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GASEOUS HYDRATED OXIDES, HYDROXIDES, AND OTHER HYDRATED MOLECULES

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(Thesis)

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Abstract

Gaseous hydrated oxides which are more volatile than the corresponding oxides are discussed and the periodic table is covered for evidence of such molecules.

The solubility of salts in high pressure steam is discussed and interpreted. The results are applied to steam turbine deposits and geological theory.

General Discussion

There have been frequent indications in the literature of increased volatility of various compounds in the presence of steam. In general, however, little attempt has been made to specify the formulas of these hydrated molecules, except those of the normally gaseous non-metallic oxides. The work of Stackelberg, Quatram, and Dressel[1] in establishing $H_3BO_3(g)$ is a particularly notable exception, while Grossweiner and Seifert[2] have also partially established three more molecules recently.

In this thesis an attempt is made to cover particularly the available indications of volatile hydroxides and hydrated oxides although some information relating to other gaseous hydrates at high pressures is also included. At the low pressures the method is identical, in principle, with that used by Grossweiner and Seifert[2] but is extended to fix the complete reaction where possible.

By means of experiments in which the activities of the possible products and reactants of a reaction are varied, it is possible to find what reaction is taking place. In a reaction:

$$wA + xB = yC + zD$$

the equilibrium constant will have the form:

$$K = \frac{(a_C)^y (a_D)^z}{(a_A)^w (a_B)^x}$$

where a = activity. In such an equilibrium if the activities of all

products and reactants except two are held constant, a power relationship between the two varied species can be found. This power relationship will in general be a small whole number or simple fraction. Thus particularly accurate determinations are not necessary.

These activity relationships, once found, may be used with confidence in further experiments where more activities are varied in the same equilibrium and further relationships may be found until the reaction is fixed. If several activities must be varied in the original determinations, then, by the results of several experiments, all relationships may be found. In this case more accurate determinations are needed.

A common method of plotting such data if only two concentrations, such as A and C, are varied is to plot log A vs. log C. The slope of such a plot gives the relationship between the power dependences of A and C since:

$$\log a_C = \frac{w}{y} \log a_A + \frac{1}{y} (\log K + x \log a_B - z \log a_D).$$

This equation has the form $y = mx + b$.

A plot such as this is of value for a first estimate of the power dependence, but it is unwise to count on it completely since it does not use the one absolute piece of information one has: namely, that the reaction can not go if one of the reactants is missing. A better method is to plot activities raised to an appropriate power. In this case the lines goes through the origin.

In the latter part of the paper, some rather new approaches to identification of the high pressure molecules are discussed along with the results.

Experimental

Three different experimental procedures were used and each had minor modifications in the various runs. The last to be discussed was not used for any of the reported results since analytical problems proved particularly obnoxious; however, it is reported since similar equipment could be valuable for experiments where the collected material could be easily dissolved.

One very quick and easy method was developed to test for hydrated gaseous molecules. A hollow copper block was placed in a vertical combustion tube furnace which was further insulated with asbestos. A chromel-alumel thermocouple was run through an asbestos cap and air space and then through a copper cap into a constant temperature zone in the block. The thermocouple was originally calibrated against the boiling point of sulfur and the melting points of Bureau of Standards copper and aluminum. However, in the course of the runs the thermocouple was broken and not recalibrated. Temperature of the furnace was controlled to about ±5° with a 20 ampere Variac and ammeter if desired; however, in many of the runs it was felt wiser to raise the temperature a fraction of a degree per minute to avoid possible heating and cooling of the sample.

Approximately 10 mg. oxide samples to be tested were placed in weighed small quartz glass tubes mounted on small glass stands. The tubes were again weighed to ±.05 mg. One tenth to one fortieth of a cc. of boiled distilled water was placed by a semi-micro pipette into 6 mm. or 7 mm. outer diameter quartz tubes. The small sample tubes were then placed inside the larger tubes. If desired, the tubes were

repeatedly evacuated and flushed with a pure gas, and sealed while still attached to a long tube filled with the gas to prevent mixing with air.

Several tubes were generally heated simultaneously to test, for instance, the effect of oxygen, hydrogen, and argon on otherwise identical water vapor filled tubes. Heating was normally for 20 to 30 minutes to assure equilibrium. The tubes were always examined, after removal, for any evidence of a concentration of condensate at a particular spot which would indicate precipitation due to thermal gradients. No such evidence was ever found.

After cooling, the tube was scratched and the bottom held in a vise so the sample would not be spilled, and the top was broken off. The outside of the sample tube was then washed and dried in an oven, and the tube then weighed. Where possible, the condensate on the walls of the outer tube was dissolved off and the sample analyzed colorimetrically.

The silica glass tubes proved remarkably strong though not consistently so. Seven millimeter outside diameter tubing generally held about 150 atmospheres internal pressure while heated to 1000°C. In the absence of a copper block an explosion commonly wrecked the furnance heating elements and damaged the insulation. However the copper block directed the explosions upward harmlessly in the later runs. In the presence of hydrogen the attack on the silica was much more severe (see Group IV A later in this report) and the weakened tubes tended to break at lower pressures. In breaking, the tubes shatter to a fine powder which can be stopped by clothing or a face

shield even though the explosion is only a foot or two away.

The second method was used at temperatures up to 1550°C and involved flowing mixtures of water vapor and other gases over a boat containing the oxide to be tested. Hydrogen, oxygen, or argon was flowed at a constant initial pressure of about 2 to 10 psi guage through calibrated capillaries, after which the gas mixed with steam from a flask heated at constant rate by Variac and Glas-Col heater. The pyrex tubing leading the gas to the furnace was sealed directly to a platinum tube in which the reaction took place. The oxide containing boat was generally Al_2O_3, porcelain, or SiO_2, since platinum could not be used for the boat as it tended to stick to the platinum tube. The boat was weighed before and after the run, sometimes with a further treatment to give back the original oxidation state of the oxide. Sometimes, also, the product was condensed in a porcelain tube, either as an analytical procedure or to prevent fouling of the platinum. If platinum itself was undesirable, a porcelain tube was inserted through the length of the platinum tube. Temperatures were measured with a pt-pt 10% rhodium thermocouple fused to the platinum tube. The gas was passed through a two foot tube before the water vapor was condensed out in a glass condensor, since water condensation proved a little unsteady and a dilution of the furnace gas mixture with the non-condensible gas had to be avoided. There was also a tendency toward fog formation, so the non-condensing gas was passed out through a long vertical tube to feed back to the water collector any fog which might otherwise escape. The water collected was then weighed. The system operated at atmospheric pressure.

The third type of equipment involved a more elaborate flow system.

The original equipment had been designed by N. L. Lofgren,[3] but was considerably modified by the author and its use attempted on the $Mo + H_2O + H_2$ system.

The system operated at less than atmospheric pressure. Hydrogen was fed at constant pressure through a calibrated capillary, the pressure being maintained constant by bubbling excess hydrogen through a sulfuric acid head. The hydrogen was passed from a fritted glass tube through a constant head of hot water at a temperature corresponding to a considerably higher vapor pressure than that desired in the experiment. (Saturation with H_2O vapor had earlier proved difficult). The hydrogen and water vapor were then led through heated tubes into a long copper coil in a constant temperature bath. Excess H_2O was condensed out to the desired vapor pressure and the possible fog trapped on glass wool. Heated tubes led to the furnace which was of McDanel porcelain. Our glass blower, H. S. Powell, was able to make beautiful glass-to-porcelain vacuum-tight seals. (See also (4)). The reacting gases were led through 2 mm. capillary tubes into the reaction zone in order to eliminate thermal diffusion errors. The reaction chamber contained molybdenum at a temperature up to about 1300°C and a high enough pressure of hydrogen was maintained to keep the molybdenum reduced. $MoO_3 \cdot H_2O(g)$ carried out into the 1 mm. capillary collector tube which was cooler than the reaction chamber and the hydrated gas condensed out. The collector tube contacted the reaction chamber at a ball joint which was lapped in with a copper die and moist carborundum. Outside of everything was another porcelain tube for maintaining the vacuum. A large glass joint, lubricated with silicon

Hi-vac grease as were all warm stopcocks, permitted removal of the capillary collector, which was held in place with a spring. Exit tubes were also heated to the point where the water vapor was condensed out in liquid air; this heating of the conducting tubes was done by resistance wires and Variacs. The hydrogen was collected in a large calibrated burette maintained at constant pressure. The rise and fall of a mercury manometer established or broke an electrical contact operating a relay and solenoid arrangement which evacuated or compressed gas in a dummy burette and moved water to or from the gas collecting burette. Temperature in the furnace was measured with a Pt-Pt 10% rhodium thermocouple and a second thermocouple actually inside the reaction chamber showed a constant value whether gas flowed or not. Gas flow rates up to about 60 cc. per minute at room temperature were used. The furnace used Globar heaters and was controlled by a Micromax automatic potentiometer.

A molybdenum (V) thiocyanate method was available[3] for analyzing as little as one microgram of molybdenum. However use of the equipment for $MoO_3 \cdot H_2O(g)$ and other possible molybdenum hydroxides was unsuccessful apparently because of the formation of very insoluble aluminum molybdates. This molybdenum would not dissolve in HCl or HNO_3 in capped glass pipe heated at 350°C for several hours. (At these temperatures and pressures nitrogen oxides seriously penetrated a teflon gasket and attacked the brass cap). Boiling NaOH and Na_2O_2, or boiling H_2SO_4 containing traces of HNO_3 were of little value. H_2O_2 with Ag^+ showed some promise, but was far from completely successful. Several of these treatments severely etched the mullite porcelain.

