

THERMOCHEMICAL ANALYSES OF THE
OXIDATIVE VAPORIZATION OF METALS AND
OXIDES BY OXYGEN MOLECULES AND ATOMS

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The active use of "near space" envisioned for the 1980's and beyond has revived interest in the effect of oxygen atoms in the gas phase on the oxidative vaporization of metals and metal oxides. Some years ago, we demonstrated that the oxidative vaporization of platinum was markedly enhanced by the presence of oxygen atoms (Ref. 1). More recently, we showed that the oxidative vaporization of Cr_2O_3 was enormously enhanced by oxygen atoms (Ref. 2). Since metal-oxygen systems such as these are numerous, a method of predicting rates of oxidative vaporization from equilibrium thermodynamic data would be valuable. Jansson and Gulbransen (Ref. 3) have utilized equilibrium thermochemical diagrams for a number of metal-oxygen molecule systems to predict oxidative vaporization behavior.

We have shown (Ref. 2) that thermochemical diagrams could be used to interpret the rates of oxidative vaporization in the chromium-oxygen atom system and to predict in a quantitative manner the effect of oxygen atom exposure in this system. Qualitatively, the effect of adding atomic oxygen to a metal-oxygen system is equivalent to increasing the chemical potential of oxygen. Enhanced oxidation in oxygen atoms should be exhibited by any metal or oxide for which there exists a stable gaseous oxide of high volatility with the metal atom in a higher oxidation state, provided the conditions of pressure and temperature are appropriate. In this paper the thermochemical method has been applied to the chromium-, platinum-, aluminum-, and silicon-oxygen systems. Maximum rates of oxidative vaporization are predicted in oxygen molecules and atoms, and oxidation enhancements in oxygen atoms are presented. Predicted results are compared with experimental results for the chromium and platinum systems.

In the chromium system, enhanced vaporization of condensed phase Cr and Cr_2O_3 is facilitated by the CrO_3 and its polymers. The enhancements calculated for the case of Cr_2O_3 with $P_{\text{O}_2}=1.5 \times 10^{-4}$ atm and $P_{\text{O}}=3.8 \times 10^{-6}$ atm vary from 10^{20} at a temperature of 200°C to 10^9 at 550°C and 10^2 at 1000°C . Experimental values at the high and low temperatures are in good agreement with predicted values of enhancement; at intermediate temperatures the experimental values of enhancement are considerable lower than predicted. The

reason for the disagreement at the intermediate temperatures may be due to (1) recombination of oxygen atoms, resulting in a concentration on the surface which is somewhat lower than that in the gas phase or (2) the destabilization of the CrO_3 polymers as the temperature increases.

Figures 1 and 2 give a thermochemical description of the platinum-oxygen system at 1400K and show regions of stability for the condensed phases Pt, Pt_3O_4 and PtO_2 and vapor pressures of gaseous PtO_2 , PtO and Pt. Both $\text{PtO}_2(\text{g})$ and $\text{PtO}(\text{g})$ lead to enhanced vaporization of platinum over the platinum condensed phase. In Figure 3 the calculated and experimental rates of platinum vaporization are given for the conditions studied by Fryburg (Ref. 1) which are $P_{\text{O}_2}=6.58 \times 10^{-4}$ atm and $P_{\text{O}}=4.61 \times 10^{-5}$ atm. The calculated and experimental values of the oxygen atom enhancements are shown in Figure 4. The lack of better agreement between the values is probably due to the large amount of oxygen atom recombination on platinum which results in a lower concentration of atoms on the surface able to react with the metal.

For the aluminum system, the AlO_2 molecule should lead to enhanced vaporization of the Al_2O_3 phase. However, the magnitude of the predicted enhancement is small compared to those for chromium or platinum. In the silicon system, $\text{SiO}(\text{g})$ should lead to enhanced vaporization of the silicon phase, whereas the SiO_2 condensed phase can be unaffected or even somewhat stabilized by oxygen atoms.

References

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3. S.A. Jansson and E.A. Gulbransen, Fourth Int'l Congress on Metallic Corrosion, Amsterdam, Netherlands, Sept. 7-14, (1969). p, 77; S.A. Jansson, J. Vacuum Sci. Technol. 7, S5 (1970).

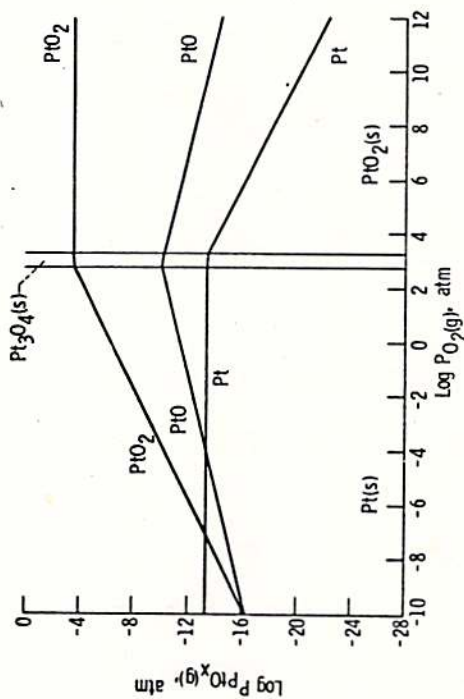


Figure 1. - Equilibrium thermochemical diagram for the platinum - oxygen system at 1400 K.

