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Low-Cost
Solar Array Project

MASTER

Silicon Preparation and Purity from the Reaction of Sodium with Silicon Tetrafluoride and Silicon Tetrachloride

A Thermochemical Study

Robert A. Rhein

April 15, 1979

Prepared for
U.S. Department of Energy
Through an agreement with
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The JPL Low-Cost Solar Array Project is sponsored by the Department of Energy (DOE) and forms part of the Solar Photovoltaic Conversion Program to initiate a major effort toward the development of low-cost solar arrays.

ABSTRACT

Thermochemical equilibrium computations for the preparation of silicon (Si) by the reaction between sodium (Na), either liquid or vapor, with silicon tetrafluoride (SiF_4) and silicon tetrachloride ($SiCl_4$) are presented. Computations indicate that SiF_4 reacts with either liquid or gaseous Na to produce temperatures sufficiently high to form molten Si. Liquid Na reacts with SiF_4 to produce substantially higher Si yields than does the free combustion reaction with Na vapor; however, the Na vapor/SiF_4 reaction, if temperature-constrained at the Si melting point, produces an expected Si yield close to 100%.

A stoichiometric mixture of liquid Na and $SiCl_4$ vapor reacts to produce liquid Si, gaseous sodium chloride (NaCl), and a small concentration of Si subhalides. Gaseous Na, however, reacts with $SiCl_4$ to form entirely gaseous reaction products and a high yield of Si (liquid) but subhalide concentrations are greater than when liquid Na is used.

The reactions of a number of impurity elements in Na, during the course of the Na-Si halide reaction, have been described. Of those considered, only calcium (Ca), magnesium (Mg), phosphorus (P), and strontium (Sr) are expected to co-exist to any extent in Na vapor and none is expected to be in the Si products if excess Si halide is used in the Na-Si halide reactions.

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Figures

SECTION I

INTRODUCTION

One of the objectives of the Silicon Material Task of the Low-Cost Solar Array Project (JPL/DOE) is the development of a process for producing Si at a price of less than \$10/kg (1975 \$). Included among the various endeavors to accomplish this objective are those using reactions of Na with silicon tetrahalides.

The preparation of Si by alkali metal reduction of Si tetrahalides is not new. Gay Lussac and Thenard in 1811 reduced SiF_4 with Na at 673-773 K. In 1896, Moissan stated that the Si product from alkali metal reduction was liable to be impure because the great heat generation of the reaction resulted in attack of the vessel in which the reaction is conducted (Reference 1).

Recently, however, attention has been directed toward the preparation of high-purity Si by this method, since the reactants can be obtained in fairly high purity. Kamanar and Grdenic (Reference 2) produced Si containing 1 ppm (by weight) Mg, 1 ppm copper (Cu), and 1 ppm iron (Fe) by the vapor-phase reduction of $SiCl_4$ and SiF_4 with Na vapor. Presently, there are three groups in the Task program attempting to prepare solar-cell-grade Si by the reaction of alkali metals and Si tetrahalides: Nanis and co-workers of SRI International by burning Na in SiF_4 (Reference 3); Olson et al of AeroChem Research Laboratories by the vapor-phase combustion of Na and potassium in SiF_4 and $SiCl_4$ (Reference 4); and Fey et al of Westinghouse by arc-heated H_2/Ar mixtures interacting with Na and $SiCl_4$ (Reference 5).

The purpose of this report is to describe the predicted reaction temperatures and product compositions resulting from computer-assisted thermodynamic analyses of the reaction of Na and the Si tetrahalides under various initial conditions and under the assumption that the reactants contain some of the elemental impurities commonly found in commercial Na.

The computer program and thermodynamic data used herein are taken from the report by Gordon and McBride (Reference 6). This report describes the equilibrium compositions of chemical species that are predicted in a chemical reaction for an isenthalpic, or combustion, reaction at one atm pressure (there, the reaction temperature is also computed), and for reactions where both the temperature and pressure (one atm) are specified. The reactants are liquid Na (370.5 K); Na vapor (1187 K); SiF_4 gas (298.15 K), and $SiCl_4$ gas (370.5 K).

The fate of certain impurity elements, assumed present in small concentrations in elemental Na, during the reaction between Na and Si tetrahalides was also computed by the thermodynamic equilibrium program. The impurity elements considered were aluminum (Al), boron (B), Ca, Cu, Fe, Mg, manganese (Mn), nickel (Ni), P, and Sr. The thermodynamic data for these elements, their fluorides, chlorides, and, where available, their silicides were obtained primarily from the JANAF tables. Some of the data were obtained courtesy of Dr. Sanford Gordon at NASA-LEWIS, and the remainder were obtained from the collections of Barin and Knacke (References 7, 8) and in a paper by Brewer et al (Reference 9).

The concern with impurities in the reaction products arises from the fact that very small concentrations of a number of impurity elements in Si can seriously degrade the efficiency of solar cells fabricated from this Si (References 10, 11). Here, the impurity elements in the reactants would become, in the reaction product, either unchanged as the element, or become the silicide or halide. It was assumed that if an impurity is in the elemental form or as a silicide in the reaction product, then it ends up in the Si product, where it may be expected to degrade the performance of a solar cell made from this Si. However, if the impurity becomes a halide in the reaction product, then it would presumably associate with the Na halide and not be in the product Si.

SECTION II

RESULTS AND DISCUSSION

A. THE REACTION OF SODIUM WITH SILICON TETRAFLUORIDE

Figure 1 shows the computed reaction temperature for Na liquid and Na vapor reacting with SiF_4 vs the ratio (moles SiF_4)/(4 moles Na). Of interest is that at stoichiometry, i.e., (moles SiF_4)/(4 moles Na) = 1.0, the reaction temperature, 1790 K, is the same for both liquid and gaseous Na reactants. Figure 2 shows that for the isenthalpic combustion of Na vapor with SiF_4, the equilibrium product composition includes substantial unreacted Na and SiF_4, a relatively poor yield of Si, and substantial amounts of Si subfluorides. Figure 3 shows that a good yield of Si is expected from the reaction of liquid Na with SiF_4. An excess of SiF_4 has little effect on the Si yield, but results in less unreacted Na and substantial quantities of Si subfluorides.

Indicated in Figure 4 are the expected concentrations at various temperatures for the temperature-constrained Na/SiF_4 reaction. Si yield is essentially the same from 1300 K to 1693 K, but the concentrations of the other species are dependent upon mixture ratio and temperature. This situation may be realized physically from the combustion of either liquid or vapor Na with SiF_3, with sufficient heat abstraction from the reaction to constrain the temperature to the given constant level.

B. THE REACTION OF SODIUM WITH SILICON TETRACHLORIDE

In Figure 1 it is shown that there is a range of mixture ratios, 0.8-1.1, wherein the combustion temperature is above the Si boiling point (2560 K) for the reaction of Na vapor with $SiCl_4$. In all cases, the combustion temperature is above the melting point of Si (1693 K). Figures 5, 6, and 7 show that, under a variety of initial conditions, the reaction of Na and $SiCl_4$ produces nearly a 100% yield of Si. Under some conditions, such as excess $SiCl_4$ and elevated temperatures, Si subchlorides are also anticipated.

C. IMPURITY TRANSFER FROM REACTANTS TO PRODUCTS

These calculations were performed assuming the impurity elements considered here originate in commercial Na and the concentrations are the maximum values found in several published tables (Reference 12).

Assuming 8 ppm (by weight) Al in the Na, Figures 8 and 9 indicate that the reaction of Na with SiF_4 is expected to produce Al fluorides that presumably would not associate with product Si. However, at 1155 K, Al has a vapor pressure of 0.01 microns (13.2 ppb) (Reference 13), indicating the presence of negligible Al concentration in Na vapor. It is seen in Figures 10 and 11 that, for the reaction of Na and $SiCl_4$, any Al impurity in the Na would end up as the chlorides of Al except at lower temperatures and excess Na reactant. These results are similar to those achieved by Harvey (Reference 14), who indicated that around 15% of Al present in the reactants transferred to Si product for the reaction of a stoichiometric mixture of Na and $SiCl_4$ and product temperatures 1700-2100 K.

Any B present in Na vapor would, in the course of reaction with SiF_4, become B fluorides. Ordinarily, however, B would not be expected in Na vapor, as the vapor pressure of B is much less than 0.1 micron at 1163 K (Reference 13). If B is present in Na, the reaction of Na with SiF_4, constrained at lower temperatures, Figure 13, would result in elemental B under conditions of excess Na. This B could presumably be present in the product Si. A similar result is indicated for the reaction of Na and $SiCl_4$, Figure 14. However, Harvey (Reference 15) indicated that, in the stoichiometric Na/$SiCl_4$ reaction, all the B initially in the Na would be in the product Si.

Some Ca impurity may be present in Na vapor, as the vapor pressure of Ca at 1187 K, computed from the data of Stull (Reference 16), is 4 torr. Figures 15-18 show that, for the reaction of Na with either SiF_4 or $SiCl_4$, the Ca ends up primarily as the halide and that a very small amount of Ca is expected in the Si product, particularly in the case of excess Si halide reactant.

If Cu is present in the Na, it was found to be totally unreactive in the presence of SiF_4 and would presumably end up in the Si product. However, in the Na/$SiCl_4$ reaction, Figure 19, it is seen that for an excess of reactant $SiCl_4$, with the reaction temperature held at 1685 K (Si melting point), a very small concentration of elemental Cu is anticipated. However, for an excess of Na, Figure 19, the Cu is computed to be unreactive, ending up in the product as elemental Cu, presumably to become an impurity in the Si product. Harvey (Reference 17) similarly concluded that, at 1900 K, all Cu in the reactants is found in the liquid Si product. The vapor pressure of Cu is sufficiently low (0.01 micron at 1215 K) (Reference 13) so that Cu would be absent in Na vapor or distilled Na.

Fe was found to be essentially unreactive in the Na/SiF_4 reaction, presumably ending up in the Si product, Figure 20. In the Na/$SiCl_4$ reaction, excess $SiCl_4$ resulted in the Fe conversion to $FeCl_2$ (temperatures 1200-1600 K), Figure 21; however, at stoichiometry and for excess Na, the Fe remains as the element, presumably to dissolve in the Si product. Harvey (Reference 12) concluded that, at 1900 K, the Fe in the reactants ends up in the Si product. Fe, however, has negligible vapor pressure (Reference 13) at 1163 K (0.01 micron at 1380 K) and hence would be absent in Na vapor or distilled Na.

Mg can be expected to be found in Na vapor as the vapor pressure computed from the data of Stull (Reference 16) at 1163 K is 105 torr.

In the combustion reactions of Na with either SiF_4 or $SiCl_4$, free Mg is expected, as shown in Figures 22 and 23. However, in the temperature-constrained reactions of Na with either SiF_4 or $SiCl_4$, see Figures 24 and 25, excess Si halide can be expected to result in a very small concentration of Mg associated with the product Si.

Mn impurity would end up in the Si product for the Na/SiF_4 reaction, as seen in Figure 26. However, in the Na/$SiCl_4$ reaction, Mn would convert to the chloride in the presence of excess $SiCl_4$, thereby presumably not associating with the Si product; for excess Na, however, the Mn would pass through the reaction unchanged, Figure 27, and likely end up in the Si. Harvey (Reference 14) stated that for reaction temperatures 1700-2100 K, approximately 74% of Mn in the reactants would end up in the Si. Using the data of Stull (Reference 16), Mn has a computed vapor pressure at 1163 K of 2.6 microns; assuming Raoult's law to apply, the Mn concentration in Na vapor or distilled Na would be negligible.

Ni forms a stable silicide in either Na/SiF_4 or Na/$SiCl_4$ reactions and thus would presumably be found in the Si product. Ni has a vapor pressure of 0.01 microns at 1415 K (Reference 13), so it would be absent in Na vapor or distilled Na.

Computations indicate that P impurity would not react in either the Na/SiF_4 or Na/$SiCl_4$ systems. Harvey (Reference 15) stated that for the Na/$SiCl_4$ reaction, for temperatures 1700-2100 K, the P content expected in Si product would be several orders of magnitude less than in the reactant; it may be assumed that a similar conclusion would apply to the Na/SiF_4 reaction. P has a boiling point of 704 K (Reference 13), and thus should be easily removed from Na by distillation if desired.

Sr at 1163 K has a computed vapor pressure of 12 torr, based upon the data of Stull (Reference 16); hence it may well be present in Na vapor. Figure 28 shows that, in the Na vapor/SiF_4 reaction, the concentration of free Sr in the products is some three orders of magnitude less than that in the reactants. Figure 29 shows that the anticipated concentration of elemental Sr in the reaction products held at 1693 K is some two orders of magnitude less in the presence of excess Na, and some four orders of magnitude less in the presence of SiF_4, than in the reactants initially. For the Na/$SiCl_4$ reaction, Figure 30 shows that, for the Na vapor reaction, elemental Sr in the product is several orders of magnitude less than in the reactants, and decreases with increasing $SiCl_4$/Na ratio. Figure 31 shows that, for the temperature-constrained reaction, elemental Sr is absent in mixtures with excess $SiCl_4$, although some elemental Sr can be expected in Na-rich mixtures. Consequently, little if any elemental Sr is expected to be in the Si product.

In some additional work, Harvey (References 14, 15, 17, 18) showed that, for stoichiometric Na/$SiCl_4$, titanium (Ti) (at 1900 K), molybdenum (Mo) (1900 K), zirconium (Zr) (1900 K), chromium (Cr) (1700-2100 K), and vanadium (V) (1700-2100 K) would transfer to liquid Si product if these elements were present initially in the reactants.

However, the vapor pressures of these elements would be very low at 1163 K (i.e., Na boiling point): Ti, 0.01 micron at 1594 K; Mo, 0.01 microns at 2260 K; Zr, 0.01 microns at 2110 K; Cr, 0.01 microns at 1335 K; and V, 0.01 microns at 1705 K. Consequently, these impurity elements can all be removed by Na distillation or the use of Na vapor as a reactant.

SECTION III

CONCLUSIONS

Based upon thermochemical equilibrium calculations and subject to the accuracy of the thermodynamic data used, it is concluded that, in the preparation of Si by the reaction of SiF_4 with Na, the reaction of liquid Na or the temperature-constrained reaction of Na vapor is to be preferred over the combustion reaction of Na vapor. In this reaction, assuming liquid Si is the desired product, both liquid and gaseous Na produce liquid Si as a reaction product, but liquid Na produces liquid Si in higher yield and fewer subhalide side-products than does the combustion reaction with gaseous Na.

In the preparation of Si by the $Na/SiCl_4$ reaction, the use of liquid Na produces liquid Si in high yield with only small quantities of subhalide by-products. However, the use of gaseous Na can produce entirely gaseous reaction products and at the same time a fairly high yield of Si. This reaction is potentially useful for processes designed to separate gaseous Si from the other gaseous reaction products.

The reaction of a number of impurity elements in Na during the course of the Na/Si halide reaction has been described. The impurity elements, including those considered by Harvey (References 12, 14, 15, 17, 18), are Al, B, Ca, Cr, Cu, Mg, Mo, Mn, Ni, P, Sr, Ti, V, and Zr. Of these, only Ca, Mg, P, and Sr may be found to any extent in Na vapor or distilled Na. Of these, P is not expected to be present in the Si product, and Ca, Mg, and Sr concentrations expected in liquid Si product would be very low if excess Si halide were used during the course of the reaction.

For SiF_4 reactant, it is recommended that either distilled Na liquid or temperature-constrained Na vapor reaction be used. For a $SiCl_4$ reactant, either distilled liquid Na or Na vapor should be used.

