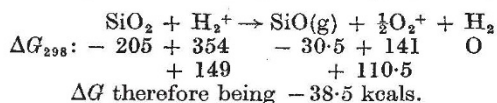


atoms produced at lower frequencies<sup>3</sup>, is sufficient to break at least one oxygen atom from the SiO<sub>2</sub> molecule to give SiO. A possible reaction, involving H<sub>2</sub><sup>+</sup> ions, is:



The formation of a volatile silicon compound strongly suggests that the second oxygen bond may be broken also. The bond energy O-SiO is not known, but it is presumably lower than that of Si-O, which is 186 kcal/mole. A comparison may be made with CO<sub>2</sub> which is broken down readily in a high-frequency field of 30 Mc/s<sup>4</sup> to give CO + O; the bond energy O-CO, which is 128 kcal/mole, is well within the range of lower frequency discharge energies. The C-O bond, however, has an energy of 256.7 kcal/mole and is too stable to be broken under such conditions.

This represents a new technique for coating objects and has the advantage that only SiO<sub>2</sub> and hydrogen are present in quantity in the system and the reaction rate is readily controlled.

F. K. McTAGGART

C.S.I.R.O.

Division of Mineral Chemistry,  
Chemical Research Laboratories,  
Melbourne.

<sup>1</sup> Emons, H. H., and Boenicke, H., *J. Prakt. Chem.*, **18**, 11 (1962).

<sup>2</sup> Weber, B. C., and Hessinger, P. S., *J. Amer. Ceram. Soc.*, **37**, 267 (1954).

<sup>3</sup> McTaggart, F. K., *Nature*, **199**, 839 (1963).

<sup>4</sup> Blackwood, J. D., and McTaggart, F. K., *Austral. J. Chem.*, **12**, 114 (1959).

### New High-pressure Polymorph of Sodium Fluoride

RECENTLY, Piermarini and Weir<sup>1</sup> found a high-pressure transition (from the face-centred cubic to the caesium chloride-type structure) between 9 and 15 kbar in anhydrous rubidium fluoride. Somewhat later transitions were also found for caesium fluoride and potassium fluoride<sup>2</sup>. Bridgman<sup>3</sup> found no evidence for high-pressure polymorphs in any of the alkali fluorides and noted that the fluorides appeared to be anomalous in this respect. For the case of sodium fluoride Bridgman<sup>4</sup> stated that "the shearing curve definitely has a maximum near the end of the pressure range, leading to the expectation of a transition. Because of the interest which any transition in this particularly simple compound would have, unusually careful exploration was made with the volume apparatus. Runs were made at 25°, 125°, 150°, and 175° C. It is certain that there is no transition with the large volume change associated with the change from face centred to body centred, which is the transition anticipated".

Pressures up to 50 kbar were generated in a piston-cylinder apparatus similar to that previously described<sup>5</sup>. Possible transitions were investigated with the volume-discontinuity method<sup>6</sup>. Hopkin and Williams AnalaR grade sodium fluoride was prepressed into a cylindrical pellet about 1 in. long by 0.5 in. in diameter, and wrapped in thin lead foil. Piston displacement versus pressure was plotted.

The curve obtained at room temperature was exceptional in that it appeared that the compressibility of sodium fluoride increased with increasing pressure—a highly unusual effect. At 157.5° C it was clear that a new high-pressure polymorph of sodium fluoride appears at 18.3 ± 1.0 kbar. The transition is exceedingly sluggish, and is not yet completed at 45 kbar. It is consequently not possible to measure the change in volume; but such change is certainly more than 5 per cent, perhaps much more. Armed with this knowledge, the room temperature curve (26.5° C) could now be interpreted as being normal with the transition at 16.8 ± 2.0 kbar. These uncer-

tainties are due mainly to the difficulty in detecting the onset of the transition. While the transition is reversible, at least at 157.5° C, it is then even more difficult to detect. The usual corrections for friction, hysteresis, etc., were made.

