GASEOUS HYDROXIDES

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I. Introduction

The hydroxides[1] are one of the four main groups of compounds in oxide-water systems, one of the oldest and most studied areas of inorganic chemistry. We classify as hydroxides solid, liquid, or gaseous compounds derived, either experimentally or formally, from an oxide and water, e.g.,

$$N_2O_5(g) + H_2O(g) = 2NO_2(OH)(g)$$

Gaseous hydroxides of both nonmetals and metals are known. The first group contains species, such as nitrogen dioxide hydroxide, $NO_2(OH)$, and boron trihydroxide, $B(OH)_3$, which have been known for a long time. Gaseous metallic hydroxides, on the other hand, have only recently been described, though they are now known to exist over the whole range between room temperature and 2000°C.

Gaseous hydroxides may be divided into two types with different equilibria underlying their formation.

(a) *Vaporization or Sublimation Equilibrium*

$$\text{Hydroxide(s,l)} \rightleftharpoons \text{Hydroxide(g)} \qquad (1)$$

Examples: $NO_2(OH)(l) \rightleftharpoons NO_2(OH)(g)$
$NaOH(s) \rightleftharpoons Na(OH)(g)$

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[1] Compounds in oxide-water systems, which are also known as aquoxides, have been divided, according to the mode of bonding of the water, into four main groups: hydroxides, oxide hydrates, hydronium compounds, and oxide aquates; cf. O. Glemser, Ergebnisse and Probleme von Verbindungen der Systeme Oxid-Wasser. *Angew. Chem.* **73,** 785 (1961).

0	I	II	III	IV	V	VI	VII	VIII
He	$LiOH$ $Li_2(OH)_2$ $Li_3(OH)_3$	$Be(OH)_2$	$B(OH)_3$ $BOOH$ $(BOOH)_3$	$CO(OH)_2$?	NO_2OH $NOOH$	O	F	Ne
Ne	$NaOH$ $Na_2(OH)_2$	Mg	$Al(OH)_3$?	$Si(OH)_4$	$PO(OH)_3$	$SO_2(OH)_2$	$ClOH$ $ClO_3(OH)$	Ar

FIG. 1. Gaseous hydroxides of elements of the second and third periods.

(b) *Reaction Equilibrium*

$$\text{Oxide(s,l)} + H_2O(g) \rightleftharpoons \text{Hydroxide(g)} \qquad (2)$$

Example: $BeO(s) + H_2O(g) \rightleftharpoons Be(OH)_2(g)$

This division is to some extent arbitrary, for some of the gaseous hydroxides now known may be considered as formed according to either Eq. (1) or Eq. (2). There is, however, a series of compounds which can be produced only according to Eq. (2). These have not yet been isolated, and their existence is inferred indirectly from equilibrium studies based on the transfer method or the effusion method, the latter being coupled with mass spectrometric studies. Such measurements enable us to postulate reactions leading to the formation of hydroxides and lead to conclusions, based on thermodynamic data, about the conditions for their existence. Furthermore, under the conditions existing in the oxyhydrogen flame, gaseous alkali metal hydroxides and hydroxylic radicals may be observed, as is described later.

The molecular structures of gaseous hydroxides has been completely elucidated only in a few instances with the aid of infrared and Raman spectroscopy, microwave spectroscopy, or electron diffraction. Often only the molecular weight can be deduced, in which case the mass spectrometer is the chief tool. It is not yet possible to say if the occurrence of gaseous hydroxides is restricted to particular groups of elements of the periodic system. Figure 1 shows the gaseous hydroxides formed by elements in the second and third periods.

II. Systems of the Type Hydroxide(s,l) ⇌ Hydroxide(g)

A. NONMETALLIC HYDROXIDES

Nitrogen dioxide hydroxide, $NO_2(OH)$, is a gaseous hydroxide which has been thoroughly investigated. Forsythe and Giauque (*25*) determined the thermodynamic data shown in Table I. Interpretation of the infrared spectrum confirmed the entropy value in Table I, and also showed the

TABLE I
PHYSICAL DATA FOR $NO_2(OH)(g)$ AND $NO(OH)(g)$

	Heat of vaporization (cal/mole)	Enthalpy of formation $\Delta H_{298.2}°$ (kcal/mole)	Standard entropy $S_{298.2}°$ in (cal/mole°C)	Free energy of formation $\Delta G_{298.2}°$ (kcal/mole)	Dipole moment D
$NO_2(OH)$	9355 (20°C)	−31.99	63.62	−10.46	2.16
$NO(OH)$	—	−18.58	61.46	−10.81	—

existence of an energy barrier of about 10 kcal/mole to the rotation of the hydroxyl group.

After Badger and Bauer (*4*) had detected the hydroxyl group in the absorption spectrum of $NO_2(OH)(g)$, the structure was determined by Maxwell and Mosley (*47*) and by Akishin *et al.* (*2*) from electron diffraction, by Cohn *et al.* (*22*) from the infrared spectrum and by Millen and Morton (*50, 50a*) from the microwave spectrum. We consider the results of the last authors, which are given in Fig. 2, to be the most reliable. Only the O—H distance is uncertain; it is assumed to be 0.96 Å, as in water.

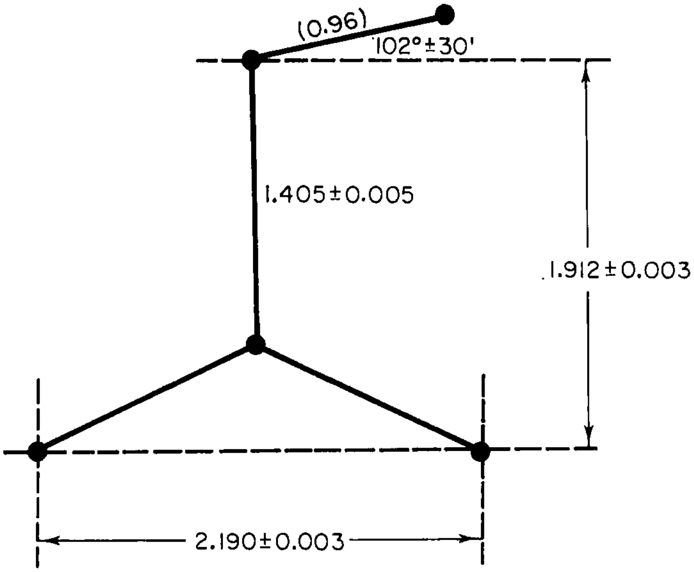


FIG. 2. Structure of the gaseous $NO_2(OH)$ molecule according to Millen and Morton.

Nitrogen oxide hydroxide, NO(OH). Some time ago Melvin and Wulff (*48*) found a number of bands between 3100 and 3900 Å in the absorption spectrum of gaseous mixtures of NO(g), $NO_2(g)$, and $H_2O(g)$ which they attributed to NO(OH)(g). This conclusion was questioned, but Porter (*57*) was able to substantiate it. In the infrared spectrum of NO(OH)(g) a doubling of most of the bands occurs owing to *cis-trans* tautomerism. [For further references, see Palm (*56*).] For this equilibrium

$$K_{25^\circ} = \frac{p_{trans}}{p_{cis}} = 2.5$$

The *cis* form is believed to be about 500 cal/mole richer in energy than the *trans* form. (The statement that the interconversion of the two forms is hindered by an energy barrier of about 12 kcal/mole is, however, open to doubt.) The structures shown in Fig. 3 have been proposed for the two forms. A third isomer in which the hydrogen atom is bonded to nitrogen can be excluded on the basis of the infrared spectrum.

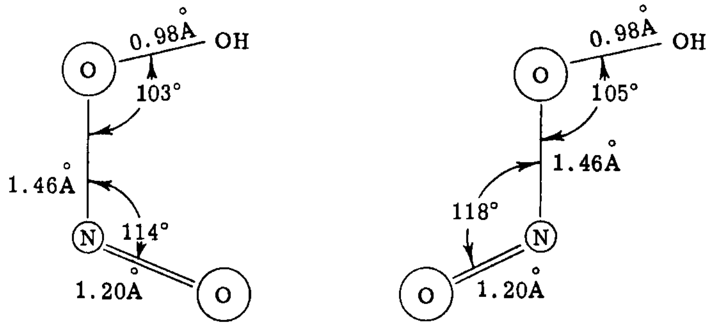


FIG. 3. Structures of *cis*- and *trans*-NO(OH)(g), according to Palm.

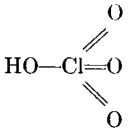
Jones *et al.* (*43*) obtained the structural data for *cis*- and *trans*-NO(OH)(g) shown in Table II from their infrared spectra. The observed N—O distance of 1.20 Å is almost that expected for a N═O bond. While these authors used the equilibrium $NO(g) + NO_2(g) + H_2O(g) \rightleftharpoons 2NO(OH)(g)$ as a basis for their infrared investigation at 25°, Ashmore and Tyler (*3*) carried out vapor pressure measurements at 20–80°C. Their thermodynamic data are given in Table I.

TABLE II
DISTANCES AND ANGLES IN *cis* AND *trans*-NO(OH)(g)

	O—H (Å)	O—N (Å)	N—O (Å)	HON (angle)	ONO (angle)
cis-NO(OH)	0.98	1.46	1.20	(103°)	114°
trans-NO(OH)	0.98	1.46	1.20	(105°)	118°

Other gaseous nonmetallic hydroxides. Hedberg and Badger (*37*) used infrared spectroscopy to detect gaseous chlorine hydroxide or ClOD in mixtures of $Cl_2O(g)$ with $H_2O(g)$ or $D_2O(g)$. Assuming the O—H distance to be 0.96 Å, as in water, and the O—Cl distance to be 1.70 Å, as in Cl_2O, the angle H—O—Cl is 113°.

The structure of gaseous chlorine trioxide hydroxide, ClO_3OH, was determined by Akishin *et al.* (*1*) by electron diffraction. Their results agree with a molecule



$$\mathrm{HO{-}Cl(=O)_3}$$

having C_{3v} symmetry. The molecular parameters are: $r(\text{Cl} = \text{O})$, 1.42 ± 0.01 Å; $r(\text{Cl} - \text{O})$, 1.64 ± 0.02 Å; HOClO; 100° ± 2°. The position of the hydrogen atom was not determined.

Vapor pressures of condensed phosphoric acids have also been investigated over a wide range of temperatures and compositions. From measurements of molecular weight at 1020°C of the vapor obtained by vaporizing phosphoric acid with varying ratios of H_2O to P_2O_5, it was concluded that a mixture of water and P_4O_{10} vapor and/or a low molecular weight ultraphosphoric acid approximating to $P_3O_7(OH)$ was present. Presumably the vapor contains water in addition to several low-molecular-weight ultraphosphoric acids, including P_4O_{10}, the end member of this series of acids (*13, 74, 76, 80*).

Gaseous phosphorus oxide trihydroxide, $PO(OH)_3$, (*17*), sulfur dioxide dihydroxide, $SO_2(OH)_2$, (*84*) and selenium dioxide dihydroxide, $SeO_2(OH)_2$ (*72*) are also known. Gaseous boron hydroxide will be dealt with in Section III.

B. METALLIC HYDROXIDES

1. *The Mass Spectrometric Method of Investigation*

The first vapor pressure measurements on alkali hydroxides were made by von Wartenberg and Albrecht (*82, 83*) and Jackson and Morgan (*40*) more than forty years ago. At that time it was impossible to make any deductions as to the nature of the species formed on vaporization, but we are now well informed on this subject as a result of recent work. In this work, the mass spectrometer has played a predominant role, since it permits the separation and identification of the separate gaseous species produced and hence enables us to determine their thermodynamic properties.

In the method of Chupka and Inghram (*19, 20*) a Knudsen cell, used for measuring vapor pressures, is combined with a mass spectrometer. The gas leaving the Knudsen cell, which is in equilibrium with the solid phase, is transferred to the ionization chamber of a mass spectrometer. The ions resulting from electron bombardment are observed in the mass spectrometer. The temperature dependence of the logarithm of the concentration of the volatile product (deduced from the observed ion intensity and the temperature) permits the calculation of the enthalpy of vaporization from the Clausius-Clapeyron equation. Absolute values of the vapor pressure may be determined by calibrating the measuring apparatus, using substances with known vapor pressure relationships. The following relationship is generally valid:

$$P_x = kTJ_{x^+} \tag{3}$$

P_x = vapor pressure of the component x; k = proportionality constant to allow for the calibration; T = temperature of the effusion cell when J_{x^+} is measured; J_{x^+} = observed ion intensity of the component.