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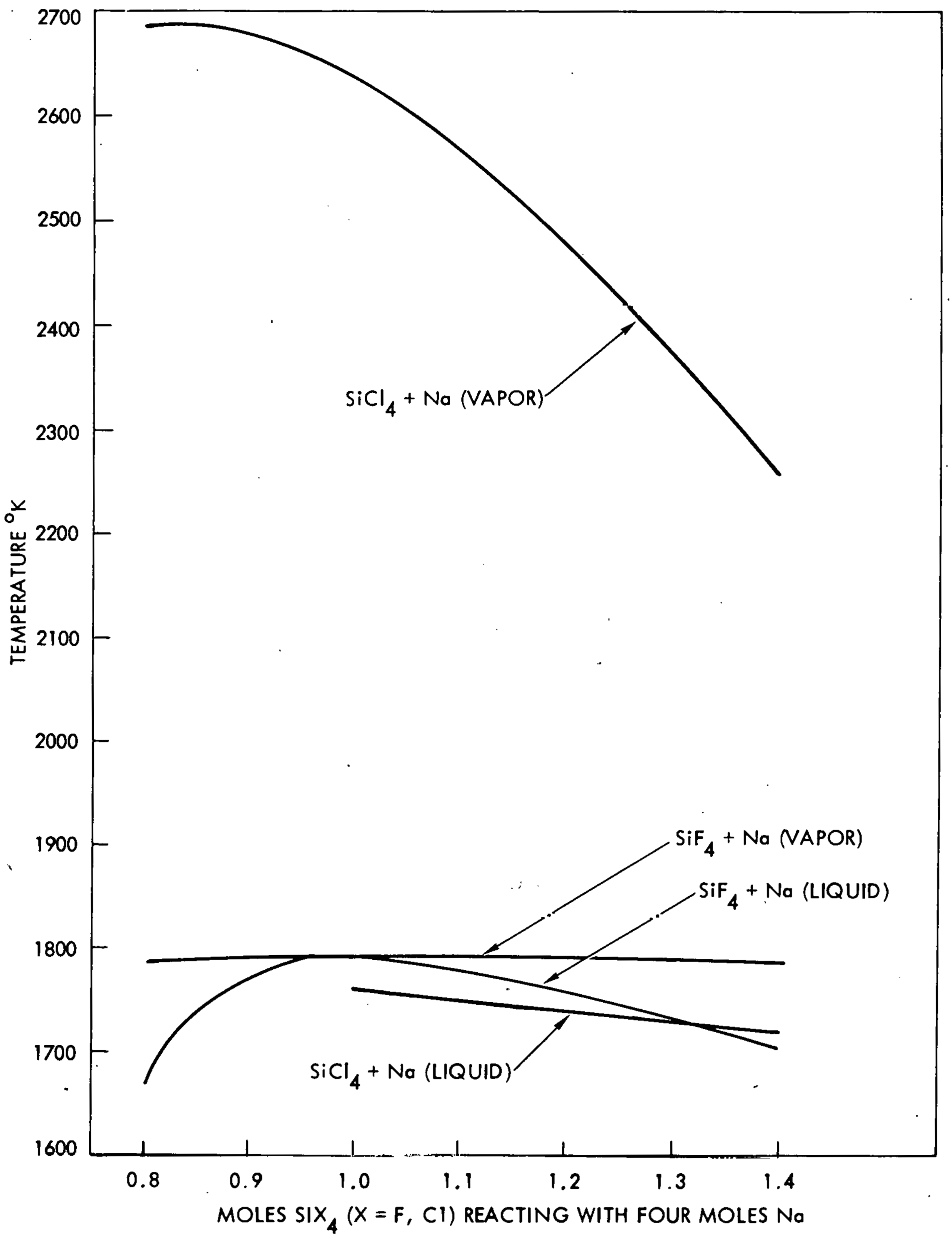

Figure 1. Computed Temperature Resulting from the Combustion of Na (Liquid and Vapor) with SiF_4 and with $SiCl_4$

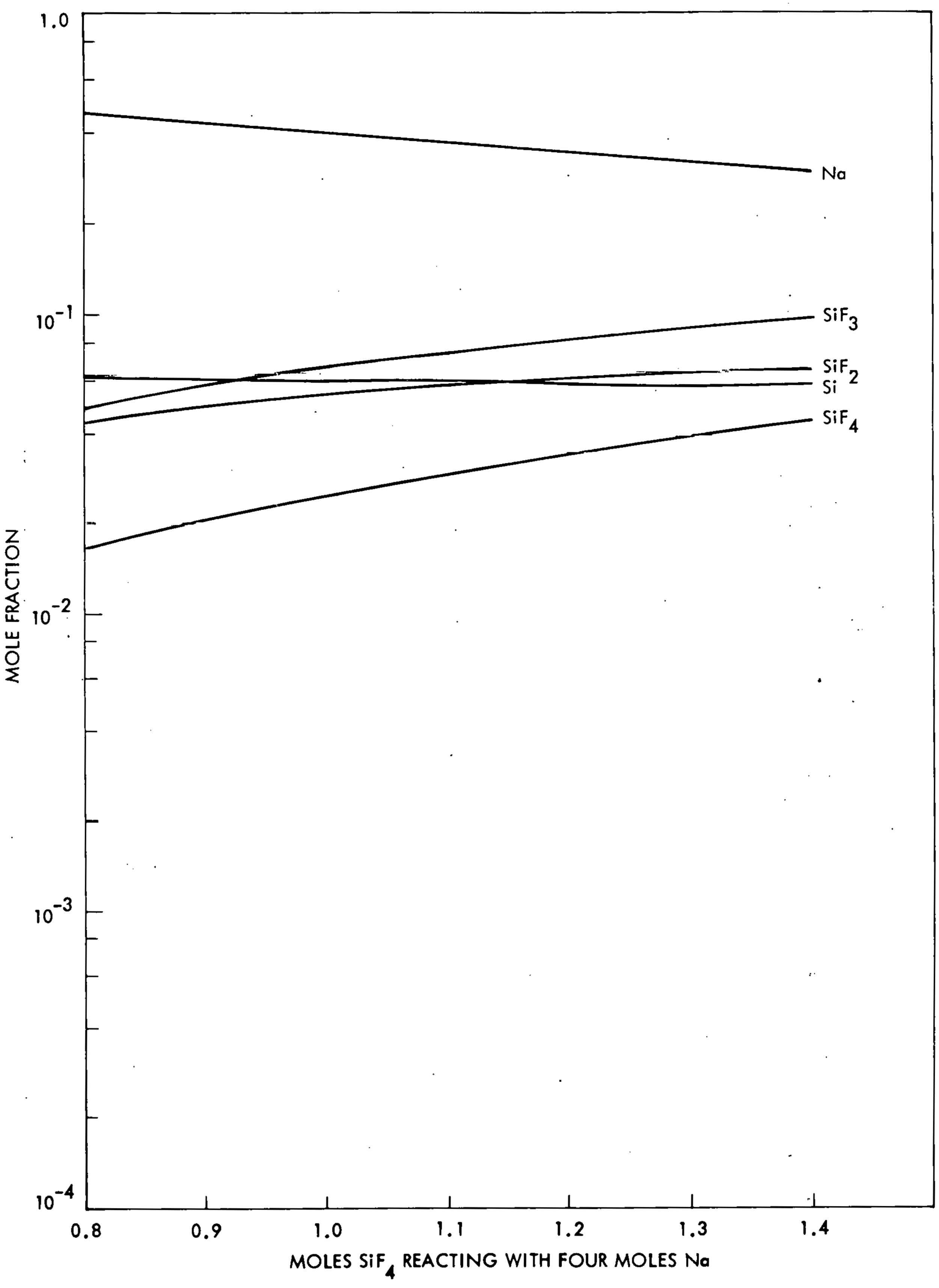

Figure 2. Computed Reaction Products from the Combustion of Na Vapor with SiF_4

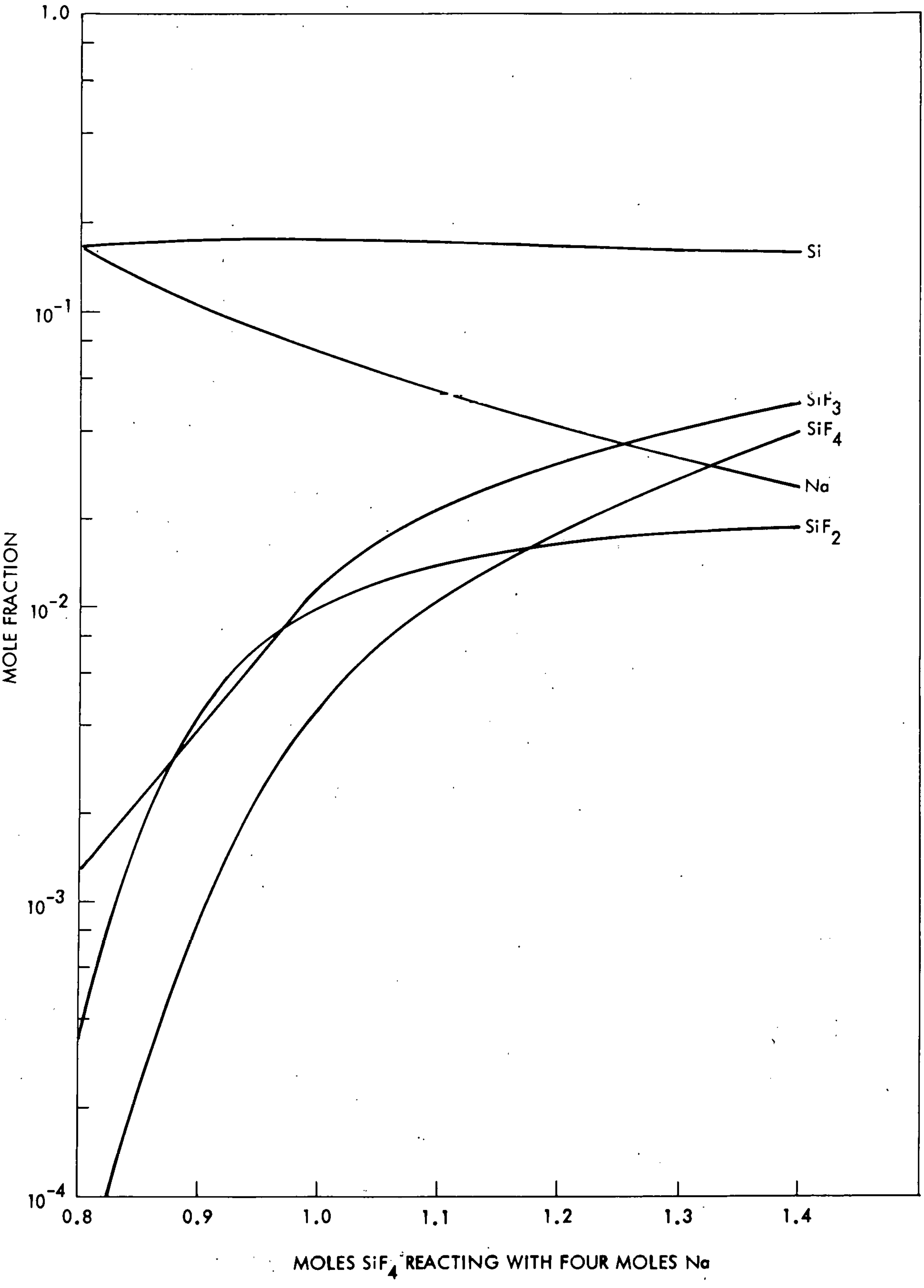

Figure 3. Computed Reaction Products from the Combustion of Na Liquid with SiF_4

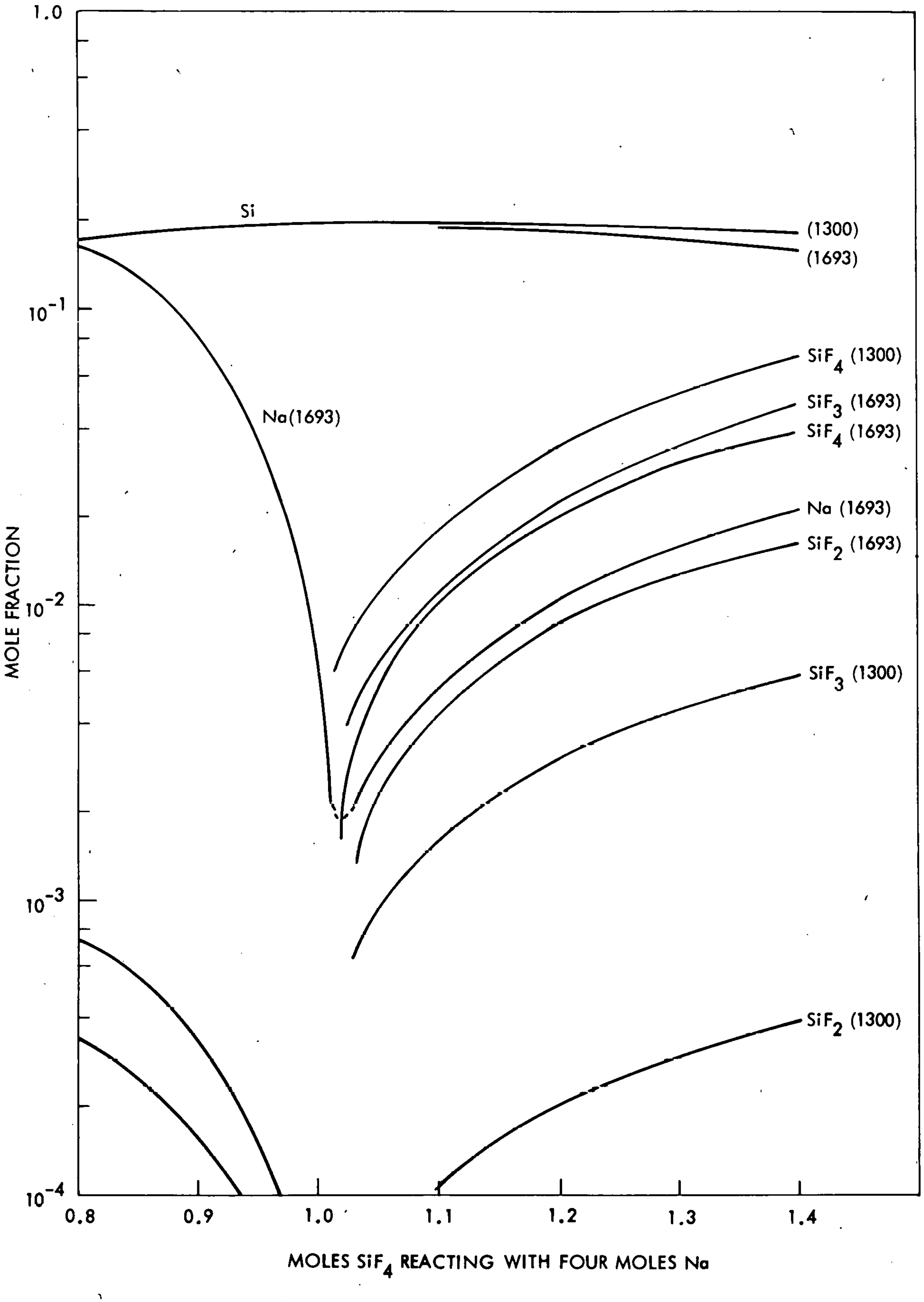

Figure 4. Computed Product Concentrations from the Reaction of Na with SiF_4 at Constant Temperature

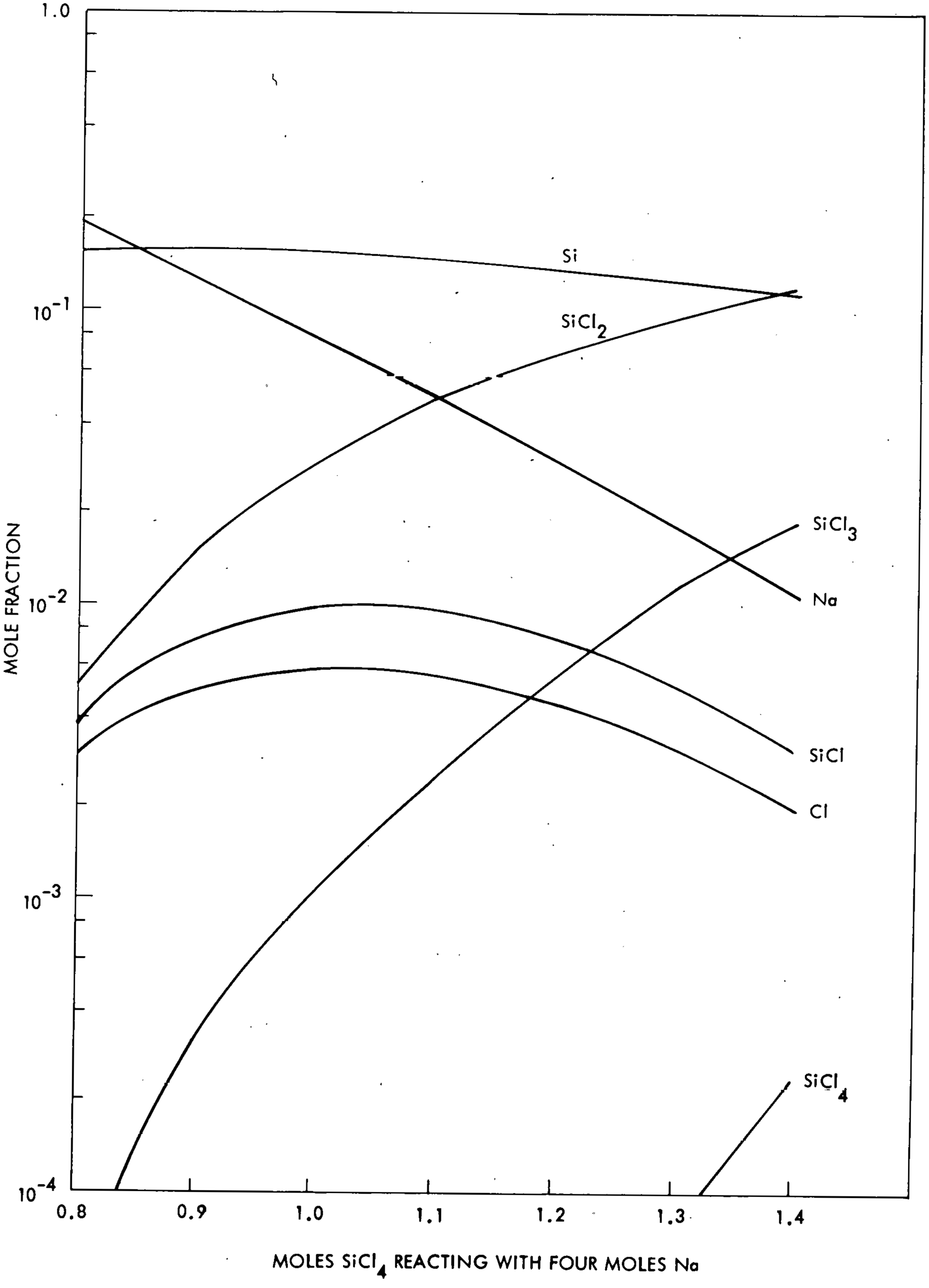

Figure 5. Computed Reaction Products from the Combustion of Na Vapor with $SiCl_4$