Section I: Volatile Hydroxides and Hydrated Oxides

Group I A

KOH and NaOH were reported to be volatile in a manometer type experiment by Von Wartenberg and Albrecht[5]. Kelley[6] gives a recalculation of these data.

Recently Margrave[7] has calculated decomposition pressures to the oxides and $H_2O(g)$ which indicate that the data of (5) could correspond to this reaction. He has also, in preliminary experiments, passed argon plus a little water vapor over LiOH and NaOH at elevated temperatures. LiOH(g) appears to be appreciably volatile while NaOH(g) does not.

Smith and Sudgen[8] have found CsOH(g) volatile in flames, but they did not find NaOH(g) or KOH(g).

From the work of Spillner (see Section II) we conclude that a molecule of constitution approximately $NaOH \cdot 7H_2O(g)$ appears at high steam pressures.

Group II A

BeO: The volatility of BeO in steam has been studied by several authors principally at Argonne National Laboratory. The work culminated in a paper by Grossweiner and Seifert[2] in which H_2O diluted with various He pressures was passed over BeO(s). The data were of good precision and only approximately fitted $BeO \cdot H_2O(g)$ as the volatile

species, the slope of a plot of log P_{BeO} complex versus P_{H_2O} being equal to 0.765. If one assumes the reaction:

$$BeO(s) + H_2O(g) = HBeOH(g) + 1/2\ O_2(g)$$

and uses the proper O_2 pressure (from water decomposition at their pressures and temperatures of around 1400°C) in a plot of log P_{HBeOH} + 1/2 log P_{O_2} versus log P_{H_2O} the slope comes out almost precisely one, corresponding to the reaction above.

For this reason we decided to test for our assumed reaction by passing H_2-H_2O and O_2-H_2O gas mixtures over BeO(s) in the second described experimental arrangement. The results on Table I, although equilibrium is not proved, exclude O_2 as a product of the major reaction which would now seem to be:

$$xBeO(s) + H_2O(g) = xBeO \cdot H_2O(g).$$

In this case from Grossweiner and Seifert and correcting a typographical error:

$$\log P_{mm} = 4.584 - \frac{9060}{T}.$$

However, both our data and those of (2) suggest a minor volatile species which does show an oxygen dependence.

Berkman and Simon[9] also show a similar trend of increased volatility in the presence of H_2 as opposed to N_2 in the carrier gas. Theirs were definitely non-equilibrium data, however, and did not prove the absence of the O_2 product.

Hutchison and Malm[10], in their early work, passed H_2O over

Table I

The Volatility of BeO in H_2-H_2O and O_2-H_2O Mixtures

Brewer and Elliott

Run No.	Temp. °C	Moles H_2O passed	Moles BeO collected x 10^4	Flow Rate Liters per minute at R.T.	P_{H_2O} atm.	P_{H_2} atm.	P_{O_2} atm.	$\frac{P_{BeO \cdot H_2O}}{P_{H_2O}}$ (10^{-5}) this paper	$\frac{P_{BeO \cdot H_2O}}{P_{H_2O}}$ (10^{-5}) Grossweiner and Seifert
1	1270	1.9_5	0.3	1.3	0.87		0.13	1	6.9
2	1285	1.8_3	0.8_4	1.7	0.74	0.26		8.4	7.6
3	1310	3.4_4	1.5_2	1.5	0.95		0.05	4.4	9.8
4	1310	2.2_7	1.1_2	1.9	0.91		0.09	4.9	9.8
5	1310	3.9	3.4_0	1.7	0.74	0.26		8.7	9.8
6	1254	3.8_8	1.5_6	1.4	0.88		0.12	4.0	5.9

beryl also. The thermodynamics are not sufficient, however, for even a limiting determination of x in $xBeO \cdot H_2O(g)$.

Von Wartenberg[11] has performed experiments which indicate H_2O or hydrated BeO gas dissolved in molten BeO in an O_2-H_2 flame.

MgO: Hutchison and Malm have found no appreciable volatility of MgO in steam at 1500°C. Straub[12] used MgO at high steam pressures and intermediate temperatures with no indication of volatility of hydrated MgO.

CaO: TiO_2 and CaO (in separate boats) were heated by van Nieuwenberg and Blumendal[13] for several days with 350 atm. steam at 415°C and did not react to form titanates. Apparently the CaO is not volatile under these conditions.

Group III B

La_2O_3: We have passed steam at high temperatures over La_2O_3 with results which were not as conclusive as would have been desired due to impurities in our sample. However, the volatility with one atmosphere of steam is 10^{-5} atmospheres from 1100°C to 1500°C.

Von Wartenberg[11] finds bubbles on cooling a molten drop of La_2O_3 heated in a H_2-O_2 flame. He interprets this to indicate dissolved gaseous hydroxides. While the interpretation is not conclusive (see Group IIIA), Al_2O_3 and BeO high temperature hydrated gases are now known.

Rare earth oxides: Von Wartenberg also tested Pr_2O_3, Nd_2O_3, and Yb_2O_3 similarly with negative results.

Group IV B

TiO_2: Morey[14] has shown TiO_2 to be carried by steam at about 2000 atmosphers and 900°C. TiO_2 was not volatile in steam with van Nieuwenberg's conditions. (See group II A).

Group V B

Nb_2O_5: We tested for volatility of Nb_2O_5 in quartz tubes with the first described experimental arrangement at 850°C. The tubes had a volume of about 3 cc. and contained up to 0.1 cc. of water at room temperature, and air was in the tubes when they were sealed. There was no evidence, on cooling the tubes, of an Nb_2O_5 precipitate on the walls.

Group VI B

van Nieuwenberg and Blumendal[13] originally showed the volatility of MoO_3 and WO_3 in steam, their work being around 400°C and 275 atmospheres. Millner and Neugebauer[15] showed there was a dependence of the volatility of both upon the water pressure, but did not attempt to identify the volatile species. Recently Grossweiner and Seifert[2] have correctly specified the volatile molecule, $WO_3 \cdot H_2O(g)$, from this work. However, we will extend their treatment to prove the formula of the molecule completely.

We did a great deal of work on the $Mo + H_2 + H_2O$ system, but due to analytical difficulties which were not at first apparent, our

early results had little meaning. However, in the course of the work we developed the third discussed equipment which could prove quite valuable with another system more amenable to chemical analysis.

$MoO_3 \cdot H_2O(g)$: We heated tubes containing MoO_3 with high pressure steam at intermediate temperatures. In the first group of tests 1.7 cc. silica tubes with MoO_3 and 25, 50, or 100 λ of liquid water and sealed in air were heated to 560°C for 40 minutes. A visual examination of the snowflake-like condensate which showed a 1:2:4 ratio, assured us of the first power dependence of the MoO_3 volatility upon water pressure even at high pressures.

As a quantitative test, we made a group of three more experiments at 550°C dissolving the MoO_3 condensate off the walls with ammonia and analyzing for Mo(V) thiocyanate as in (3). The results are shown on Table II.

Table II

The Volatility of MoO_3 in High Pressure Steam.

Brewer and Elliott

Volume of Tube cc.	Water Present cc. liquid	µg Mo Volatilized
1.54	0.100	27.5 ± 2.5
2.35	0.100	25.0 ± 2.5
1.54	0.025	7.5 ± 5

The MoO_3 vaporized is clearly a linear function of the amount of water present indicating a first power dependence on the H_2O.

The oxidation state is established by the work of Millner and Neugebauer[15] who found that MoO_3 carried with steam in the presence of much O_2. This oxygen would have quenched a reaction involving a volatile species with a lower oxidation state of Mo.

From (15) one can get for the reaction around 600°C and assuming the product:

$$MoO_3(s) + H_2O(g) = MoO_3 \cdot H_2O(g) \qquad \Delta H = +40.3 \text{ kcal./mole}, \quad \Delta S = +27 \text{ cal/degree/mole}$$

These data can be combined with those of Ueno[16]* for the vapor pressure of MoO_3 to yield for the reaction:

$$MoO_3(g) + H_2O(g) = MoO_3 \cdot H_2O(g) \qquad \Delta H = -23.4 \text{ kcal./mole}, \quad \Delta S = -23 \text{ cal/degree/mole}$$

If $MoO_3(s)$ vaporizes as a monomer, the ΔS of the reaction above is strong indication of the formula chosen, since 20 to 25 e.u. is the expected range if two moles of gases yield one mole of gas.

Further interest in the molecular weight of MoO_3 vapor exists because of the unexplained difference in the entropies of vaporization of MoO_3 and WO_3, which could be explained by polymerization of the $MoO_3(g)$.

We made several determinations attempting to find the density of MoO_3 vapor just above its boiling point. Equipment generally involved a weighed SiO_2 tube containing MoO_3, with a capillary hole which was heated over the boiling point, cooled, and weighed again to find the weight of MoO_3 gas in a given volume at 1 atmosphere

---

*Feiser's[17] corresponding data were taken with some H_2O present.

pressure. The determinations were uncertain because of large corrections for the decomposition of MoO_3 to lower oxides. However several determinations indicate the formula is less than $(MoO_3)_{1.5}$ and the probability is that polymerization is quite unimportant at 1200°C.

