

Characterization of silicon-containing catalysts by ^{29}Si solid-state NMR

Spectroscopic background: ^{29}Si nuclei have a spin of $I = 1/2$ and, therefore, no quadrupole moment. The ^{29}Si isotope has a natural abundance of 4.7 % and, in this state, a sensitivity of 3.7×10^{-4} in comparison with ^1H nuclei (1.0). Therefore, it is at the limit for solid-state NMR studies being possible to investigate without isotopic enrichment. For basic principles of solid-state NMR, see lectures “Solid-State NMR Spectroscopy” for Bachelor students or PhD seminars, accessible via the link “Lectures for Students”.

The framework of crystalline aluminosilicates, such as zeolites, contains tetrahedrally coordinated silicon with Si-O-Si and Si-O-Al bridges. These local structures result in five different Q^4 silicon environments, denoted as **Si(*n*Al) or Si((4-*n*)OSi,*n*OAl) units**, with the number ***n* = 0, 1, 2, 3 or 4** of the aluminum atoms in the second coordination sphere. Each type of the various Si(*n*Al) units in **Fig. 1, top**, yields ^{29}Si MAS NMR signals in different ranges of chemical shifts between $\delta_{^{29}\text{Si}} = -120$ and $\delta_{^{29}\text{Si}} = -70$ ppm [1, 2].

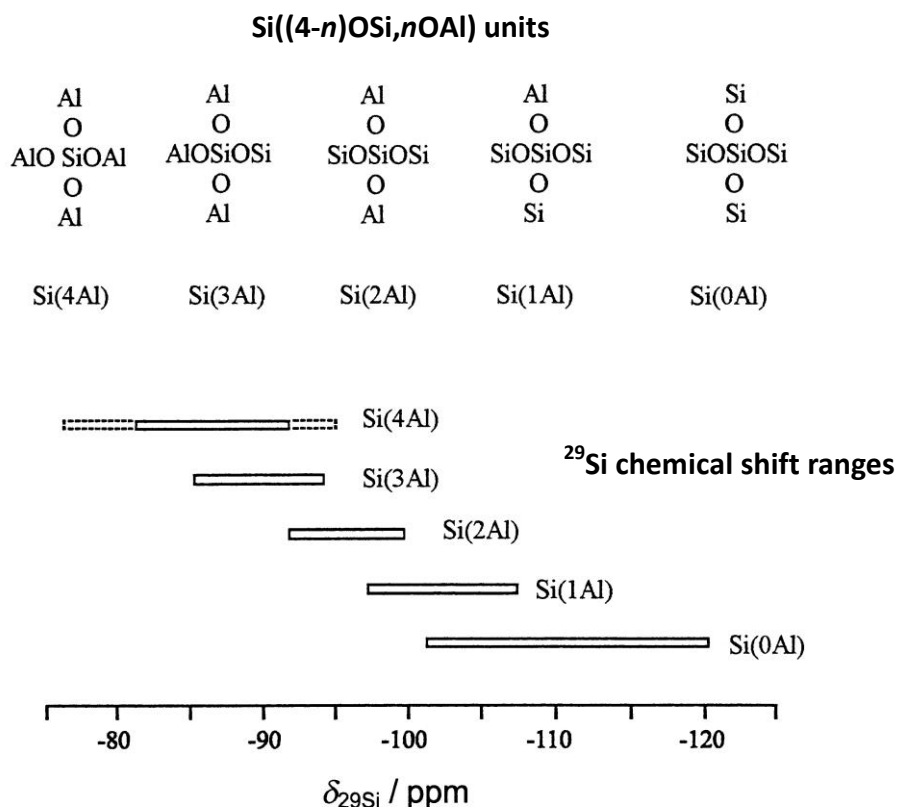


Fig. 1

For zeolite Y with a single crystallographic T-site, ^{29}Si MAS NMR spectra of aluminum-containing samples consist of $\text{Si}(n\text{Al})$ signals (**Fig. 2, top spectra**) with