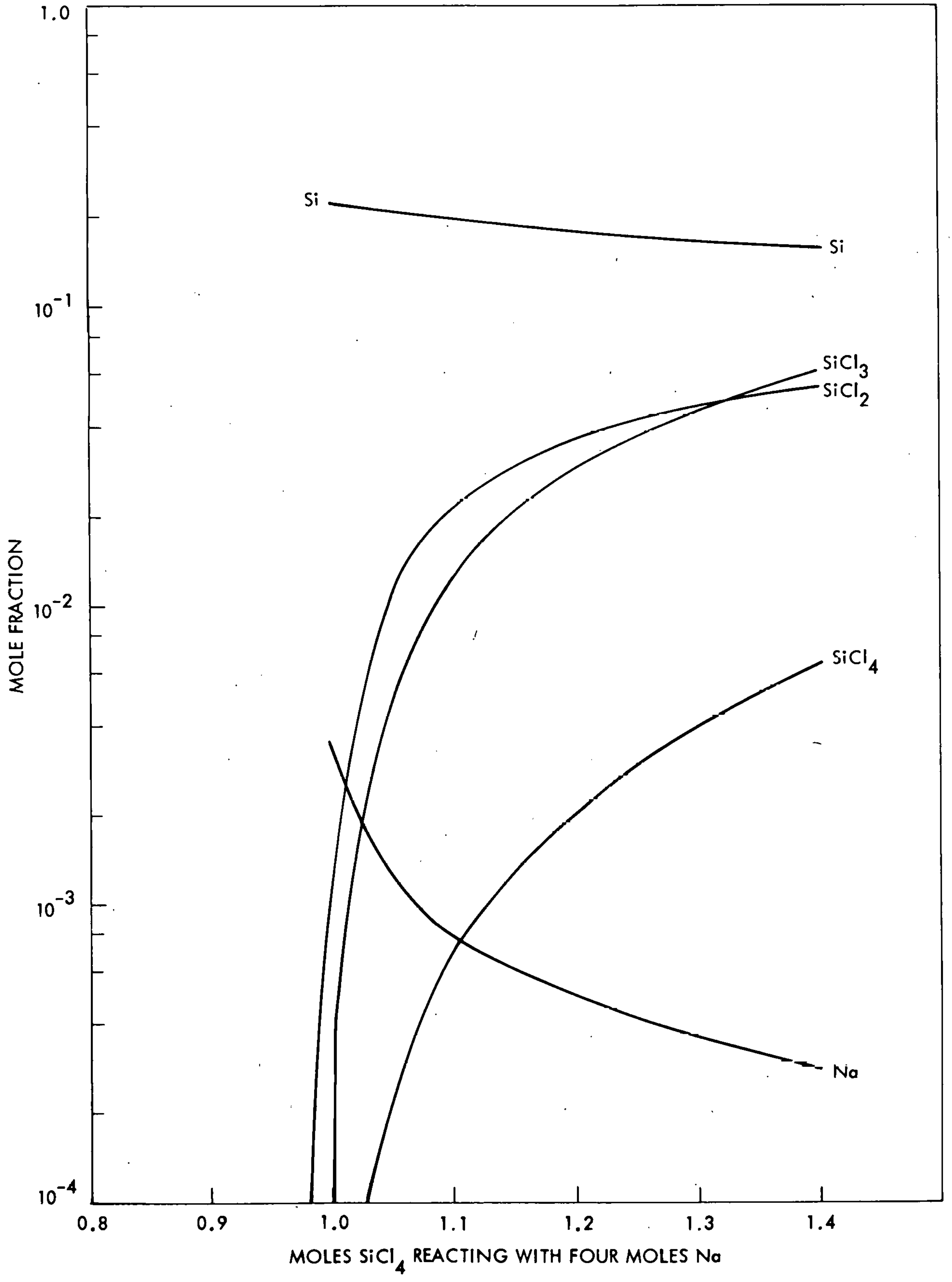

Figure 6. Computed Reaction Products from the Combustion of Na Liquid with $SiCl_4$

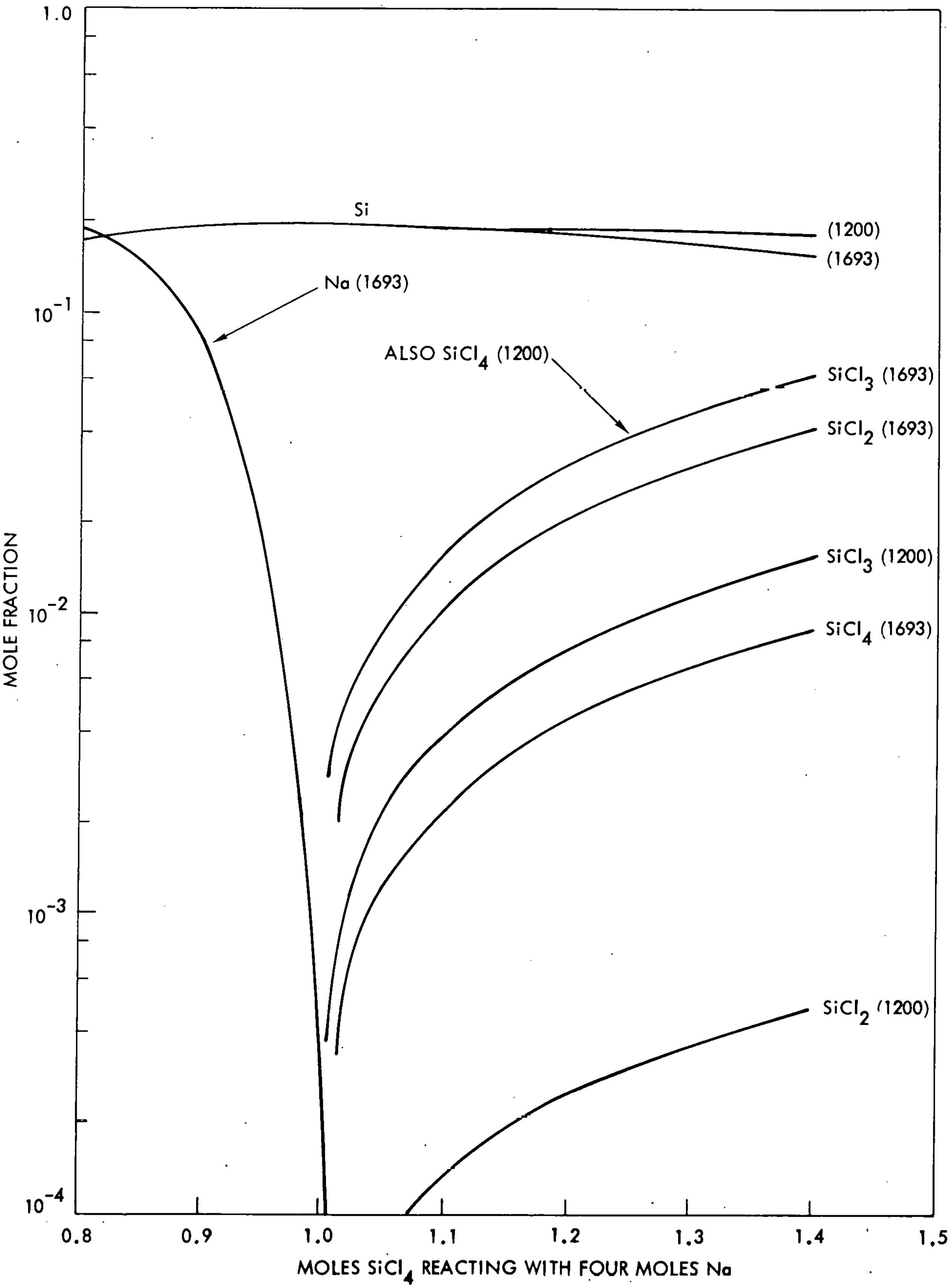

Figure 7. Computed Product Concentrations from the Reaction of Na with $SiCl_4$ at Constant Temperature

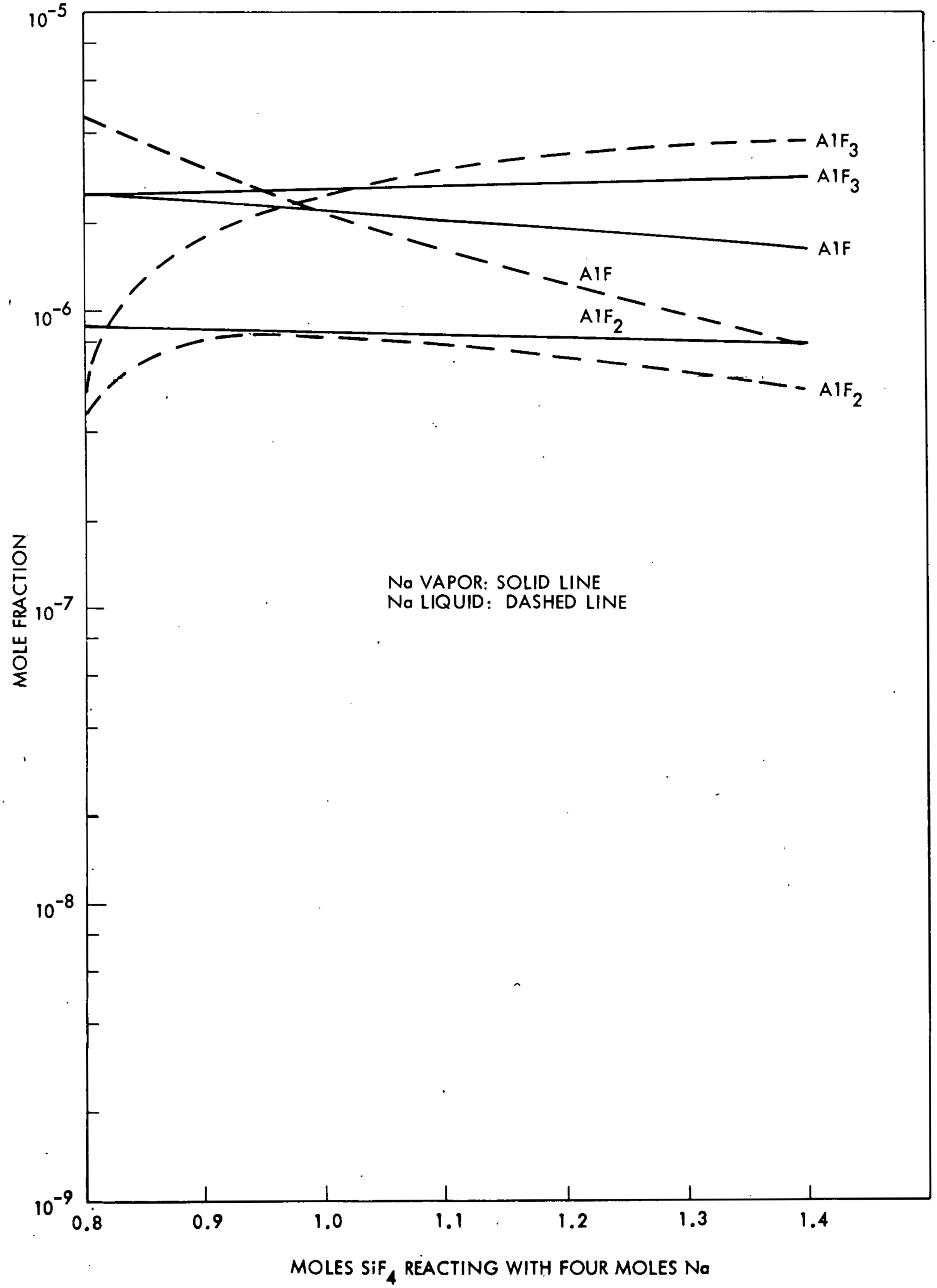

Figure 8. Computed Concentrations of Al Species Resulting from the Combustion of SiF_4 with Na (Liquid and Vapor) Containing 8 ppm (wt) Al

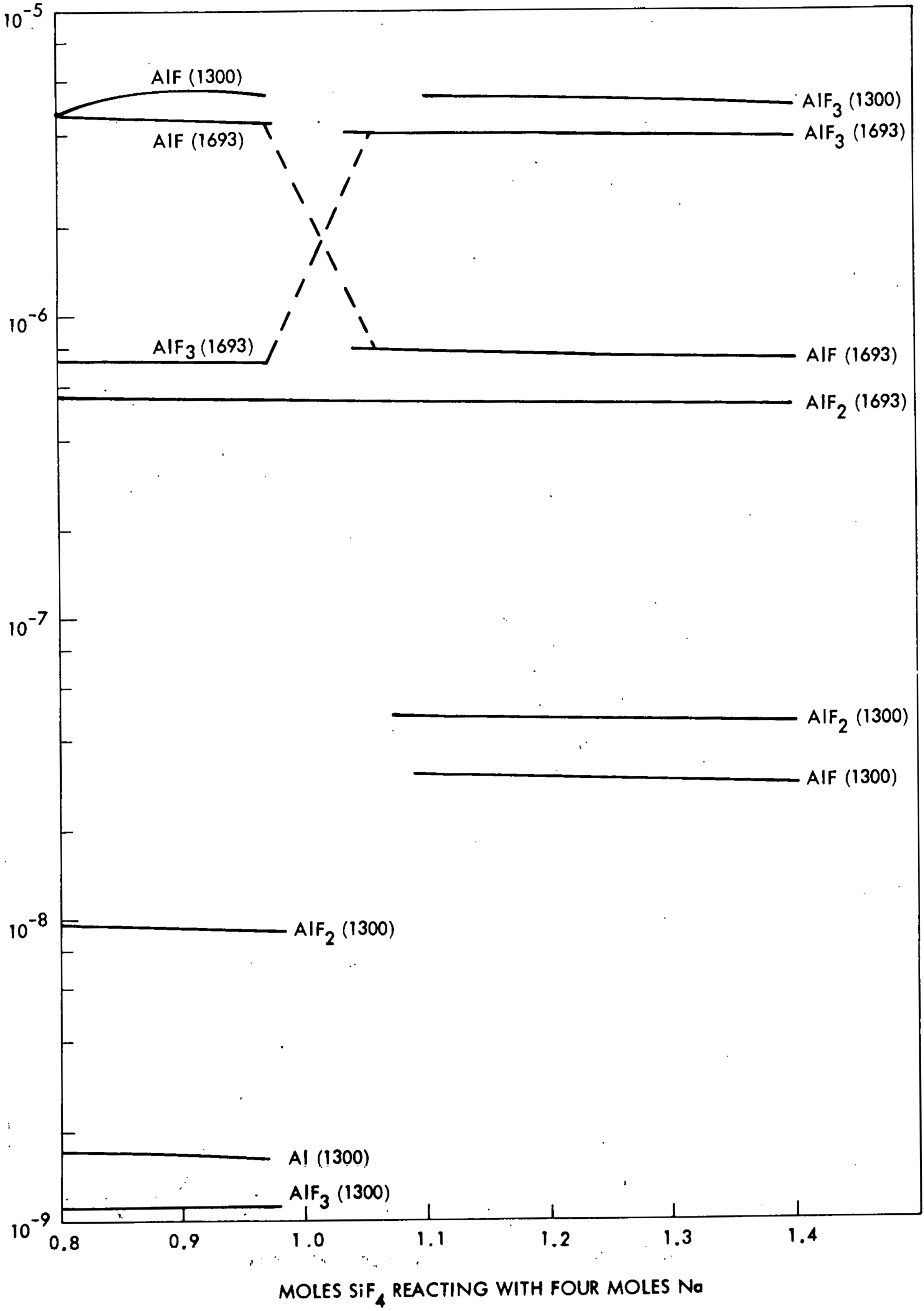

Figure 9. Computed Concentrations of Al Species Resulting in the Isothermal Reaction of SiF_4 with Na Containing 8 ppm Al