By analogy with $WO_3 \cdot H_2O(g)$ and considering the preceding discussion, the formula $MoO_3 \cdot H_2O(g)$ seems reasonably certain.

$WO_3 \cdot H_2O(g)$: The gas flow data of Millner and Neugebauer[15] combined with available thermodynamics fix the formula of this molecule, if equilibrium is assumed in their work. Table III does indicate a close approach to such equilibrium. One can discard the second point on the table because it was taken with an extremely slow gas flow-rate which permitted excessive movement of WO_3 by ordinary gaseous diffusion and precipitation. The first point is also uncertain since only 1.2 mg. of WO_3 moved, of which about a fourth carried unhydrated as $WO_3(g)$. (See data of Ueno[16]). The free energies of formation of the solids, extrapolated from Brewer[18,19], are internally consistent, although they may be off in absolute magnitude. The consistency of the free energy of formation of $WO_3 \cdot H_2O(g)$ from the various data establishes (a) the oxidation state of the W, (b) the single combined water molecule, and (c) the single WO_3 molecule in the gas.

We tested WO_3 volatility in high pressure steam in tubes as described under "Experimental". The volatility was not large enough for us to measure until a temperature of about 1000°C was reached. The quartz could not be heated much hotter, and the

Table III

The Volatility of Wolfram Oxides in Steam Mixtures

(From data of Millner and Neugebauer[15] at 1000°C.)

Solid Present	ΔF form.* of solid	ΔF form* of $H_2O(g)$	$P_{H_2O}(g)$ atm.	$P_{O_2}(g)$ atm.	$P_{H_2}(g)$ atm.	$P_{WO_3 \cdot H_2O}(g)$ atm.	K of vaporization Reaction	ΔF form. of $WO_3 \cdot H_2O(g)$
WO_3	-116.5	-42.4	.004	.996		(8.7×10^{-7})	(2.18×10^{-4})	(-137.7)
			.02	.98		(3.87×10^{-5})	(1.94×10^{-3})	(-143.1)
			.29	.71		1.03×10^{-4}	3.55×10^{-4}	-138.8
			.75	.25		3.41×10^{-4}	4.55×10^{-4}	-139.4
			1.00			5.23×10^{-4}	5.23×10^{-4}	-139.7
W_4O_{11}	-428		.86		.14	3.65×10^{-4}	2.70×10^{-4}	-139.2
WO_2	-78.8		.59		.41	1.00×10^{-4}	1.18×10^{-4}	-140.7

*Data extrapolated from Brewer[18, 19].

volatility was just outside the amount we could weigh or dissolve and analyze. A visual comparison of the condensates indicated that at high pressures of steam the molecule $WO_3 \cdot H_2O(g)$ still predominates.

Group VII B

We have no evidence for increased volatility of these oxides if H_2O is present.

Group VIII

Fe: Strohecker and Sierp[20] found a vaporization of iron in a steam current at 100°C. This volatility may have been due to impurities such as halides.

Molly Gleiser[21] has reported a volatility of iron of 3.6×10^{-4} atmospheres at 1450°C and with an H_2/H_2O ratio sufficient to keep the iron reduced to the metal. We found FeO carried to no more than 10^{-6} atm. in 1 atmosphere of steam at about 1500°C. The discrepancy argues for a volatile species such as perhaps FeOH, in which the iron valence is less than 2. Since Miss Gleiser intends to work further on the subject, we did not try any runs with H_2 present.

Iron in some form carries in high pressure steam boilers and deposits on turbine blades many stages inside the turbine while other salts largely precipitate out, due to the pressure drop, on the first few blades. This condition argues for a low degree of hydration of the volatile molecule at about 100 atm. and 400°C.

NiO: We passed H_2O, $H_2O + H_2$, and H_2O + A over Baker's C.P. NiO, several percent of the sample being volatilized in the first four runs. The results are shown on Table IV using the data from Brewer[19] for the thermal dissociation of $H_2O(g)$. The data except for run 5 extrapolate well to Johnston and Marshall's[22] work, assuming either vaporization to the elements, or as NiO(g). (See Brewer and Mastick[23]). Run 5 leads to a vapor pressure higher than that of pure Ni and indicates we had reduction to the metal under these conditions, the reoxidation being incomplete after the run. The data do not indicate important hydrated oxide species under these conditions.

$PtO_2(g)$: We find no hydrated oxides at 1500°C in the presence of both oxygen and steam. Our data for the volatility of PtO_2 are plotted (Fig. 1) as they show the volatile species and also the absence of any important hydrates.

Schneider and Esch[24] have determined the volatility of PtO_2, but Esch's thesis data were discontinuous and it was uncertain how great were the errors introduced. It turns out that if one plots log P_{PtO_2} versus log P_{H_2O}, a theoretical slope of one goes well through the points and probably gives about as good a value for the equilibrium constant as we get from our data. An estimate of the entropy of the vaporization reaction from the value for $Pt(s) + Cl_2(g) = PtCl_2(g)$ leads one to expect about $\Delta S = 4$ to 8. (See Brewer[19]). Combining our data with those of Schneider and Esch leads to a ΔS of 8.7 e.u. for $Pt(s) + O_2(g) = PtO_2(g)$. At 1500°C our data yield $K = 3.1 \times 10^{-5}$, while those of Schneider and Esch would best fit $K = 1.7 \times 10^{-6}$ at 1200°C.

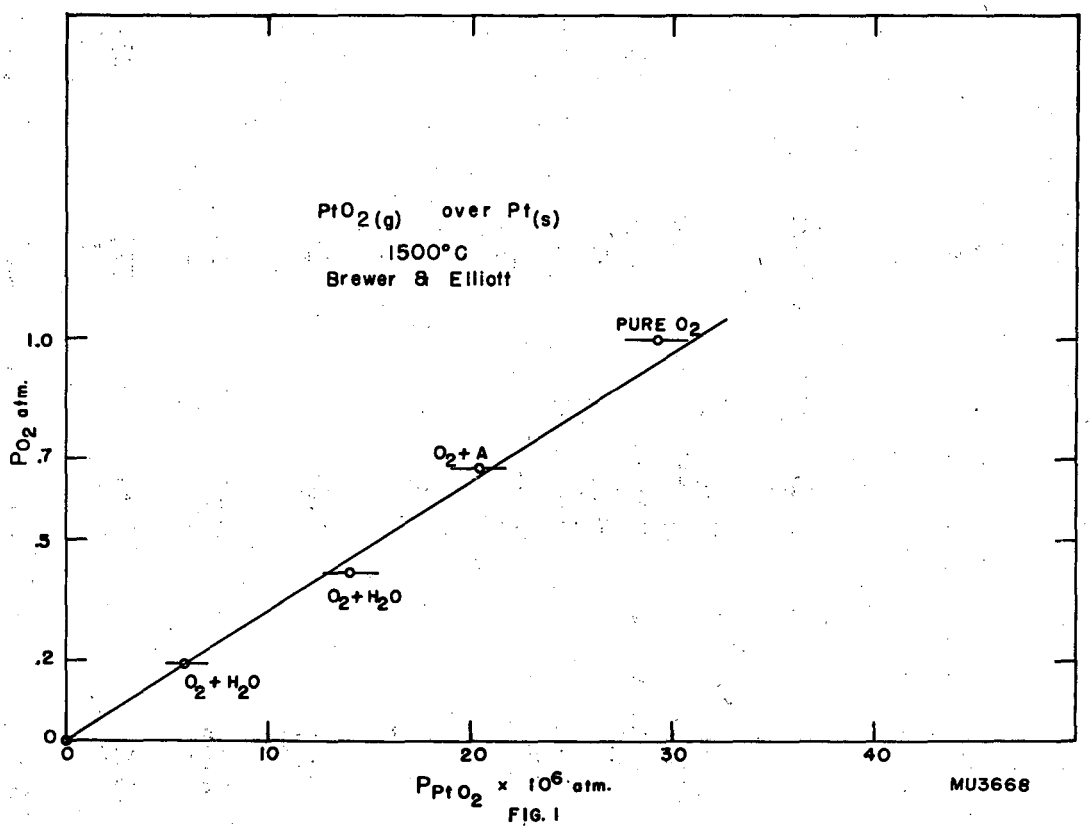
PtO2(g) over Pt(s)
1500°C
Brewer & Elliott
PURE O2
O2+A
O2+H2O
O2+H2O
1.0
.7
.5
.2
0
PO2 atm.
0
10
20
30
40
PPtO2 x 10^6 atm.
MU3668

FIG. 1

Table IV

The Volatility of NiO in H_2-H_2O and O_2-H_2O Mixtures

Brewer and Elliott

Run No.	T °C	Moles H_2O Passed	Moles NiO Vaporized x 10^5	Flow Rate Liters per Min: at R.T.	P_{H_2O} atm.	P_{H_2} atm.	P_A atm.	$(P_{Ni})(P_{O_2})^{1/2}$ x 10^7
1	1500 ± 5	0.7_2	0.67	0.90	1			2.6
2	1508 ± 5	6.4_5	4.02	0.66	1			1.8
3	1506 ± 6	7.4_9	4.95	1.07	1			1.8
4	1508 ± 6	7.1_0	6.36	2.07	$.64_2$		$.35_8$	1.5
5	1507 ± 5	1.0_8	76.5	1.52	$.72_3$	$.27_7$		0.6

Group I B

Cu: Strohecker and Sierp[20] also report Cu to be volatile in steam at 100°C. Again we did not check their work, but we were not looking for small traces.