It is, of course, a prerequisite for valid observations that thermodynamic equilibrium is attained and that the ions observed are correctly assigned to the primary neutral species. The investigation therefore also involves a series of further measurements and observations, the nature of which is determined by the complexity of the problem and the presence of disturbing effects; these will not be dealt with more fully here.

The use of this method is not restricted to the determination of vapor pressures. It has been possible to apply it, after some modification, to the study of reactions between oxides and water, which is of special interest here. According to Chupka *et al.* (*21*), the effusion cell and ionization chamber may be evacuated separately. In this way, the mass spectrometer may be used with relatively high pressures of water vapor introduced by means of a needle valve in the effusion cell.

2. Results

From infrared spectroscopic studies of the gas phase over solid NaOH. KOH, and RbOH, Spinar and Margrave (*71*) believed gaseous hydroxides of the composition $M^+(OH)^-$ to be present. Porter and Schoonmaker (*58, 59, 61, 65, 67*) and also Berkowitz *et al.* (*8*), used the combined method, (involving the effusion cell and mass spectrometer) which has already been described to study the vaporization and sublimation equilibria of some alkali metal hydroxides. They also studied mixed solid phases of the type $Me_aMe_b(OH)_2$, where Me_a and Me_b are two metals of the series sodium, potassium, rubidium, and cesium. It was not possible, for reasons which will be mentioned shortly, to include LiOH in this investigation, but application of a modified technique to the system $Li_2O + H_2O$ was successful.

The essential conclusion from the study of these equilibria is that gaseous hydroxides are in fact formed. Tables III and IV summarize the results for the reactions studied and data derived from them. The authors discuss a number of interesting observations and conclusions arising from the work. Thus, Berkowitz, Meschi, and Chupka deduce a nonlinear structure for lithium hydroxide from a comparison with the lithium halides. In agreement with the structure proposed for Li_2F_2 and in keeping with the structures of other dimeric lithium halides and of Li_2O, they assume the planar diamond-shaped structure for $Li_2(OH)_2$, shown in Fig. 4. The thermodynamic functions determined with this model have been used to evaluate the observed results by applying the third law (cf. Section III,A,*2*,*b*). The $\Delta H_T°$ values so obtained are compared in Table IV with $\Delta H_T°$ values determined by the slope method [Section III, Eq. (17)].

Agreement is very satisfactory, except for the dimerization reaction $2LiOH(g) = Li_2(OH)_2(g)$, for which the authors consider the third-law value of 64 kcal to be more reliable.

TABLE III

ENTHALPY VALUES FOR THE SUBLIMATION-VAPORIZATION OF SODIUM AND POTASSIUM HYDROXIDES

	ΔH_T (kcal/mole)[a]		T (°K)	
	Na	K	Na	K
I $MeOH(s) \leftrightarrows MeOH(g)$	46.4 ± 3	43.9[b]	298	298
II $MeOH(l) \leftrightarrows MeOH(g)$	43 ± 3	44.6 ± 3	660	298
III $2MeOH(s) \leftrightarrows Me_2(OH)_2(g)$	—	36 ± 2	—	626
IV $2MeOH(l) \leftrightarrows Me_2(OH)_2(g)$	28 ± 3	—	660	—

[a] In reactions III and IV the percentage of dimer is given.

[b] Kelley, from the data of von Wartenberg.

When the solid phase consists of a mixture of various hydroxides, as in the investigations of Porter and Schoonmaker, gaseous species of the type $Me_aMe_b(OH)_2(g)$ are found. Equilibrium constants for the reaction $(Me_a)_2(OH)_2 + (Me_b)_2(OH)_2 \rightleftharpoons 2Me_aMe_b(OH)_2$ are given in Table V. The experimental values correspond approximately with the value $K = 4$, which is to be expected from entropy considerations $\Delta_R H \approx 0$ for the above reactions. Since polymeric gaseous alkali halides exist, the formation of gaseous alkali hydroxide halides [e.g., $Na_2(OH)F$] is also very likely *(68)*.

TABLE IV

ENTHALPY VALUES FOR REACTION IN THE FORMATION OF GASEOUS LITHIUM HYDROXIDE

	ΔH_T (kcal/mole)		T°K	
	A[a]	B[b]	A	B
$Li_2O(s) + H_2O(g) \leftrightarrows LiOH(g)$	78 ± 3	80 ± 2	1300	1300
$Li_2O(s) + H_2O(g) \leftrightarrows Li_2(OH)_2(g)$	14 ± 2	16 ± 4	1250	1500
$2LiOH(s) \rightleftharpoons Li_2(OH)_2(g)$	44 ± 3	45 ± 3	500	600
$Li_2(OH)_2(g) \leftrightarrows 2LiOH(g)$	58 ± 3	64 ± 4	1300	1300

[a] Estimated from the slope of the graph of ln K vs $1/T$.

[b] Estimated by the "third-law" method.

The occurrence of polymeric gaseous species as products of the vaporization process is not restricted to alkali hydroxides but is a phenomenon which is observed with many oxides. Aggregation numbers lie between 2 and 4 or higher. Brewer *(10)* has shown that there is a simple relationship between the dimerization energy, ΔH_D, and ΔH_1, the enthalpy of vaporization of the monomer, according to which the ratio between monomer and dimer or polymer is established as a function of temperature. Thus if $\Delta H_D > \Delta H_1$,

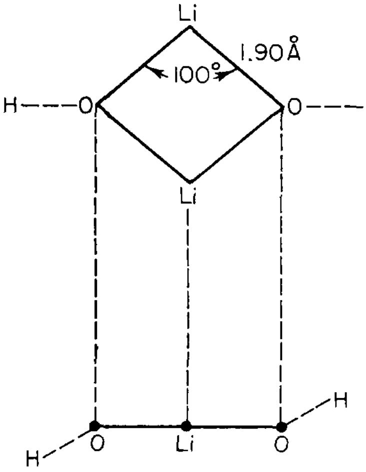


FIG. 4. Proposed structure for $Li_2(OH)_2$.

the dimeric species will be the main product of vaporization at lower temperatures; with rising temperatures the monomeric species will predominate. This relationship is found for sodium and potassium hydroxides.

TABLE V
EQUILIBRIUM CONSTANTS FOR THE REACTION
$(Me_a)_2(OH)_2(g) + (Me_b)_2(OH)_2(g) \rightleftharpoons 2Me_aMe_b(OH)_2(g)$

$Me_aOH—Me_bOH$	K	T(°K)
RbOH—CsOH	4.2 ± 0.1	673
KOH—RbOH	5.2 ± 1.0	693–718
NaOH—KOH	4.9 ± 0.3	883
NaOH—RbOH	2.8 ± 0.3	823
KOH—CsOH	3.5 ± 1.0	629

Energies of dimerization for the various alkali hydroxides are set out in Table VI. Apart from the value for LiOH, results for the dimerization energies are obtained with mixed solid phases. The value for LiOH was obtained directly and is thus independent of the values for the other alkali hydroxides, which are relative. It agrees with the observed trend of decrease in dimerization energy with increase in atomic number of the alkali metal.

The sublimation equilibrium of lithium hydroxide could not be studied

TABLE VI

ENTHALPIES OF DIMERIZATION OF VARIOUS ALKALI HYDROXIDES

$2MeOH(g) \rightleftharpoons Me_2(OH)_2(g)$

MeOH	ΔH_T (kcal/mole of Dimer)	T°K
LiOH	−64	1300
NaOH	−54	660
KOH	−48	883
RbOH	−45	823
CsOH	−40	692

in the way used for the other alkali metal hydroxides; the decomposition equilibrium

$$2LiOH(s) \rightleftharpoons Li_2O(s) + H_2O(g) \quad (4)$$

lies so far to the right at the operating temperature that the resulting partial pressure of H_2O interferes with the use of the mass spectrometer.[2] It is necessary, therefore, to study the reverse reaction in the presence of a much smaller partial pressure of water vapor than corresponds to the decomposition of LiOH.

Schoonmaker and Porter (*68*) worked in the temperature range 780–900°C, but with a maximum water vapor partial pressure of 10^{-2} mm of mercury. They discussed the possible influence of the water vapor partial pressure on the ratio of monomer to dimer, and concluded that the low pressure used was unfavorable for the formation of dimer or excluded the production of this species. They also worked with mixtures of Li_2O and Na_2O as the solid phase under the same reaction conditions. From this investigation it was found that the energy of dimerization to $Li_2(OH)_2$ was about 4 to 6 kcal/mole of dimer different from that to $Na_2(OH)_2$; this leads to a value of 58–60 kcal for LiOH, in agreement with that obtained by the slope method.

Berkowitz *et al.* were able with their technique to control the water vapor partial pressure at about 0.1 mm Hg. They worked in the temperature range 830–1130°C and found that the main product was LiOH(g), with smaller amounts of $Li_2(OH)_2(g)$ and traces of $Li_3(OH)_3(g)$.

These investigations, in which the gaseous hydroxide is prepared by reaction of the metal oxide with water vapor, are of interest not only as a

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[2] Direct observation of sublimation (vaporization) was practically impossible because of the strongly corrosive nature of LiOH. Even in work with KOH and NaOH the activity of the fused alkali hydroxide was observed to be influenced by the crucible material (MgO). This results in a slight uncertainty in the data in Table III, which was pointed out in ref. *60*, without numerical corrections being made.

contribution to our knowledge of the gaseous alkali hydroxides, but also because they deal with a type of reaction in which the (apparent) increase in the vapor pressure of an oxide is brought about by a foreign gas (H_2O). This is further discussed in Section III. Mass spectroscopic studies of these reactions (so far as metal oxides are involved) are not yet available.

The relationship is made clearer by the work of van Arkel *et al.* (*77*). It was shown that Li_2O has an increased vapor pressure in the presence of water vapor, and this leads to greater vaporization of the oxide in the oxygen stream than when water vapor is absent. The product vaporized in these experiments was trapped by means of a cool finger and identified by X-ray methods as LiOH. (As the authors pointed out, the nature of the gaseous product was not necessarily proved by this method.) In view of the work of Smith and Sugden (*70*), who showed that LiOH is stable at 2000°, van Arkel, Spitzbergen, and Heyding assumed the reaction

$$Li_2O(g) + H_2O(g) \rightleftharpoons 2Li(OH)(g) \tag{5}$$

C. Investigations in the Oxyhydrogen Flame

Sugden and his co-workers (*73*) assume the formation of gaseous alkali hydroxides in an oxyhydrogen flame into which aqueous alkali metal salt solutions (mostly nitrates or acetates) are sprayed. Both vaporization and ionization of the metal atoms take place. Assuming equilibrium is obtained (though this has not been proved directly for the part of the flame studied), the electron concentration may be calculated by Saha's method (*64*). It may also be determined experimentally by measuring the absorption of microwave radiation. Only for sodium do the values agree; the discrepancies for the other alkali metals may be understood if the formation of gaseous alkali hydroxide and OH^- ions is assumed.

$$Me \rightleftharpoons Me^+ + e^- \tag{6}$$

$$OH + e^- \rightleftharpoons OH^- \tag{7}$$

$$Me + OH \rightleftharpoons MeOH \tag{8}$$

A further possible way of studying such flames is by the photometric examination of the flame spectra in the visible and ultraviolet region. The spectra of the alkali and alkaline earth metals have been known for a hundred years and are used in determining them by flame photometry. Formerly molecules such as Ca_2 or the oxides were assumed to be carriers for the spectra of the alkaline earth metals. From a comparison with the halide spectra, and from spectrophotometric measurements, James and Sugden (*41*), Lagerquist and Huldt (*45*) and Gaydon (*29*) came to the conclusion that the band spectra in these flames arose mainly from the radicals CaOH, SrOH, and BaOH.

Magnesium salts in the oxyhydrogen flame show a characteristic band spectrum in the near ultraviolet which is due to MgOH (*16*). Under similar conditions GaOH, InOH, and TlOH (*15*), MnOH (*55*), and CuOH (*14*) occur; the last of these is said to be responsible for the well known green coloration of flames by copper salts.

