Original Paper

Thermodynamic assessment of the Ge−Si−O−Cl−H system

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An assessed thermodynamic dataset for the Ge−Si−O−Cl−H system useful for application in the glass fiber industry is presented. The focus of the work is on the germanium-bearing species. Taking into account the available vapor pressure measurements on the Ge−O, Ge−Cl, Ge−Cl−H, and Ge−O−Cl systems, modifications have been made to the recommended data for the important oxide and halide species. The GeO_2−SiO_2 and $GeCl_4$−$SiCl_4$ binary systems have been thermodynamically optimized using simple models. The current dataset, when combined with the data from the FactSage™ database for the other required species/phases, can be used to make useful calculations of glass vapor equilibria pertinent to the manufacture of germanium-doped silica glass fibers using vapor deposition methods.

1. Introduction

GeO_2 is one of the dopants used to modify the refractive index of silica glass fibers. In the flame hydrolysis method of chemical vapor deposition used in the manufacture of silica glass fibers, a mixture of $SiCl_4$ and $GeCl_4$ is blown over a hot flame at high temperatures resulting in the formation of an $(Si,Ge)O_2$ glass powder ("soot"). The soot is further treated, consolidated, and drawn to the fiber form. The availability of an assessed dataset on the thermodynamic properties of the Ge−Si−O−Cl−H system is useful for thermodynamic analysis aimed at understanding the influence of parameters such as deposition temperature, $SiCl_4$/$GeCl_4$ ratio, and flame atmosphere in the vapor deposition process. Thermodynamic analysis can be used to gain information on partial pressures of gaseous species and compositions of the condensed phases involved in the reactions. For example, the evaporation of GeO from silica-germania glasses during the collapsing process is a known problem that causes a central dip in the refractive index of the glass. The ability to calculate the vapor pressure of this component in the reaction atmosphere is therefore of great interest to glass fiber manufacturers. In this paper we assess the thermodynamic data for the Ge−Si−O−Cl−H system that are pertinent to the vapor deposition process used in the glass fiber industry.

The thermodynamic dataset for the Ge−Si−O−Cl−H system presented here combines the assessed thermodynamic properties of the germanium-bearing species, based largely on the compilation of Gurvich et al. [1], with the thermodynamic data for the silicon-bearing species from the FactSage™ database [2]. The focus of this paper is on the thermodynamic properties of germanium-bearing spe-

cies; the data on the other species have been previously assessed and included in the FactSage™ database [2]. Thermodynamically evaluated phase diagrams are presented for the GeO_2−SiO_2 and $GeCl_4$−$SiCl_4$ binary systems. In all the calculations presented here, the gas phase was assumed to be an ideal mixture. The thermodynamic data for the germanium-bearing species presented here can be used in conjunction with the FactSage™ software [2] for performing thermodynamic calculations relevant to the vapor deposition process involving a GeO_2−SiO_2 glass in equilibrium with a gas phase. The sources of the thermodynamic data are discussed below, followed by an evaluation of the data for the critical species (mainly oxides and halides) based on published experimental vapor pressure measurements.

2. Thermodynamic data

Table 1 gives the assessed data on the pure gas, liquid, and crystalline phases. These are briefly discussed below.

2.1 Ge and Ge_2(g)

For the crystalline, liquid, and gaseous forms of germanium and for Ge_2(g), we have taken the thermodynamic data from Gurvich et al. [1]. The values for crystalline and liquid germanium are the same as those adopted by CODATA (International Council for Science, Committee on Data for Science and Technology). There has been, however, some reservation about the value of the standard enthalpy of formation of Ge(g) adopted in [1]. Shim et al. [3] argued that because Gurvich et al. [1] used the Knudsen cell data from Severin et al. [4] to obtain the enthalpy of formation, there

Table 1. Assessed thermodynamic properties relative to elements. H^0 and S^0 are the standard state (298.15 K, 10^5 Pa) enthalpy of formation from the elements and absolute entropy. The numbers under columns a to h represent isobaric heat capacity, C_p, coefficients given by: $C_p = a + b(10^{-3})T + c(10^5)T^{-2} + d(10^{-6})T^2 + e(10^{-9})T^3 + fT^{-1} + gT^{-0.5} + h(10^8)T^{-3}$.