Straub[12] has used copper in his bombs at about 400°C and 100 atmospheres and finds no conductivity error from the copper used.

We heated copper in a quartz tube containing H_2O and sealed in air to about 100 atmospheres of steam and 800°C with no coating of the tube with any noticeable copper deposits. From Straub's work and ours, we conclude that hydrated copper species are not important in the vaporization of copper or its oxides.

Au, Ag: Spillner[25] reports that Ag can be used in high pressure steam without attack. Strohecker and Sierp do not find either silver or gold volatile in steam at 100°C.

Group II B

Zn: Kitchener and Ignatowics[26] have passed H_2 + H_2O mixtures over Zn at 1100°C and up to .05 atm. H_2O. Their work checks CO-CO_2 equilibrium data and shows no evidence of volatile hydrates, however their water pressure was low.

Strohecker and Sierp[20] got evidence of Zn carried in steam at 100°C, but one can not tell in what form the metal was carried.

Group III A

$H_3BO_3(g)$: The molecules $H_3BO_3(g)$ and possibly $HBO_2(g)$ have been almost completely established by the work of Stackelberg, Quatram, and Dressel[1]. Even their lone assumption related to the degree of polymerization of the gas can be resolved by reference to the thermodynamics of $H_3BO_3(s)$ and $HBO_2(s)$ as given in the N.B.S. tables[27]. Neglecting ΔCp of formation leads to the following free energies of formation at 382°K:

$$\Delta F_f^\circ[H_3BO_3(s)] \text{ at } 382^\circ K = -220.7 \text{ kcal./mole}$$

$$\Delta F_f^\circ[HBO_2(s)] \text{ at } 382^\circ K = -165.7 \text{ kcal./mole}$$

$$\Delta F_f^\circ[H_2O(g)] \text{ at } 382^\circ K = -53.7 \text{ kcal./mole}$$

Then from the data given by Stackelberg, Quatram, and Dressel[1] for the reactions:

$$H_3BO_3(s) = H_3BO_3(g) \qquad \Delta F^\circ_{382^\circ K} = 5.4 \text{ kcal./mole}$$

$$HBO_2(s) + H_2O(g) = H_3BO_3(g) \qquad \Delta F_{382^\circ K} = 4.0 \text{ kcal./mole}$$

(by easy extrapolation)

Combining to get the free energy of formation of $H_3BO_3(g)$ by two paths, we find:

$$-220.7 + 5.4 = -115.3 \text{ kcal./mole at } 382^\circ K$$

$$-165.7 - 53.7 + 4.0 = -115.4 \text{ kcal./mole at } 382^\circ K$$

The correspondence of these figures shows that $H_3BO_3(g)$ is not

polyermized.

Earlier workers[29,30] also considered H_3BO_3 vaporization.

The authors[1] give for the vaporization of $H_3BO_3(s)$ at about 140°C:

$$\Delta H_V^\circ = +23.43 \text{ kcal./mole}$$

$$\log P = 13.206 - \frac{5125}{T}$$

and for the relationship between $H_3BO_3(g)$ and $HBO_2(g)$ at 160°C,

$$K = \frac{P_{H_3BO_3(g)}}{P_{H_2O(g)}\ P_{HBO_2(g)}} = 0.06$$

Al_2O_3: Other group III hydrated oxides are not well studied, although there are several indications and suggestions of volatile aluminum hydrates.

Best evidence is that of Morey[14] who found Al_2O_3 moving through the gas in a temperature about 1000°C and 3000 psi steam.

Von Wartenberg[11] found what he interpreted as dissolved gaseous hydroxides of Al_2O_3 in a molten drop of Al_2O_3 in an H_2-O_2 flame. The bubbles found on solidification of the molten drop could equally well be explained by a solution of H_2O in the liquid. In a recent paper[31] he definitely shows a volatility of Al_2O_3, probably hydrated, in an H_2-O_2 flame.

Spillner[25] found little evidence of steam attack on Al_2O_3 at moderate temperatures and high pressures.

Strohecker and Sierp[20] report traces of aluminum carried

at 100°C in a current of steam. It is uncertain if H_2O was involved in this transport.

In these laboratories we have passed steam and steam-oxygen mixtures over Al_2O_3 at 1500°C and atmospheric pressure. Under these conditions the vapor pressure of the hydrated species is below 10^{-6} atmospheres, this figure being confirmed in several runs where Al_2O_3 was used for a container.

Group IV A

C: Carbon has many gaseous hydrates such as H_2CO, HCOOH, etc., which are well known.

Si: The high pressure species $SiO \cdot 4H_2O(g)$ (or $SiO_2 \cdot 3H_2O(g)$) is discussed at length in the second section of this report.

At temperatures around 1500°C and steam pressures under one atmosphere, SiO_2 becomes volatile with a different principal gaseous species. Preston and Turner[32] have demonstrated this volatility at 1400° and 1500°C.

In attempting to get an entropy from the data above, we found that a species involving SiO would give a more reasonable fit than would one involving SiO_2. Our attempts to fix the formula of the volatile species led to the data on Table V.

It is seen that oxygen quenches the reaction, that there is a first power dependence upon H_2O, and that hydrogen greatly enhances the volatility. Equilibrium was apparently not attained in the hydrogen run where much more SiO_2 had to vaporize. However, the

Table V

The Volatility of SiO_2 in Steam Mixtures at High Temperatures

Brewer and Elliott

Run No.	Temp. °C	Moles H_2O passed	P_{H_2O} atm.	P_{O_2} atm.	P_A atm.	P_{H_2} atm.	Moles SiO moved x 10^6	Flow Rate Liters per min.	P_{SiO_2} atm. x 10^6	$\frac{(P_{SiO.4H_2O})(P_{O_2})^{1/2}}{(P_{H_2O})}$
1	1502	3.8	0.90	0.10			0.00	0.70	0	
2	1490	2.7	1.00				7	0.45	2.6	7.0×10^{-8}
3	1480	15.5	0.50		0.50		32	1.46	1.0	4.3×10^{-8}
4	1492	0.75	0.79			0.21	22	1.86	23	4.2×10^{-9}

equilibrium constant is nearly constant and would be far off constancy with other assumed reactions. Guessing the single Si in the mole leads to the reaction:

$$SiO_2(s) + H_2O(g) = SiO \cdot H_2O(g) + 1/2\ O_2(g)\ .$$

Conclusions from Section I.

Hydrated oxides exhibiting a greater volatility than that of the oxide in the absence of water are scattered over the whole periodic table rather than being associated with particular groups. The phenomena are not restricted to a single oxidation state.

Only a few hydrated gaseous molecules appear possible for a particular oxide. Thus an oxide molecule cannot gradually add more and more waters to get more and more volatile. This effect will be more pronounced for the compounds discussed in Section II.

These hydrates could be quite important economically. For instance if $SiO(g)$ and $SiO \cdot H_2O(g)$ are kept down by an O_2 atmosphere, bubbles entering in the making of quartz glass might be cut appreciably by use of oxygen. Also $SiO(g)$ and $SiO \cdot H_2O(g)$ seem to be involved in the crystallization of quartz glass. One can clear up the white film on worked quartz glass by flaming in a high O_2 plus H_2 flame. The flame remelts the crystals, and the O_2 keeps down $SiO(g)$ and $SiO \cdot H_2O(g)$, thus preventing crystallization at the sides of the flame.

Likewise, low grade ores of Mo, for instance, could be concen-

trated by passing steam, possibly at high pressures, over the powdered ore. Oxygen could be added to maintain $MoO_3(s)$ available for hydration as $MoO_3 \cdot H_2O(g)$.

Section II: Solubility of Solids in High Pressure Steam

Because of its importance to the operation of high pressure steam turbines and to geological theory, much work has been done on the volatility of several substances in high pressure steam. To our knowledge the only attempts to identify these volatile molecules were done for the vaporizing SiO_2. Straub[12] suspected silicic acid or a hydrate of it. Grossweiner and Seifert[2] suggested a formula.

In the work reported in the first section of this paper, treatment of the data as gaseous molecules was obvious. High pressure work, on the other hand, has generally been treated by a more general method similar to that used for the more complicated liquid situation. We hoped, as proved to be the case, that high pressure data could be treated by the former method to yield some workable conclusions as to the processes involved in gaseous solution.

In this discussion we will first consider the volatilization of NaCl since here the data are most complete and lead to interesting conclusions.

$NaCl \cdot 7H_2O(g)$: Straub[12] has done much very careful work on the solubility of NaCl(s) in superheated steam at about 100 atmospheres pressure and 400°C. At a constant temperature and pressure of water vapor he showed that the amount of NaCl carried by steam was proportional to the concentration of NaCl dissolved in the solution over which the steam passed. This shows that there is a single NaCl in the volatile molecule.

Spillner's work[25] shows that the pH of the salt solution obtained on condensing steam carrying salt is nearly neutral, a fact indicating that the NaCl is not hydrolyzing and carrying as NaOH hydrate and HCl gas. A further indication lies in the fact that NaOH, from Spillner's data, has about as much hydration of its volatile species as does NaCl. This would not leave enough water to hydrate the HCl.

Straub has reported the volatility of NaCl in steam at constant pressure and varying temperature. From his data the plot of Fig. 2 was constructed. In this figure at any one temperature the successive points plotted are for pressures of 46.1, 72.5, 105.1, and 150.5 atmospheres respectively. The curves for the various temperatures are displaced vertically in order to make the graph more easily readable, but all are plotted on the same scale. The length of the horizontal line at each plotted point is indicative of the uncertainty involved in the experimental location of the point.