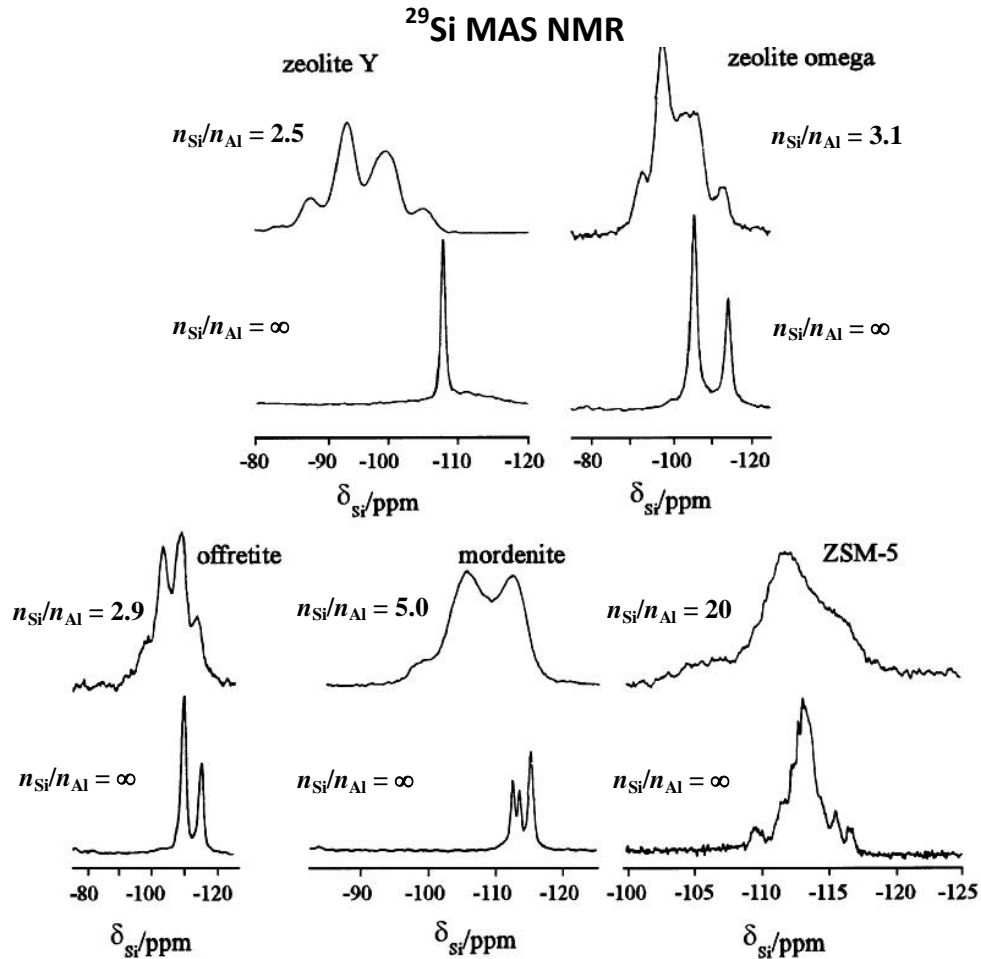


Fig. 2

intensities $I_{\text{Si}(n\text{Al})}$, which are a function of the framework composition, i.e. of the aluminum content. Therefore, the framework $n_{\text{Si}}/n_{\text{Al}}$ ratio of these materials can be calculated from the ^{29}Si MAS NMR intensities using the formula [2]:

$$n_{\text{Si}} / n_{\text{Al}} = \sum_{n=0}^4 I_{\text{Si}(n\text{Al})} / \sum_{n=0}^4 0.25 \cdot n \cdot I_{\text{Si}(n\text{Al})} \quad (1)$$

By a comparison of the framework $n_{\text{Si}}/n_{\text{Al}}$ ratio, calculated via **Eq. (1)**, with the bulk composition determined by chemical analysis, the amount of aluminum atoms at extra-framework positions can be obtained. However, in each zeolite, SiOH groups

exist, bound to silicon atoms (**Q³ units corresponding to Si(3OSi,1OH)**) located at the outer surface of the zeolite particles or at framework defects. The chemical shifts of Si(3OSi,1OAl) units ($\delta_{29\text{Si}} = -95$ to -105 ppm) are in the same range like those of Si(3OSi,1OH) units ($\delta_{29\text{Si}} = \mathbf{-103}$ to $\mathbf{-100}$ ppm) [1, 2]. Therefore, the number of SiOH groups limits the range of $n_{\text{Si}}/n_{\text{Al}}$ ratios, which can be derived by ^{29}Si MAS NMR spectroscopy, or their number must be previously determined by a complementary method, such as ^1H MAS NMR spectroscopy.

