



# Phase equilibrium data for potentially hazardous binary mixtures involving dichlorosilane, trichlorosilane and silicon-tetrachloride



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## ABSTRACT

Isothermal (vapour + liquid) equilibrium data were obtained for potentially hazardous binary mixtures of (dichlorosilane + trichlorosilane), (dichlorosilane + tetrachlorosilane), and (trichlorosilane + tetrachlorosilane) using an apparatus based on the “static-analytic” method. The apparatus was specially developed and designed to ensure safe measurement of the flammable, toxic, and corrosive components. The (dichlorosilane + trichlorosilane) system was measured at  $T = (343.04, 353.04 \text{ and } 363.00) \text{ K}$ , and the (dichlorosilane + tetrachlorosilane) system at  $T = (343.28 \text{ and } 353.07) \text{ K}$ , and the (trichlorosilane + tetrachlorosilane) system at  $T = (323.17, 333.11 \text{ and } 343.03) \text{ K}$ . The resulting data were correlated with the Peng–Robinson equation of state coupled with the Wong Sandler mixing rule. The model provided accurate description of all isotherms of the binary systems using temperature-independent interaction parameters regressed for all isotherms.

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## 1. Introduction

Trichlorosilane plays an important role in both the solar and electronics industry, as it is a key immediate used in the production of polysilicon [1]. Trichlorosilane, produced via hydrochlorination of metallurgical grade silicon metal, can be purified from a mixture of simple chlorosilanes ( $\text{SiH}_x\text{Cl}_y$ ) by distillation [2]. Distillation and distillation-like separation methods exploit the affinity of mixtures to progress toward the state of phase equilibrium; although it should be noted that very seldom does equilibrium actually occur at the stages within a distillation column. Distillation-type methods are highly energy intensive, hence distillation column synthesis and design must be optimized effectively; thus, the experimental phase equilibrium data, on which the optimization is based, must be of high quality. Unfortunately, highly accurate (vapour + liquid) equilibrium (VLE) data involving mixtures of simple chlorosilanes ( $\text{SiH}_x\text{Cl}_y$ ) are scarce in open literature. VLE data involving binary systems of simple chlorosilanes are rare; to the best of our knowledge only two binary VLE sets including trichlorosilane have been published. These include firstly, isobaric binary VLE data at 98.659 kPa for the binary system of (trichlorosilane + tetrachlorosilane (silicon-tetrachloride)) measured by Zanta and Laskafeld [3] in 1969, and secondly, isobaric binary VLE at  $P = (0.70, 1.39 \text{ and } 2.07) \text{ MPa}$  for the binary system of (dichlorosilane

+ trichlorosilane) measured by Olson in 1989 [4]. The lack of such data may be attributed to the difficulty involved in working with chlorosilanes. The highly flammable, toxic and corrosive nature of chlorosilanes makes VLE measurement non-trivial.

In order to undertake measurements on these experimentally difficult systems, a specially designed inert enclosure was built in which the (vapour + liquid) equilibrium apparatus and all associated charging and analytical equipment were also housed. A detailed description of the experimental setup is available in the thesis of Nelson [5].

VLE measurements were undertaken for the (dichlorosilane + trichlorosilane) system at  $T = (343.04, 353.04 \text{ and } 363.00) \text{ K}$ , the (dichlorosilane + tetrachlorosilane) system at  $T = (343.28 \text{ and } 353.07) \text{ K}$ , and the (trichlorosilane + tetrachlorosilane) system at  $T = (323.17, 333.11 \text{ and } 343.03) \text{ K}$ .

The experimental data are modelled using an equation of state approach, the details of which are presented in detail in section 2.4.

## 2. Experimental

### 2.1. Chemicals

Dichlorosilane ( $\text{SiH}_2\text{Cl}_2$ , CAS number: 4109-96-0), trichlorosilane ( $\text{SiHCl}_3$ , CAS number: 10025-78-2), and tetrachlorosilane ( $\text{SiCl}_4$ , CAS number: 10026-4-7) were supplied by Sigma-Aldrich. Chemical purities (mass basis) stated by Sigma-Aldrich, and detector area percentages determined via gas chromatography (after

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**TABLE 1**

Purities and critical property data for the chemicals used for the phase equilibrium measurements.

Component	SiH <sub>2</sub> Cl <sub>2</sub> (g)	SiHCl <sub>3</sub> (l)	SiCl <sub>4</sub> (l)
Mass fraction purity (supplier) <sup>a</sup>	0.999	0.99	0.9999
GC <sup>b</sup> area percentage	>99.5 <sup>c</sup>	>99 <sup>c</sup>	>99.9 <sup>c</sup>
T <sub>c</sub> /K	459.0 [11]	479.0 [11,19]	507.0 [11]
P <sub>c</sub> /MPa	4.529 [11]	4.054 [19]	3.589 [11]
ω	0.0985 [11]	0.1935 [19]	0.1935 [19]

<sup>a</sup> Chemicals supplied by Sigma–Aldrich.

<sup>b</sup> Gas chromatograph.

<sup>c</sup> Analysed using a thermal conductivity detector, components and impurities separated via a ZB-1ms capillary column.

degassing) are listed in table 1. All chemicals were degassed thoroughly via periodic vapour withdrawal. A quantitative analysis regarding the purity of each chemical was not undertaken, as the respective impurities of each chemical were unknown. Further purification of the chemicals was not performed due to their hazardous nature. Furthermore, refractive indices and densities of the chemicals were not measured due to their corrosive nature.