At this point a discussion of the validity of drawing conclusions from our plot is in order. Theoretically a plot such as ours should employ fugacities rather than pressures and fugacities for the hydrated NaCl are obviously not available. However, if it can be shown that, at a given pressure, $(f/p)^7_{H_2O}$ approximates $(f/p)NaCl \cdot 7H_2O$, where f is fugacity and p is pressure, and presuming our results, then conclusions may be drawn.

Thus for the reaction:

$$NaCl(g) + 7H_2O(g) = NaCl \cdot 7H_2O(g)$$

$$K = \frac{\left[f_{NaCl \cdot 7H_2O(g)}\right]}{\left[f_{H_2O(g)}\right]^7} = \frac{\left[(f/p)_{NaCl \cdot 7H_2O(g)}\right]}{\left[(f/p)_{H_2O(g)}\right]^7} \frac{\left[P_{NaCl \cdot 7H_2O(g)}\right]}{\left[P_{H_2O(g)}\right]^7}$$

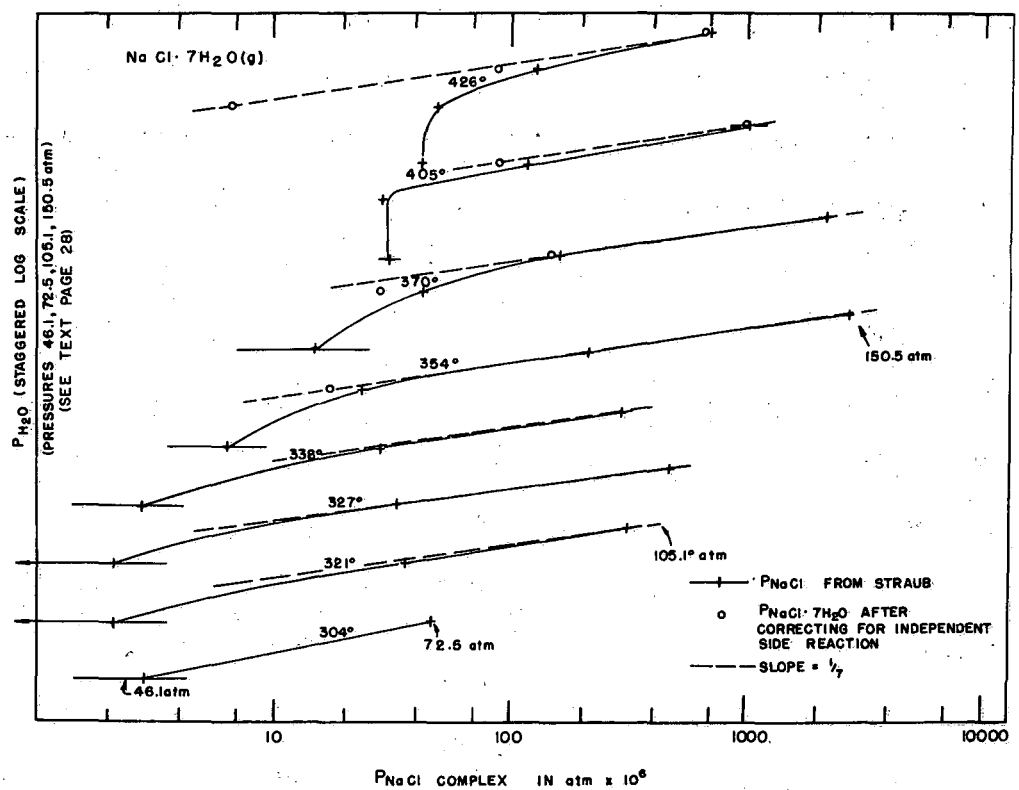
Na Cl· 7H2O(g)
426°
405°
370°
354°
338°
327°
321°
304°
150.5 atm
105.1° atm
72.5 atm
46.1atm
PNaCl FROM STRAUB
PNaCl· 7H2O AFTER CORRECTING FOR INDEPENDENT SIDE REACTION
SLOPE = 1/7
PH2O (STAGGERED LOG SCALE)
(PRESSURES 46.1, 72.5, 105.1, 150.5 atm)
(SEE TEXT PAGE 28)
10
100
1000.
10000
PNaCl COMPLEX IN atm x 10^6

FIG. 2

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A semi-theoretical justiciation of plotting pressures may be obtained from the following considerations. With seven water molecules around an NaCl molecule, the whole gaseous molecule may appear to other gaseous waters to be similar to other water agglomerates which are surely present at these pressures. If each of the seven water molecules exercises an almost normal attraction on another water molecule approaching it, then the seven molecules will exercise, in total, seven times the attraction of a single molecule. In this case, using van der Waals type reasoning:

$$\left(\frac{f}{P}\right)^{7}_{H_2O(g)} \approx \left[e^{\left(\frac{a_{H_2O}}{RT} - b_{H_2O}\right)P/RT}\right]^{7}$$

$$\left(\frac{f}{P}\right)_{NaCl\cdot 7H_2O(g)} \approx e^{\left(\frac{7a_{H_2O}}{RT} - b_{NaCl\cdot 7H_2O}\right)P/RT}$$

These two exponents are practically equal and the pressure plot is somewhat justified.

This reasoning is admittedly questionable, and a further justification of our plots can be obtained by examining the error involved.

As an example at 137 atm. and 400°C the fugacity to pressure ratio for water is 0.820, graphically integrated from the Steam Tables[33]. The change of free energy of the solid due to pressure changes amounts to a maximum of about 5% in the pressures of NaCl found. Certainly the water and hydrated NaCl will largely cancel each other's errors when pressures are used instead of fugacities. Even if one plotted the fugacity of water versus the pressure of the hydrate, he would conclude about eight for the number of hydrating molecules.

A log-log plot such as we make is quite insensitive to small deviations, and a check for gross errors in our assumptions can be made by looking for fluctuations in the slopes found on our plot. No such fluctuations are apparent.

The points are plotted (Fig. 2) with the width of the horizontal line corresponding to what we feel is a fair estimate of the uncertainty in precision of the data. The dashed lines are all drawn in with a slope of one seventh which would be observed if seven water molecules reacted with one salt molecule, while the circled points were obtained by subtracting an "NaCl" blank pressure, corresponding to volatility observed with the lowest water pressure, from further points in the same temperature series.

Straub analyzed by measuring conductivity and total chloride. The subtracted "NaCl" pressure is probably not due to NaCl(g) or a polymer, since Zimm and Mayer[34] have accurately measured the volatility of NaCl near these temperatures. An extrapolation of their data leads to a much lower vapor pressure than that observed by Straub.

However $FeCl_2(g)$ from attack on the iron container offers a very reasonable explanation for the water independent volatility. Kelley[6] reports a vapor pressure equation for $FeCl_2(l)$ which leads to a pressure of 6×10^{-6} atmospheres at 405°C. Each $FeCl_2$ molecule carried would analyze as two NaCl molecules. Other halides possibly have even higher volatilities. For instance Baker's C.P. NaCl has 0.001% each of Br^- and I^-, leading to the possibility of vaporizing $FeBr_2(g)$ or $FeI_2(g)$. If one considers the extrapolation involved,

the fact that fugacities are not equal to pressures, and the possibility of several concurrent water independent side reactions, the agreement with the observed "blank" is good.

The $FeCl_2(s)$ would get into the reaction chamber rapidly if there were any trace of acidity in the bomb. Even if there were no acidity a reaction similar to the following would take place:

$$H_2O(g) + FeO(s) + 2NaCl(s) = FeCl_2(s) + 2NaOH(s).$$

Combining data from several sources leads to an approximate $K_{405°C} \approx 10^{-18}$. At high steam pressures the NaOH volatility is similar to that of NaCl and the NaOH would be removed driving the reaction to the right. Once in, the $FeCl_2$ would be removed in Straub's procedure only by vaporization.

Apparently there is only a single important hydrated species present over this temperature and pressure range, namely $NaCl.7H_2O(g)$. This conclusion was very surprising. If seven water molecules will make NaCl quite volatile, why won't six also make it appreciably volatile?

The conclusion regarding the single hydrated species may well apply to liquid water also near the critical point where it is a poorly ionizing solvent (see Spillner[25]). It is possible that the assignment of seven waters of hydration may be off by one or two, but the conclusion of a single important species seems undeniable.

It is to be emphasized that calculations such as ours can not replace engineering data for the turbine operator. However, they do provide a means of interpolating and roughly extrapolating the

existing data, and do contribute to theory as discussed in a later section of this report.

Other Hydrated Salts

Spillner[25] has studied several salts well, but not as completely as did Straub[12] with NaCl. Spillner's volatilities in steam are reported here as recalculated to yield pressures. NaCl being also reported to show that the author's results yield similar conclusions.

If one assumes a reaction in Spillner's case with NaCl at 407°C similar to the one so apparent with Straub's data, and subtracts from all other points a vapor pressure corresponding to the "NaCl" at the lowest water pressure, then here also one obtains a theoretical slope of seven. (Fig. 3a). In this case the blank corresponds to a somewhat higher volatility than with Straub's NaCl. This difference might be due to a difference in analytical procedure by the author, or to the presence of more of the other halides, for instance, in Spillner's salt.