This new transition appears to be the long-looked-for transition from face-centred cubic to the caesium chloride structure. Confirmation by means of high-pressure X-ray studies would be very welcome. Although this transition is exceptionally sluggish, it is unmistakable in our apparatus, and it is not clear why Bridgman<sup>3,4</sup> failed to detect it.

CARL W. F. T. PISTORIUS  
L. J. ADMIRAAL

National Physical Research Laboratory,  
South African Council for  
Scientific and Industrial Research,  
Pretoria.

<sup>1</sup> Piermarini, G. J., and Weir, C. E., *J. Chem. Phys.*, **37**, 1887 (1962).

<sup>2</sup> Weir, C. E. (personal communication).

<sup>3</sup> Bridgman, P. W., *Phys. Rev.*, **48**, 893 (1935).

<sup>4</sup> Bridgman, P. W., *Proc. Amer. Acad. Arts Sci.*, **72**, 45 (1937).

<sup>5</sup> Kennedy, G. C., and Newton, R. C., *Solids under Pressure* (McGraw-Hill Book Co., Inc., New York, 1963).

<sup>6</sup> Jayaraman, A., Klement, W., Newton, R. C., and Kennedy, G. C., *J. Phys. Chem. Solids*, **24**, 7 (1963).

### Separation of Permanent Gases by Open Tubular Adsorption Columns

IN conjunction with investigations aimed at reducing the size, weight, and carrier gas consumption of a space-borne chromatograph for breathing atmosphere analysis, an open tubular (Golay) adsorption column, capable of separating fixed gases, has been designed. Separation was achieved for hydrogen, oxygen, nitrogen, and methane. Base-line resolution of oxygen and nitrogen was obtained as shown in Fig. 1. So far as I know, the separation of permanent gases with coated open tubular columns has not yet been reported.

Petitjean and Leftault<sup>1</sup>, and Mohnke and Saffert<sup>2</sup>, described open tubular adsorption columns prepared by activating the inner walls of capillary tubing. More recently, Halasz and Horvath<sup>3</sup>, Schwartz, Brasseaux and Shoemaker<sup>4</sup>, and Kirkland<sup>5</sup> discussed the preparation of

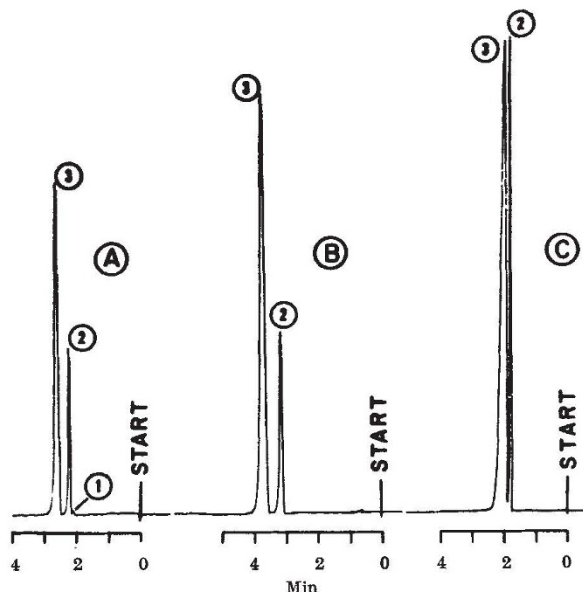


Fig. 1. Separation of (1) hydrogen, (2) oxygen and (3) nitrogen. Column: 75 ft. × 0.040 in. internal diam. open tubular column with molecular sieve 5 Å deposited on the inside wall. Temperature of analysis: 26° C. Miniature thermistor detector; 5 mV recorder. Sample sizes and carrier gas (helium) flow-rates: (A) 10 μl., 12 ml./min; (B) 10 μl., 1.5 ml./min; (C) 1 μl., 12 ml./min