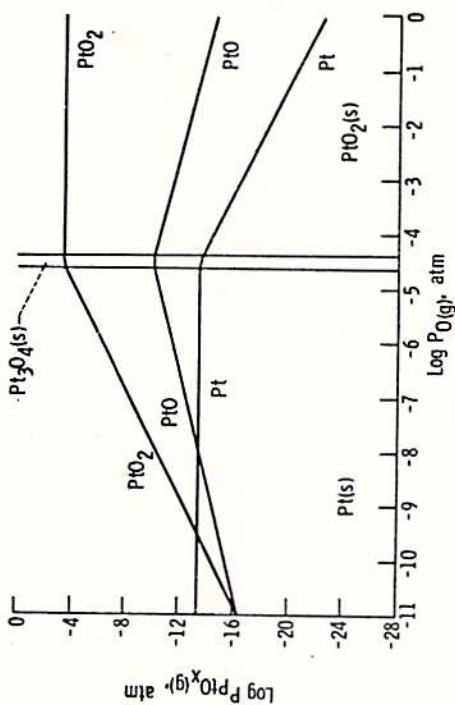


Figure 2. - Equilibrium thermochemical diagram for the platinum - atomic oxygen system at 1400 K.

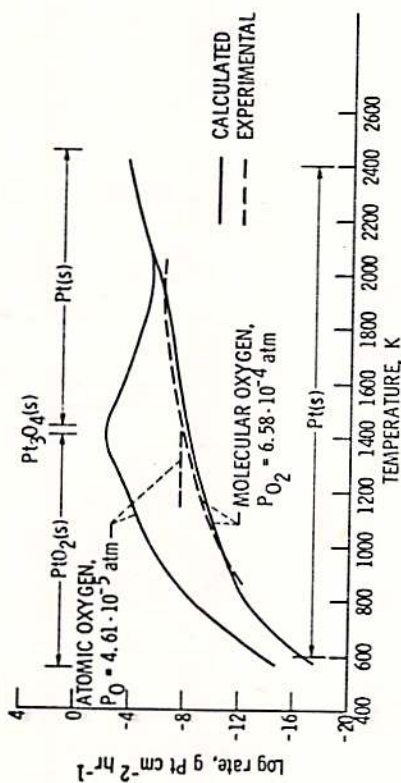


Figure 3. - Calculated and experimental rates of oxidative vaporization of platinum and platinum oxides in partially atomic and molecular oxygen.

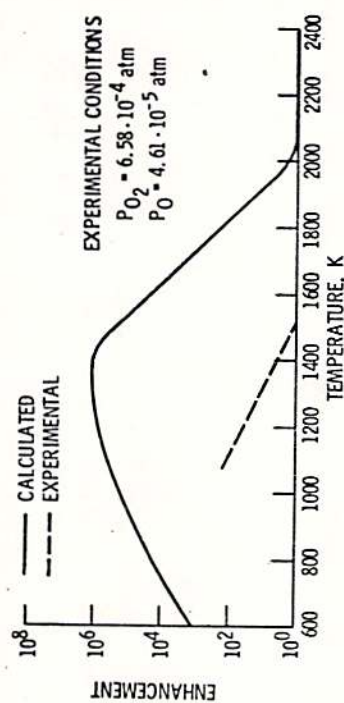


Figure 4. - Enhancement of oxidative vaporization of platinum in partially atomic oxygen.

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Enclosed is a copy of the long abstract which we have submitted to ECS.

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Regards,
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(Title of paper) Thermochemical Analyses of the Oxidative Vaporization of Metals and
Oxides by Oxygen Molecules and Atoms

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Equilibrium thermochemical analyses are employed to describe the vaporization processes of metals and metal oxides upon exposure to molecular and atomic oxygen. The effect of adding atomic oxygen to a system is equivalent to increasing the chemical potential of oxygen. As a consequence, enhanced oxidation in oxygen atoms should be exhibited by any oxide for which there exists a stable, gaseous oxide of high volatility with the metal atom in a higher oxidation state. Specific analytic results for the chromium-, platinum-, aluminum-, and silicon-oxygen systems are presented. Maximum rates of oxidative vaporization predicted from thermochemical considerations are compared with experimental results for chromium and platinum.

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Leisz, Denise (Summer Employee), 5132

Examination of Oxidative Vaporization Processes by Means of Thermochemical Diagrams

Equilibrium thermochemical diagrams can be used to graphically display the behavior of various systems under specified conditions. The purpose of this work was to determine if these diagrams could be used to predict the rates of reactions of metals or metal oxide condensed phases with atomic oxygen. Diagrams describing the oxidative vaporization of various metals or oxides with molecular oxygen have been employed successfully in the past to illustrate the mode of vaporization for a number of metal-oxygen systems including chromium, silicon, molybdenum, and tungsten.

The main thrust of the present work was threefold: (1) to construct diagrams for the atomic and molecular oxygen reactions with condensed phases; (2) to compare the theoretically predicted behavior of atomic versus molecular oxygen; i.e., enhancement or depression of the vaporization rates with atomic oxygen; and (3) to correlate these theoretical predictions with the experimental results described in the chemical literature.

The systems for which diagrams were completed are Al, B, Pt, C, Re, Si, Ir, W, and Mo. The diagrams are plots of partial pressures of the metal atoms and various oxide molecular species versus oxygen pressure at a given temperature. The temperature range for which diagrams were drawn for a specific system varied, but fell between 600 and 2400K.

For the systems Al, B, Pt, C, Re, and Ir, overall rates of oxidative vaporization were calculated at a particular oxygen molecule or atom pressure. From these results, enhancement curves were obtained. All of the systems for which diagrams were completed showed a theoretical enhancement except for silicon.

The results for the platinum system were compared exhaustively with the experimental data. Good agreement between the theoretical and experimental results were demonstrated. No experimental data were available for Al, B, or Ir. Comparisons have yet to be made for C, Re, Mo, and W. In addition, calculations for the U-O system were begun.

It is our hope that some of these results may be incorporated into a future publication after additional work and deliberation are completed. This project was a cooperative effort with Fred Kohl, George Fryburg, and Carl Stearns.