OAK RIDGE NATIONAL LABORATORY
operated by
UNION CARBIDE CORPORATION
for the
U.S. ATOMIC ENERGY COMMISSION

ORNL-TM-475

COPY NO. - 4

DATE - February 5, 1963

THERMAL AND RADIATION STABILITY OF SUGGESTED ALTERNATIVE GAS COOLANTS

W. T. Rainey, Jr.
R. L. Bennett

ABSTRACT

A literature survey has been made to evaluate the thermal and radiation stabilities of several gases which have been proposed tentatively as reactor coolants. Available thermodynamic stability data are listed. For each gas a summary is presented of the available information concerning stabilities and chemical reactivity with reactor materials and contaminants.

Because of their low thermal stabilities, B_2H_6, SiH_4, and NF_3 are not recommended. Radiolytic decomposition and expense of removal of B^{10} probably eliminate the use of BF_3. Little data are available concerning MoF_6, MoF_5 and NbF_5, but these compounds do not appear to have large stabilities. Radiolytic damage to CF_4 gives a G value for the production of fluorine of 0.28. No radiation information is available for SiF_4 and SF_6. An experimental investigation of the more promising gases (SF_6, SiF_4 and CF_4) is proposed. This would include radiation at ambient and high temperatures as well as reactivity studies with carbon and reactor contaminants.

A literature survey has been made to collect information relative to the thermal and radiolytic stability of materials suggested as possible coolants by Lackey and Samuels in their letter of September 24, 1962. Information indicating compatibility with other reactor materials has been included also. Only SiF_4, CF_4 and SF_6 are suggested as possible satisfactory coolants.

The equilibrium constants for decomposition of the molecules into elements are given in Table I. These constants were calculated from the standard free energies of formation at the stated temperatures. No consideration was given to any other possible reactions for decomposition or to possible reactions between reactants and construction materials.

Table I

Molecule	Log K_p		
	800°K (981°F)	1200°K (1700°F)	1600°K (2420°F)
BF_3	-62.47	-46.01	-33.64
B_2H_6	+13.20	+11.86	+11.59
CF_4	-111.27	-51.64	-31.78
NF_3	-9.94	-0.81	+1.86
SiF_4	-196.31	-94.37	-60.39
SiH_4	+8.28	+6.58	+6.11
SF_6	-139.38	-60.57	-33.05

where $K_p = \frac{\text{Elements}}{\text{Molecule}}$

These data reflect the thermodynamic stability of each compound and could be used to calculate compositions of the gases at equilibrium. However, kinetic data, which would be of more practical value, are limited. In the absence of experimental results, even thermal decomposition kinetic data would be of questionable value in estimating stabilities in radiation environments. A summary of available information for each gas listed in Table I is presented below.

<u>Boron Trifluoride</u> (BF_3)

This compound reacts with iron at red heat, but does not react with hydrogen under normal conditions. It fumes in moist air. Its use in reactors would require the removal of high cross-section B^{10}. This could be done by known techniques. Pile radiation of 10^{20} nvt resulted in decomposition of the compound, about 25% due to radiation damage plus an additional 27% due to transmutation of B^{10}. BF_3 is very irritating and should be handled as HF. No toxicological data are available, but workers handling the material have not shown bad effects on continued exposure to small amounts.

<u>Diborane</u> (B_2H_6)

Diborane is very unstable. It ignites below -100°C upon exposure to air. It disproportionates at 100-200°C into hydrogen and B_4H_{10}. At 300°C, it decomposes into boron and hydrogen.

<u>Carbon Tetrafluoride</u> (CF_4)

This fluorocarbon has extremely high thermal stability and resistance to hydrolysis. It has been decomposed by pile radiation into fluorine and unidentified products (probably polymers). With 2×10^{18} nvt about 1.4 volumes of F_2 was produced per 100 volumes of

CF_4. The G value for production of fluorine was 0.28 molecules per 100 ev of energy absorbed. CF_4 is not extremely toxic, showing no noticeable physiological effects in low concentrations.

Nitrogen Trifluoride (NF_3)

Thermodynamic stability of NF_3 is low, but it is only weakly chemically active because of kinetic effects. Mixtures with H_2, CF_4, or CO ignite only upon heating. It has low toxicity (mice endured 1 hr exposure to 0.2% NF_3).

Silicon Tetrafluoride (SiF_4)

Thermodynamic computations indicate that SiF_4 cannot be reduced by H_2, H_2S, C, or P. These conclusions are confirmed by experiments. It is reduced by red-hot iron due to marked exothermy of formation of iron silicide. It fumes in moist air, but is difficult to hydrolyse completely under conditions allowing contact of product with the HF produced. Toxicity data are not available, but, due to hydrolysis, it should be handled with the same caution as HF. It is an irritating gas.

Silicon Hydride (SiH_4)

Silane is extremely reactive with oxygen. At -180° exposure to air results in explosive oxidation. At red heat it breaks up into Si + H_2.

Sulfur Hexafluoride (SF_6)

Sulfur hexafluoride is stable upon heating to $800^{\circ}C$. Chemical inertness is due largely to kinetic considerations. For example, hydrolysis does not occur readily even though thermodynamically possible. SF_6 is non-toxic but might form small amounts of S_2F_{10} in practical use. S_2F_{10} is extremely toxic, even more so than phosgene. The proposed ACGIH maximum allowable concentration is 0.025 ppm. Exposure of mice to SF_6-O_2 atmosphere resulted in no bad effects.

MoF_5, MoF_6, NbF_5

Molybdenum pentafluoride is of questionable stability. Not much data is available on it. The hexafluoride reacts rapidly with water, gaseous ammonia, and glass. Organic compounds reduce it. It reacts slowly with C, S, P, I_2, and metals. Although little information is available on NbF_5, it appears to be stable to 255°C. It does not react with oxygen but is reduced by hydrogen upon heating. It reacts with bromine, chlorine, sulfur, and water. It attacks glass.

Conclusions

The low thermal stability of B_2H_6, SiH_4, and NF_3 would prevent the use of these gases. Radiolytic decomposition and expense of isotope separation are disadvantages of BF_3. Radiolytic decomposition is known to occur in the case of CF_4 also, but may not be enough to prevent its use. It is entirely possible that all fluorides would be undesirable if traces of free fluorine would be incompatible with construction materials. Fluorine reacts with amorphous carbon to give CF_4 but with graphite an interstitial fluoride is formed with nearly double the original volume.

An experimental investigation of radiation damage to the more promising gases (SF_6, SiF_4 and possibly CF_4) would be required before definite recommendations could be made. A Co^{60} source could be used to measure damage at ambient and high temperatures before considering pile radiation. Relatively simple quartz or nickel capsule tests would be sufficient to measure decomposition rates and determine product compositions. A study should also be made to determine the reaction rates with carbon and trace impurities such as hydrogen, water and carbon oxides. Irradiation in-pile would be used only on those compounds which appeared promising after the preliminary study.

Distribution

1-3. DTIE, AEC
4. M. J. Skinner
5. Laboratory Records