III. Systems of the Type Oxide(s,l) + $H_2O(g) \rightleftharpoons$ Hydroxide(g)

Experiments have shown that various oxides react with water vapor to form gaseous products. The observations may be described in terms of the hypothesis of an increase in the vapor pressure of the oxide in presence of water vapor. For high pressures and with strong attractive forces such effects as solubility of solid bodies in gases are known. For the systems considered here, however, the increase in vapor pressure at atmospheric pressure is appreciably greater than would be expected from a simple physical model. It is apparent from this that there must be considerable interaction between the oxide and water vapor, which may be formulated by the reaction scheme in Eq. (1), in which

$$\text{Oxide(s,l)} + m\text{H}_2\text{O(g)} \rightleftharpoons [\text{Oxide }(\text{H}_2\text{O})_m](\text{g}) \qquad (9)$$

the expression on the right denotes only over-all composition, no indication of the mode of bonding being given. A study of this heterogeneous equilibrium yields information about the association number, m, and the interaction energy between oxide and water vapor, and hence about the nature of the gaseous compound formed. In our case it provides information on the possibility of forming a gaseous hydroxide. Reactions which can be described by the equilibrium of Eq. (9) may be divided into two groups: A. Reactions at atmospheric pressure; B. Reactions at higher pressures.

A. REACTIONS AT ATMOSPHERIC PRESSURE

Heterogeneous reactions at high temperatures may be represented as approximately obeying the ideal gas laws. From (9) it follows that

$$k_m = \frac{p_{[\text{oxide}(\text{H}_2\text{O})_m]}}{p^m_{\text{H}_2\text{O}}}$$

or, in shortened form

$$k_m = \frac{p_{\text{hyd}}}{p^m_{\text{H}_2\text{O}}} \qquad (10)$$

The equilibria in question may be examined by vapor pressure measurements, preferably made by the transfer method or, at pressures $<10^{-5}$ to 10^{-6} atm, by the Knudsen effusion technique. Measurements with the Knudsen cell in association with the mass spectrometer have been made for the equilibria under consideration here in the cases of lithium hydroxide and the boron hydroxides. Infrared emission spectroscopic studies have also been made for the system B_2O_3(l)-H_2O(g), and the results agree well with those obtained by mass spectrometric and transfer methods. The transfer method has various advantages arising from the ease of manipulation, the reliability of the measurements, and the possibility of varying the conditions of the experiment widely. It is understandable, therefore, that this method has been used frequently for the study of the reactions under consideration. However, in spite of the simple technique involved in the transfer method, some precautions must be taken to obtain dependable measurements. Because of their general interest, we will now consider briefly the method and the limitations attending the interpretation of the results obtained.

1. *The Transfer Method of Investigation*

In this method water vapor or mixtures of it with other gases (N_2, O_2) are passed over the oxide at the temperature of the experiment, and the gas stream becomes saturated to the equilibrium pressure. In this way, material is drawn from the reaction zone without disturbing the equilibrium, provided the experiment is conducted properly. The material is condensed outside of the reaction zone, so that its quantity may be determined. In the simplest case this is done by weighing (the loss in weight of the specimen in the reaction tube may also be measured). The amount of material transferred per unit volume of carrier gas is then determined as a function of the partial pressure of water vapor and the temperature. In essence it is a question of making sure, by choice of the conditions of the experiment, that the amount of substance transferred by the carrier gas in unit time ($\dot{n}$) under otherwise identical conditions varies linearly with its flow rate ($\dot{v}$). This function, $\dot{n} = f(\dot{v})$ in a general case is shown in Fig. 5. The extent of the regions A, B, and C depends on the conditions of the experiment. In A a transfer due to diffusion is added to that due to the equilibrium pressure of the substance. Region B represents the ideal case of proportionality, while in C the transfer gas is not saturated. The supersaturation in region A may be overcome experimentally by increasing $\dot{v}$. The risk of unsaturation in C may be reduced by reducing the gas space over the sample and by increasing the length of the cell. It is possible to make region B sufficiently large by suitable construction of the transfer cell. Further details of the theory and technique may be obtained from recent publications (*38*).

Data are collected in Table VII in order to give an impression of the results of transfer experiments with WO_3, MoO_3, TeO_2, and BeO. They also illustrate the apparent increase in vapor pressure, resulting from the interaction of the solid oxide with gaseous water, which was mentioned earlier.

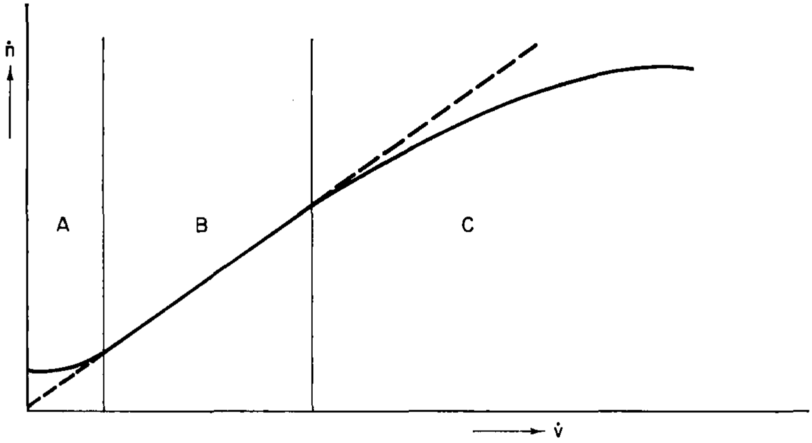

FIG. 5. Amount of substance, $\dot{n}$, transferred per unit time as a function of the flow rate, $\dot{v}$.

TABLE VII
RESULTS OF MEASUREMENTS BY THE TRANSFER METHOD

	T	Carrier gas O_2	Carrier gas H_2O	Carrier gas p_{H_2O}	Apparent vapor pressure of oxide	Oxide transported as gaseous compound	Approximate duration of experiment
	(°K)	l(STP)	l(STP)	(mm Hg)	(mm Hg)	(mg)	(hr)
WO_3	1323	9.13	0.57	44	0.151	21.0	1.6
	1323	—	9.10	751	2.43	305.0	1.5
MoO_3	933	13.69	0.36	19	0.140	17.1	2.3
	933	1.84	13.2	650	1.021	132.6	2.5
TeO_2	923	30.78	3.28	71	0.020	6.7	5.6
	923	—	32.00	748	0.141	42.8	5.3
BeO	1586	—	62.30	736	0.089	8.4	15.2
	1822	—	6.46	738	0.533	5.2	7.8

2. Evaluation of Results

The mixture of water vapor with a gas (the dilution component) which is inert with respect to the system will be referred to as the carrier gas. The volume V of the dilution component is determined, for example, with the aid of a flow meter or a small gas holder.

The water vapor component, m_{H_2O}, is obtained by weighing the water frozen out after separating the substance transferred. The reaction temperature T, the total pressure P (which is almost the same as the barometric pressure) and the mass of the substance transferred, m^{+}_{oxide}, are also known.

Applying the usual corrections, and knowing, or assuming, the molecular weight of the gaseous compound produced (cf. Section III,A,*13*), partial pressures may be calculated from Dalton's law as:

$$p_{H_2O} = \frac{n_{H_2O}}{\Sigma n_i} \cdot P \qquad p^+_{\text{oxide}} = \frac{n^+_{\text{oxide}}}{\Sigma n_i} \cdot P \tag{11}$$

The term n_i denotes the number of moles of the components i.e., $\Sigma n_i = n_v + n_{H_2O} + n^+_{\text{oxide}} = n_{\text{carrier gas}} + n^+_{\text{oxide}}$; $n^+_{\text{oxide}} = (m^+_{\text{oxide}}/M^+_{\text{oxide}})$; n_v = number of moles of dilution component; M_{oxide} = molecular weight of the gaseous product. It frequently happens that $n^+_{\text{oxide}} \ll n$ carrier gas, so $\Sigma n_i \approx n_{\text{carrier gas}}$. The term p^+_{oxide} may be defined as the apparent vapor pressure of the oxide under the conditions used. This is the sum of the saturation pressure of the oxide, p^s_{oxide},[3] and the vapor pressure of the reaction product, p_{hyd}; from this it is possible to determine the association number m and the equilibrium constant k_m.

a. Association Number m and the Equilibrium Constant k_m. If p^+_{oxide} is plotted against p_{H_2O} as an isotherm, a straight line is obtained for the association number $m = 1$; the slope of this gives the equilibrium constant k_m.

$$p^+_{\text{oxide}} = p_{\text{hyd}} + p^s_{\text{oxide}} \tag{12}$$

From this expression, by combination with Eq. (10), we obtain

$$p^+_{\text{oxide}} = k_m p^m_{H_2O} + p^s_{\text{oxide}} \tag{13}$$

If there were not interaction between the oxide and water vapor this straight line would be parallel to the abscissa: $p^+_{\text{oxide}} = p_{\text{oxide}}$. In Fig. 6, results for the system $WO_3 + H_2O$ are shown; they are typical also of the other systems studied. The linear relationship between p^+_{oxide} and p_{H_2O} shows that the association number m is unity in this case. As will be seen later, the association number for the boron hydroxides can have values other than unity. In the general case when $m \neq 1$, its value is derived from the equation

$$\log p_{\text{hyd}} = m \log p_{H_2O} + \log k_m = \log (p^+_{\text{oxide}} - p^s_{\text{oxide}}) \tag{14}$$

b. Thermodynamic Data. The experimental relationship between the increase in the saturation pressure of the oxide, p^s_{oxide}, by p_{hyd} and the partial pressure of H_2O in the reaction equilibrium at different tempera-

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[3] This is true in the case when the degree of polymerization, x, of the gaseous oxide [e.g., $(MeO)_x$] is equal to y, that for the gaseous hydroxide [e.g., $Me_yO_{y-1}(OH)_2$]. If $x \neq y$ we obtain $p^+_{\text{oxide}} = p_{\text{hydroxide}} + p^s_{\text{oxide}} \cdot (x/y)$, assuming that other possible vaporization or reaction products have a negligible effect. If $p^+_{\text{oxide}} \gg p^s_{\text{oxide}}$, which is often observed at lower temperatures, this relationship is simplified. It then follows that $n^+ = n_{\text{hydroxide}}$; $p^+_{\text{oxide}} \approx p_{\text{hydroxide}}$.

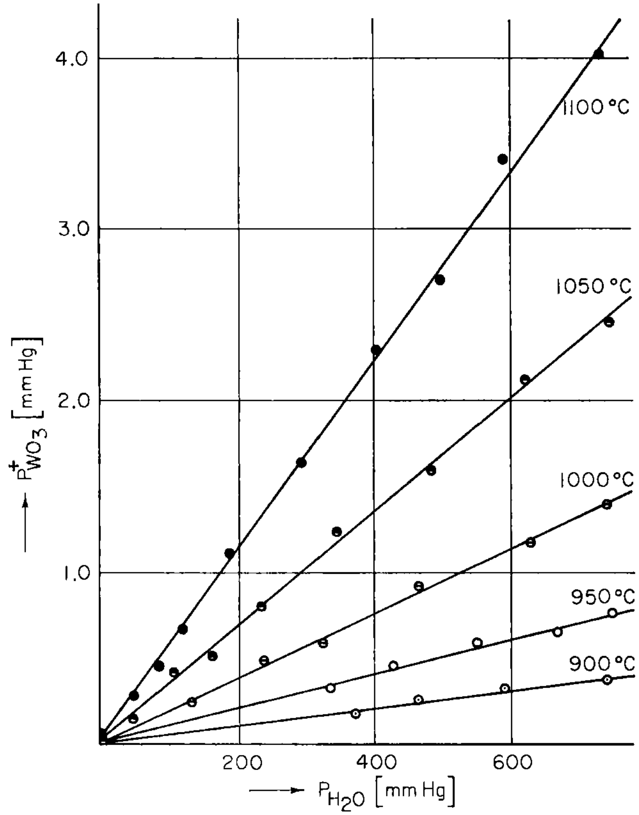


FIG. 6. Apparent vapor pressure of WO_3 as a function of the partial pressure of water vapor.

tures may be interpreted in terms of an association (without compound formation) involving dipole-dipole forces or hydrogen bonds. Since, however, the association number is definite and small it is possible to make more far-reaching conclusions. It is necessary to differentiate between the stoichiometrically equivalent alternatives of the formation of a gaseous oxide hydrate and a gaseous hydroxide; hydroxide formation is very likely if the interaction energy is relatively large.

The enthalpy of the homogeneous reaction Oxide(g) + $H_2O(g) \rightleftharpoons$ Hydroxide(g) provides a measure of the interaction energy, which is obtained from the enthalpy of sublimation (or vaporization) of the pure oxide and the enthalpy of the heterogeneous reaction. The latter may be determined from the temperature dependence of the equilibrium constants.

$$\frac{d \ln k_m}{dT} = \frac{\Delta H^\circ}{RT^2} \tag{15}$$

Using a power series for C_p, integration of this equation leads to an expression of the form

$$R \ln k_m - \Sigma \nu_i \left(a_i \ln T + \frac{b_i T}{2} + \frac{c_i T}{6} \right) = C - \frac{\Delta H^\circ}{T} \tag{16}$$

where ΔH° and C are integration constants.