phase/species	T in K	H^0_{298} in J mol⁻¹	S^0_{298} in J mol⁻¹ K⁻¹	C_p in J mol⁻¹ K⁻¹							
				a	b	c	d	e	f	g	h
Ge (crystal)	298 to 1211	0	31.090	24.096	2.987	−1.57					
Ge (liquid)	1211 to 4900	35492	58.644	27.600							
Ge (gas)	298 to 1500	367800	167.903	45.978	−35.137	−5.62	18.223	−3.135			
	1500 to 10000			18.722	2.677	37.11	−0.523	0.033			
Ge₂ (gas)	298 to 1500	471500	256.450	61.949	−44.434	−8.55	31.261	−7.373			
	1500 to 6000			36.071	1.265	36.56	0.511	−0.086			
GeO (gas)	298 to 1500	−41000	223.887	26.484	21.868	−0.80	−15.984	4.128			
	1500 to 6000			32.340	4.839	9.50	−1.527	0.180			
Ge₂O₂ (gas)	298 to 3000	−268950	312.731	85.203	−0.444	−6.33			−2823		
Ge₃O₃ (gas)	298 to 3000	−479840	417.492	136.530	−0.742	−4.42			−4937		
GeO₂ (rutile)	298 to 3000	−580200	39.710	82.123		−40.23				−114.93	5.28
GeO₂ (quartz)	298 to 3000	−558355	56.698	100.892						−822.41	−0.30
GeO₂ (glass-liquid)	298 to 980	−542589	67.418	64.297	13.915	−15.69					
	980 to 3000			73.858	4.092						
GeO₂ (gas)	298 to 1500	−106172	241.244	41.162	42.057	−3.66	−31.135	8.043			
	1500 to 6000			62.208	0.075	−26.41	−0.014	0.001			
GeCl (gas)	298 to 1500	69031	245.901	41.014	6.156	−4.53	9.973	3.551			
	1500 to 6000			45.546	−5.283	−23.47	1.450	−0.101			
GeCl₂ (gas)	298 to 1500	−170800	295.825	56.742	3.138	−3.29	−2.455	0.660			
	1500 to 6000			58.197	0.002	−4.50	−0.0003	0.00002			
GeCl₃ (gas)	298 to 1500	−267559	329.902	80.266	6.179	−6.10	−4.828	1.296			
	1500 to 6000			83.136	0.004	−8.52	−0.001	0.0001			
GeCl₄ (liquid)	298 to 2000	−530380	248.237	151.670							
GeCl₄ (gas)	298 to 1500	−495000	348.393	103.050	10.782	−8.60	−8.408	2.253			
	1500 to 6000			108.069	0.009	−12.83	−0.002	0.0001			
Ge₂Cl₆ (gas)	298 to 2500	−564840	451.872	192.046	4.310	−35.40					
GeH₃Cl (gas)	298 to 2000	−70249	263.508	56.093	48.276	−13.61	−12.601				
GeH₂Cl₂ (gas)	298 to 2200	−220246	308.654	83.900	17.255	−18.13	−3.782				
GeHCl₃ (gas)	298 to 1400	−359280	328.026	86.209	25.364	−8.77	−9.615				

could be an increased error in this value. Severin et al. [4] assumed the gas phase to be composed entirely of Ge(g), whereas it is known that the vapor phase contains germanium polymers up to Ge₇ in addition to Ge(g), and this could introduce further error [3]. This will most likely not have any significant impact on calculations for applications in glass manufacturing because Ge(g) is expected to become an important constituent of the vapor only under highly reducing conditions.

2.2 GeO(g), Ge₂O₂(g), and Ge₃O₃(g)

The vapor phase over pure GeO₂ is composed essentially of GeO(g) and O₂(g) (GeO₂ undergoes congruent vaporization) up to high temperatures, as has been determined in mass spectrometric studies in the temperature range 1294 to 1480 K [5 to 8]. Towards the higher end of this temperature range, in addition to GeO(g), minor amounts of GeO₂(g), Ge₂O₂(g), and Ge₃O₃(g) are also present in the gas phase [8 to 10].