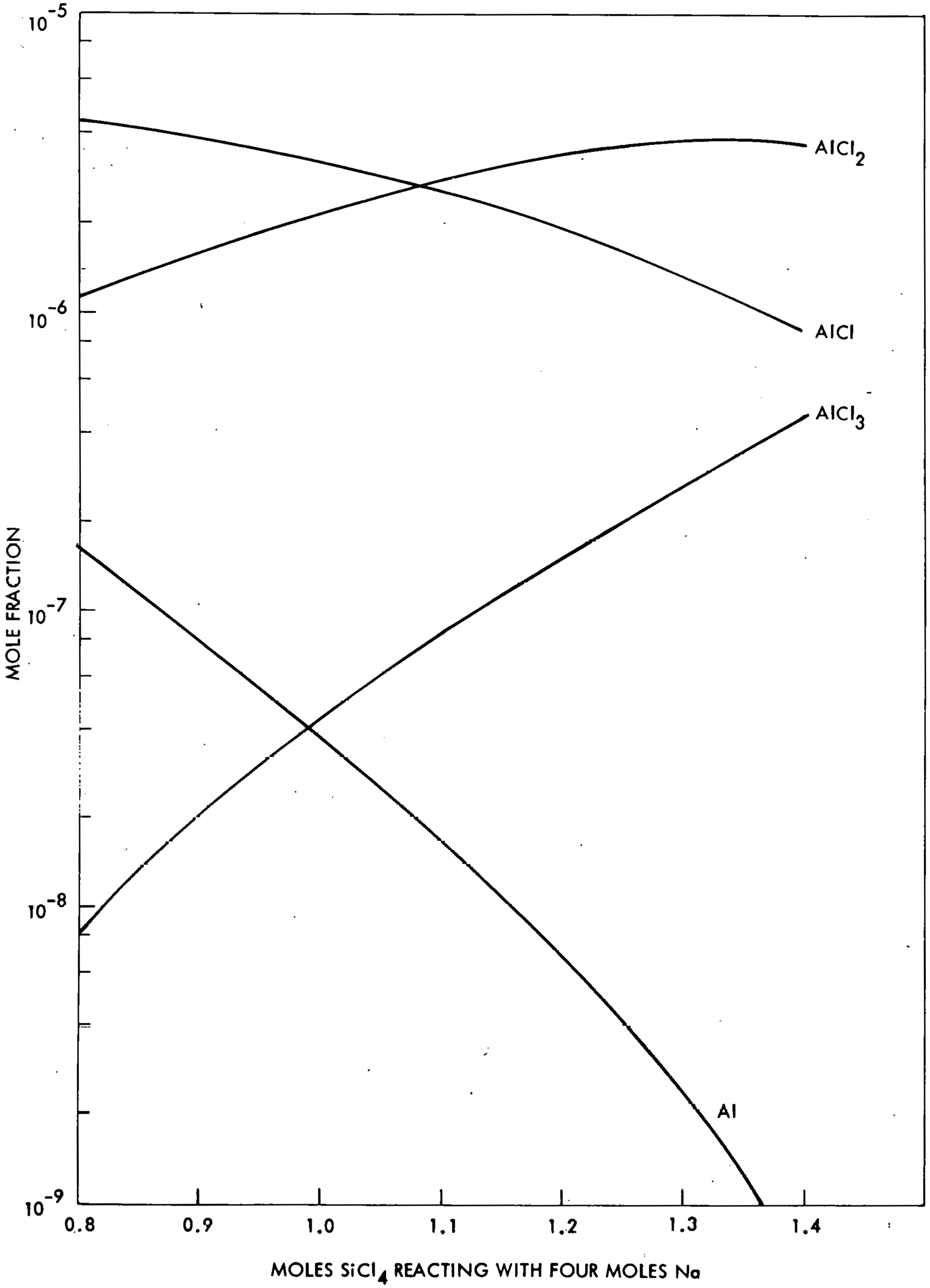

Figure 10. Computed Concentrations of Al Species Resulting from the Combustion of $SiCl_4$ with Na Vapor Containing 8 ppm (wt) Al

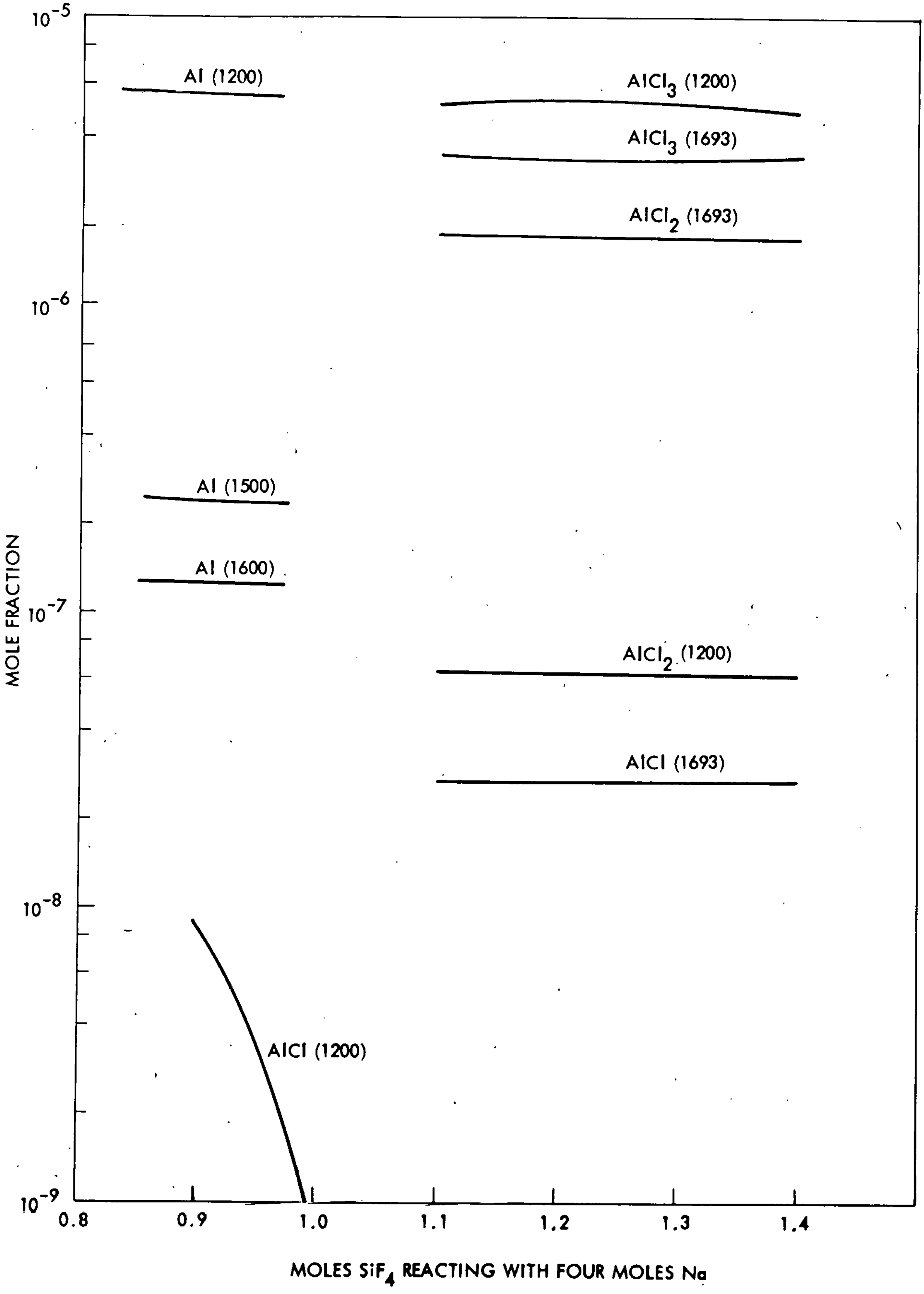

Figure 11. Computed Concentrations of Al Species Resulting in the Isothermal Reaction of $SiCl_4$ with Na Containing 8 ppm Al

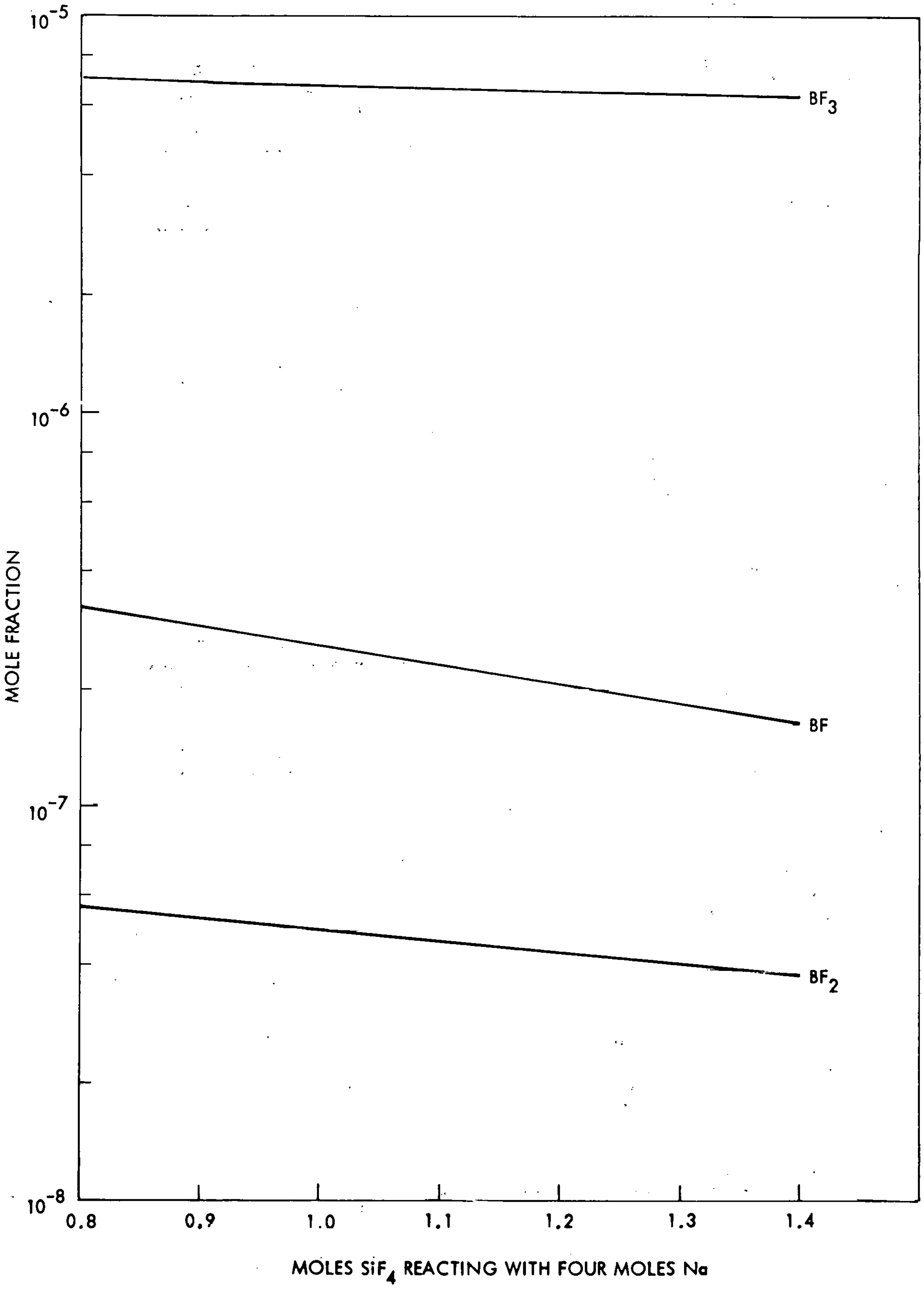

Figure 12. Computed Concentrations of B Species Resulting from the Combustion of SiF_4 with Na Vapor Containing 4 ppm B

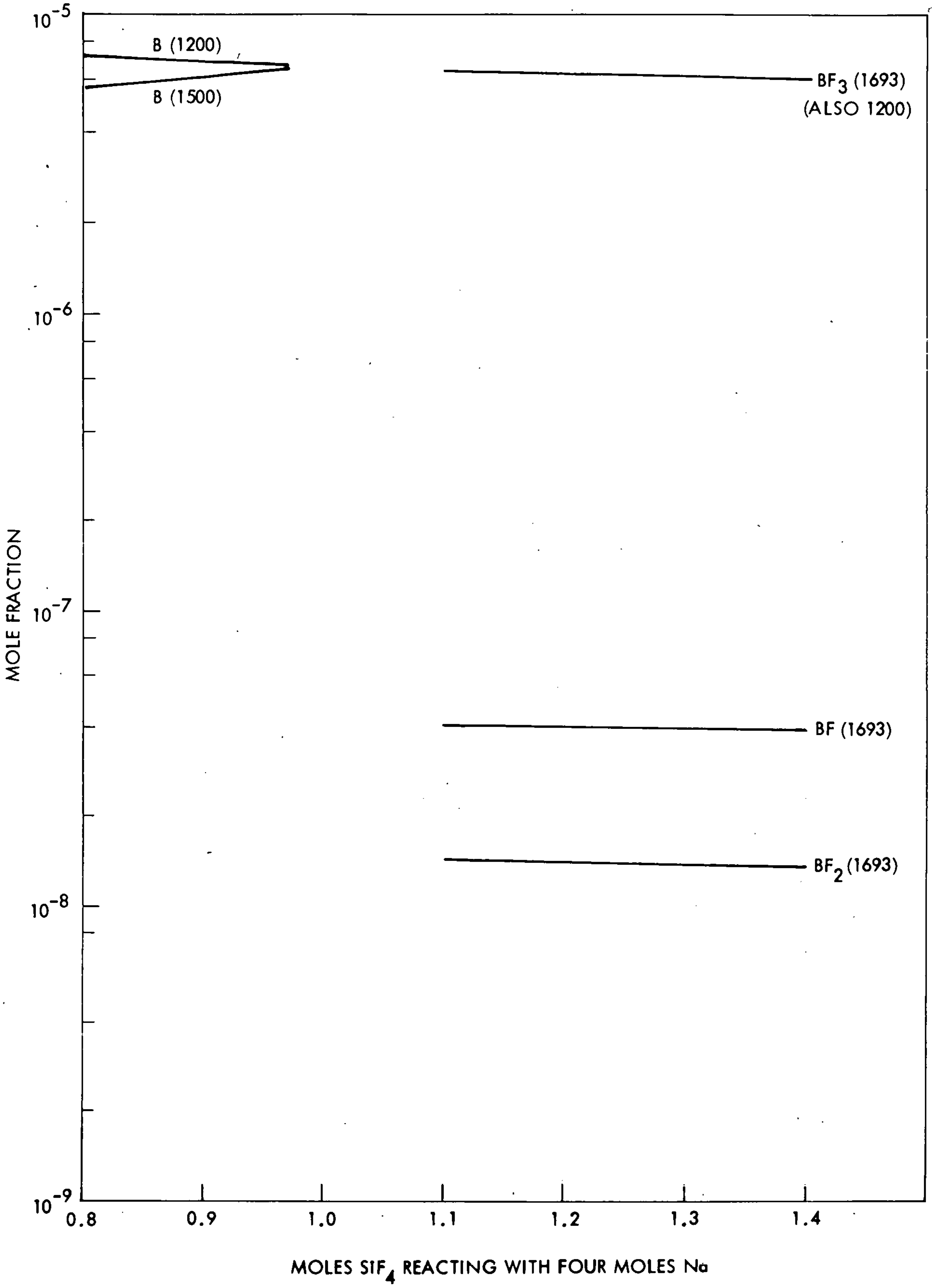

Figure 13. Computed Concentrations of B Species Resulting from the Isothermal Reaction of SiF_4 with Na Containing 4 pm B

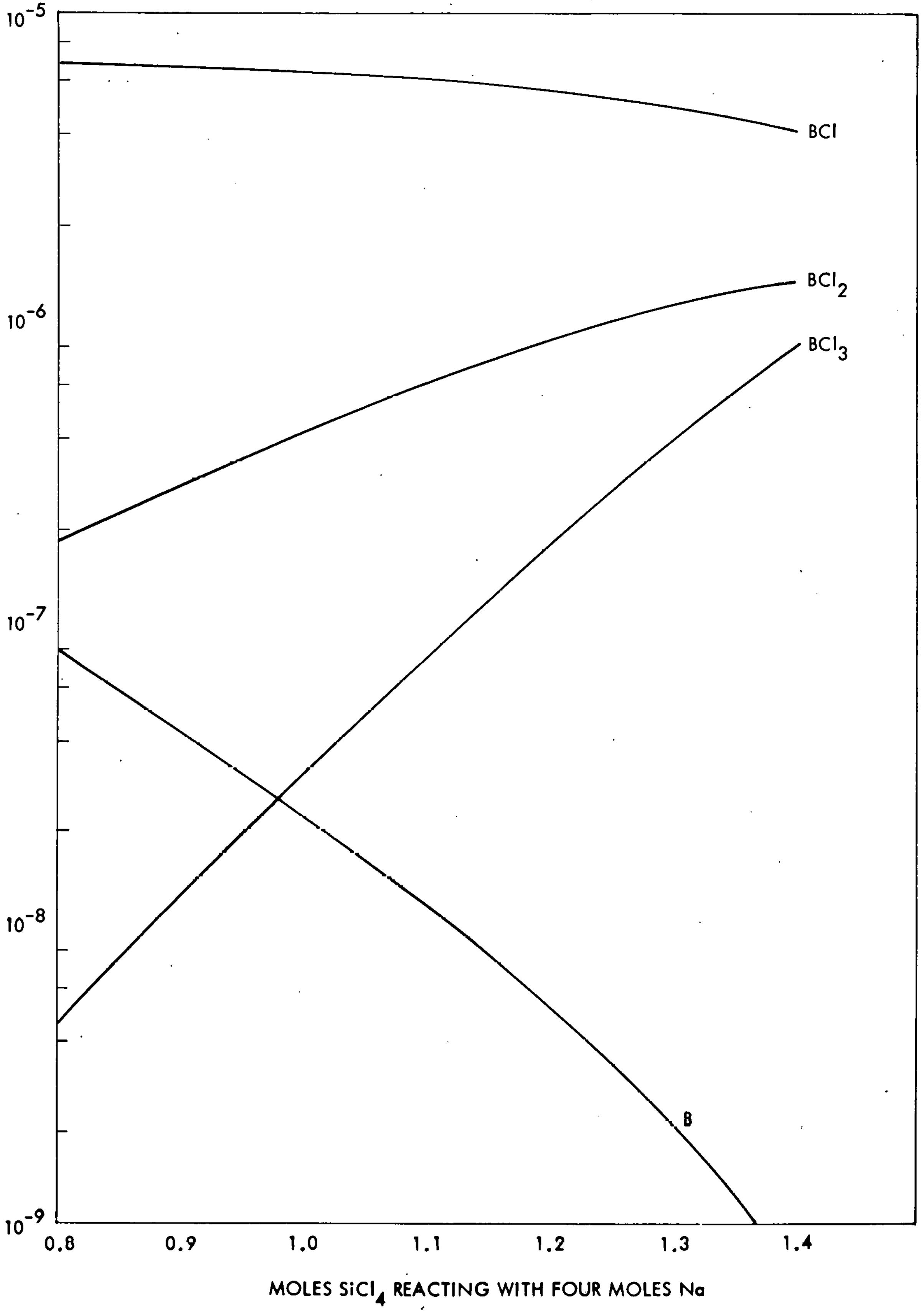

Figure 14. Computed Concentrations of B Species Resulting from the Combustion of $SiCl_4$ with Na Vapor Containing 4 ppm B