As a rule it is not necessary to evaluate the observations in terms of this relationship since further simplifications may be introduced. For a limited temperature range $\Delta C_p \approx 0$, and one then obtains the expression

$$R \ln k_m = \frac{-\Delta H^\circ}{T} + C \left(\text{or, generally, } \log k_m = \frac{-A}{T} + B \right) \tag{17}$$

which is used by nearly all authors in the first evaluation of their experimental results, together with the following relationship:

$$\Delta G_\theta^\circ = \Delta H_{T'}^\circ - \theta \Delta S_{T'}^\circ = -R\theta \ln k_m \tag{18}$$

In this expression ΔH_T° and $\Delta S_{T'}^\circ$ are taken as constant for a limited temperature range T'

$$\Delta H_T^\circ = \Delta G_T + T \Delta S_T^\circ \tag{19}$$

Alternatively, ΔH_T may be evaluated by the "third-law" method; ΔG_T is calculated from values for k_m and T, and if ΔS_T is known ΔH_T may be obtained. ΔS_T may be calculated from tabulated values. Entropy values for compounds which have not yet been investigated may be estimated or determined by the methods of statistical mechanics on the basis of assumptions about the molecule.

The "free energy function" (referred to 0°K)

$$\frac{G_T^\circ - H_0^\circ}{T} = \frac{H_T - H_0^\circ}{T} - S_T^\circ \tag{20}$$

or, for a chemical reaction

$$\Delta \left(\frac{G_T^\circ - H_0^\circ}{T} \right) = \frac{\Delta G_T^\circ}{T} - \frac{\Delta H_0^\circ}{T}, \tag{21}$$

is frequently used in these calculations. The ΔH_0° values may be calculated for various values of ΔG_T and T. From this a mean value may be determined, from which statements about the scatter of the separate measurements can be made. ΔH_0° may be recalculated for any required temperature. Comparison of the values of ΔH_T° obtained by applying the third law with those determined from Eq. (17) is revealing, for from their good agreement far-reaching conclusions about the consistency of the calculation and the model assumed can be drawn.

3. Limitations of the Method of Evaluation of Results

From the experimental point of view both the determination of the increase in vapor pressure of the oxide in presence of water vapor and the association number *m* are quite definite. On the other hand information obtained from the enthalpy of the reaction can be interpreted, even with caution, only if some hypothesis is used to provide a value for the molecular size of the stoichiometrically equivalent reaction product. The measurements give no information on the molecular size of the compound produced. For example, in formulating the heterogeneous equilibrium such as

$$x\,\mathrm{WO_3} + \mathrm{H_2O} \rightleftharpoons \mathrm{W}_x\mathrm{O}_{3x-1}(\mathrm{OH})_2 \qquad (22)$$

a value of x must be assumed. The significance of the determined enthalpy value is then doubtful. Reactions involving more than one unit of oxide, e.g., with $x = 3$, cannot be excluded, since Berkowitz *et al.* (*6*) observed trimeric gaseous molecules of W_3O_9 in studying the sublimation equilibrium of WO_3, and corresponding results have been reported for MoO_3 (*7*) and BeO (*21*). In order to limit this uncertainty when evaluating equilibrium data, it is sometimes possible to postulate several models for the gaseous reaction product formed, corresponding to the several gaseous products of sublimation observed with the mass spectrometer. Enthalpy values determined in this way demonstrate the tendency for a strong interaction between the oxide and water.

More concrete deductions can be made if additional considerations, such as the estimates of entropy and notions of structures, are taken into account. For example, as will be seen later, it may be shown that in the reaction of WO_3, $x = 1$.

In order to make sound deductions it is necessary to determine the molecular magnitude. This can be done in several ways. The use of the mass spectrometer is especially important, since it makes possible the individual observation of each reaction product; this consideration is also important when other complications, such as the combination of the reaction products and the existence of competing equilibria, occur.

4. Results

The interaction with water vapor described at the beginning of this section is observed for seven oxides, namely, B_2O_3, Li_2O, BeO, ZnO, MoO_3, WO_3, TeO_2. In all cases the reaction products are described as gaseous hydroxides. Too few systems have been investigated for it to be worth attempting a systematic interpretation, but further studies in this field should broaden our knowledge and make it possible to establish more general relationships. The impulse for such further work will come, as hitherto, from problems connected with the properties of materials and corrosion, from preparative and geochemical work, and, not least, from general studies. It seems safe to predict that further oxides will be found to form volatile hydroxides in presence of water.

A review of the results of work up to the present time is given in Table VIII, in which thermodynamic data on the reactions studied are collected. Apart from the reactions with Li_2O and B_2O_3 for which the third law method was used, the data were determined on the basis of Eq. (17). Table VIII also includes values for the constants A and B in the expression $\log k_m = (-A/T) + B$ [cf. Eq. (17)] and references.

a. Gaseous Boron Hydroxides. It may be shown by the transfer method (*46, 46a*) that the reaction between $B_2O_3(l)$ and $H_2O(g)$ at higher temperatures can be described essentially by the equation

$$\tfrac{1}{2}B_2O_3(l) + \tfrac{1}{2}H_2O(g) \rightleftharpoons BOOH(g) \tag{23}$$

It was concluded from the investigation that BOOH(g) was not the only reaction product, though it was the most important. Other possible reactions may be formulated, such as

$$\tfrac{1}{2}B_2O_3(l) + \tfrac{3}{2}H_2O(g) \rightleftharpoons B(OH)_3(g) \tag{24}$$

$$\tfrac{3}{2}B_2O_3(l) + \tfrac{3}{2}H_2O(g) \rightleftharpoons (BOOH)_3(g) \tag{25}$$

As was explained in the introduction it is not possible to elucidate fully several simultaneous reactions by the transfer method without introducing hypotheses.

The position is clearer when the mass spectrometer is used, and the work of Meschi *et al.* (*49*) will therefore be discussed first. These authors studied the reaction in the system $B_2O_3(l)$ and $H_2O(g)$ at 1060°–1450°K with the combined use of the effusion method and the mass spectrometer, as described in Section II. The partial pressure of water in these experiments could be varied from 0.05 to 0.14 mm of mercury. The ions H_2O^+, $BOOH^+$, $(BOOH)_3^+$, and $B(OH)_3^+$ were found. The most interesting result was that the main product detected was BOOH(g): both the trimeric species and $B(OH)_3(g)$ were present to the extent of $<1\%$ of the amount of monomer. White *et al.* (*86*) confirmed this result.

The occurrence of $BOOH^+$ as a secondary product, formed perhaps from $(BOOH)_3(g)$, was shown to be very unlikely on the basis of intensity measurements. The observed dependence of the $BOOH^+$ peak intensity on the partial pressure of water made this quite certain. The authors found a relationship corresponding to an association number $m = 0.5$ [cf. Eq. (13)] rather than $m = 1.5$, which would have been expected if the main product had been the trimer. The enthalpy of the reaction was found from Eq. (17) to be 42.3 kcal/mole (T = 1060°–1450°K). This value agreed

TABLE VIII

THERMODYNAMIC DATA ON REACTIONS OF SOME OXIDES WITH $H_2O(g)$

	T' °K	$-A$	B	$\Delta H_{T'}$ (kcal/mole)	$\Delta S_{T'}$ e.u.	$\Delta G\theta$ (kcal/mole)	θ (°K)	Reference
$\frac{1}{2}B_2O_3(s) + \frac{1}{2}H_2O(g) \rightleftharpoons BOOH(g)$	1060–1450	—	—	42.3	—	—	—	(*49*)
$Li_2O(s) + H_2O(g) \rightleftharpoons (2LiOH(g)$	1100–1400	—	—	7.90	43.6	21.8	1310	(*8*)
$BeO(s) + H_2O(g) \rightleftharpoons Be(OH)_2(g)$	1462–1823	9060	1.63	41.5	7.4	29.0	1673	(*35*)
$ZnO(s) + H_2O(g) \rightleftharpoons Zn(OH)_2(g)$	1573–1623	—	—	102.2	48.8	25.3	1573	(*30*)
$MoO_3(s) + H_2O(g) \rightleftharpoons MoO_2(OH)_2(g)$	873– 963	7731	5.45	35.3	24.9	16.20	963	(*32*)
$WO_3(s) + H_2O(g) \rightleftharpoons WO_2(OH)_2(g)$	1173–1373	8725	4.10	39.9	18.8	14.11	1373	(*32*)
$TeO_2(s) + H_2O(g) \rightleftharpoons TeO(OH)_2(g)$	923– 973	7290	4.11	33.4	18.8	18.70	973	(*32*)

within the limits of error with the value of $\Delta H_T°$ determined by the third law method. Values for the homogeneous reaction

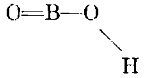
$$\tfrac{1}{2}B_2O_3(g) + \tfrac{1}{2}H_2O(g) \rightleftarrows BOOH(g) \qquad (26)$$

were calculated from a direct determination of the equilibrium constants by the third-law method; the mean value was $\Delta H_T° = -1.4$ kcal.

The enthalpy of sublimation of B_2O_3 may be determined from the $\Delta H_T°$ values for the homogeneous reaction (26) and the heterogeneous reaction (24).[4] This then serves as a check. Values of $\Delta H_{298}°$ and hence $\Delta H_0°$ values were determined for both reactions from the free energy function. Twice the difference [$\Delta H_0°$ for reaction 15 − $\Delta H_0°$ for reaction (26)] gives the enthalpy of sublimation, $\Delta H_0°$, for B_2O_3; Meschi *et al.* found the value 99 ± 6 kcal/mole, while White [private communication; cf. (*8*)] finds 94.5 kcal/mole.

Although the agreement of the above value is apparent, it is very interesting to compare them with the results of other investigations. The system B_2O_3-H_2O affords a beautiful example of how the most varied methods give results which are in agreement and which therefore enable us to draw firm conclusions. It is very desirable that several methods should be applied to other systems, and indeed the first experiments in this direction are in hand.

White *et al.* (*86*) have studied the infrared emission spectrum of the gas phase of the system $B_2O_3(l)$-$H_2O(g)$ in the temperature range 1250 to 1450°K with water vapor pressures from 1 to 15 mm Hg. Their results show the production of BOOH(g) as the main product of the interaction. The spectroscopic data are consistent with the structure



containing a linear O=B—O group. The authors found an enthalpy change $\Delta H_T°$ of 39 ± 2.5 kcal/mole (T = 1350°K) for reaction (23), a value which agrees with the mass spectrographic result. The value was obtained from the variation in intensity of the 2030 cm^{-1} band with temperature. In this connection, Fig. 7 shows the results of observations of the equilibrium $\tfrac{1}{2}B_2O_3(l) + \tfrac{1}{2}D_2O \rightleftarrows BOOD(g)$ in the form of a plot of the logarithm of partial pressure of BOOD(g) against $1/T$.

The band at 2030 cm^{-1} was the strongest of those observed under the conditions used. It lies very close to 2040 cm^{-1}, at which frequency a strong band is observed in the investigation of the B_2O_3 vaporization equilibrium.

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[4] Otherwise values for the homogeneous reaction are calculated from the enthalpy values for the pure oxide and those for the heterogeneous reaction.