Drowart et al. [5] in their mass spectrometric study in the temperature range of 754 to 950 K identified that the predominant species in the high-temperature vapor over GeO (amorphous) or [GeO₂ (quartz) + Ge (crystal)] are GeO(g), Ge₂O₂(g), and Ge₃O₃(g). The polymeric species Ge₂O₂(g) and Ge₃O₃(g) make a considerable contribution to the vapor pressure over [GeO₂ + Ge(crystal)] even at temperatures as low as 900 K [8].

Thermodynamic data for GeO(g) have been taken from [1]. As discussed later, in order to obtain better agreement with the published experimental data on GeO partial pressures, the GeO(g) data have to be modified. For Ge₂O₂(g) and Ge₃O₃(g), data were taken from [11]. These were obtained from critical evaluation of molecular constant and thermodynamic data. We have fitted the original heat capacity versus temperature data (kindly provided by R. H. Lamoreaux) to a $C_p(T)$ polynomial as shown in figures 1a and b. We shall further discuss the modifications of the Ge₂O₂(g) and Ge₃O₃(g) data in the section on vapor pressure calculations.

2.3 GeO (amorphous)

Amorphous GeO is metastable and disproportionates to a mixture of Ge (crystal) + GeO₂ (quartz or amorphous) at 800 to 975 K [5, 12 to 14]. Unfortunately, from the available thermodynamic data on this phase [5, 14 to 16], a reliable Gibbs energy expression cannot be obtained. Therefore, we do not consider this phase further in this paper.

2.4 GeO₂

Gurvich et al. [1] and Richet [17] have independently reviewed the literature on the thermodynamic properties of GeO₂ phases and have presented recommended datasets for the crystalline, glass, and liquid forms. Two GeO₂ poly-
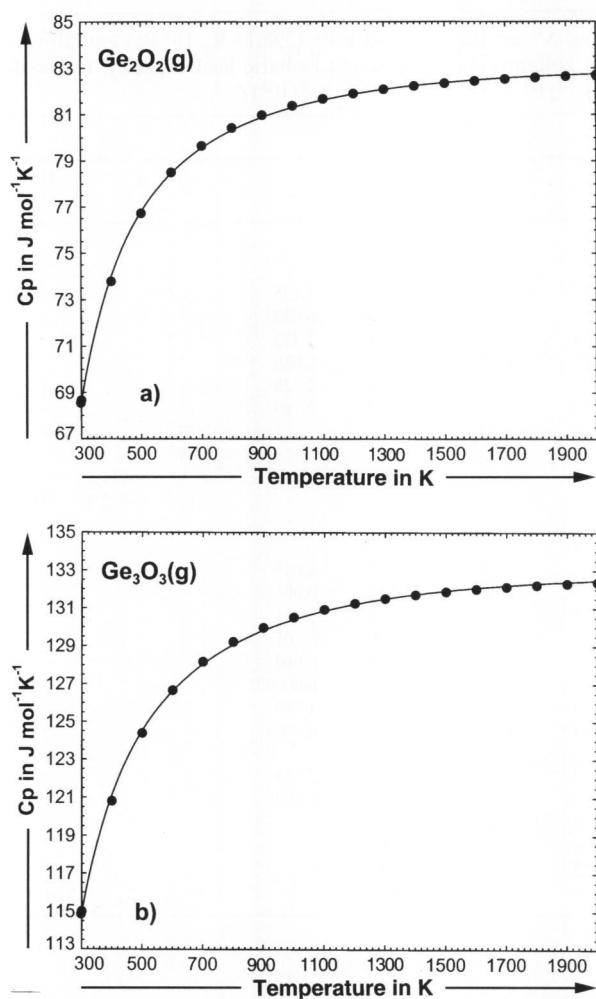
Figures 1a and b. Isobaric heat capacity a) $Ge_2O_2(g)$ and b) $Ge_3O_3(g)$; solid circles −original data from [11] (kindly furnished by R. H. Lamoreaux), curve −fitted in this work.

