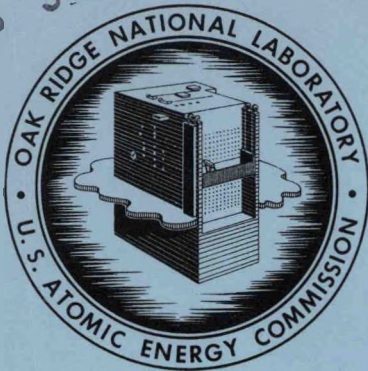


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THERMAL, RADIATION AND CHEMICAL STABILITY OF SULFUR DIOXIDE

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A search for information regarding the thermal and radiation stability of sulfur dioxide has been made. In addition, the chemical reactivity with some reactor materials has been examined. These topics are discussed separately below although it is obvious that they would be inter-related in a reactor system.

Thermal Stability

Sulfur dioxide is relatively stable thermally. It can be heated to above 2000°C without appreciable decomposition. At high temperatures, the dissociation products are S₂, O₂, SO, SO₃, S and O. Thermodynamic calculations of the equilibrium products have been made by St. Pierre and Chipman (1) for 1823°K and 1 atm and by Dr. R. F. Newton (2), Reactor Chemistry Division consultant, for 900°K and 90 atm.

Table 1. Calculated Equilibrium Products of SO₂
Partial Pressures

	1823°K, 1 atm	900°K, 90 atm
	atm	atm
O ₂	1.29 x 10 ⁻³	8.7 x 10 ⁻¹⁴
S ₂	4.49 x 10 ⁻⁸	4.2 x 10 ⁻⁵
SO ₃	4.25 x 10 ⁻⁴	1.7 x 10 ⁻⁴
SO ₂	0.998	90
SO	3.00 x 10 ⁻³	5 x 10 ⁻¹⁰
S	2.1 x 10 ⁻⁶	-
O	6.0 x 10 ⁻⁶	-
S ₈	-	10 ⁻¹⁸

Radiation Stability

Although no experimental information is available on radiation damage, it is the opinion of Dr. P. S. Rudolph (3) of the Chemistry Division that SO_2 will decompose in a radiation field. This is based on the cracking pattern of SO_2 (4) for 50 ev electrons shown in Table 2.

Table 2. Cracking Pattern of SO_2 for 50 ev Electrons

m/e	Ion	Relative Abundance
16	O^+	5.2
24	SO^{++}	0.8
32	S^+	10.4
48	SO^+	49.3
64	SO_2^+	100.0

Even greater decomposition would be expected with irradiation of high pressure gas or liquid. Sulfur and oxygen are probable products.

Chemical Stability

When sulfur dioxide is passed over carbon at high temperatures the following substances may be present: carbon, sulfur, sulfur dioxide, carbon monoxide, carbon dioxide, carbonyl sulfide and carbon disulfide. Owens, Sykes and Thomas (5) have calculated equilibrium composition of this rather complex system at temperatures above 1000°K . These are given in Table 3.

Table 3. Calculated Equilibrium Partial Pressures of C + SO_2

	1000 $^\circ\text{K}$	System 1200 $^\circ\text{K}$	1400 $^\circ\text{K}$
CO	0.4830 atm	0.7330 atm	0.7800 atm
CO_2	0.1132	0.00875	0.0009
COS	0.3019	0.0991	0.0326
CS_2	0.0940	0.1455	0.1646
S_2	0.0081	0.0163	0.0220
SO_2	4.3×10^{-8}	8.6×10^{-9}	2.2×10^{-9}

Siller (6) has made an extensive series of kinetic measurements using anthracite coal as the carbon source. The agreement with the above data was satisfactory, especially at higher temperatures when equilibrium was more quickly approached. However, the type of carbon used was important. When metallurgical coke was substituted, very little CS_2 was formed. Siller attributed this to the well known low chemical activity of impurities. Some earlier workers (7) found that solid carbon reacted with SO_2 at 700-1200°C, but with catalysts such as Fe_2O_3 the temperature could be lowered to 500°C. In another study (8) of the same reaction, it was found that with charcoal the reaction began at 500°C but was hardly noticeable at 800°C with coal.

Carbon Monoxide

Sulfur dioxide reacts with carbon monoxide to form carbon dioxide, free sulfur, and some carbonyl sulfide at temperatures as low as red heat (9).

Moisture

The reaction $3SO_2 + 2H_2O \rightarrow S + 2H_2SO_4$ is favored by high concentration, pressure, and temperature and is autocatalyzed by sulfur (10).

Beryllium Oxide

Budnikov and Belgaev (11) report BeO does not react with SO_2 although conditions are not stated.

Construction Metals

Iron, steel, monel and Inconel are common materials found satisfactory for dry or hot SO_2 but above the dew point corrosion takes place readily. Inconel is especially resistant to very hot SO_2 gas (12, 13). The

protective film on stainless steel is reported to be destroyed by hot gases containing sulfur oxides (14).

Summary

Although sulfur dioxide has a very high thermal stability it is very reactive with carbon, especially at temperatures above 500-800°C. If this objective is eliminated, the question of radiation damage remains. Even though the radiation stability is not promising, this could be investigated if other factors are favorable.

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