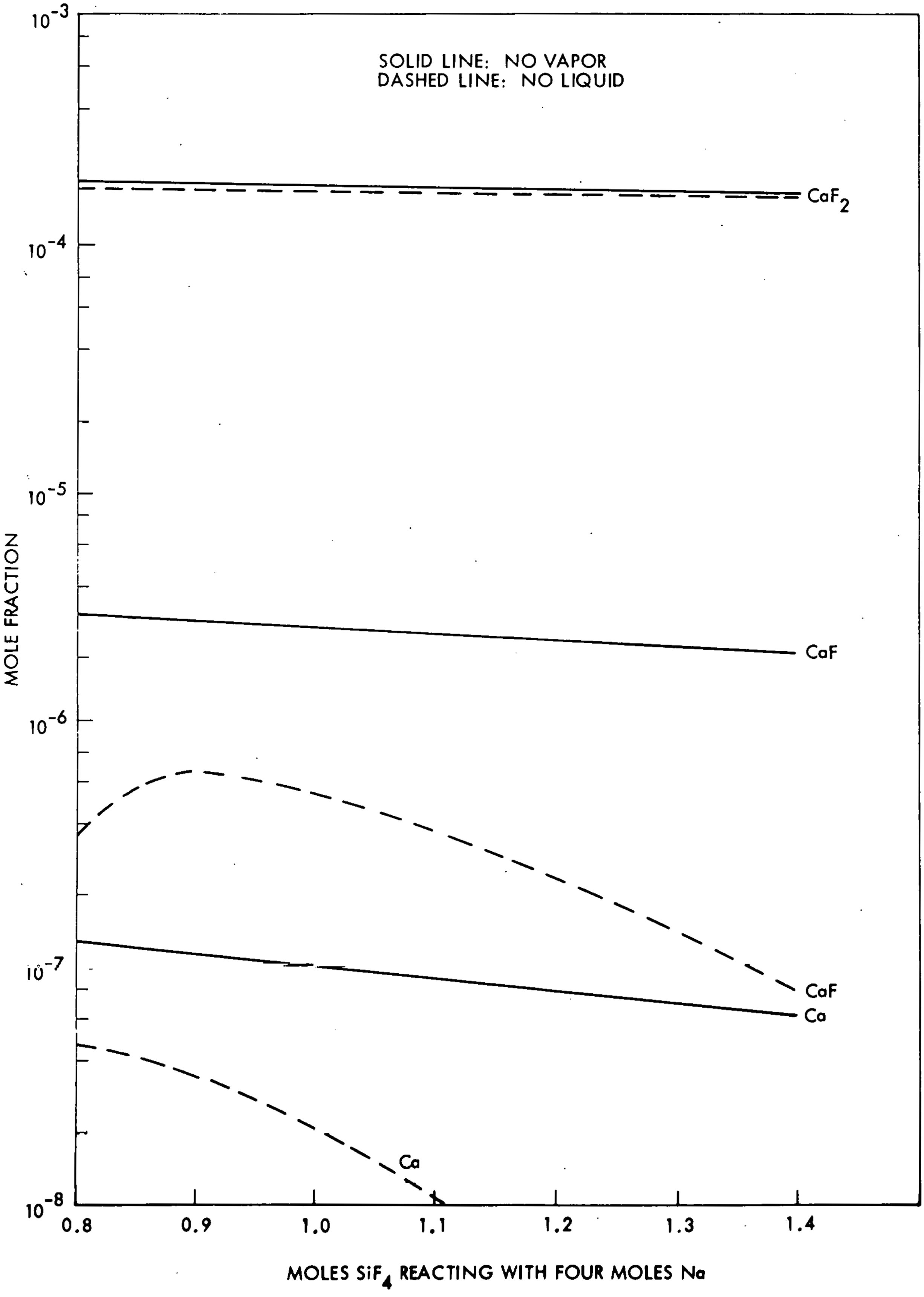

Figure 15. Computed Concentrations of Ca Species Resulting from the Combustion of SiF_4 with Na (Vapor and Liquid) Containing 400 ppm Ca

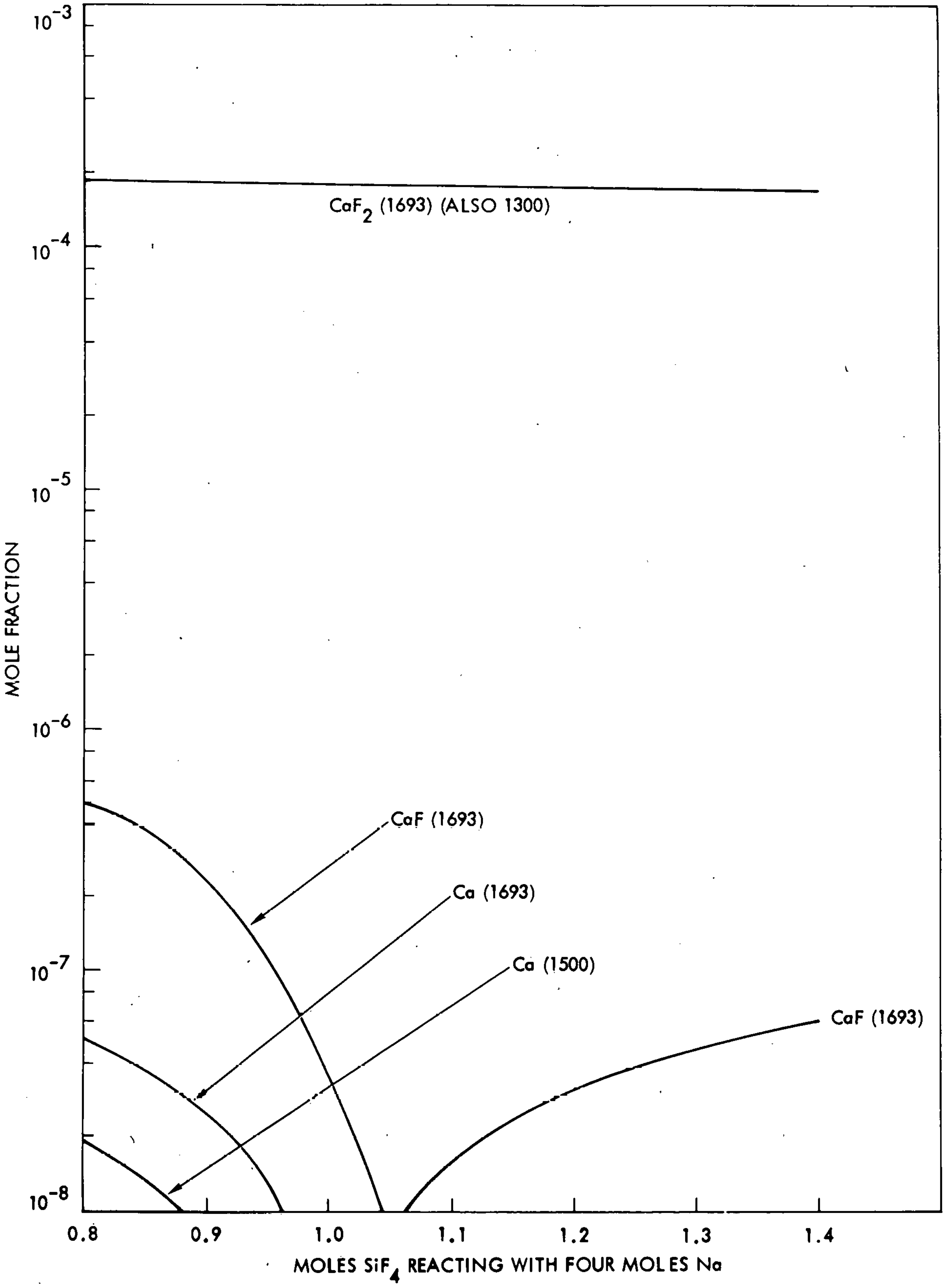

Figure 16. Computed Concentrations of Ca Species Resulting from the Isothermal Reaction of SiF_4 with Na Containing 400 ppm Ca

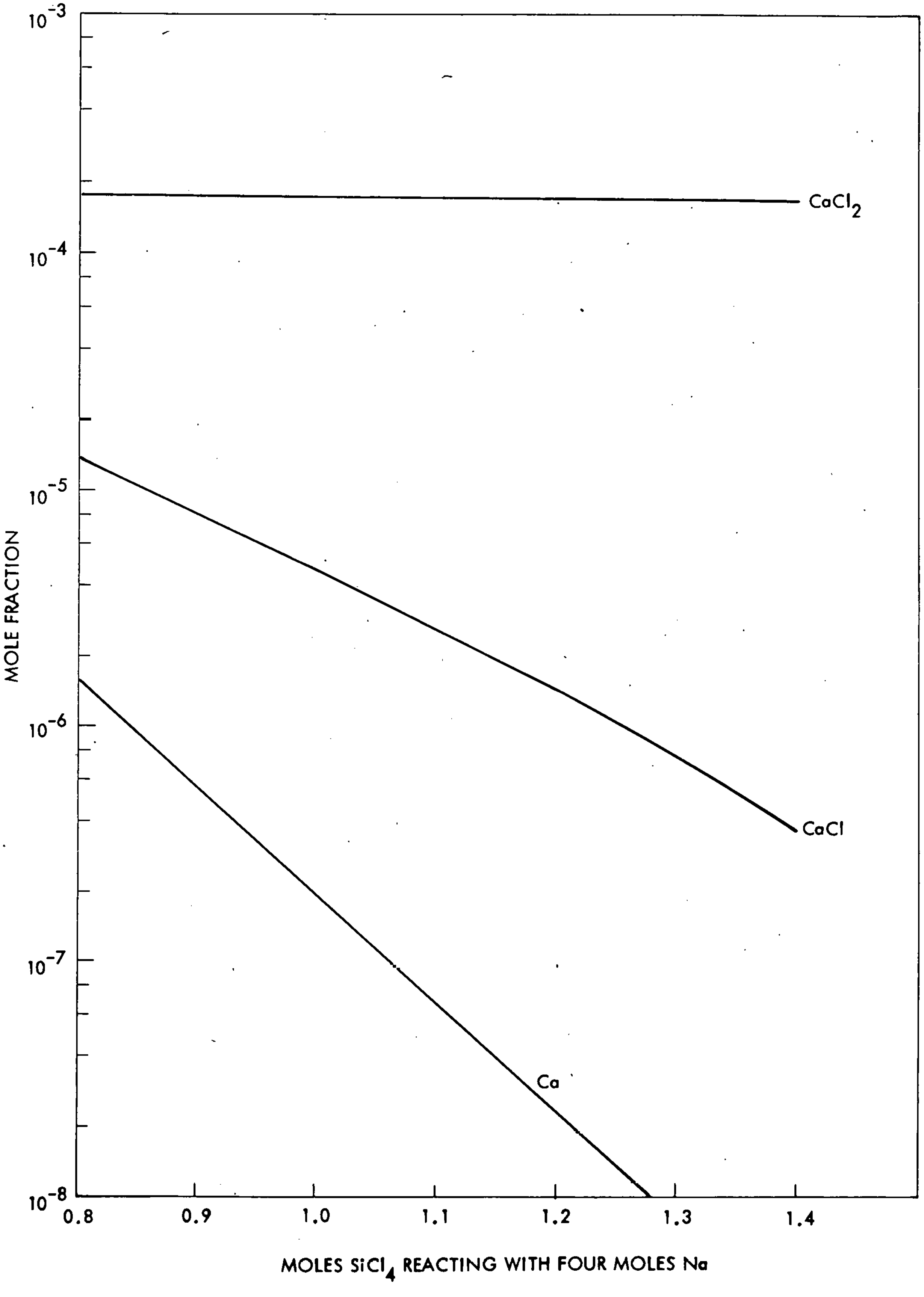

Figure 17. Computed Concentrations of Ca Species Resulting from the Combustion of $SiCl_4$ with Na (Vapor) Containing 400 ppm Ca

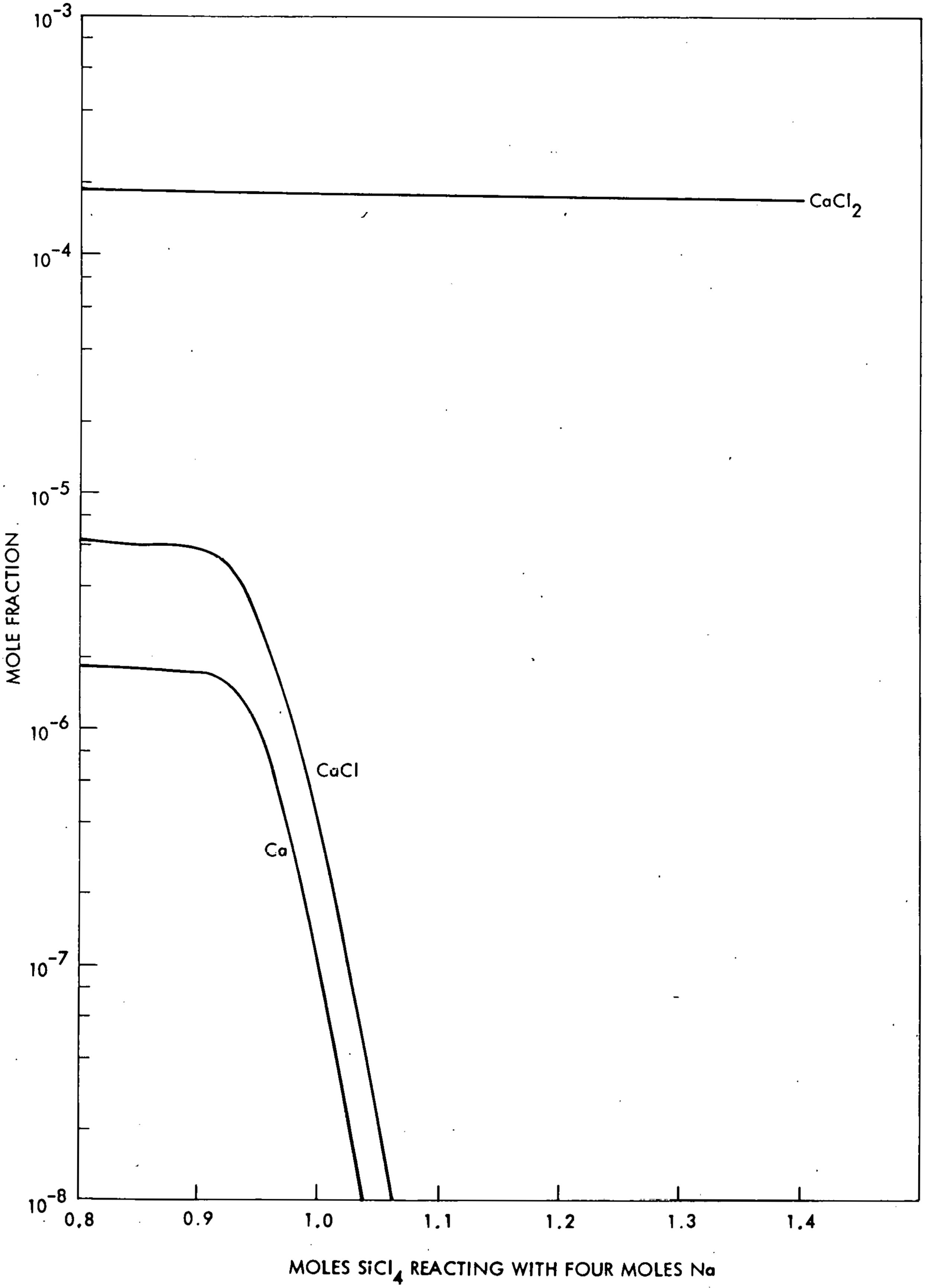

Figure 18. Computed Concentrations of Ca Species Resulting from the Reaction, at 1693 K, of $SiCl_4$ with Na Containing 400 ppm Ca