$KCl \cdot 7H_2O(g)$: Data from Spillner are shown (Fig. 3b), however, this time no attempt has been made to correct for a reaction with the container since the low pressure points are more erratic. KCl appears to have 6 or 7 combined water molecules in its volatile species. The single KCl in the molecule is a guess.

NaCl data appear also in another form in Spillner's work. He passed equilibrium steam pressures over NaCl solutions, varying his temperatures and thereby his pressures. His data show an increasing

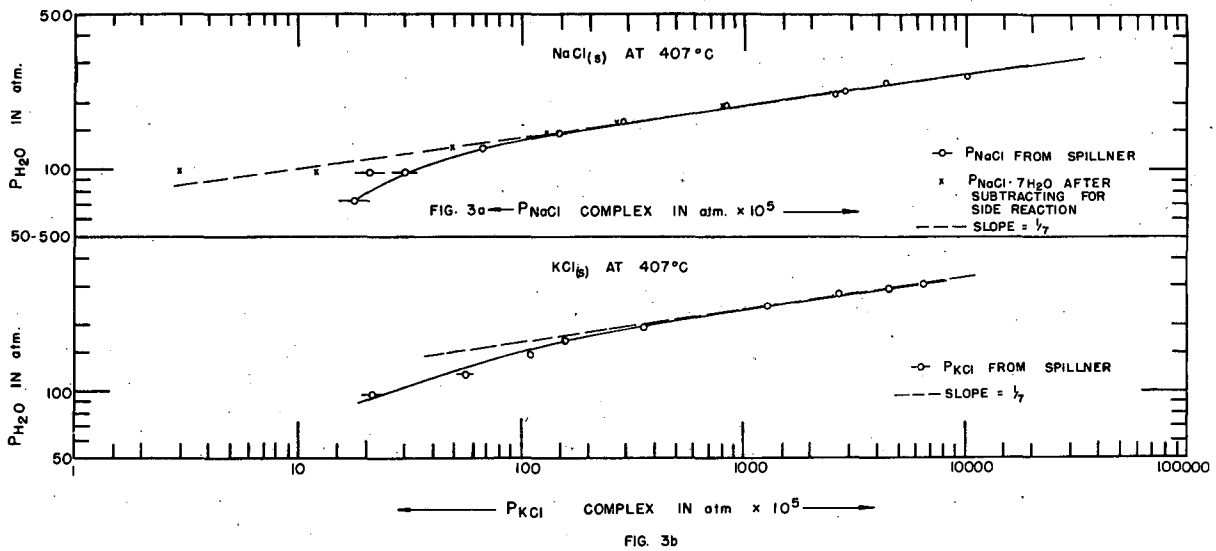

FIG. 3b

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pressure of NaCl in the vapor for an increase in concentration of NaCl in the solution up to a concentration of about 0.4 gm. NaCl per kg. of water. At about this point the NaCl pressure abruptly stops its rise with "concentration" increase in solution and remains almost constant. Straub thinks, possibly correctly, that Spillner had a precipitation of solid NaCl due to mechanical carry-over and precipitation in a possibly overheated portion of Spillner's bomb. Another explanation might lie in the possibility that the solution becomes saturated with NaCl at about this point, the fine precipitate being suspended uniformly in the highly agitated solution, so that Spillner analyzed a proper concentration of NaCl in his room temperature analyses. Straub has noted a similar anomaly, though less consistently, in his own work. At three temperatures he gets a change to zero slope of his NaCl gas pressure versus solution concentration data at about 0.9 gm. NaCl per kg. of water. The fourth, and higher, temperature data do not change slope. If the slope change is truly valid, it gives evidence of a gradual and continuous change from aqueous to gaseous solution at the critical point, since the gaseous solubility ($\approx$0.5 gm. H_2O/KgH_2O) is quite comparable to the liquid concentration at this point where the vapor pressure stops rising. (The critical point of the solution is uncertain and is probably raised by the dissolved salt. See Morey[14]).

$NaOH \cdot 7H_2O(g)$: If there were both solid and liquid present at equilibrium in Spillner's solutions, and if the solubility of solid in liquid were not changing much with temperature, then,

since the two phases are approaching an identity at the critical point, the equilibrium constant relating liquid concentration gaseous would not change much with temperature. That is:

$$\frac{d \ln K}{dT} = \frac{\Delta H}{RT^2} \rightarrow 0.$$

If so plots such as (Fig. 4a, 4b) are valid, the temperatures being neglected in plotting log P_{H_2O} versus log $P_{hydrate}$. This plot of NaCl is less complicated (lower temperature) due to the water independent side reaction. In this case the limiting slope of the curve near the critical point will represent the number of water molecules reacting to form the hydrated gaseous salt. These data lead to about eight waters of hydration for the NaCl and $NaOH \cdot 7H_2O(g)$ for the formula of the gaseous NaOH, assuming the solid is not hydrated. The single NaOH near the critical point in the species is established by the work of Straub, who found a first power relationship between NaOH in solution and in gas. Here again there is evidence for only a single hydrated gaseous species.

$BaCl_2$: Spillner also tested the solubility of $BaCl_2$ in steam but found only HCl carried in the vapor and had much attack upon his bomb.

Hydrated Sulfates: The gaseous solubility of sulfates may well be very slight. Spillner and Straub have both tested Na_2SO_4 and Secoy[35] has shown that the solubility of UO_2SO_4 goes to near zero at the critical point. Spillner reports that Schroer[36] was able to see the color of $CuSO_4$ in the gaseous phase.

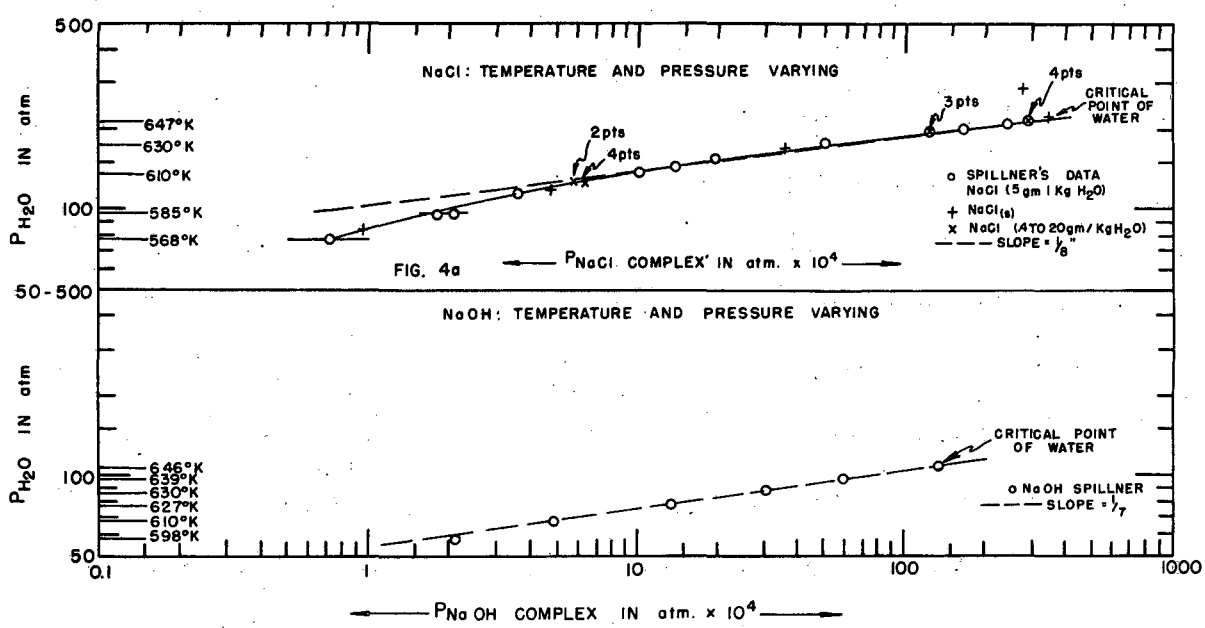

FIG. 4b

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Na_2SiO_3: This molecule or some similar one appears to be volatile in steam since Morey and Hesselgesser[37] found more SiO_2 in steam if Na_2O were present in the solid than if it were not.

$SiO \cdot 4H_2O(g)$ (or $SiO_2 \cdot 3H_2O(g)$): The volatility of SiO_2 in steam has been studied by many workers. Of these, three are outstanding in the field, however.

