X-Ray Diffraction Study of Liquid Silicon Tetrachloride*

CARL T. RUTLEDGE† AND GLEN T. CLAYTON

Department of Physics, The University of Arkansas, Fayetteville, Arkansas 72701

(Received 16 October 1969)

The angular intensity distribution of x rays scattered from liquid $SiCl_4$ has been measured at temperatures of −65 and +23°C by use of theta–theta reflection diffractometry. Molecular nearest neighbors reside in two well resolved shells of radii 3.9 and 6.8 Å. There are about 4.25 and 7.5 molecules in the respective shells at the lower temperature, and about 3.75 and 7.0 at the higher temperature. This agrees well with the macroscopic density of the liquid. The inner shell of neighbors is interpreted as resulting from short range orientational effects due primarily to molecular shape.

INTRODUCTION

The compound $SiCl_4$ has been studied in the gaseous state by electron diffraction[1] and the Si–Cl and Cl–Cl bond lengths determined. An x-ray diffraction study of the liquid state has been made,[2] using the transmission method, which seemed to indicate considerable molecular ordering, but which was deficient in several respects: (1) In transmission studies it is difficult to properly correct the intensity for scattering by the sample holder.[3] (2) Analysis of the electronic radial distribution function (ERDF) was made using effective atomic numbers and symmetrization of peaks rather than by calculation of ideal peaks according to the method of Waser and Schomaker.[4] (3) The intermolecular coordination was interpreted from the ERDF in terms of pairs of chlorine atoms belonging to different molecules, without mention of silicon atoms, supplemented by a peak representing molecular pairs. (4) The shortest distance between molecular centers was given as 6.4 Å, with a coordination number of four molecules. Even with the Cl–Cl peaks added, such a packing yields at most a macroscopic density which is much too small when compared to the measured density of the liquid.

For these reasons, it was apparent that a new study of liquid $SiCl_4$ would be desirable. Furthermore, such a study should provide information on the effect of molecular openness, as determined by the ratio of the radii of the central and corner atoms of the tetrahedral molecules, on the intermolecular structure by comparing the short range molecular coordination numbers with those previously obtained for CCl_4[5] and CF_4.[6] Finally, a study near the triple point as well as at room temperature might show interesting intermolecular structure changes.

EXPERIMENTAL AND ANALYSIS

X-ray diffraction patterns were obtained by use of a theta–theta reflection diffractometer. Molybdenum K-α radiation was used and the beam was monochromated by use of a bent and ground single crystal monochromator. The x-ray beam was $\frac{1}{2}°$ divergence, 2500 counts per point were taken, and three patterns were completed at each of two temperatures to insure consistency. The temperatures chosen were −65°C, which is about 5°C above the melting point, and 23°C, which was the equilibrium room temperature.

Sample containment was similar to that described for liquid Br_2,[7] and analysis was essentially the same as previously described for CF_4 and CCl_4.

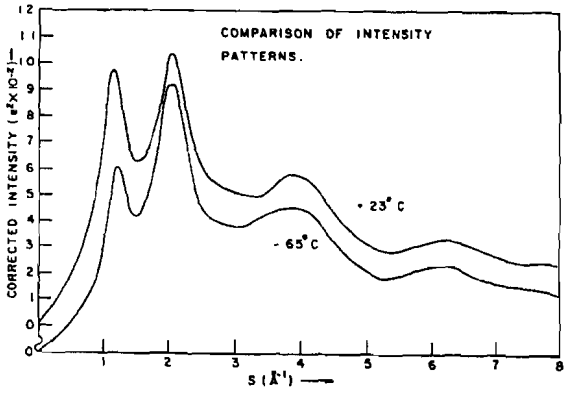

FIG. 1. A comparison of the intensity patterns at +23° (top) and −65° (bottom).

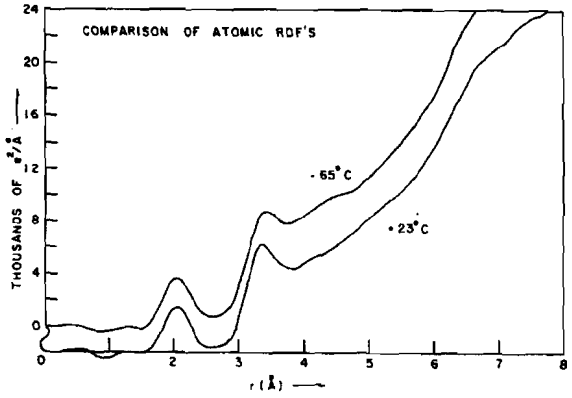

FIG. 2. A comparison of the atomic ERDF's at −65° (top) and +23° bottom).