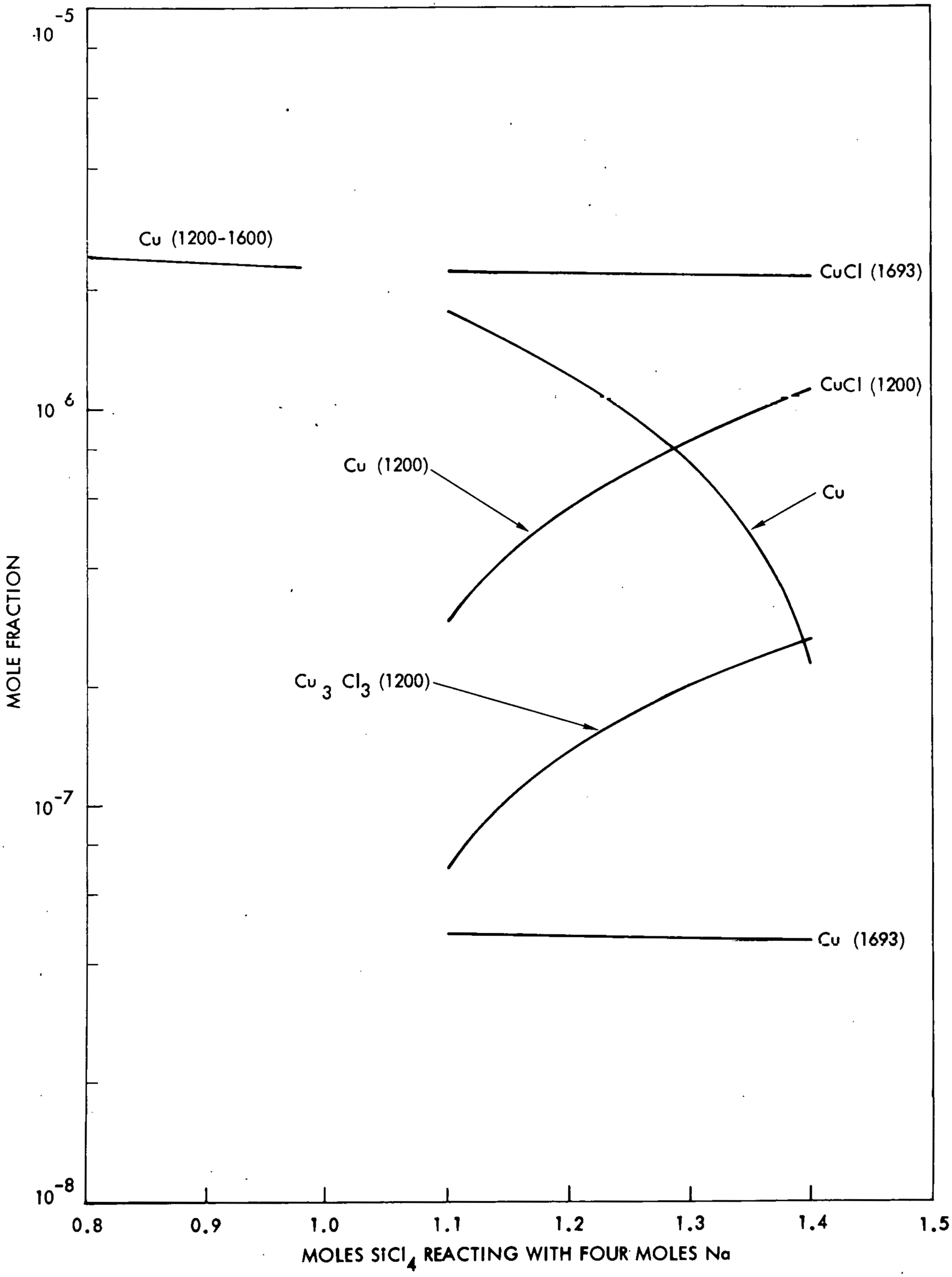

Figure 19. Computed Concentrations of Cu Species Resulting from the Isothermal Reaction of $SiCl_4$ with Na Containing 8 ppm Cu

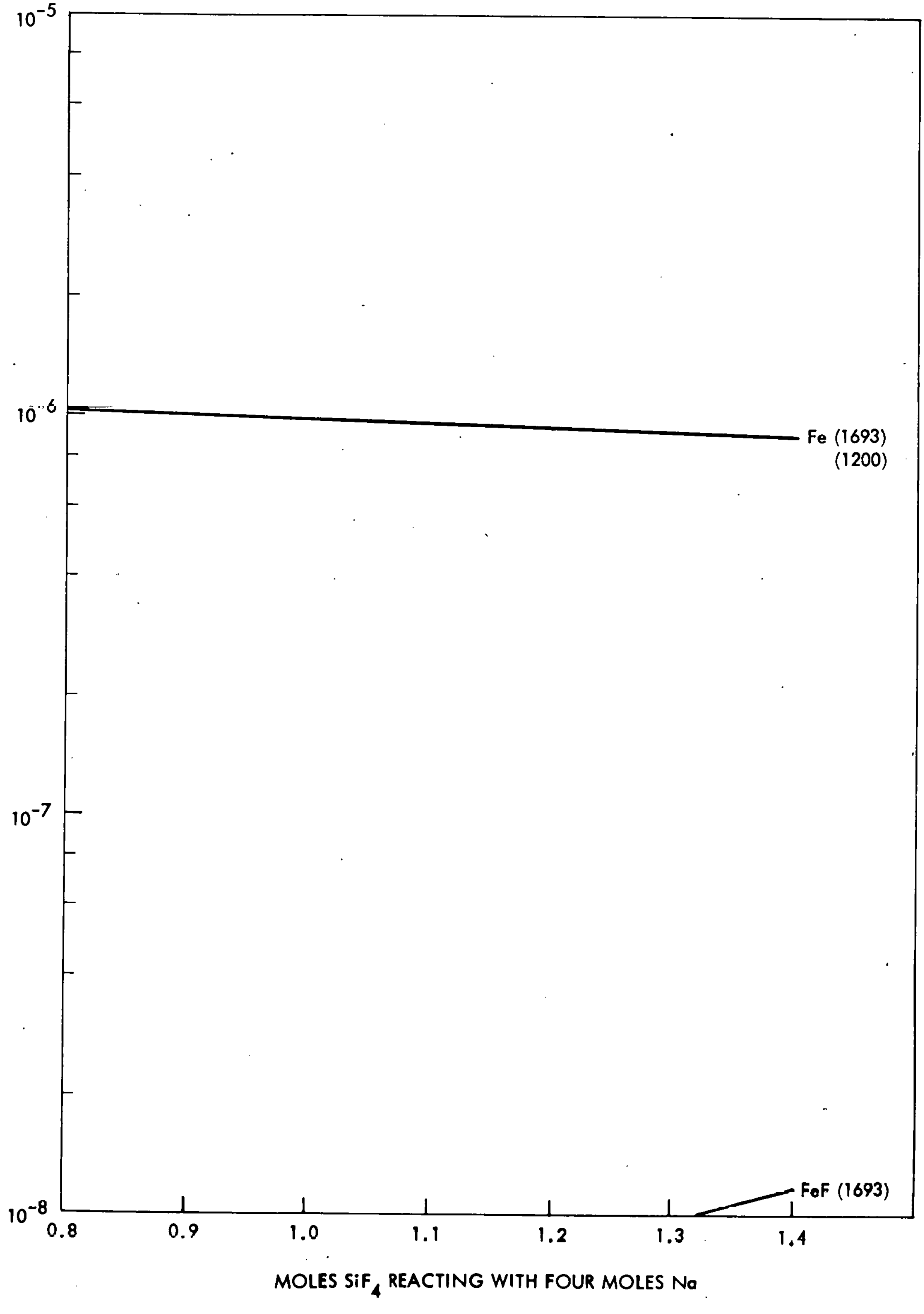

Figure 20. Computed Concentrations of Fe Species Resulting from the Isothermal Reaction of SiF_4 with Na Containing 3 ppm Fe

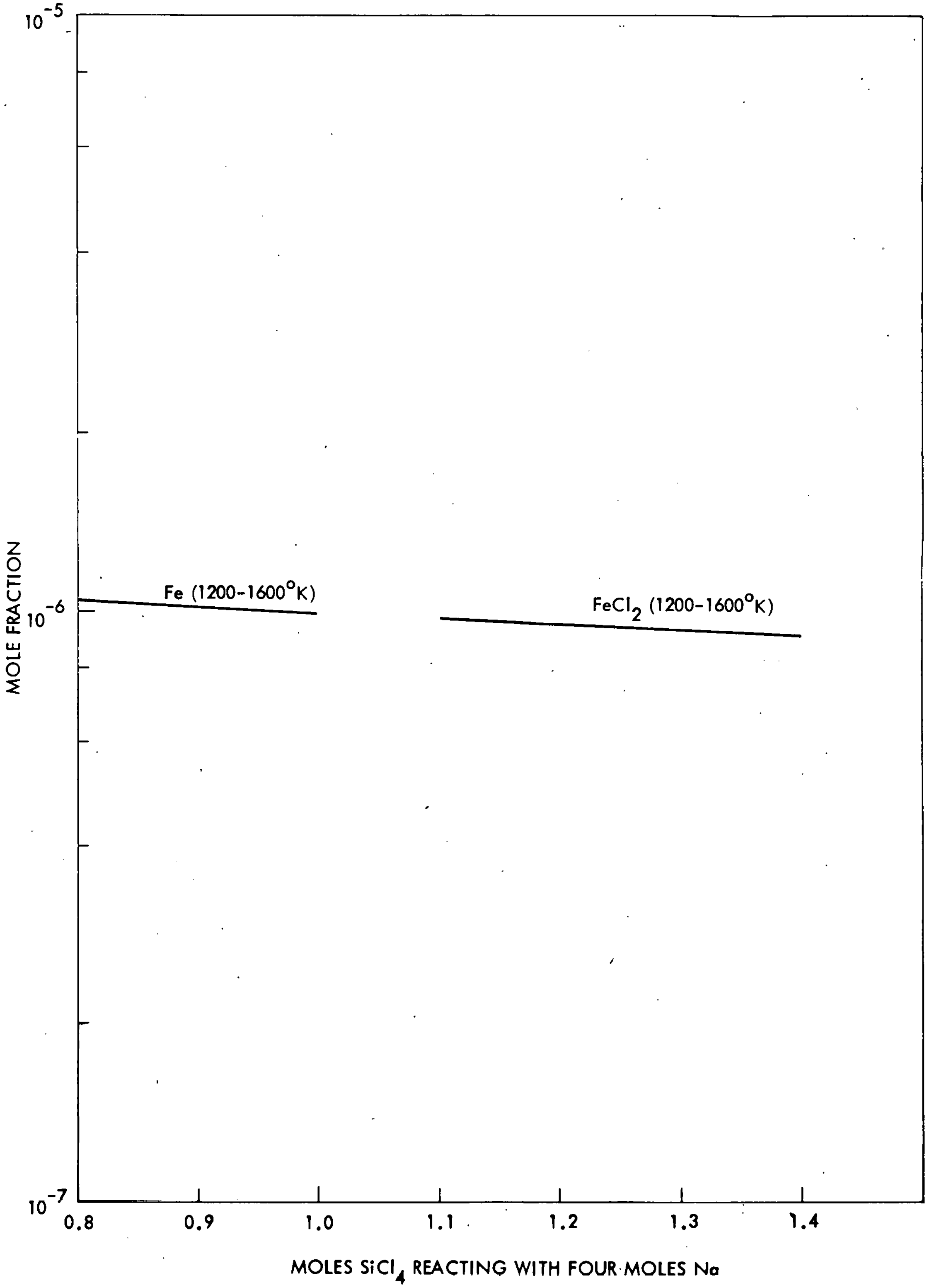

Figure 21. Computed Concentrations of Fe Species Resulting from the Isothermal Reaction of $SiCl_4$ with Na Containing 3 ppm Fe

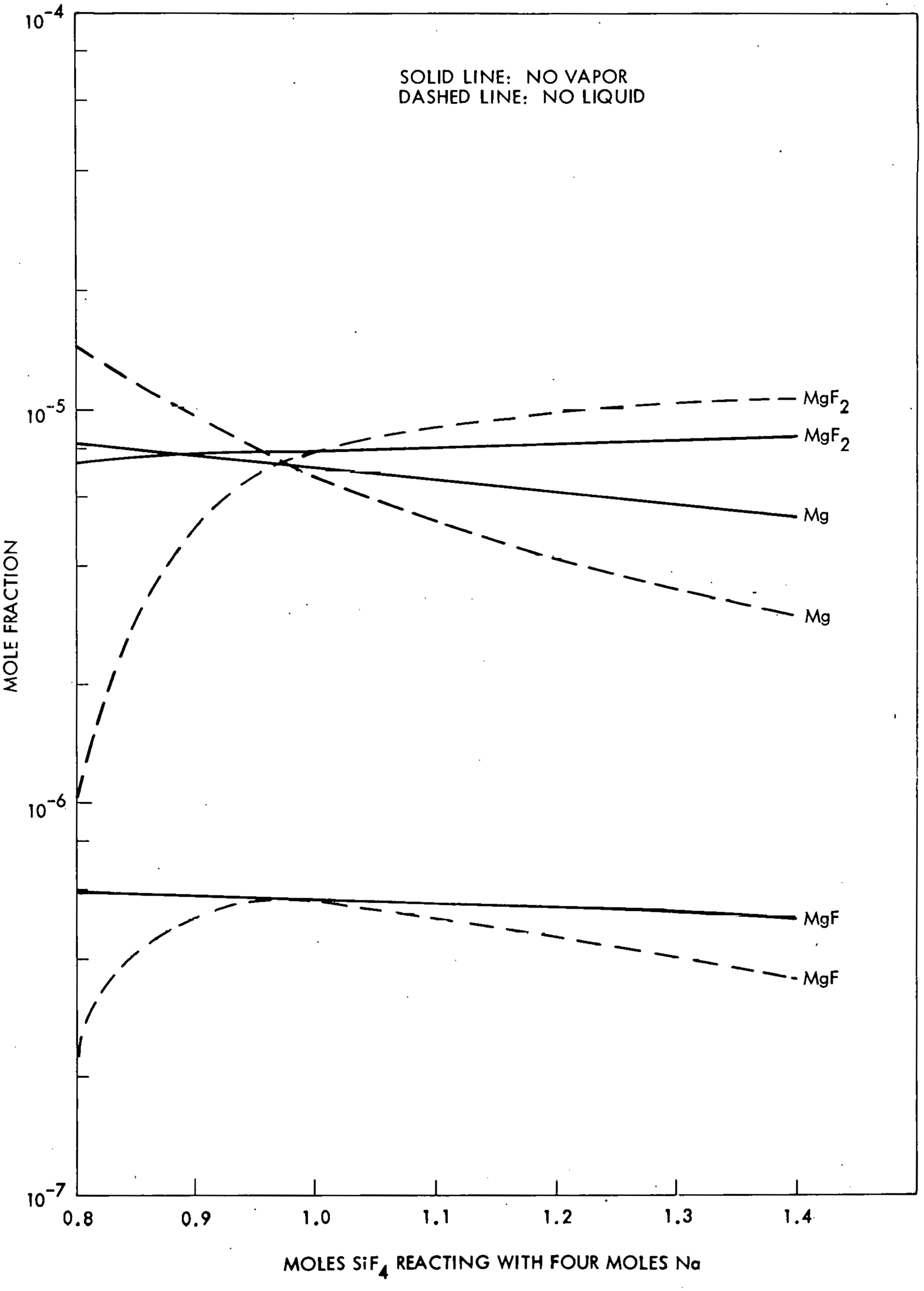

Figure 22. Computed Concentrations of Mg Species Resulting from the Combustion of SiF_4 with Na (Vapor and Liquid) Containing 20 ppm Mg