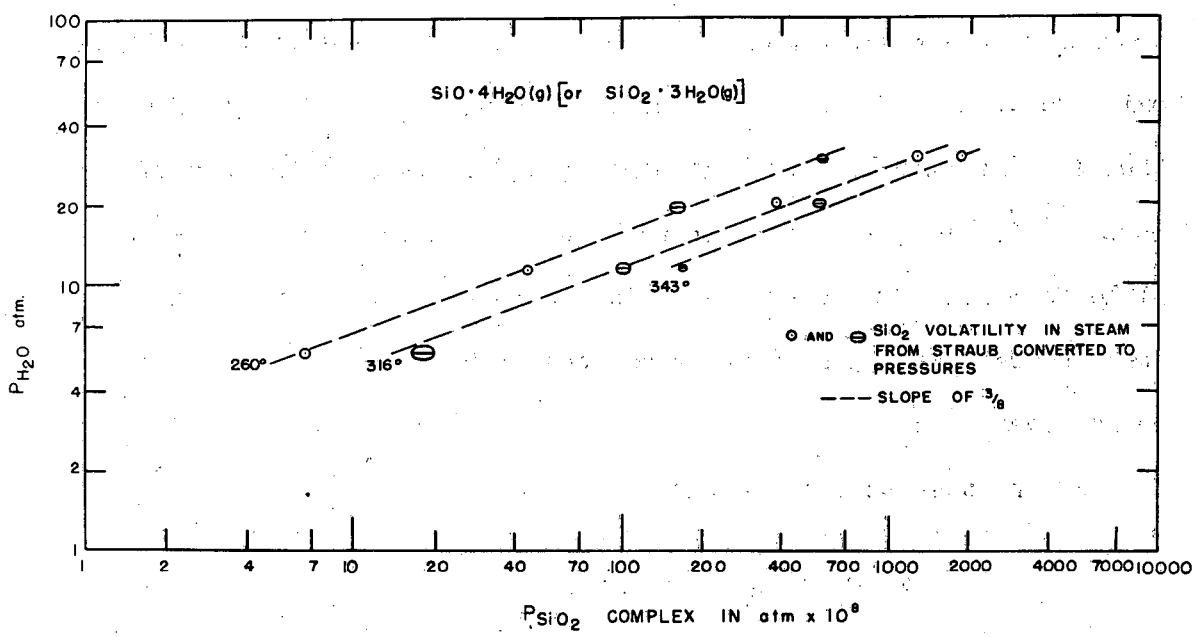
van Nieuwenberg[13] and coworkers showed a remarkable understanding of what was going on in the system in their very early work. Results of their experiments are principally reported with the other oxide volatilities which are discussed in the first section of this thesis. The excellent work of Morey and Hesselgesser[37] and of Straub[12], along with our own work, have been used to fix the possible formulas of this species. The positive assignment of this species must await more work by someone with better equipment than we had available.

If one assumes the reaction:

$$xSiO_2 + yH_2O = \text{volatile species} + zO_2$$

one can fix the single silicon atom from Straub's first power dependence of SiO_2 volatility upon the concentration of SiO_2 in solution at a constant pH and water pressure.

A plot of log P_{H_2O} versus log P_{SiO_2} complex for Straub's data is shown on Fig. 5, the assignment of the possible formulas of the volatile species being based largely on this work for reasons we will discuss shortly. The slope found with the low temperature data is 3/8, although 1/3 is conceivable as a true value if fugacities


SiO·4H2O(g) [or SiO2·3H2O(g)]
260°
316°
343°
⊙ AND ⊖ SiO2 VOLATILITY IN STEAM FROM STRAUB CONVERTED TO PRESSURES
SLOPE OF 3/8
PH2O atm.
PSiO2 COMPLEX IN atm x 10^8
100
70
40
20
10
7
4
2
1
1
2
4
7
10
20
40
70
100
200
400
700
1000
2000
4000
7000
10000

MU3667

FIG. 5

were taken into account. At the higher temperatures the slopes are not exactly constant apparently because the gas imperfections which seem so evident at 400°C (Fig. 6) now appear noticeably.

At this point in the reasoning the assignment of the number of reacting water molecules must await a determination of the oxygen dependence of the reaction. If no oxygen is evolved the volatile species is $SiO_2 \cdot 3H_2O(g)$ with the theoretical slope equal to one third. If 1/2 O_2 is evolved in the reaction, the molecule is $SiO \cdot 4H_2O(g)$ with the theoretical slope being three eighths, the reasoning being that O_2 from the H_2O decomposition is negligible here and therefore 1/2 $P_{SiO \cdot 4H_2O(g)}$ approximates P_{O_2}. Then:

$$K = \frac{(P_{SiO \cdot 4H_2O})(1/2\ P_{SiO \cdot 4H_2O})^{1/2}}{(P_{H_2O})^4}$$

$$\left(\frac{K}{\sqrt{2}}\right)^{2/3} = \frac{(P_{SiO \cdot 4H_2O})}{(P_{H_2O})^{4 \times 2/3}}$$

In order to compare Straub's results with those of Morey and Hesselgesser we made the plot shown on Fig. 6. The function plotted is a little unfair to the latter authors since a best fit of their 500°C data would indicate about a third power dependence on the water pressure. At this temperature their points group fairly well on the plot shown although on extrapolating Straub's data one would expect the group to lie about a factor of ten higher. The 400°C data do not fit at all. This plot must not be interpreted to indicate errors by Morey and Hesselgesser. The error lies in the

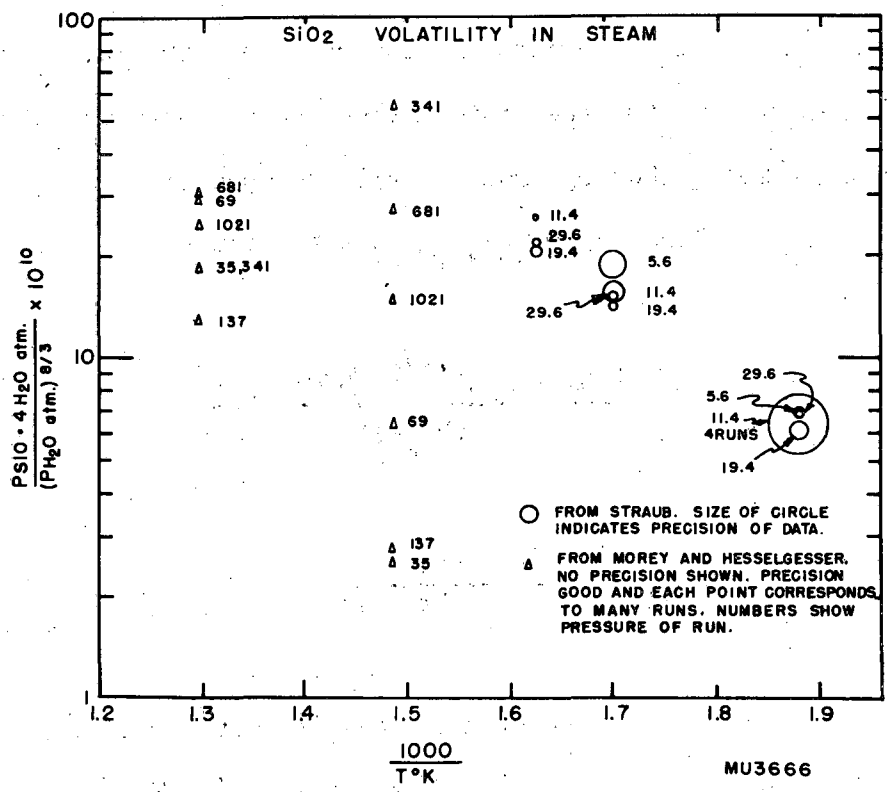

SiO2 VOLATILITY IN STEAM
100
10
1
1.2
1.3
1.4
1.5
1.6
1.7
1.8
1.9
1000 / T°K
PSiO • 4 H2O atm. / (PH2O atm.)8/3 x 10^10
341
681
69
1021
35,341
137
681
1021
69
137
35
11.4
29.6
19.4
5.6
11.4
19.4
29.6
29.6
5.6
11.4
4RUNS
19.4
FROM STRAUB. SIZE OF CIRCLE INDICATES PRECISION OF DATA.
FROM MOREY AND HESSELGESSER. NO PRECISION SHOWN. PRECISION GOOD AND EACH POINT CORRESPONDS TO MANY RUNS. NUMBERS SHOW PRESSURE OF RUN.
MU3666

FIG. 6

insufficiency of our treatment of the data.

There are several conditions prevailing with hydrated silica which did not appear with the hydrated sodium chloride. One is that higher pressures are involved in some of the data. A second is that the silica is less highly hydrated and the outer surface of the molecule is less similar to water. Third, if oxygen is a product, as we believe, its fugacity is not equal to that of $SiO \cdot 4H_2O(g)$ as the plot assumes. Fourth, the error involved in neglecting change of the solid free energy with pressure ($V\Delta P$) is not negligible. The error in the fugacity of the hydrated silica seems to be the largest since approximate corrections of the other errors did not approach bringing these data into line on a log-log plot such as that used for Straub's data.

The excellent internal consistency of Morey's and Hesselgesser's work can be checked by examining their SiO_2 (glass) versus quartz data. They felt that SiO_2 condensing out on glass would necessarily take on a quartz structure. However, this idea conflicts with their own data which show a remarkable consistency for the SiO_2 glass pressures and, except for one point, a nearly constant ratio at a given temperature between the vapor pressure of the glass and quartz. Another case of the silica hydrate not condensing out, as the thermodynamically stable quartz, is found in the coating of glass which developes in steam turbines.

The ratios of gaseous hydrated silica from the corresponding glass and quartz data of these authors are shown in Table VI.

A ΔF for conversion of silica glass to quartz at each of these temperatures can be fairly accurately obtained since gas imperfections

Table VI

Comparison of Silica Glass and Quartz Data.

(From Morey and Hesselgesser)

Temperature °C	P_{H_2O}	$\frac{P_{SiO_2} \text{ from Glass}}{P_{SiO_2} \text{ from Quartz}}$		
		Measured	Solid corrected for VAP	Average
400	2000	6.4	6.5	
	5000	2.7	2.23	2.14
	10000	1.92	2.04	
500	5000	1.65	1.69	
	10000	1.88	1.97	1.80
	15000	1.62	1.75	

practically cancel out. Combining with the data of Moseman and Pitzer[38] and Kelley's[39] high temperature heat content of glass and correcting for the change of solid free energy with pressure leads to a ΔH of fusion at 1983°K of crystoballite of 2273 cal. per mole. This value is from an average of the values of Morey and Hesselgesser at a particular temperature, excluding one questionable point, and is a surprisingly close confirmation of Kracek's value of 1835 cal. per mole selected by Moseman and Pitzer, from quite uncertain data. The variation of the ΔF with temperature checks very closely, this being compared with much more certain data.