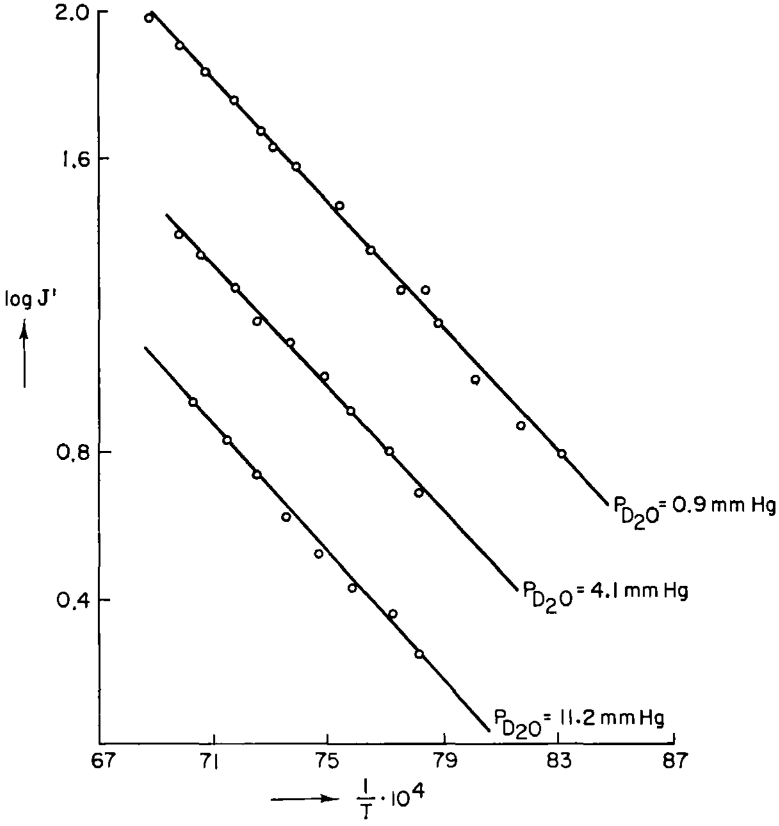

FIG. 7. Variation of the intensity of the 2030 cm^{-1} band of BOOD with temperature for different partial pressures of water vapor. J' is put equal to $JT \exp (h\nu)/(kT)$ in order to relate the observed intensity (J) to the partial pressure of the species observed. D_2O is used instead of H_2O for technical reasons.

The authors were able to show beyond question that at 2030 cm^{-1} a gaseous species other than $B_2O_3(g)$ is present: for example, the intensity of the band at 2030 cm^{-1} was already appreciably developed at temperatures at which bands of the $B_2O_3(g)$ spectrum were scarcely observable. Variation of the intensity with temperature gave a different picture from that observed in the vaporization of $B_2O_3(l)$. More convincing is the fact that the intensity depended on the D_2O partial pressure, being almost zero when the D_2O partial pressure was zero.

This relationship between intensity and D_2O partial pressure may also be used to make deductions about the stoichiometry of the reaction. Corresponding measurements, evaluated according to Eq. (13), gave association numbers of 0.5 to 0.7. The theoretical value for the formation of BOOH(g) according to Eq. (23) is 0.5; for the formation of $B(OH)_3(g)$ or $(BOOH)_3(g)$ it would be 1.5. The experimental results therefore indicate clearly that the course of the reaction follows Eq. (23).

It has been pointed out already that the mass spectrographic results agree well with those obtained by infrared spectroscopy and by the transfer method. Table IX, in which the values found for the enthalpy of formation of BOOH(g) by various methods are collected, demonstrates this correlation.

TABLE IX
ENTHALPY OF FORMATION IN KCAL/MOLE BORON HYDROXIDE DETERMINED BY VARIOUS METHODS

Method	Mass spectroscopic (*49*)	Infrared spectroscopic (*86*)	Transfer method (*62*)
HBO_2	−137.5[a]	−135 ± 3	−134.9 ± 1
$(HBO_2)_3$	−540 ± 10	537 ± 10	−537.5 ± 3

[a] All units are kcal/mole.

It must not be overlooked that the good agreement would be still more convincing if the measurements by the transfer method related to a wider range of materials. One of the advantages of this method is that the partial pressure of water vapor can be varied widely. Randall and Margrave (*62*) have done this, though they limited themselves to a few measurements. Interpretation of their results gives an association number $m \simeq 1.5$ at 1073°K: only at higher temperatures (1273°K) is a value of $m \simeq 0.5$ observed. This was found only at low H_2O partial pressures (10^{-1} to 10^{-2} atm), while at H_2O partial pressures $> 10^{-1}$ atm a value of $m \simeq 1.5$ resulted. They thus showed that, as already mentioned, there are probably several gaseous species in the system $B_2O_3(l)$-$H_2O(g)$ as the temperature and H_2O partial pressure are varied. This is in agreement with theoretical considerations (*24*) and also with the results of other investigations.

For all the methods the determination of the enthalpy of formation of $(BOOH)_3(g)$ is less certain (cf. Table IX), though it is clear that the detection of this species is not in question. Meschi *et al.* obtained a positive $\Delta H_T{}^\circ$ value for the reaction $\frac{3}{2}H_2O(g) + \frac{3}{2}B_2O_3(l) \rightleftharpoons (BOOH)_3(g)$ using Eq. (16) as a method of evaluation, while a negative value was given by the third law method. They concluded from this that equilibrium was incompletely established at lower temperatures; under these conditions the partial pressure of the trimer is too small for reliable evaluation. Conditions are more favorable at higher temperatures. Using the reaction $B(OH)_3(g) + B_2O_3(l) \rightleftharpoons (BOOH)_3(g)$ the authors used the equilibrium constant at 1451°K to deduce a value of $\Delta H_{1451}{}^\circ$ of -3 kcal/mole by the third law method. From this they found the enthalpy of formation of the trimer to be −540 kcal/mole.

With the other methods of investigation it is necessary to make assumptions about the partial pressures of the species $B(OH)_3(g)$, $BOOH(g)$ and $(BOOH)_3(g)$ which are postulated. These may be supported by data on the known behavior of $B(OH)_3(g)$ and by conclusions based on changes in the reaction conditions (*24*).

Any report on gaseous boron hydroxides would be incomplete without consideration of the volatility of $B(OH)_3$ at lower temperatures, which has been known for a long time (*34*, *75*, *75a*). According to von Stackelberg *et al.* (*81*) the system $B(OH)_3$-H_2O at 110° to 180°C may be described by the following equations:

$$B(OH)_3(g) \rightleftharpoons B(OH)_3(g) \qquad (27)$$

$$BOOH(s) + H_2O(g) \rightleftharpoons B(OH)_3(g) \qquad (28)$$

The vapor pressure of $B(OH)_3$ is independent of the water vapor partial pressure at 140°C.[5] At this temperature the solid phase $B(OH)_3(s)$ is transformed into $BOOH(s)$. Above 140° one observes a proportionality between p_{H_2O} and $p_{B(OH)_3}$ and relationships which are the same as for other oxide-water systems. The authors used the transfer method; their results are summarized in Fig. 8.

Let us consider the isotherms for 149, 160, and 180°C, for which the relationship $p^+ = p_{B(OH)_3} + p^s_{\text{oxide}} = k_m \cdot p_{H_2O} + p^s_{BOOH}$ holds. The term p^s_{BOOH} is the saturation pressure of the solid phase $BOOH(s)$. The linear relationship between p^+ and p_{H_2O} indicates the association number $m = 1$, which supports the formulation shown in Eq. (28).

In contrast to these the 109° isotherm takes the form $p^s = p^s_{B(OH)_3}$ because of the change in the solid phase; in this case p^+ is equal to $p^s_{B(OH)_3}$, since it is independent of p_{H_2O}. Thermodynamic data derived from the measurements are to some extent uncertain, though this fact does not alter the main conclusions on the reactions under discussion. The enthalpy of sublimation of $B(OH)_3(g)$ was determined as 23.4 kcal/mole and that of $BOOH(s)$ as 27 kcal/mole (uncertain). An enthalpy of reaction of −19 kcal/mole (uncertain) was found for the homogeneous reaction

$$BOOH(g) + H_2O(g) \rightleftharpoons B(OH)_3(g) \qquad (29)$$

These investigations on the volatility of boric acid formed part of a study of the system B_2O_3-H_2O, and were the first quantitative work on

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[5] An investigation of the solubility of $B(OH)_3$ in saturated and superheated water vapor between 1–200 atm (M. A. Styrikovich, D. G. Tschiraschwilli, and D. P. Nelierdize, *Doklady Akad. Nauk. S.S.S.R.* **134,** 615 (1960); D. G. Tschiraschwilli and D. P. Nelierdize, *Doklady Akad. Nauk Grus. S.S.R.* **23,** 695 (1959), showed that $B(OH_3)$ molecules go from the saturated solution into the vapor.

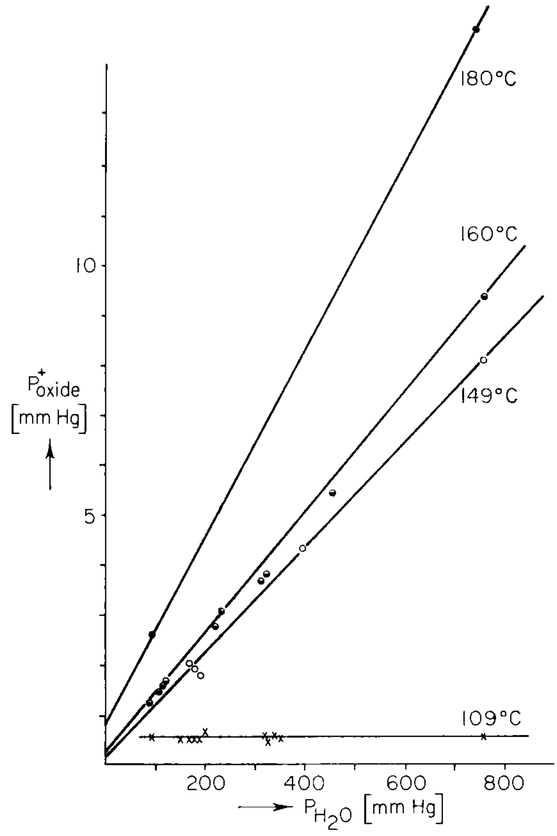

FIG. 8. Volatility of $B(OH)_3$ at various temperatures as a function of vapor partial pressure.

the formation of gaseous compounds starting from oxide and water. It is noteworthy that even in this investigation the method of determining association numbers was explored and discussed in order to establish the stoichiometry of the reaction (the authors actually used the expression "degree of hydration"). von Stackelberg *et al.*, considered that water vapor could be regarded as a "gaseous solvent" and were thus able to formulate variations in its concentration very simply. The conclusions drawn by the authors from their studies of the system B_2O_3-H_2O, and particularly those relating to the existence of BOOH(g), are not incompatible with later experimental findings as outlined in the earlier part of this section.

b. Gaseous Beryllium Hydroxide. If the interaction between oxide and water vapor is considered more from the preparative and technical point of view, the main interest centers on the phenomenon of the apparent increase in the vapor pressure of the oxide under the influence of water vapor i.e., the increase in volatility. The system $BeO\text{-}H_2O$ is a striking example of this. Malm and Hutchison (*39, 39a*) made preparative studies on the purification of BeO. They found that they could obtain a separation of BeO by allowing it to react with water vapor at higher temperatures, when it was carried over in the vapor form and recondensed as a solid. Separation from impurities which were not volatile under these conditions was thus achieved. In order to explain the reaction the authors assumed the existence of a gaseous product formed from BeO and H_2O. This conclusion agrees with the work of Berkmann and Simon (*5*), who likewise studied the volatility of BeO in water vapor. Hutchinson and Malm established that the volatility of BeO at a given temperature increases with the water vapor pressure. Von Wartenberg (*83*) concluded from their observations that a gaseous beryllium hydroxide was formed and this result was then confirmed by Grossweiner and Seifert (*35*) and firmly established by further measurements.

