid this interference, the concentration of Hg-EDTA complex was lowered to 0.0001 *M* and the concentration of metal complex, MeY, increased to 0.01 *M*.

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RECEIVED FEBRUARY 20, 1956

ELECTRONIC AND VIBRATIONAL STATES OF THE NITRITE ION[1]

Sir:

The electronic spectrum of the nitrite ion has been studied under conditions of moderately high resolution, in an effort to determine the symmetry properties of the first excited singlet electronic state and the fundamental vibrational frequencies in the ground state and in the first excited state. The absorption spectrum of crystalline $NaNO_2$ at low temperature has been studied previously by other workers,[2,3] but a detailed analysis has not been offered. In agreement with Eberhardt and Trawick,[3] the origin of the lowest absorption transition at 25960 cm.$^{-1}$ is polarized perpendicular to the plane of the NO_2^- ion, although the lattice and vibrational additions do show some absorption for light polarized in the plane of the NO_2^- ion. The vibrational analysis of the absorption spectrum is quite straightforward. Long progressions of a single frequency of 632 ± 4 cm.$^{-1}$, with the intensity maximum in the fourth member of the progression, combine with single quantum additions of a frequency of 1018 cm.$^{-1}$ to each of the bands to account for all of the prominent bands in the transition. Irradiation of crystalline $NaNO_2$ at 77°K. with the λ 3650–3660 Å. lines of the mercury arc produced a weak but detectable fluorescence spectrum, which is reported here for the first time. The fluorescence and absorption spectra have a common origin, and are mirror images of each other. Long progressions of a frequency of 829 cm.$^{-1}$, with the intensity maximum also in the fourth member of the progression combine with single quantum additions of a 1337 cm.$^{-1}$ frequency to each of the bands in the progression.

Since the absorption and fluorescence spectra possess a common origin, the electronic transition must be allowed by symmetry. The symmetry of the site, crystal and molecule are all C_{2v},[4] so the O–O band cannot be induced by the crystal. The polarization properties then prove that the transition is allowed by symmetry and is polarized perpendicular to the NO_2^- plane, in complete agreement with the predictions of Walsh for an 18-electron molecule of C_{2v} symmetry,[5] but in disagreement with recent predictions by McGlynn and Kasha.[6] In further agreement with Walsh, calculations based on the method of Craig[7] indicate that the bond angle has increased slightly in the excited state.

Vibrational assignments for the NO_2^- ion in crystalline $NaNO_2$ are given in Table I for the ground electronic state and for the first excited singlet electronic state. The vibrational frequencies deduced from the analysis of the fluorescence spectrum agree within the limits of error with the frequencies observed in infrared absorption. It should be noted that ν_3 is lower in frequency than ν_1, in agreement with the Raman polarization studies of Langseth and Walles.[8] The resemblance with ozone[9] in this respect is apparent.

TABLE I
VIBRATIONAL FREQUENCIES OF NO_2^-

	Ground electronic state (0 cm.$^{-1}$)	Excited electronic state (25960 cm.$^{-1}$)
ν_1, symmetric stretching	1337 ± 4	1018 ± 4
ν_2, bending	829 ± 2	632 ± 4
ν_3, asymmetric stretching	1270 ± 4	Not obsd.

It is hoped that additional work at 4°K. which is now in progress will lead to a detailed analysis of the lattice and vibrational states of the NO_2^- ion, and that a complete analysis may eventually be obtained from studies of $N^{15}O_2^-$.

(1) Supported by the Office of Ordnance Research, under Contract DA-30-115-Ord-620 with the University of Rochester.

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(3) W. H. Eberhardt and W. G. Trawick, *J. Chem. Phys.*, **22**, 1462 (1954).

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RECEIVED APRIL 10, 1956

VAPORIZATION OF BORIC OXIDE AND THERMODYNAMIC DATA FOR THE GASEOUS MOLECULES B_2O_3, B_2O_2 AND BO

Sir:

Vaporization of liquid B_2O_3 at high temperatures has been difficult to interpret since there has been uncertainty about the molecular species involved in the process. Recent mass spectrographic studies,[1,2] together with effusion[3] and flow[4] vapor

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(4) (a) J. R. Soulen, P. Sthapitanonda and J. L. Margrave, *J. Phys. Chem.*, **59**, 132 (1955); (b) J. R. Soulen, Ph.D. Thesis, University of Wisconsin, 1955.