## 2.2. Apparatus

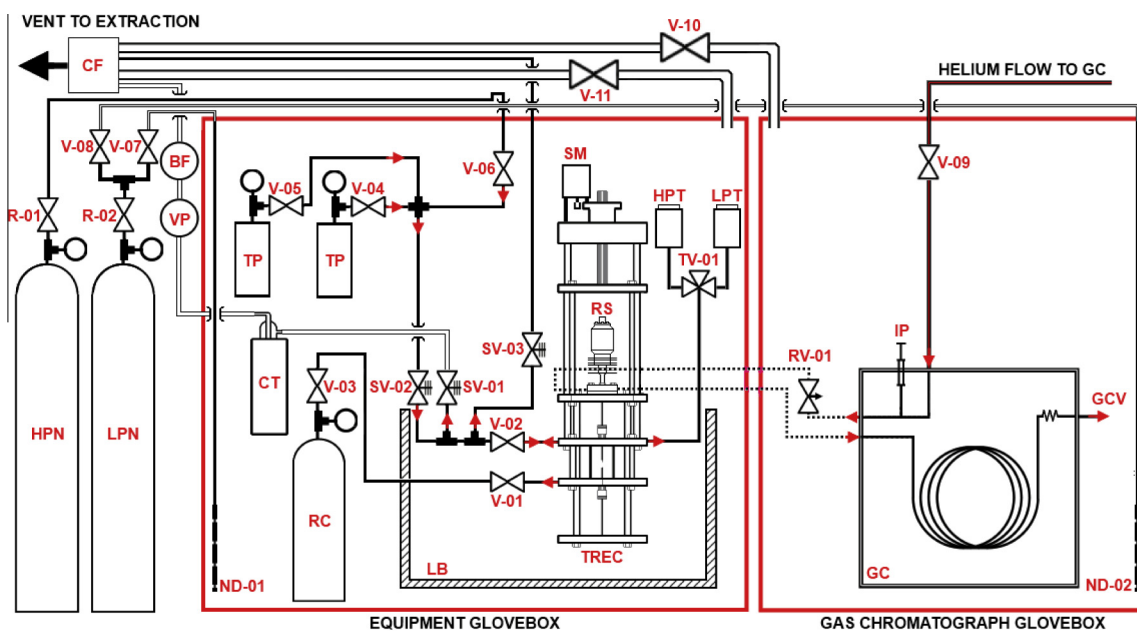
The apparatus used in this work incorporated the “static-analytic” measurement principle. The small-volume sapphire equilibrium cell (approximately 18 cm<sup>3</sup> total volume), the equilibrium cell housing, as well as the sampling and agitation technique used in this study are a reproduction of the apparatus developed by Narasigadu *et al.* [6]; further information on the small-volume equilibrium cell can be found in the work of Narasigadu *et al.* [6].

Isothermal conditions within the equilibrium cell were attained by submerging the cell into an isothermally regulated liquid solution contained within a 50 L steel bath. The temperature of the bath fluid was controlled using a Polyscience controller (Model 7312); the temperature stability of the controller stated by the manufacturers is  $T = \pm 0.01$  K. Silicone oil was used as the thermostating fluid.

The temperature of the equilibrium cell was measured by two three-wire WIKA model REB 1/10 DIN Pt-100s. The Pt-100 probes were inserted into wells drilled into the top and bottom flanges that support and seal the sapphire tube. The pressure within the equilibrium cell was measured using a 0–8 MPa gauge WIKA model P-10 precision transmitter (accuracy:  $\leq 0.05\%$  of span). The pressure transmitter was housed within a thermo-regulated aluminium block to avoid temperature disturbances to the pressure transmitter due to changes in ambient temperature (although WIKA do state that there is no additional temperature error between (273 and 323) K. A portion of the pressure transmitter line, protruding above the isothermal bath fluid, connecting the pressure transmitter to the equilibrium cell was heat-traced to avoid temperatures differing with the isothermal bath temperature. The signals of the pressure transmitters and temperature probes, measuring the conditions within equilibrium cell, were transmitted to a data acquisition unit (Agilent; Model 34970A), which was connected (by a RS-232 connection) to a desktop computer, allowing real-time pressure and temperature measurement and recording.

Evacuation of the equilibrium cell and all transfer lines was achieved with an Edwards RV3 vacuum pump. The evacuation loop consisted of 8 mm OD (outer diameter) Isoversinic (superior resistance to corrosive chemicals) tubing attached to the inlet of a glass cold-trap; the cold-trap (contained within a flask of liquid nitrogen) was attached before the inlet of the vacuum pump.

The composition of the equilibrium phase samples were analysed using a Shimadzu 2010 gas chromatograph (GC) equipped with a thermal conductivity detector (TCD). The equilibrium phase samples were transferred from the equilibrium cell to the GC via a single mobile Rapid On-Line Sampler Injector (ROLSI™) sampler. The position and motion of the ROLSI™ capillary tip within the equilibrium cell was controlled with a 2.5 N · m<sup>-1</sup> stepper motor. The lines connecting the ROLSI™ to the GC were heat traced to ensure sample homogeneity. A Phenomenex Zebron ZB-1ms (100% dimethylpolysiloxane) capillary column (length – 15 m; ID – 0.25 mm; film thickness – 0.25 μm) was used for sample analysis, with helium as the carrier gas.



**FIGURE 1.** Process flow diagram: BF – ballast flask; CF – carbon filter; CT – cold-trap; GC – gas chromatograph; GCV – gas chromatograph vent; HPN – high-pressure nitrogen; IP – injection port; LB – liquid bath; LPN – low-pressure nitrogen; ND – nitrogen distributor; TP – thermal press; PT – pressure transducer; SM – stepper motor; SV – solenoid valve; R – regulator; RC – storage cylinder RS – ROLSI™; RV – pressure relief valve; TREC – thermo-regulated equilibrium cell; TV – three-way valve; V – valve; VP – vacuum pump. Red arrows indicate the direction of gas flow. Red lines indicate the glove box boundaries. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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