In the same manner, as above-mentioned for ^{29}Si MAS NMR spectroscopy on aluminosilicate-type zeolites, the chemical compositions of zincosilicates [3] and gallium-modified ZSM-5 (Ga-MFI) [4] can be determined. In the ^{29}Si MAS NMR spectra of the titanosilicate ETS-10 and the titanoaluminosilicate ETAS-10, signals of **Si(4OSi)** units at $\delta_{29\text{Si}} = \mathbf{-103}$ ppm, **Si(3OSi,1OTi)** units at $\delta_{29\text{Si}} = \mathbf{-97}$ ppm to $\mathbf{-94}$ ppm, and **Si(2OSi,1OAl,1OTi)** units, **ca. 4 ppm low-field shifted (left shifted) from the signal of Si(3OSi,1OTi)** units, occur [5]. Utilizing **Eq. (1)** with Si((4- n)- m)OSi, n OGa, m OTi instead of Si((4- n)OSi, n Al), and setting the corresponding factors n and m in the denominator, the framework $n_{\text{Si}}/n_{\text{Ga}}$ and $n_{\text{Si}}/n_{\text{Ti}}$ ratios, respectively, can be determined [3, 4].

Numerous zeolite frameworks are characterized by crystallographically non-equivalent T-sites, but chemically equivalent environments, being responsible for a chemical shift distribution and/or a split of the ^{29}Si MAS NMR signals of framework silicon atoms. Dealumination and ultrastabilization of zeolite frameworks, e.g. by steaming and calcination, result in an elimination of all Si(n Al) units and a strong decrease of the ^{29}Si MAS NMR signal widths [6-9]. Therefore, the ^{29}Si MAS NMR spectra shown in **Fig. 2, bottom**, of each pair consists exclusively of narrow Si(4OSi) signals.

While the ^{29}Si MAS NMR spectrum of zeolite Y shows a single Si(4OSi) signal only, corresponding to one crystallographic T-site, most of the other zeolites cause ^{29}Si MAS NMR spectra with Si(4OSi) signals of at least two crystallographically non-equivalent T-sites. The intensity ratios of these lines, e.g. of 2 : 1 for zeolites omega and offretite, correspond to the population ratios of these different T-sites in the crystallographic structure. In **Table 1**, the ^{29}Si chemical shift data of some selected zeolites are summarized.

Zeolites	$n_{\text{Si}}/n_{\text{Al}}$	T Sites	$\delta_{29\text{Si}}/\text{ppm}$					Refs.
			Si(4Al)	Si(3Al)	Si(2Al)	Si(1Al)	Si(0Al)	
zeolite A (LTA)	1.0	T	-89.6					[16]
	∞	T					-112.9	[17]
zeolite Y (FAU)	2.5	T	-83.8	-89.2	-94.5	-100.0	-105.5	[16]
	∞	T					-107.8	[18]
omega (MAZ)	3.1	T1		-89.1	-93.7	-98.8	-103.4	[19]
		T2	-89.1	-93.7	-98.8	-107.0	-112.0	[19]
	∞	T1					-106.0	[2]
		T2					-114.4	[2]
offretite (OFF)	2.9	T1		-93.5	-97.5	-101.9	-106.9	[20]
		T2		-97.5	-101.9	-106.9	-112.5	[20]
	∞	T1					-109.7	[2]
		T2					-115.2	[2]
mordenite (MOR)	5.0	T1 - T4			-100.1	-105.7	-112.1	[21]
	∞	T1					-112.2	[2]
		T4					-113.1	[2]
		T2 + T3					-115.0	[2]
ZSM-5 (MFI)	20	T1 - T12				-106.0	-112.0	[22]
ZSM-39 (MTN)	∞	T1					-107.8	[13]
		T2					-115.0	[13]
		T3					-120.3	[13]
MCM-22 (MWW)	∞	T2 + T6					-105.5	[23]
		T1 + T3					-110.8	[23]
		T13					-111.5	[23]
		T5					-112.6 – -112.0	[23]
		T4 + T7 + T12					-113.7 – -113.0	[23]
		T9 + T10					-116.7 – -115.8	[23]
		T8 + T11					-120.3 – -119.9	[23]