These authors worked with the transfer method in the temperature range 1200–1400°C. They found an association number of unity and formulated the reaction as

$$BeO(s) + H_2O(g) \rightleftharpoons Be(OH)_2(g) \qquad (30)$$

on the assumption of monomeric gaseous species. Technical aspects of the subject were also involved in the work of Young (*88*), who studied the reaction of water vapor with beryllium, chrysoberyl, and $BeO\cdot 3Al_2O_3$. The objective was to reduce the chemical potential of beryllium oxide in order to reduce complications associated with the use of BeO in reactor technique as a result of the volatility of the oxide in presence of water vapor. The transfer method was used and the results were evaluated on the assumption of a monomeric gaseous reaction product $Be(OH)_2$. The reactions

$$\tfrac{3}{2}BeO\cdot Al_2O_3(s) + H_2O(g) \rightleftharpoons \tfrac{1}{2}BeO\cdot 3Al_2O_3(s) + Be(OH)_2(g) \qquad (31)$$

$$BeO\cdot 3Al_2O_3(s) + H_2O(g) \rightleftharpoons 3Al_2O_3(s) + Be(OH)_2(g) \qquad (32)$$

were investigated in addition to the reaction with BeO as the solid phase. The thermodynamic data from this investigation are collected in Table X together with values from the work of Grossweiner and Seifert. From Young's work it was found that the equilibrium pressure $p_{Be(OH)_2}$ over $BeO\cdot 3Al_2O_3$ at 1600°C was $\frac{1}{2}$ to $\frac{2}{3}$ of the value measured over pure BeO as the solid phase. This is agreement with formation of mixed crystals and ideal behavior. The resulting reduction in the volatility of beryllium was thought not to be sufficient to overcome health risks and corrosion defects which occur when moist gases are used in cooling BeO moderators in high temperature reactors.

c. Gaseous Molybdenum and Tungsten Hydroxides. Some time ago

TABLE X

THERMODYNAMIC DATA FOR SOME REACTIONS LEADING TO THE FORMATION OF $Be(OH)_2(g)$, ACCORDING TO YOUNG

	Temperature range T' (°K)	$\Delta H_{T'}$ (kcal/mole)	$\Delta S_{T'}$ (e.u.)	ΔG_{1823} (kcal/mole)	Reference
$BeO(s) + H_2O(g) \leftrightarrows Be(OH)_2(g)$	1462–1823	41.5	7.4	27.9	(*35*)
$BeO(s) + H_2O(g) \leftrightarrows Be(OH)_2(g)$	1576–1839	42.5	8.8	26.4	(*88*)
$\frac{3}{2}BeO \cdot Al_2O_3(s) + H_2O(g) \leftrightarrows \frac{1}{2}BeO \cdot 3Al_2O_3(s) + Be(OH)_2(g)$	1604–1848	49.4	11.2	29.0	(*88*)
$BeO \cdot 3Al_2O_3(s) + H_2O(g) \leftrightarrows 3Al_2O_3(s) + Be(OH)_2(g)$	1626–1832	43.2	7.1	30.3	(*88*)

Millner and Neugebauer (*51*) found that there was a considerable loss in weight by WO_3, W_4O_{11}, WO_2, and MoO_3 in presence of water vapor or water vapor + hydrogen (for lower tungsten oxides) at 1000° (for all tungsten oxides) and at 600–700°C (for molybdenum oxide). They were able to show from this investigation that the cause of the corrosion phenomena in tungsten wire incandescent lamps must lie in the volatility of tungsten oxide in presence of water vapor. Brewer and Elliott (*12*) suggested that earlier determinations of the vapor pressure of WO_3 had probably been influenced by the formation of gaseous hydroxide as a result of the presence of water vapor. According to Ruff and Grieger (*63*) the vapor pressure of WO_3 at 1393°K is 10 mm Hg, but later measurements with the mass spectrometer (*6*) give 4.1×10^{-3} mm Hg.[6]

Newer measurements have now provided more information about the formation of a gaseous tungsten hydroxide (*31*, *32*). Figure 6 shows that there is association number $m = 1$ for the reaction between $WO_3(s)$ and $H_2O(g)$. From this, assuming that monomeric species are formed, it follows from the thermodynamic data that the equilibrium involved is

$$WO_3(s) + H_2O(g) \rightleftharpoons WO_2(OH)_2(g) \tag{33}$$

A representative temperature dependence of the equilibrium constants for other systems is shown in Fig. 9. The enthalpy of reaction, $\Delta H_T°$, for the heterogeneous reaction (33) was found to be 39.9 kcal/mole (T = 900–1100°C).

A fuller discussion of the results, based on the assumption that monomeric species are formed in the reaction, is given in the following section. It may be mentioned at this point that mass-spectrographic reexamination (*18*) of the system WO_3-H_2O has shown that at higher temperatures the reaction product is correctly formulated as $WO_2(OH)_2$. More highly aggregated species were not observed by the mass-spectrographic method. The findings and general considerations on the occurrence of a monomeric gaseous tungsten hydroxide can certainly be applied to the corresponding molybdenum compound. It is thus possible to formulate the reaction for which Glemser and von Haeseler found an association number $m = 1$ as:

$$MoO_3(s) + H_2O(g) \rightleftharpoons MoO_2(OH)_2(g) \tag{34}$$

The authors found an enthalpy $\Delta H_T° = 35.5$ kcal/mole for this reaction at T = 600–690°C.

[6] This explanation agrees with newer measurements (*31*). It seems from this that Ruff and Grieger determined the vapor pressure of WO_3 in a water vapor atmosphere ($p_{H_2O} \approx 760$ mm Hg), which is unlikely. It is therefore not known what caused the discrepancy in Ruff and Grieger's measurements. The matter cannot be checked since the statement by the authors (in "Landolt-Bornstein Tabellen," Suppl. II, Ergänzungsband Part 2, p. 1301) is based on a private communication.

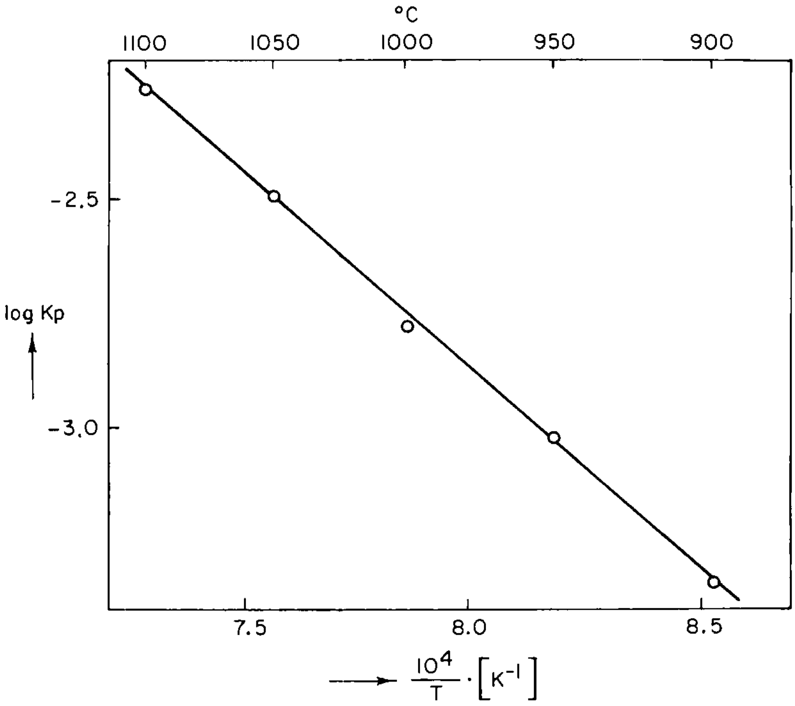

FIG. 9. Temperature dependence of the equilibrium constant for reaction (33).

Glemser and Wendlandt (*33*) also studied the system WO_3/MoO_3-H_2O from the preparative viewpoint. For a composition of the mixed solid phase WO_3/MoO_3 with a mole fraction $x_{MoO_3} < 0.1$, the results at 600° to 700°C and with $p_{H_2O} \approx 760$ mm Hg are compatible with mixed crystal formation.

d. Gaseous Tellurium Oxide Hydroxide and Zinc Hydroxide. In further investigations by the transfer method the reactions between $TeO_2(s)$ and $H_2O(g)$ and between $ZnO(s)$ and $H_2O(g)$ were examined. In both cases proportionality between p_{H_2O} and $p_{\text{oxide}}{}^+$ was established. Using the experimentally determined association number $m = 1$ and assuming monomeric gaseous reaction products, the reactions may be formulated as:

$$TeO_2(s) + H_2O(g) \rightleftharpoons TeO(OH)_2(g) \quad (35)$$

$$ZnO(s) + H_2O(g) \rightleftharpoons Zn(OH)_2(g) \quad (36)$$

The reaction with TeO_2 was studied at 600–700°C and that with ZnO at 1300–1350°C.[7]

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[7] Compare also J. Kasarnowsky, *Z. physik. Chem.* **109,** 289 (1924). The demonstration of the formula $TeO(OH)_2$ given in this work is incorrect.

Finally, let us consider Table XI, in which are collected enthalpy values of interest in discussing gaseous hydroxides in the homogeneous reaction

$$\text{Oxide(g)} + H_2O\text{(g)} \rightleftarrows \text{Hydroxide(g)}$$

The values have been determined (except for the value for the reaction of B_2O_3 which, as described previously, was determined directly) from the enthalpy of the heterogeneous reaction (cf. Table VIII) and the sublimation (vaporization) enthalpy of the pure oxide. These data are also included in Table XI. The enthalpies of sublimation of MoO_3 and WO_3 are given for the equilibrium $MeO_3(s) \rightleftarrows MeO_3(g)$ (Me = W, Mo).[8] The value for the reaction of B_2O_3 with H_2O(g) clearly differs from those for the other reactions. It is not possible, however, to conclude from this that there is any essential difference in the formulation of the reaction products, for the system B_2O_3-H_2O has been studied in detail by various authors.

TABLE XI

ENTHALPIES OF REACTIONS OXIDE(g) + H_2O(g) $\rightleftarrows$ HYDROXIDE(g)

Oxide	Gaseous product	Sublimation (vaporization) enthalpy of pure oxide (kcal/mole)	Enthalpy of heterogeneous reaction[a] $\Delta H_{T'}$ (kcal/mole)	Enthalpy of homogeneous reaction[b] $\Delta H_{T'}$ (kcal/mole)	Temperature range T' (°K)
B_2O_3	BOOH		42.3	−1.4	1060–1450
Li_2O	LiOH	98.5	79.0	−19.5	1100–1400
BeO	$Be(OH)_2$	150.0	41.5	−108.5	1673
ZnO	$Zn(OH)_2$	117.2	102.2	−15.0	1573–1623
MoO_3	$MoO_2(OH)_2$	102.0[c]	35.3	−66.7	873–963
WO_3	$WO_2(OH)_2$	127.0[c]	39.9	−87.1	1173–1373
TeO_2	$TeO(OH)_2$	54.9	33.4	−21.5	923–973

[a] Oxide(s) + H_2O(g) $\leftrightarrows$ Hydroxide(g).

[b] Oxide(g) + H_2O(g) $\leftrightarrows$ Hydroxide(g).

[c] See Footnote 8.

5. *Discussion of Results*

Among the compounds which result from the reaction equilibrium *I*/2, we are best informed about lithium hydroxide and the various boron hydroxides. For them we know the molecular weights and, in part, the molecular structures in addition to the thermodynamic data. For all of the

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[8] This value ($= \Delta H_1$) follows from the measured enthalpy of the reaction $3MeO_3(s) \rightleftarrows (MeO_3)_3(g)$ ($= \Delta H_2$) and the enthalpy of depolymerization $(MoO_3)_3(g) \rightleftarrows 3MoO_3(g)$ ($= \Delta H_3$) as $\Delta H_1 = 1/3\ (\Delta H_2 + \Delta H_3)$. Values of ΔH_2 are well known for both oxides: cf. (7), (8). The value of ΔH_3 is from the work of R. P. Burns, G. De Maria, J. Drowart and R. T. Grimley, *J. Chem. Phys.* **32,** 1363 (1960).

oxides, including the less studied oxides of beryllium, zinc, tungsten, and tellurium, there is no doubt that a strong interaction with water vapor can be observed at higher temperatures. By analogy with Li_2O and B_2O_3, which react with water vapor to form gaseous hydroxides, and on the basis of thermodynamic data and the small and definite association number of unity, it is very probable, therefore, that interaction of the other oxides and water vapor at higher temperatures also leads to the formation of gaseous hydroxides.

In this connection, if we start from the fact that, for example, in the system BeO-H_2O a solid hydroxide $Be(OH)_2$ exists which decomposes at 180°C to $BeO(s)$ and $H_2O(g)$, it is possible to understand the apparent difficulty that the same solid oxide at 1300°C again reacts to form a gaseous hydroxide of the same stoichiometric composition. Let us first of all consider the occurrence of the gaseous compound. Here it must first be remembered, as Brewer (*11*) emphasized recently, that thermodynamic calculations, which serve to determine the behavior of the system in the higher temperature range, do not suffice to describe the behavior at lower temperatures. Calculations based on the compounds known at lower temperatures become unreliable if new species are formed with increasing temperature. In other words, it is doubtful whether the comparison of solid beryllium hydroxide with gaseous beryllium hydroxide is justifiable if all gaseous hydroxides of the type under discussion are considered. In the case of the gaseous hydroxides of molybdenum, tungsten, and tellurium we already know from investigations which are now going on that such a comparison is not possible. Molybdenum and tungsten in the solid state do not form hydroxides [apart from compounds such as $H_6(H_2W_{12}O_{40})$, which are prepared under special conditions] but only oxide-hydrates (*69*, *69a*), while for tellurium the facts known so far justify only the formulation $TeO_2(aq)$, i.e., an oxide-hydrate. For molybdenum, tungsten, and tellurium, therefore, the gaseous hydroxides formed from the oxides and water vapor must be considered as separate compounds which are distinct from the oxide-hydrates of those elements occurring in the solid state. If we assume this to be so in the case of lithium, beryllium, and zinc, it must be a matter of chance that the formula for the gaseous hydroxides (the stoichiometric ratio Be:OH = 1:2) is the same as that for the solid compound.