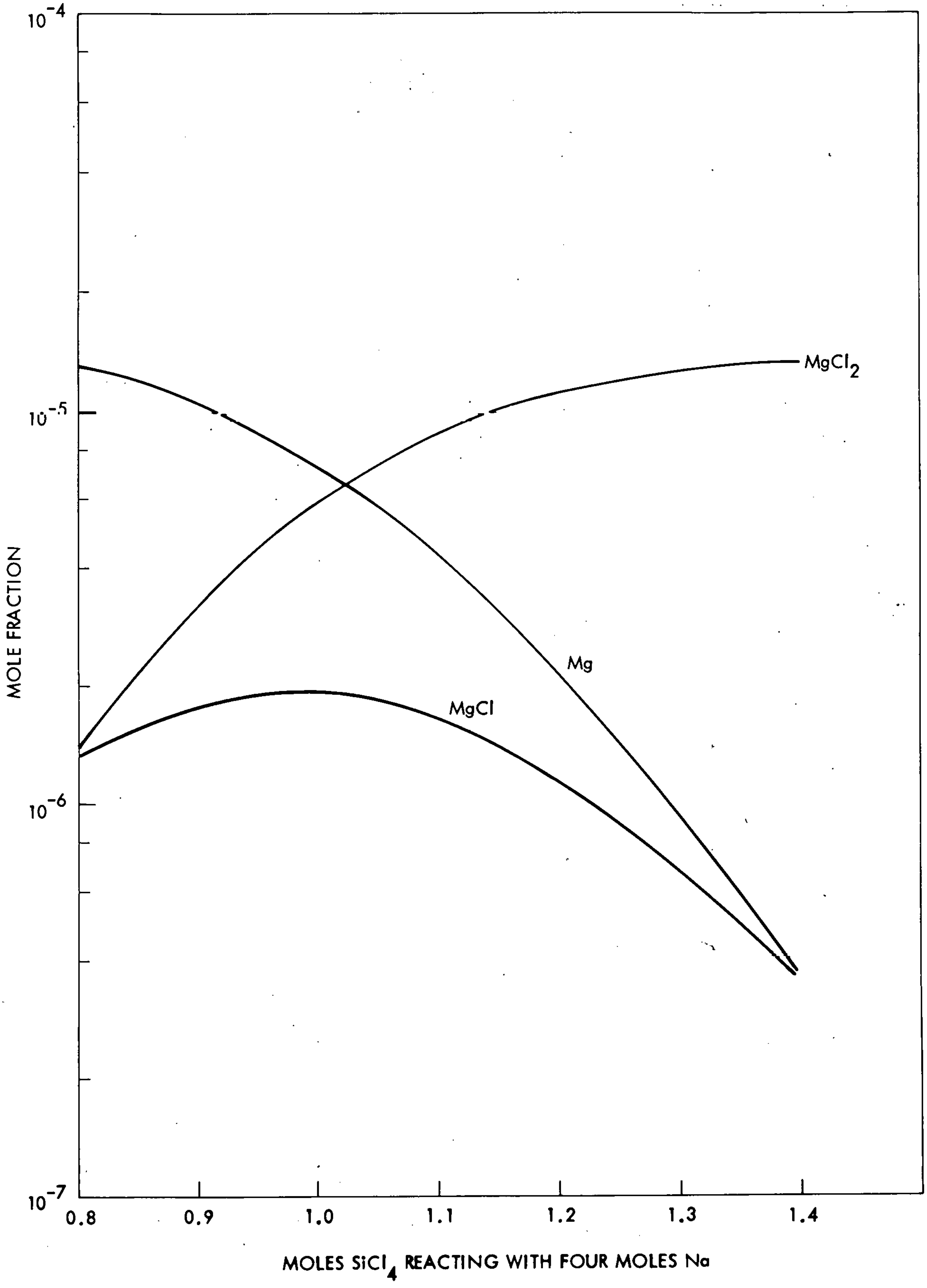

Figure 23. Computed Concentrations of Mg Species Resulting from the Combustion of $SiCl_4$ with Na (Vapor) Containing 20 ppm Mg

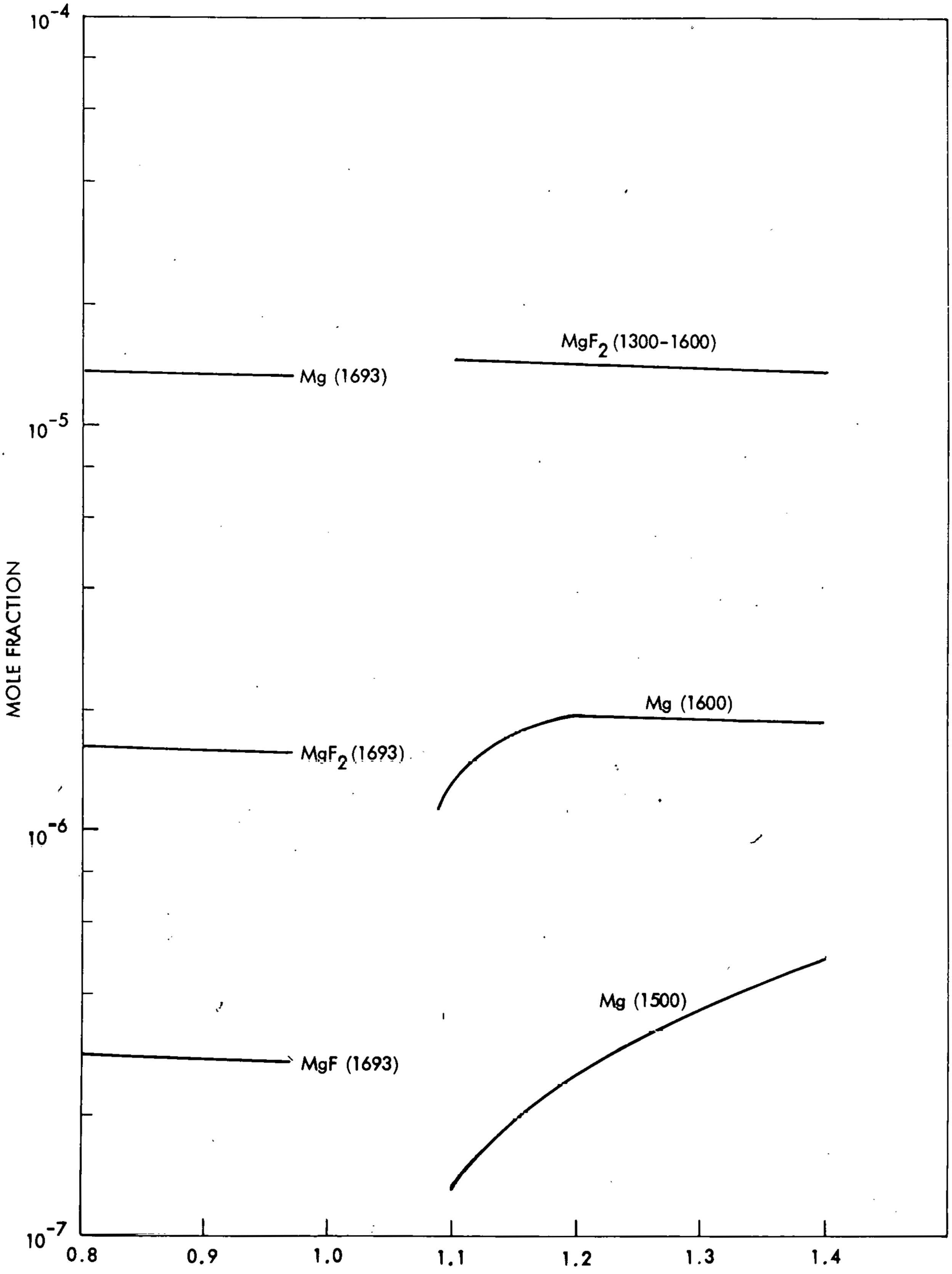

Figure 24. Computed Concentrations of Mg Species Resulting from the Isothermal Reaction of SiF_4 with Na Containing 20 ppm Mg

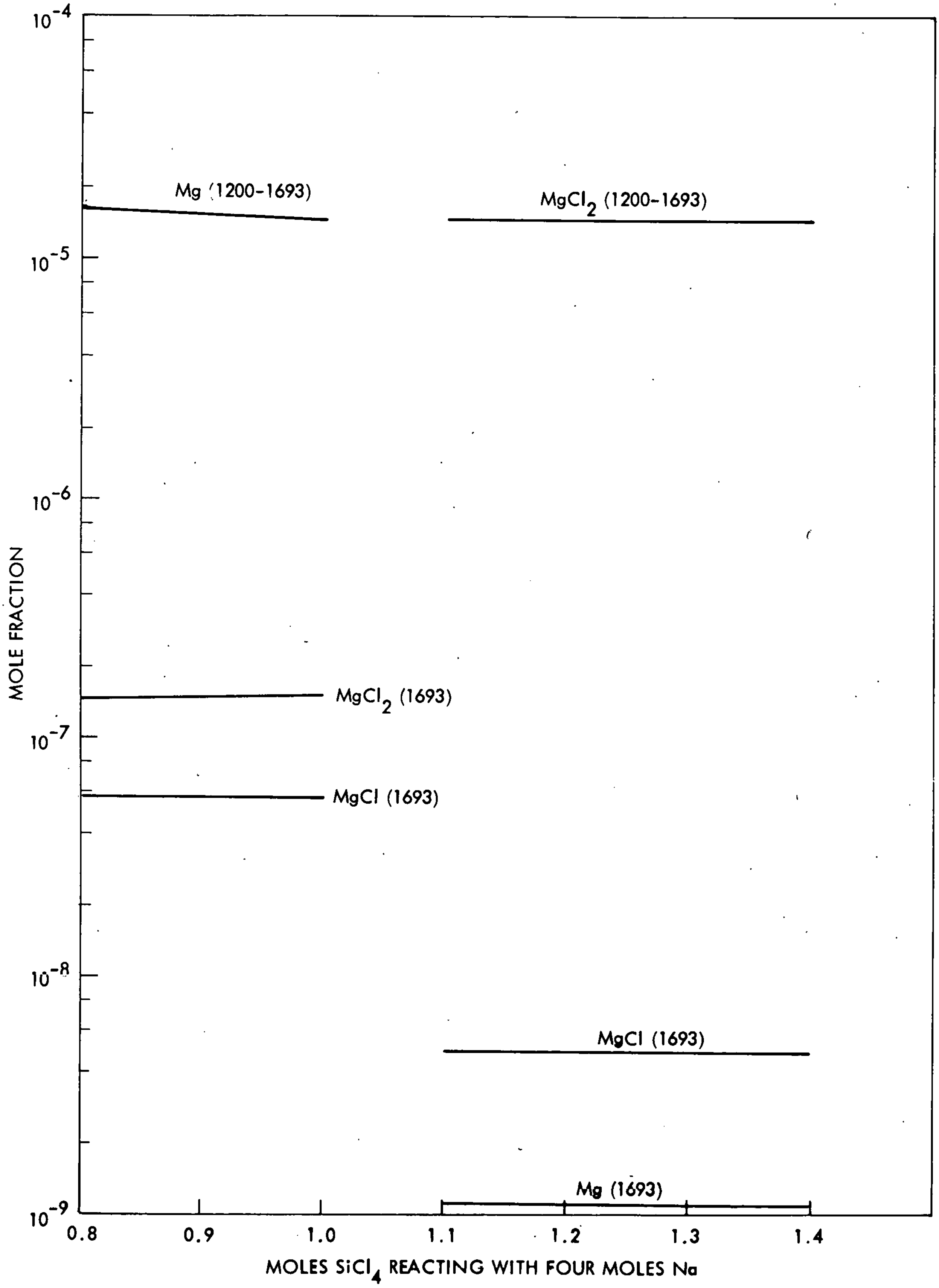

Figure 25. Computed Concentrations of Mg Species Resulting from the Isothermal Reaction of $SiCl_4$ with Na Containing 20 ppm Mg

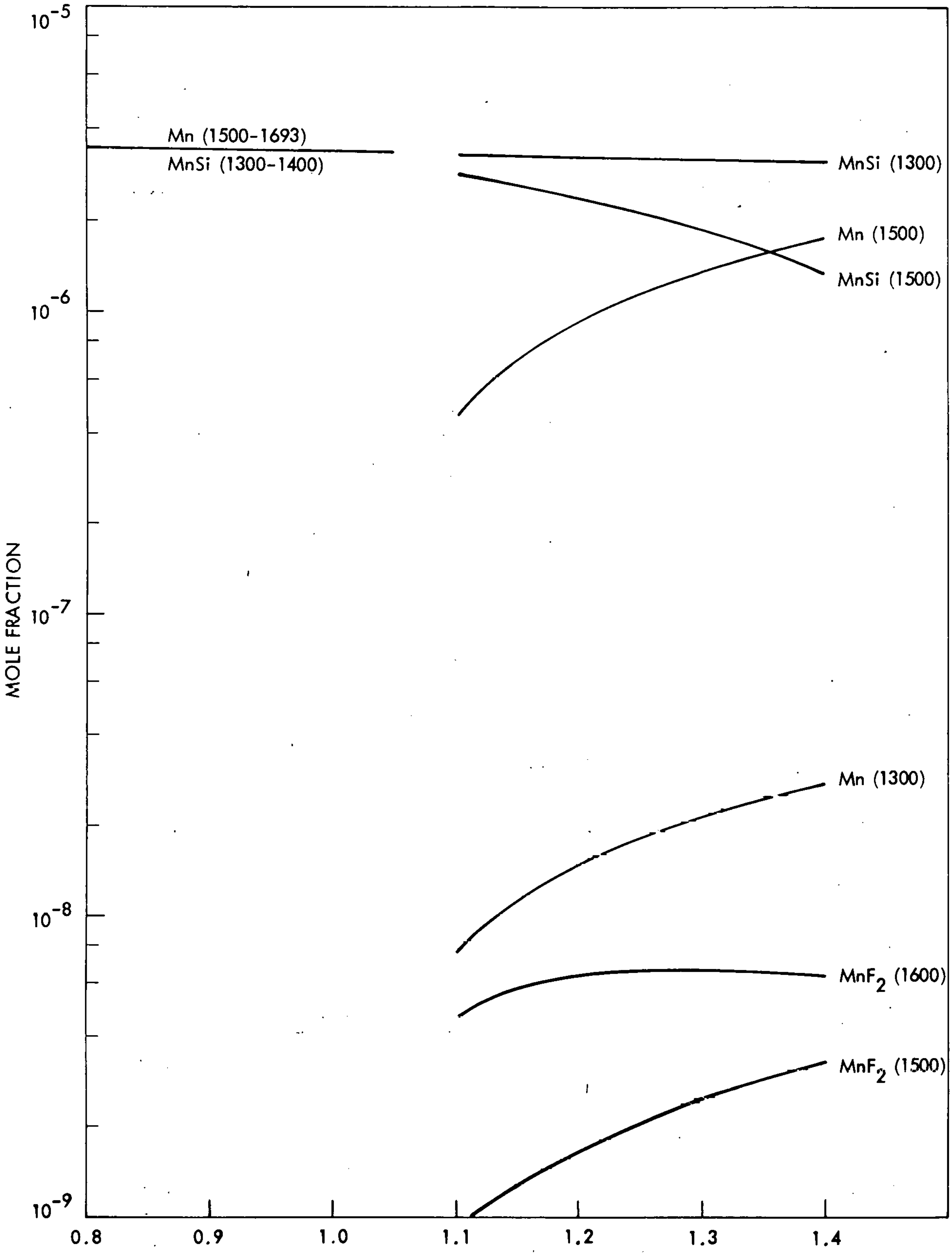

Figure 26. Computed Concentrations of Mn Species Resulting from the Isothermal Reaction of SiF_4 with Na Containing 10 ppm Mn

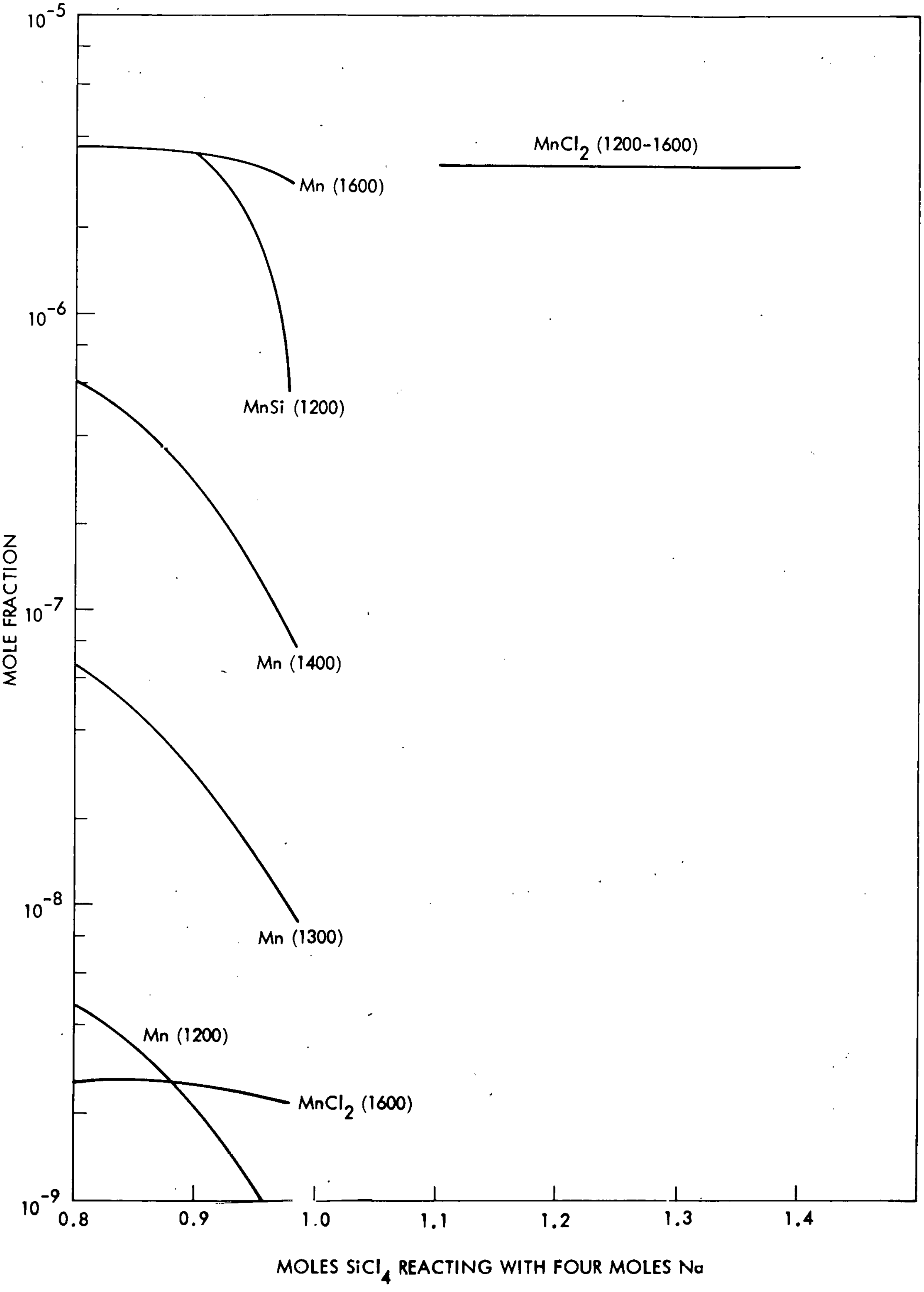

Figure 27. Computed Concentrations of Mn Species Resulting from the Isothermal Reaction of $SiCl_4$ with Na Containing 10 ppm Mn