Table 1

As more sophisticated examples, the ^{29}Si MAS NMR spectra of a MWW-type zeolite **MCM-22** ($n_{\text{Si}}/n_{\text{Al}} = 11$) and its **dealuminated material** ($n_{\text{Si}}/n_{\text{Al}} = 20$) are shown in **Figs. 3a and 3b**, respectively [10]. Because of the low aluminum content of dealuminated MCM-22, the ^{29}Si MAS NMR spectrum consists mainly of signals caused by Si(4OSi) units. At least five ^{29}Si MAS NMR signals at $\delta_{29\text{Si}} = -118.5$ ppm,

-115.3 ppm, -112.3 ppm, -110.3 ppm, and -104.0 ppm due to Si(4OSi) units are required to describe the spectrum in **Fig. 3b** [10]. These signals are due to framework silicon atoms crystallographically non-equivalent T-sites. For highly siliceous zeolite MCM-22 ($n_{\text{Si}}/n_{\text{Al}} = \infty$), up to seven ^{29}Si MAS NMR signals can be resolved [23].

In the case of the zeolite MCM-22 with $n_{\text{Si}}/n_{\text{Al}} = 11$, i.e. a significantly higher aluminum content (**Fig. 3a**), a corresponding set of Si(3OSi,1OAl) signals appears, which is shifted to more positive ^{29}Si chemical values by about $\Delta\delta_{29\text{Si}} = 5$ to 6 ppm (compare $\delta_{29\text{Si}}$ values of other aluminum-containing zeolites in **Table 1**). Therefore, the ^{29}Si MAS NMR spectra in **Figs. 3a and 3b** were simulated using two sets of five signals: Five for Si(4OSi) and five for Si(3OSi,1OAl) units. Utilizing the relative intensities of the two sets of Si(3OSi,1OAl) and Si(4OSi) signals of 1:1.75 for the parent MCM-22 and 1:4 for the dealuminated MCM-22, the simulation of the ^{29}Si MAS NMR spectra in **Figs. 3a and 3b** yielded the resonance positions of the five Si(3OSi,1OAl) signals of $\delta_{29\text{Si}} = -112.5$ ppm, -110.5 ppm, -107.5 ppm, -104.5 ppm, and -98.0 ppm. In addition, the simulation of the ^{29}Si MAS NMR spectrum of the parent MCM-22 (**Fig. 3a**) required the assumption of a signal at $\delta_{29\text{Si}} = -102$ ppm due to surface SiOH groups (Q^3 corresponding to Si(3OSi,1OH)) with a relative intensity of ca. 5% [10].

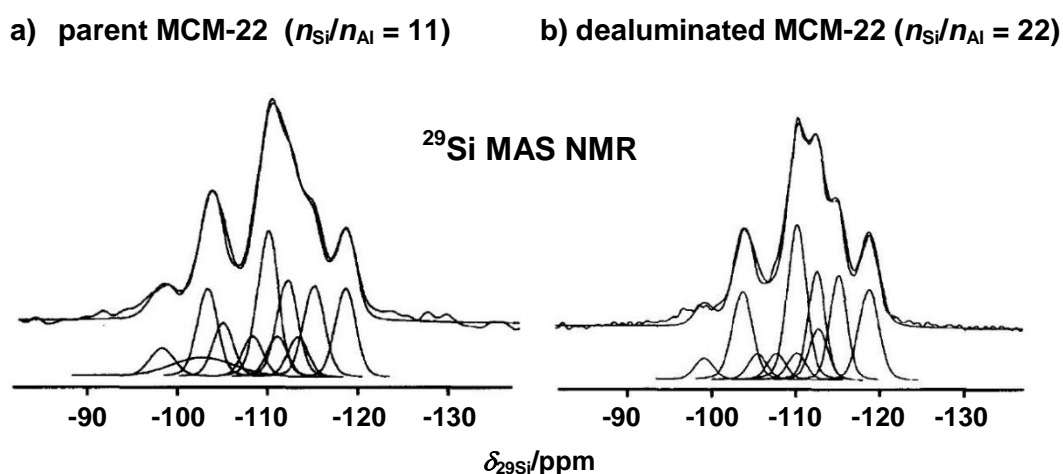


Fig. 3

Differences in the ^{29}Si chemical shifts of framework silicon atoms located on crystallographically non-equivalent T-sites are mainly caused by different local geometries of the SiO_4 tetrahedra. Empirical correlations and theoretical