Which data then, apart from the enthalpy of formation, must be considered in describing the thermodynamic stability? For the reaction of $BeO(s)$ and $H_2O(s)$ an enthalpy change of about 108 kcal was found. As Grossweiner and Seifert mentioned, this is too large for a simple molecular association corresponding to the equation:

$$BeO(s) + H_2O(g) \rightleftharpoons BeO{\cdot}H_2O(g)$$

and the observed values of $\Delta H°$, $\Delta G°$, and $\Delta S°$ accord better with the formation of a gaseous hydroxide.

$$BeO(s) + H_2O(g) \rightleftharpoons Be(OH)_2(g)$$

The value for the Be—OH bond energy supports this view. This conclusion may in all probability be extended to the other reactions studied. It is supported by the examples of the reactions of B_2O_3 and Li_2O with H_2O, which have already been described and for which mass-spectrographic and infrared methods have brought about a notable widening of the experimental basis of the subject.

Some further comments may be made on the possible formulation of the gaseous hydroxides. As has been explained several times, polynuclear oxides have been detected in the vapor over solid BeO, MoO_3, and WO_3. Figure 10 gives the proposed structural formulas for these gaseous hydroxides.

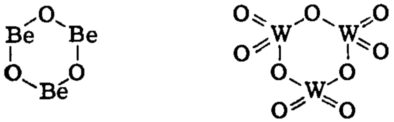
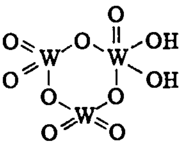
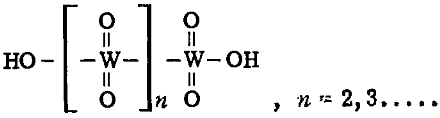


FIG. 10. Structure of gaseous oxides of beryllium and tungsten.

It will be seen that the metal atom in the trimeric gaseous molecule has an increased coordination number compared with that in the monomer. In these essentially covalent compounds between metal and oxygen, however, an increase in coordination number is associated with increase in the volatility of the molecule. In the gaseous state coordination numbers of 2 and 4 are favored by beryllium and tungsten respectively. If we allow BeO(s) to react with $H_2O(g)$ the possible species with a coordination number of two are HO—Be—OH or the polynuclear compound HO—$[Be—O]_n$—BeOH ($n = 2, 3, \ldots$), the formula of which would certainly not be linear. The latter is not very likely. In the reaction of $WO_3(s)$ with $H_2O(g)$ it would be possible to have a ring structure (A) with a coordination number of five for the tungsten atom or a nonlinear chain formula (B), with a coordination number of four.



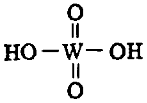
(A)



$$HO-\left[\begin{array}{c}O\\ \|\\ -W-\\ \|\\ O\end{array}\right]_n\begin{array}{c}O\\ \|\\ -W-OH\\ \|\\ O\end{array}, \quad n = 2, 3, \ldots$$

(B)

On the other hand a coordination number of four for all the tungsten atoms is attained in the monomer $WO_2(OH)_2$, and this represents the most



$$HO-\overset{\overset{\displaystyle O}{\|}}{\underset{\underset{\displaystyle O}{\|}}{W}}-OH$$

probable formulation. As already mentioned, its existence has been established mass-spectrographically (*18*).

B. Reactions at Higher Pressures of Water Vapor

In addition to reactions of an oxide with water vapor at a total pressure of one atmosphere, experiments have been made at water vapor pressures substantially greater than this value and mostly above the critical pressure of water. A formal relationship between measurements in the two pressure regions may be demonstrated only when the experimental methods are considered.

The experimental method most frequently used with higher water vapor pressures may be compared with the transfer method. In the latter we determine the amount of solid material carried by a known volume of the transfer medium, i.e., we determine the (apparent) increase in the vapor pressure of the oxide [see Eq. (13)] or the "solubility" of the solid oxide in the transport medium. This is exactly the objective in investigating the reaction of oxides at higher pressures of water vapor.

Two experimental approaches may be mentioned. In one method (*53*) a sample is taken from the reaction space and the content of dissolved substance is determined. The other method gives the solubility indirectly from the loss in weight of the oxide. In investigating the solubility of quartz the loss in weight is derived in a highly original way from the change in frequency of a quartz plate set up to act as an oscillator (*44*).

Questions on the behavior of oxides in the supercritical region of water, or in superheated steam at higher pressures, have arisen earlier, especially in connection with geochemical, technological, and preparative problems.[9] The system SiO_2-H_2O has been prominent in this connection. van Nieuwenburg and Blumendal (*78*) and van Nieuwenburg and van Zon (*79*) demonstrated the transport of SiO_2 through the gas phase, and this result was confirmed later by other authors and put on a quantitative basis.

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[9] cf. C. W. Correns, Einführung in die Mineralogie, Springer, Berlin-Göttingen-Heidelberg, 1949, p. 189 *et seq.*, See also P. Niggli, Das Magma und seine Produkte, Akademische Verlagsges. Leipzig, 1937; O. Fuchs, Z. Elektrochemie, **47,** 101, 1941; R. Nacken, Chemiker-Zeitung, **74,** 745 (1950). See also Booth and Bidwell (9), Morey (*52*) and Franck (*27*, *27a*).

Today we know from a great number of investigations how the system SiO_2-H_2O behaves if the water component is varied over a wide range. There are a number of possible ways of presenting the results; we will consider here only those which link up with the thermodynamic considerations of the previous section.

A first method of presentation, which is generally applicable, is to consider the dependence of solubility on the water pressure; this is done in Fig. 11, which gives the results of Morey and Hesselgesser (*53*). This gives qualitatively the relationship between the increase in solubility and the increase in pressure.

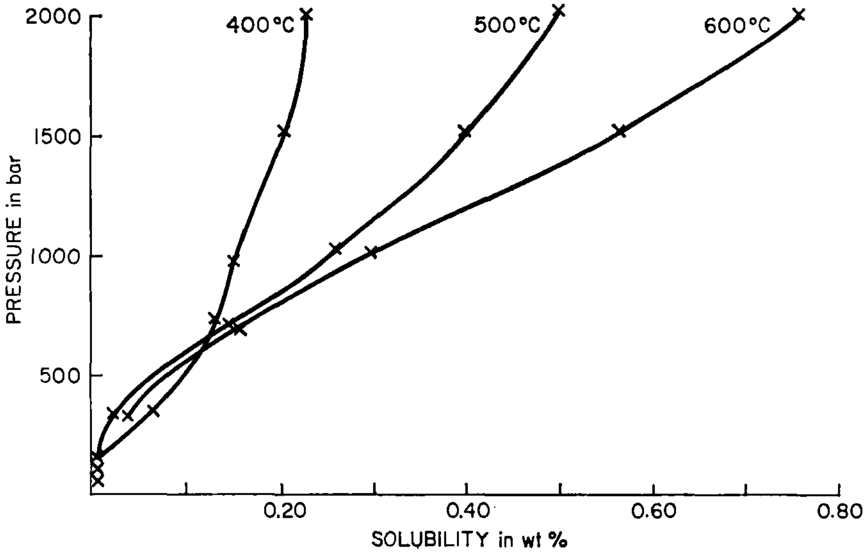

FIG. 11. The dependence of the solubility of quartz in water vapor on the pressure at various temperatures.

Kennedy (*44*) introduced the density d or the reciprocal volume as a measure of the water concentration. He was then able to represent results up to a pressure of 1000 bar in the form

$$S = -Af(T) \log \frac{1}{d} \qquad \begin{aligned} S &= \text{Solubility} \\ A &= \text{Constant} \end{aligned} \tag{37}$$

Jasmund (*42*) showed that the solubility of SiO_2 in water at high pressures and temperatures could be described by the general expression

$$L = \text{constant} \times D^n \tag{38}$$

where L stands for the solubility isotherm, D is the density, and n denotes an association number. Finally, Mosebach (*54*, *54a*) discussed the solubility of SiO_2 as a heterogeneous gas reaction and gave a relationship equivalent to that above in the form

$$\log L = m \cdot \log D + b \tag{39}$$

where L = solubility expressed as g of SiO_2/kg of H_2O; D = density of the vapor phase, m = association number; b = a temperature-dependent constant. Figure 12 shows the solubility isotherms for SiO_2 in compressed water vapor. From the slope of the lines an association number $m = 2$ is derived [cf. Eq. (14)].

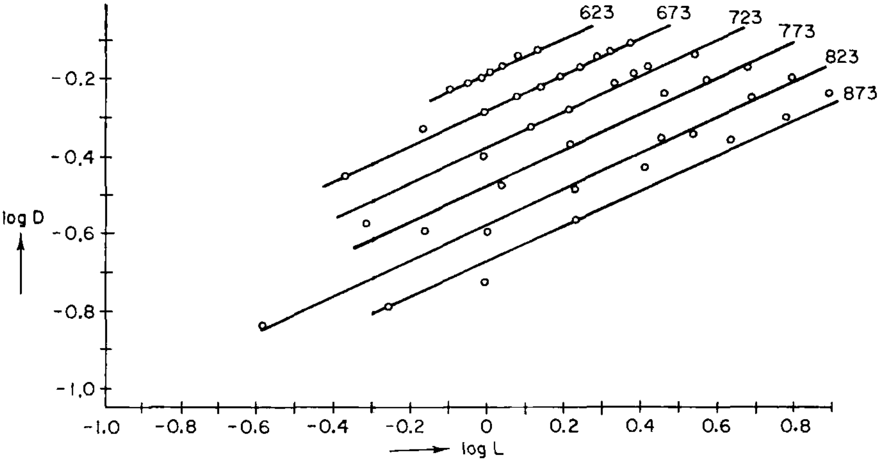

FIG. 12. Solubility isotherms for SiO_2 in compressed water vapor at different temperatures.

Mosebach expressed the temperature dependence of the solubility in the form

$$\log L = m \log D - \frac{A}{T} + B \tag{40}$$

which, putting $\log L - m \log D = -(A/T) + B = \log K_n$, corresponds formally with Eq. (17). Evaluating all experimental results then available, Mosebach determined the constants for the solubility of quartz as $A = +2.071$ and $B = +3.68$. Experimental results may be expressed by this empirical relationship with an accuracy of ±10%. Bearing in mind the difficulties associated with the measurements, this agreement may be regarded as very satisfactory.

Mosebach and Franck (*27*, *27a*) and Wasserburg (*85*) find a mean association number of $m = 2$; Wood (*87*) also finds $m \approx 2$ at 460°C and 700 bar. The most plausible formulation with $m = 2$ is $SiO_2 + 2H_2O \rightleftharpoons$

$Si(OH)_4$, i.e., volatile $Si(OH)_4$ is formed. According to Mosebach, this reaction with quartz has an enthalpy of association of 9.47 kcal/mole in the temperature range 200–600°C and up to a pressure of 2000 atm.

Possibly, polynuclear hydroxides are formed at higher pressures.[10] Franck (*26*) considers that the assumption of a partial dissociation of $Si(OH)_4$ into H^+ and $SiO(OH)_3^-$ ions which has been discussed (*54*, *54a*) is not very probable because conductivity measurements in the system SiO_2-H_2O at about 600°C and 1000–1500 atm pressure show no difference from pure water.

In interpreting this reaction of SiO_2 with H_2O there is a point of resemblance to the experiments at atmospheric pressure in that, in both cases, the increase in vapor pressure of the solid may readily be detected but it is difficult to elucidate the nature of the products. It must not be overlooked, however, in this connection that, depending on the technique used, a wide range of results may be obtained in the determination of molecular weights, the identification of reaction products, and the investigation of the thermodynamics of equilibria, for reactions at atmospheric pressure. The experimental difficulties in the high pressure region are greater, especially if it is a question of determining the criteria just mentioned. It may be expected, however, that further investigation will lead to progress in this case too.