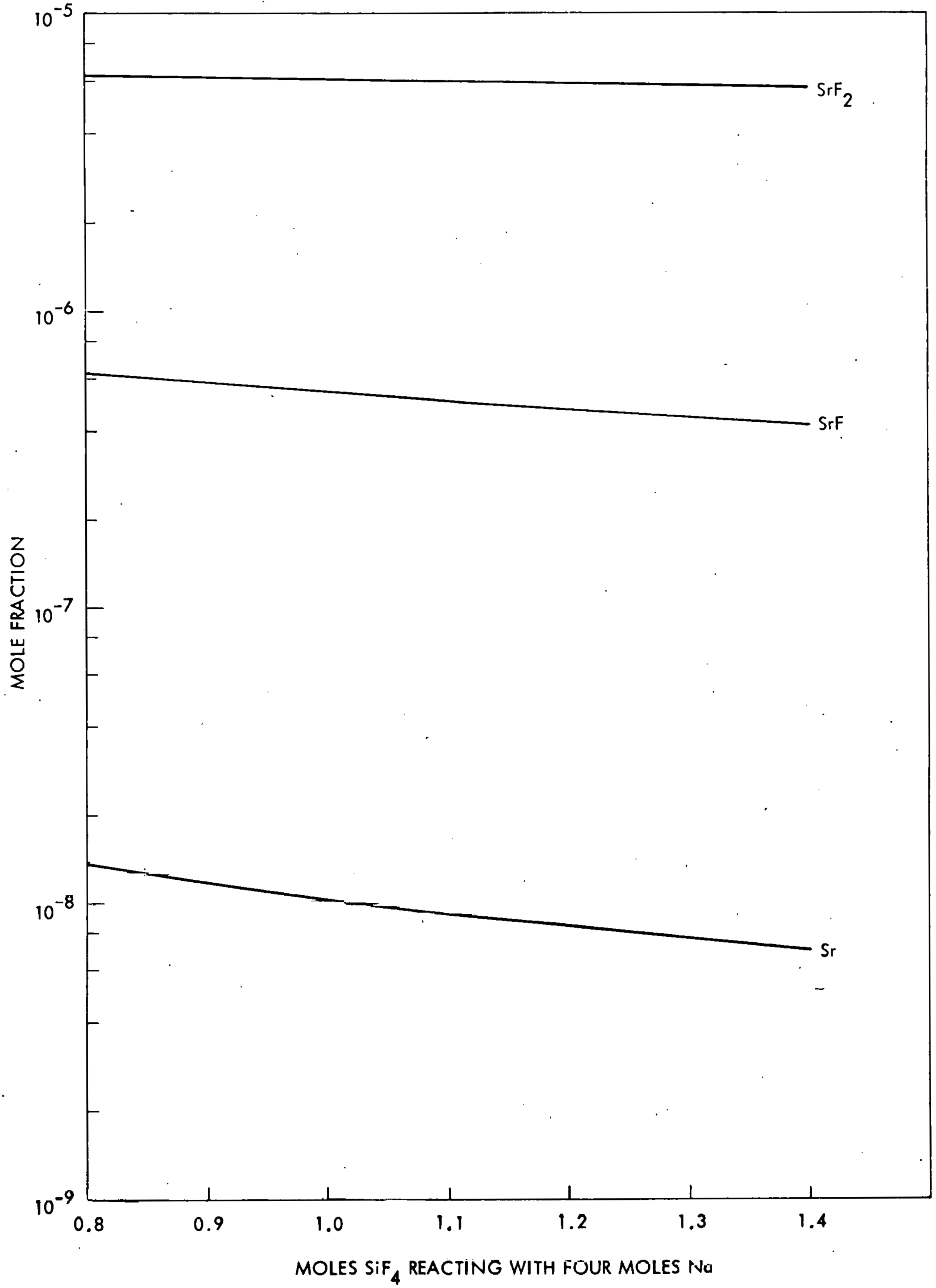

Figure 28. Computed Concentrations of Sr Species Resulting from the Combustion of SiF_4 with Na (Vapor) Containing 30 ppm Sr

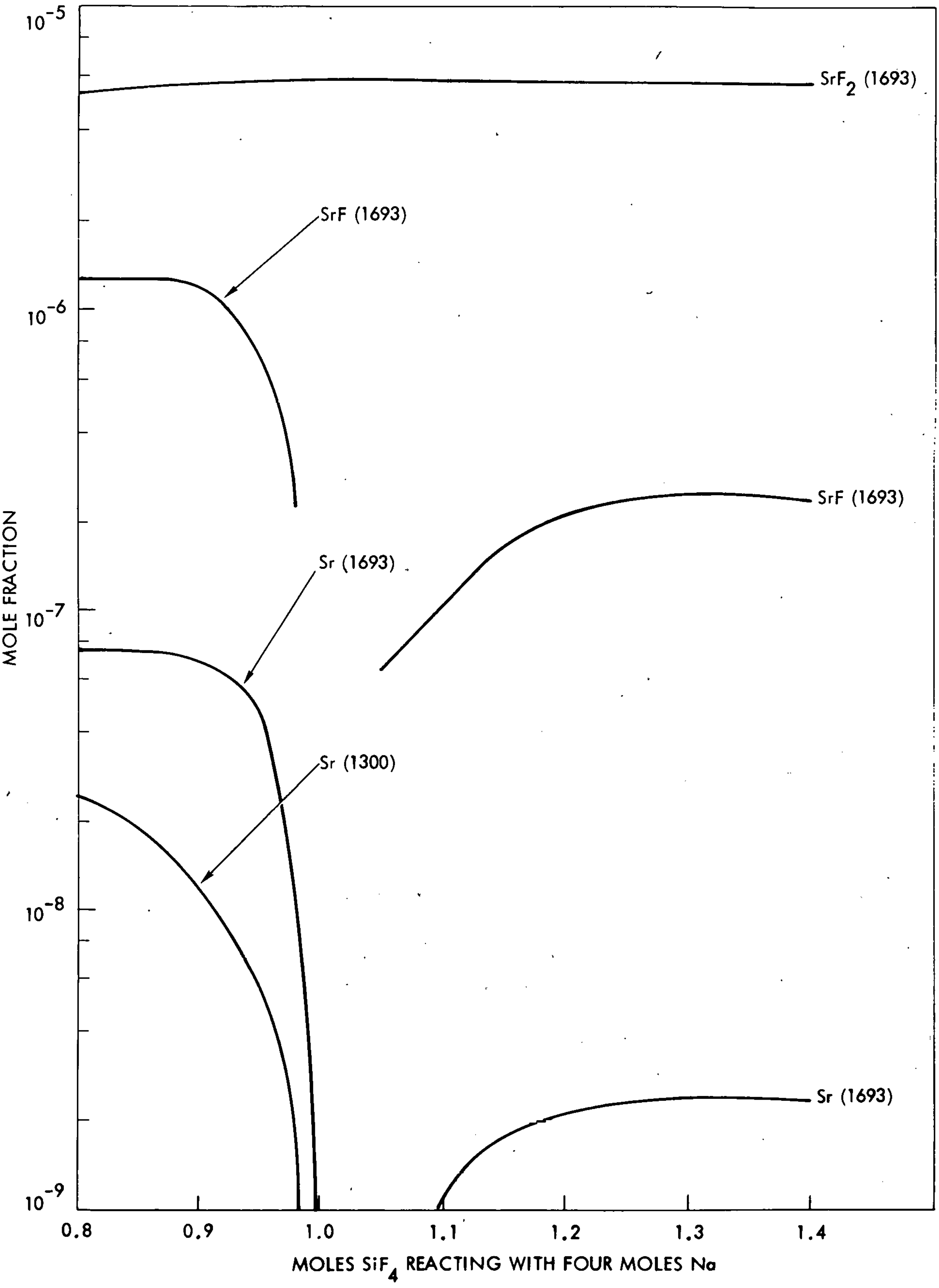

Figure 29. Computed Concentrations of Sr Species Resulting in the Isothermal Reaction of SiF_4 with Na Containing 30 ppm Sr

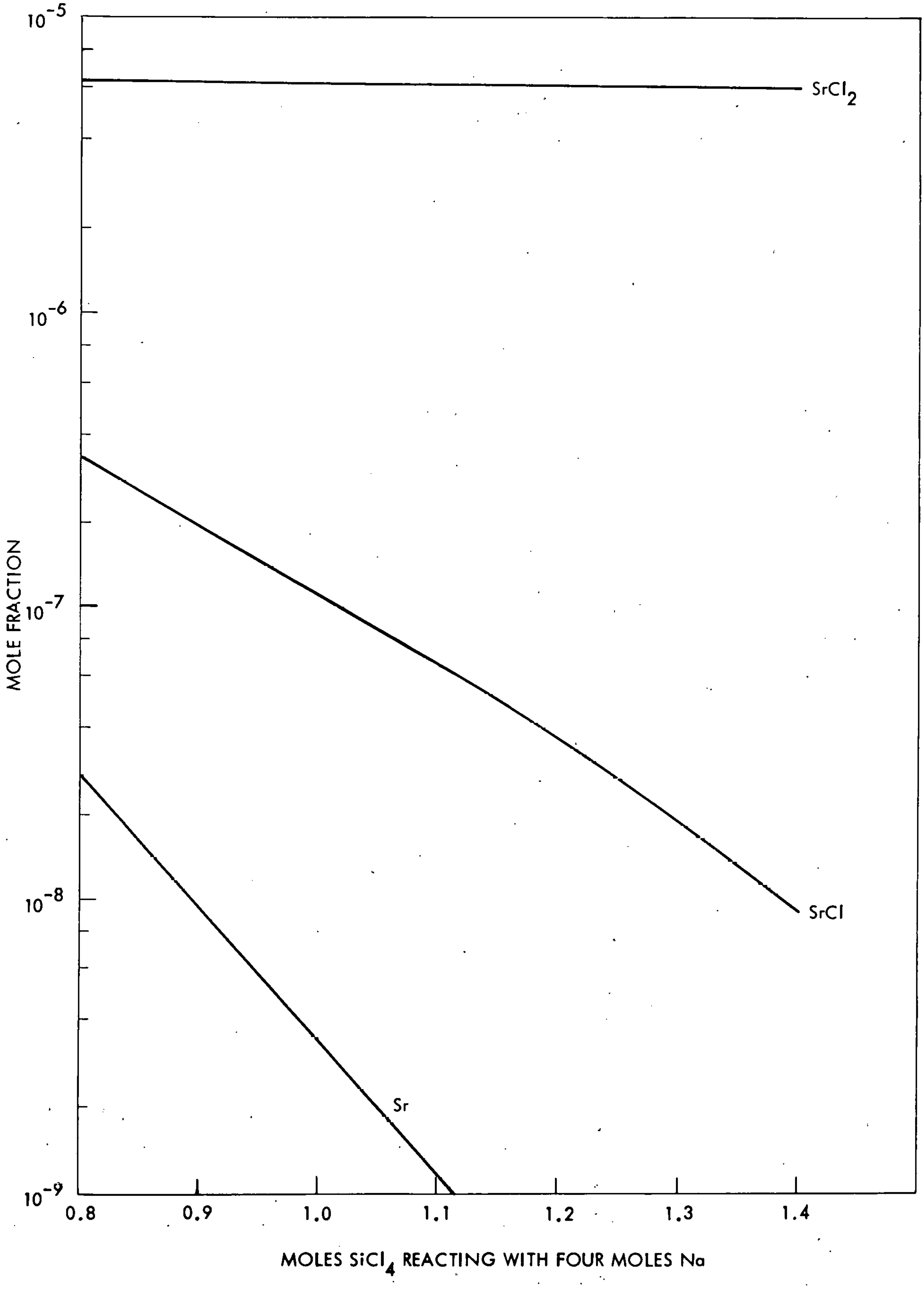

Figure 30. Computed Concentrations of Sr Species Resulting in the Combustion of $SiCl_4$ with Na (Vapor) Containing 30 ppm Sr

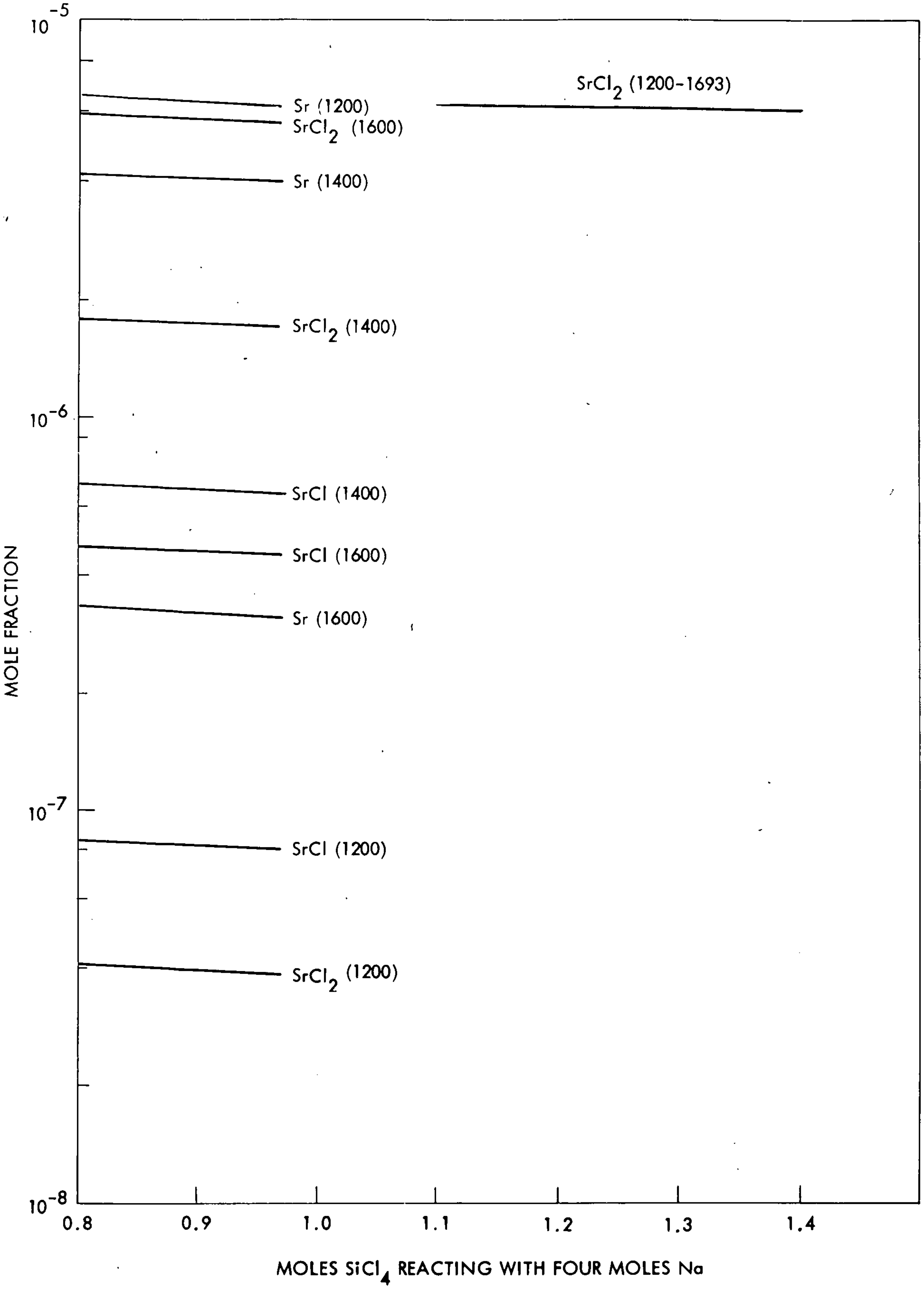

Figure 31. Computed Concentrations of Sr Species Resulting in the Isothermal Reaction of $SiCl_4$ with Na Containing 30 ppm Sr

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