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considerations yielded that the ^{29}Si chemical shifts, δ_{Si} , of $\text{Si}((4-n)\text{OSi}, n\text{Al})$ units are linearly correlated to the mean value, $\bar{\alpha}$, of the four Si-O-T bond angles. With linear regression analysis, quantitative relationships between the values of δ_{Si} and $\bar{\alpha}$ have been derived. For $\text{Si}(4\text{OAl})$ units in sodalite, cancrinite, thomsonite, and zeolites A, X, Y, and ABW, the following correlation [11]:

$$\delta_{\text{Si}} / \text{ppm} = -5.230 - 0.570 \cdot \bar{\alpha} \quad (2)$$

was obtained. The correlation between δ_{Si} and $\overline{\cos \alpha / (\cos \alpha - 1)}$ was theoretically derived [12]:

$$\delta_{\text{Si}} / \text{ppm} = -223.9 \overline{\cos \alpha / (\cos \alpha - 1)} + 5n - 7.2 \quad (3)$$

where n corresponds to the number of aluminum atoms in the first coordination sphere of T-sites. Applying **Eqs. (2)** and **(3)**, the ^{29}Si NMR shifts of silicon atoms at crystallographically non-equivalent T-sites of zeolite frameworks can be calculated from the Si-O-T bond angles, which are obtained by XRD. Therefore, this method allows the examination of structure models derived by XRD.

Three-dimensional connectivities between crystallographically non-equivalent T-sites in zeolites have been investigated applying COSY (Correlation Spectroscopy) and INADEQUATE (Incredible Natural Abundance Double Quantum Transfer Experiment) pulse sequences. The COSY experiment is based on the measurement of the J-coupling (direct bond coupling) within a molecular structure [13]. **Fig. 4a** shows the pulse sequence consisting of: (i) the preparation of the ^{29}Si spin system by magnetization transfer from the abundant S-spins (^1H nuclei) to the dilute I-spins (^{29}Si nuclei) by cross-polarization (CP), (ii) the evolution of the ^{29}Si spin system during the time period t_1 , (iii) a fixed delay (FD) before and after a $\pi/2$ pulse, and (iv) the acquisition (AQ) of the free induction decay of the ^{29}Si magnetization during the time period t_2 [13]. The 2D ^{29}Si COSY MAS NMR spectrum of zeolite ZSM-39 in **Fig. 4c** was recorded with 128 increments in t_1 and 64 scans for each t_1 [13]. The contour plot in **Fig. 4d** shows diagonal peaks of silicon atoms at T1, T2 and T3 sites and off-diagonal peaks (cross-peaks) originating from silicon atoms at T1 and T2 (cross-peak T1T2) and at T2 and T3 (cross-peak T2T3) sites. Hence, the cross-peaks clearly indicate connectivities between silicon atoms on T1 and T2 sites and between silicon

atoms on T2 and T3 sites. These results agree with the structure model of zeolite ZSM-39 in **Fig. 4b** [13].