The solubility of solids in highly compressed gases has been known since the work of Hannay and Hogarth (*36*) and has been put on a sound theoretical basis.[11] The inclusion of the system water-oxide (solid) in these studies occurred relatively late, not least because of the considerable experimental difficulties of working with water under the reaction conditions already described. The measured increase in vapor pressure (volatilization or solubility) of the oxide in compressed water vapor cannot be explained by a purely hydrostatic action; in the case of SiO_2 this effect is negligibly small. Interaction of the molecules in the water vapor with the solid is the decisive factor in increasing the vapor pressure. Naturally, such effects

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[10] A similar interpretation which is difficult to understand [that $Si(OH)_4$ exists at higher and $Si_2O(OH)_6$ at lower pressures] is due to E. L. Brady, *J. Phys. Chem.* **57**, 706 (1953). It seems rather unlikely that the conclusions of G. R. B. Elliott (Univ. of Calif. Thesis 952, UCRL-1831), that the product of the action of water vapor under pressure on silica is $SiO{\cdot}4H_2O$, can be correct. Wood (*84*) postulated the formation of higher aggregation products such as $(H_4SiO_4)_2$, $(H_4SiO_4)_3$ etc. at high pressures, but these formulas are, naturally, not proved.

[11] An introductory treatment is given by Denbigh (*23*). Booth and Bidwell (*9*) have collected solubility measurements. Morey (*52*) considers theoretical aspects of the solubility of solids in gases and reports new measurements. Franck (*28*) reviews and extends the theoretical treatment, and particularly discusses the role of water as a strongly polar gaseous solvent with reference to his own measurements.

generally depend on the specific interaction between gas and solid. According to Franck, the relationship

$$\ln \frac{x_2}{x_2^\circ} = \frac{V_{2F} \cdot P}{RT} + m \ln \frac{k_m}{V} \qquad (41)$$

holds in the limiting case of high densities and strong interaction. (x_2 = mole fraction of solute; x_2° = mole fraction of the solute under its own vapor pressure; V_{2F} = molar volume of the solid; P = total pressure; m = association number; $1/V$ = total density; k_m = constant.)

If the Poynting effect [the first of the two terms in Eq. (41)] is neglected, this expression agrees with the Eq. (39) used for the expression of the solubility relationships in the system SiO_2-water. Let us now return to Eq. (39), which Mosebach postulated on the assumption of a heterogeneous gas reaction. Such an interpretation would be understandable for the supercritical region on the basis that there is here yet another phase which may be considered as a gas phase. It cannot be overlooked in this discussion that, as Franck showed, the supercritical phase becomes more and more like a liquid as the density is increased, since formation of association complexes and electrolytic dissociation occur, as in liquid water. The heterogeneous reaction model therefore cannot be used without reservations in the interpretation of experimental data. This is evident if the hydrothermal solubility data for BeO given in Table XII are compared with those obtained by extrapolation of data for the equilibrium $BeO(s) + H_2O(g) \rightleftharpoons Be(OH)_2(g)$; the results differ by two or three orders of magnitude.

TABLE XII

SOLUBILITY OF OXIDES IN WATER VAPOR AT 500°C AND 1050 ATM

Oxide	Solubility (ppm)	Oxide	Solubility (ppm)
BeO	120	SnO_2	3.0
Al_2O_3	1.8	Nb_2O_5	28.0
VO_2	0.2	Ta_2O_5	30.0
SiO_2	2600	Fe_2O_3	90.0
GeO_2	8700	NiO	20.0 (at 2100 atm)

Studies on the solubility of oxides in the supercritical region of water have not been confined to SiO_2. Morey and Hesselgesser and Morey and Chen [see Morey (*52*)] have studied the solubility of a series of other oxides in water vapor at 510°C and 1050 atm. A summary of their results is given in Table XII. According to Franck and Tötheide (*28*) the formation of gaseous $CO(OH)_2$ from CO_2 and H_2O at 600°C and 900–1600 atm is not established.

It would be of great interest in the investigation of volatile compounds in oxide-water systems if the solubility of the oxides in Table XII and of further oxides in highly compressed water vapor at various pressures and temperatures could be determined. This would enable association numbers to be determined and formulas for the volatile compounds to be discussed, as in the systems SiO_2-H_2O.

Investigation of the action of water on oxides which, like MoO_3, react at atmospheric pressure at higher temperatures, is of special interest. If different compounds are formed at higher pressures, it can be established whether they are related to those obtained at lower pressures or to the polyanions formed in aqueous solution at ordinary pressures. The discussion of such relationships is also of interest for the SiO_2—H_2O system. We will conclude with a discussion of these questions.

Let us suppose the system

$$x \text{ Oxide(s)} + m \text{ H}_2\text{O(g)} \rightleftharpoons [\text{Oxide}_x \cdot m\text{H}_2\text{O}](\text{g}) \tag{42}$$

is investigated at various temperatures and pressures. As already discussed in detail in Section III,A, analysis shows how much oxide, m_{oxide}, is transported under equilibrium conditions for a given quantity of water, m_{H_2O}. Since $n_{H_2O} \gg \overset{+}{n}_{\text{oxide}}$, $P_{\text{total}} \approx P_{H_2O}$,

$$\overset{+}{x}_{\text{oxide}} = \frac{\overset{+}{n}_{\text{oxide}}}{n_{H_2O}} \tag{43}$$

and since the influence of the saturation vapor pressure can be neglected it follows that

$$x_{\text{hyd}} = \frac{n_{\text{hyd}}}{n_{H_2O}} \tag{44}$$

We will now evaluate m, the association number. In order to do this we must express x_{hyd} as a function of the concentration of water in the gas phase, and in doing so the character of the gas or supercritical phase as well as the pressure dependence of the chemical potential of the solid phase must be taken into account.

We assume that there is no appreciable interaction between molecules of the compound which is formed or between these molecules and water molecules. Since the fugacity coefficients of the compound formed are unknown, we will present the results of the measurements as a function of the experimentally determined PVT data for water (*38a*), represented by the density.

We define

$$C_{\text{hyd}} = \frac{n_{\text{hyd}}}{V} \qquad C_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{V} \tag{45}$$

with

$$V \approx V_{\text{H}_2\text{O}} = \frac{n_{\text{H}_2\text{O}}}{\rho_{\text{H}_2\text{O}}}; \qquad V_{\text{hyd}} \ll V_{\text{H}_2\text{O}} \tag{46}$$

We then obtain

$$K_c = \frac{C_{\text{hyd}}}{C^m_{\text{H}_2\text{O}}} = \frac{n_{\text{hyd}}}{n_{\text{H}_2\text{O}}} \cdot \frac{\rho_{\text{H}_2\text{O}}}{\rho^m_{\text{H}_2\text{O}}} \tag{47}$$

or

$$K_c = x_{\text{hyd}} \cdot \frac{1}{\rho^{m-1}_{\text{H}_2\text{O}}} \qquad \text{where } \rho = \text{density} \tag{48}$$

The pressure dependence of the chemical potential of the solid phase is given by

$$\frac{d\mu_{\text{SiO}_2}}{dp} = V_{\text{SiO}_2} \qquad \text{where } V_{\text{SiO}_2} = \text{molar volume} \tag{49}$$

Integrating from a pressure $p^1 = 1$ atm to the reaction pressure P, and assuming the pressure dependence of the molar volume, it follows that

$$\mu^P_{\text{SiO}_2} - \mu^O_{\text{SiO}_2} \cong P \cdot V_{\text{SiO}_2} \tag{50}$$

From this

$$\log a = \frac{V_{\text{SiO}_2}}{4.574} \cdot \frac{P}{T} \tag{51}$$

The experimental data may then be represented by the equations

$$K_c{}^a = \frac{x_{\text{hyd}}}{a^x_{\text{SiO}_2} \cdot \rho^{m-1}_{\text{H}_2\text{O}}} \tag{52}$$

$$\log \frac{x_{\text{hyd}}}{a^x_{\text{SiO}_2}} = (m-1) \log \rho_{\text{H}_2\text{O}} + K_c{}^a \tag{52a}$$

Equation (52a) may be evaluated for a reaction of type (42). Since, however, the investigation extends over a large range of densities, e.g., from 0.08 gm/cm^3 to 0.8 gm/cm^3, the possibility that several reactions may occur must be taken into account. It may be assumed that there are ranges of density corresponding with the existence of separate species, though the existence of transition regions in which more than one species can occur is not excluded. With this proviso, Eq. (52a) becomes the equation for the tangent for the curve corresponding with the existence of the ith species and enables us to determine the ith association number and the ith equilibrium constant. The experimentally determined relationships are in fact simpler and the curves corresponding with the existence of the separate species are good approximations to straight lines.

Results will first be evaluated using an estimated value of x. The determination of the association number is not affected, though the equilibrium constant is uncertain by the factor x. This first approximation shows whether there are several reactions leading to different species in the density range under examination. If this is so the evaluation is repeated with the most probable value for x.

Consider now the results obtained in using Eq. (52a) to evaluate the measurements of G. C. Kennedy (*44*) and G. W. Morey and J. M. Hesselgesser (*53*). Three association numbers are found. At low densities $m = 2$, at densities around 0.05 gm/cm³ $m = 3$ and at high densities $m = 1$. The solubility increases with increasing density. These findings may be interpreted stoichiometrically and the following equations are proposed:

	Density range	
$SiO_2(\text{quartz}) + 2H_2O(g) \rightleftharpoons Si(OH)_4(g)$	up to 0.05 gm/cm³	(53)
$2SiO_2(\text{quartz}) + 3H_2O(g) \rightleftharpoons Si_2O(OH)_6(g)$	up to 0.45 gm/cm³	(54)
$SiO_2(\text{quartz}) + H_2O(g) \rightleftharpoons SiO(OH)_2(g)$	>0.65 gm/cm³	(55)

The density ranges shown are only a rough indication of the limits for the separate regions and do not define them precisely. The compound $SiO(OH)_2$ is probably not a monomer, though further experimental work is needed to clarify this problem.

In the case of the system MoO_3—H_2O it is already known that the gaseous hydroxide $MoO_2(OH)_2$ occurs at higher temperatures. The highest water vapor pressure used hitherto in investigations to determine the association number was 1 atm. When the water vapor pressure is increased, no change in the association number is found up to about 160 atm. The only reaction up to this pressure is the heterogeneous gas reaction with an association number of unity. From 160 atm a reaction between $MoO_3(s)$ and $H_2O(g)$ is found which has an association number $m = 3$. In this there is a considerable increase in the solubility of the MoO_3. Its formulation as

$$MoO_3(s) + 3H_2O(g) \rightleftharpoons Mo(OH)_6(g) \qquad (56)$$

is therefore excluded on stoichiometrical grounds. The formulation

$$7MoO_3(s) + 3H_2O(g) \rightleftharpoons [Mo_7O_{18}(OH)_6](g) \qquad (57)$$

can however be reconciled with an association number of three and with the experimental results. At still higher pressures, from about 330 atm, it seems that there is another reaction with an association number of two.

When the reaction product in Eq. (57) is compared with the polyanions known in aqueous solution we see that the compositions are similar. It is now known that the only ions to occur in acidified molybdate solutions are $[Mo_7O_{24}]^{6-}$ and $[Mo_8O_{26}]^{4-}$. In our experiments on the action of water on MoO_3 at high densities and temperatures (*33*) we observed that the reaction product formed at >160 atm shows in the expanded aqueous phase behavior like that of the polymolybdate ion $[Mo_7O_{24}]^{6-}$. A further analogy may be shown to exist between the results of investigations of the heterogeneous reaction and observations on molybdate ions in aqueous solution. There is a limiting concentration which must be exceeded if polymolybdate ions are to be formed in aqueous solution. It is about $2 \cdot 10^{-4}$ g-atom molybdenum/1 (*68a*). In the reaction between $MoO_3(s)$ and $H_2O(g)$ with an association number of unity this concentration is not exceeded when the concentration of the gaseous hydroxide is expressed in the units referred to. The limiting concentration is, however, exceeded in the case of the reaction with an association number $m = 3$.

The results of the foregoing investigations show, as has been mentioned already, that the specific interaction between oxide and water determines the magnitude of the effect which, in the last examples, may be explained in terms of solvation. A simple solvation model is, however, unsatisfactory. The change in the dielectric constant of water with pressure at a given temperature runs somewhat parallel to the observed increase in the molar fraction x_{hyd} with density. It is not surprising, therefore, that compounds occur at higher pressures and temperatures which are already known in aqueous solution. From the experimental point of view this relationship suggests the possibility of using measurements at different pressures as an approach to the study of the interesting field of polyanion chemistry.

ACKNOWLEDGMENT

We thank Dr. E. Schwarzmann and Dr. H. K. Hofmeister for active support and stimulating discussion.

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