We believe, but as yet have not proved, that the volatilization reaction is:

$$SiO_2(s) + 4H_2O(g) = SiO \cdot 4H_2O(g) + 1/2\ O_2(g).$$

Circumstantial evidence comes from the fact that the volatile high temperature species involves hydrated SiO, not SiO_2. (See earlier section of this report). Also SiO_2 itself vaporizes by decomposition to $SiO(g) + 1/2\ O_2(g)$. Morey found sodium silicate to be considerably more volatile in his preliminary[14] than in his later runs[37]. As the presence of some reducing material might greatly increase the silica carried in steam, we wrote to Morey, asking if a rusting of his earlier bomb were a possible means of O_2 removal. He replied that there was no such rusting and that he believes oxygen or hydrogen to be "vanishingly small", although he has not measured or controlled them. As mentioned earlier, the hydrated silica pressures measured in the reported work are larger than the corresponding oxygen pressures

from water decomposition.

To test this oxygen reaction product, we first heated two otherwise identical water containing silica tubes, one filled with argon and the other with oxygen, to about 400° and left them in about 20° temperature gradient for a day. Water pressures were about 100 atmospheres. Although some air undoubtedly got into both tubes as they were being sealed off, there was a large difference in the oxygen pressures in the two tubes. After several hours, noticeable attack had taken place in the argon upon the glass, while the O_2 tube was clear. Finally, after a day, the argon tube was heavily etched (as in an old NaOH bottle) while the oxygen tube showed only traces of etching.

If the rate of diffusion of the gas to the cold portion and SiO_2 precipitation there is rate determining, the data indicate the oxygen dependence of the reaction. If the rate of dissolving off the SiO_2 originally is rate determining and if, further, this rate of dissolution is oxygen dependent, then the conclusions of an oxygen dependence in the equilibrium is not justified.

To get a truly equilibrium measurement of the oxygen dependence, two silica glass tubes were tested simultaneously by holding them at 550°C in a constant temperature copper block for 23 minutes. The first tube, of volume 12.1 cc. when sealed, contained 100 λ of water and about one atmosphere of H_2 at room temperature. The second tube was sealed at 11.1 cc. with 100 λ of water and O_2 at about 1 atmosphere. (See "Experimental" in earlier section). The oxygen filled tube was not etched noticeably, but a microscope showed peculiar

striations almost like finger prints running around the axis of the hydrogen filled tube and indicating a marked equilibrium solubility in this case. The experiment is not conclusive here, either, since the water would dissolve some SiO_2 before it evaporated.

We then tried to dissolve a weighed SiO_2 fiber suspended in the liquid in a copper tube sealed after filling with hydrogen. The copper tube was very difficult to seal either with silver solder or by melting the copper plug to fuse it to the body of the bomb and we were unable to get any runs in which H_2 remained in the bomb.

If silicon would react with H_2O in the tube, we would have a way of introducing H_2 by our reaction, and the silicon plus silica should prove much more volatile than SiO_2 alone. It turned out that we had to heat the tube to about 1000°C before the reaction even started appreciably. In this case a brick red color appeared on the walls of the tube. Again the results are inconclusive, however, because we already know (first section of this paper) that at 1400°C there is an oxygen dependence on the silica carried.

All the evidence we found is indicative of, though not conclusively for, the molecule $SiO \cdot 4H_2O(g)$ as the high pressure volatile species for SiO_2 solubility in steam. Grossweiner and Seifert[2] have reported this molecule as $SiO_2 \cdot 2H_2O(g)$ based on the same work of Straub. They must have made an error in their calculations, since with their treatment which neglected oxygen, they should have obtained three waters of hydration in combination with the SiO_2. Straub, himself, believed he had silicic acid or a hydrate of it.

Section III: Application to Steam Turbine Operation and Geological Theory.

Turbine Operation

The implications of this report are quite important to turbine operations if steam pressures are high. However, the conclusions regarding quartz vaporization cannot be considered absolute until they are confirmed by quantitative studies with varying oxygen (or hydrogen) pressures plus steam in an arrangement like those of Morey and Hesselgesser[37] or Straub[12].

Turbine blade deposits are a subject of enough importance so that a good many theories have been developed to account for them. The theory developed here does not, in general, discredit the older accepted theories. Rather it enlarges upon them and changes the emphasis somewhat. For instance, there is little to be argued between thinking of true solution in a highly compressed gas or compound formation leading to greater volatility. However the idea of specific compound formation explains more than the broader concept of solubility.

Splittgerber's[40] specific data along with other generally known facts available from several authors will be used to show how treatment as gaseous hydrates leads to an understanding of the various types of blade deposits.

NaCl and NaOH show a seventh power dependence on the pressure of water vapor. $SiO \cdot 4H_2O(g)$ shows about a third power dependence (actually 8/3) as discussed earlier. If water vapor is saturated with these

gases, and then the water pressure is cut in half, the pressure of $NaOH \cdot 7H_2O(g)$ and $NaCl \cdot 7H_2O(g)$ will each fall to about $(1/2)^7 = 1/128$ of their former value; on the other hand the $SiO \cdot 4H_2O(g)$ will fall only to about $(1/2)^3 = 1/8$ of its former value. Thus one sees that the pressure drop has some sixteen times the effect on NaOH or NaCl as it does on the SiO_2.

In turbine operations, the gas does not often dissolve enough of the solid to be saturated with respect to it. For this reason the gas may take a considerable pressure drop before it is saturated with respect to a particular solid, thus permitting the solid to separate out. The first few turbine blades may be almost free of deposits. Also along this line, Straub's[12] idea of refluxing the evaporating steam so that the condensing liquid will strip out dissolved salts looks extremely good.

From the power dependence one would expect, as Splittgerber shows, that NaOH and NaCl would predominate in the earlier turbine blades and would then largely disappear. SiO_2, while precipitating on early blades, too, would persist much farther. On the early blades it would react with NaOH to form Na_2SiO_3, however hydrated Na_2SiO_3 apparently carries also in the steam and complicates the interpretation of Splittgerber's data. Sulfates will carry a little, but data are not sufficient to establish any of those volatile molecules. Iron seems to carry with a low H_2O hydrate and for this reason appears all through the turbine blades.

The different character of the SiO_2 precipitates also fits into our picture. If the temperature and pressure are high enough

$SiO \cdot 4H_2O(g)$ reacts with $1/2\ O_2(g)$ to give back $SiO_2(s)$ plus $H_2O(g)$, the system being near enough to equilibrium so that SiO_2 can reach its most stable quartz form. If the gas has cooled and the pressure dropped too much, the $SiO \cdot 4H_2O(g)$ separates out without first oxidizing the SiO to SiO_2. SiO(s) decomposition and oxidation is notorious for yielding glasses rather than crystalline quartz. This latter condition would account for the red, iron-amorphous silica deposit on turbine blades where the steam is almost spent.

Power[41] reports that SiO_2 catalyzes stress corrosion due to NaOH on the steel. If one considers that SiO_2 vaporization frees oxygen, possibly even forming peroxides, one might explain the increased corrosion at that point.

However, by far the most important conclusion to be drawn from the oxygen dependence of the SiO_2 volatility is that it provides a means of controlling the SiO_2 carried. Since SiO_2 is the principal water insoluble precipitate encountered on turbine blades, and since its removal necessitates chipping or the use of harmful NaOH, it is the most important molecule to be controlled in turbine operation.

If high pressure steam plus hydrogen at a few atmospheres is in contact with SiO_2 in the boiler the amount of $SiO \cdot 4H_2O(g)$ will become very large. This is because the equilibrium constant discussed in an earlier section must be maintained. The hydrogen will keep the water from oxidizing the iron. Oxygen may now be bled in and the $SiO \cdot 4H_2O(g)$ will condense out to SiO_2 on the walls. This SiO_2 coating operation could be so controlled as to yield a glassy coating, which would protect the iron. Then O_2 could be deliberately

fed into the operating boiler to prevent SiO_2 carry-over in further operations.

It would take very little oxygen to control the SiO_2 carried. At a constant water pressure and temperature the product of the pressure of $SiO \cdot 4H_2O(g)$ and the square root of the oxygen pressure must be a constant. Thus if the oxygen pressure is increased 100 times (to a total pressure of about 10^{-3} atm., for instance) the $SiO \cdot 4H_2O(g)$ would drop to one tenth of its former value. Some Na_2SiO_3 might carry out, but it would be water soluble.

Geological Theory

Morey's work has been directed toward geological questions. His work explains, for instance, the earlier beliefs that a few percent of water will liquify solid rock if the pressure is high. A better explanation is that even a slight temperature gradient at high pressures will permit steam to transport silica and many other minerals. If pressure is released from steam containing dissolved minerals, the minerals will deposit roughly according to their power dependence on water pressure. The behavior would be quite analagous to the turbine deposits and would account for the concentration of minerals non-uniformly through quartz veins.

More study of these high pressure hydrates can do much for the theory of vein formations.

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Index of Compounds

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Au	20
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Yb_2O_3	11
Zn	20

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