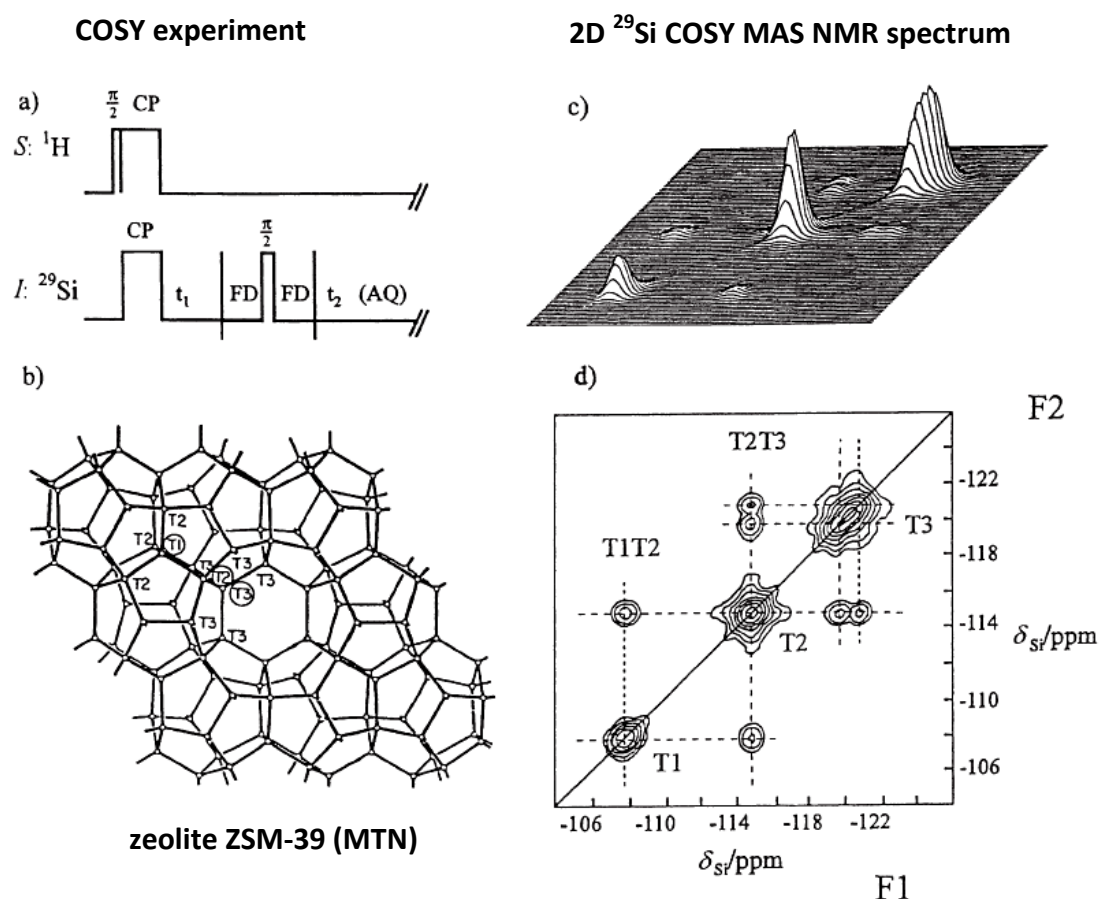


Fig. 4

For a survey on ^{29}Si MAS NMR spectroscopy of silicon-containing solid catalysts, see Refs. [1], [2], and [20]. Refs. [14] and [15] are reviews on recent advances in the application of ^{29}Si liquid and solid-state NMR spectroscopy for the study of synthesis mixtures, gels, and zeotype materials as well as their ^{29}Si NMR parameters.

Catalyst preparation: Hydrated as well as dehydrated catalyst samples can be investigated by ^{29}Si MAS NMR spectroscopy. In the case of studies of dehydrated samples, adsorption of O_2 can be helpful to decrease the T_1 time due to the paramagnetic properties of oxygen molecules.

^{29}Si MAS NMR studies: For decreasing the ^{29}Si MAS NMR line width, high-power ^1H decoupling should be applied for ^{29}Si MAS NMR studies. Typically, the nuclear spins of ^{29}Si nuclei in aluminosilicates have T_1 relaxation times requiring ^{29}Si MAS NMR <https://michael-hunger.de>

measurements with a repetition time of at least 30 s. With decreasing aluminum content, however, the T_1 time can increase up to some minutes, which requires a correspondingly higher repetition time. In the case of exciting the ^{29}Si nuclei by cross-polarization (CP), the repetition time is limited by the T_1 time of the ^1H nuclei, which is typically significantly shorter than the T_1 time of ^{29}Si nuclei. In the case of ^{29}Si CP MAS NMR studies, however, the signal intensities do not correlate with the real spin numbers, which hinders the quantitative evaluation of obtained ^{29}Si CPMAS NMR spectra by Eq. (1). Chemical shifts are referenced to octakis(trimethylsiloxy) silsesquioxane powder (Q_8M_8 , $\delta_{^{29}\text{Si}} = 11.7$ ppm) at spinning rates of $\nu_{\text{rot}} = 2$ to 3 kHz. This reference is easier to handle in MAS NMR rotors than liquid tetramethylsilane (TMS, $\delta_{^{29}\text{Si}} = 0$ ppm) with a boiling point of $T = 299$ to 301 K.

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