morphs are thermodynamically stable at ambient pressure: a rutile structure (space group $P4_2/mnm$) from low temperature to about 1308 K, and a high-temperature quartz structure (space group $P3_221$) stable from 1308 K to its melting temperature of 1388 K. The transition temperatures quoted here are those from [1]. The published temperatures (T_t) and enthalpies (ΔH_t) of the rutile-quartz transition vary significantly: T_t = 1275 to 1322 K; ΔH_t = (19.9±1.0) to (35.6±4.1) kJ mol^{-1}. The melting transition of the quartz form is much better determined, with a melting temperature (T_m) at (1388±3) K and an enthalpy of fusion (ΔH_m) between (15.1±0.3) and 17.9 kJ mol^{-1}.

Mernagh and Liu [18] questioned the generally accepted view that GeO$_2$ (rutile) is the stable form at low temperatures. In their study, various preparation methods of GeO$_2$, including oxidation of pure germanium at ambient pressure and up to 874 K, yielded GeO$_2$ (quartz), suggesting its low temperature stability. However, the evidence from other studies, including phase equilibrium [19 to 21], calorimetry [22], and ab initio calculations [23 and 24], points to the stability of GeO$_2$ (rutile) at low temperatures.

Richet [17] reported a consistent thermodynamic dataset for crystalline, glassy, and liquid GeO$_2$ by combining his own relative enthalpy measurements with carefully chosen

earlier calorimetric measurements. For the rutile form, the C_p data of Richet [17] and Gurvich et al. [1] are very close except in the temperature range 400 to 500 K where a maximum difference of 1.8 J mol^{-1} K^{-1} (about 3 %) is seen. For the quartz polymorph, the C_p data from the same two sources are very close up to about 1200 K, after which a maximum difference of 2.4 J mol^{-1} K^{-1} (3 %) is seen in the range of 1200 to 1400 K. Excellent agreement has been reported between the calorimetric C_p data of Richet and the C_p data from two independent vibrational (infrared and Raman data) modeling studies to 1500 K [25 and 26]. Hence, we have accepted the C_p data for the GeO$_2$ polymorphs from [17].

Neither Gurvich et al. [1] nor Richet [17] referred to the Gibbs energy data of O'Neill [27] obtained from an EMF study on the two GeO$_2$ polymorphs in the temperature range 860 to 1070 K. For GeO$_2$ (rutile), the data from Gurvich et al. are about 4 kJ mol^{-1} lower (more negative), while the Richet data are about 3 kJ mol^{-1} higher than O'Neill's data. For GeO$_2$ (quartz), the data of Gurvich et al. are 3 kJ mol^{-1} lower, and the Richet data 3 kJ mol^{-1} higher than O'Neill's data. We do not have any reason to consider O'Neill's data to be superior to the other two datasets.

For GeO$_2$ (glass-liquid), the major thermodynamic data sources are again [1] and [17]. A maximum difference of 2 J mol^{-1} K^{-1} was obtained for the glass liquid C_p data between the two sources. The Richet [17] C_p values are about 3 % higher than the data obtained by Dingwell et al. [28] in the temperature range of 313 to 963 K. From the mean heat capacity plots (drop-calorimetric data) Richet obtained a glass transition temperature (T_g) of approximately 980 K, whereas from differential calorimetric and dilatometric data Dingwell et al. reported a T_g of about 855 K (other T_g values are given in [29 to 31]). We have adopted Richet's T_g value for GeO$_2$ because we have taken the C_p data (that cover a wide temperature range) for the glass-liquid from this source. It may also be mentioned that the C_p data and T_g for SiO$_2$ glass-liquid from Richet and coworkers have been taken as standard values by CODATA. Thus, overall consistency is maintained between the C_p data and T_g values.

The different values of H^0_{298} and S^0_{298} for the GeO$_2$ phases adopted in [1] and [17] pose a selection problem. This difference can have a significant effect on the computed glass/gas equilibria [32]. We have chosen the data of Gurvich et al. [1] on the basis of the vapor pressure calculations discussed later; this dataset is generally more consistent with the experimental vapor pressure data (see below).

For GeO$_2$(g) we have taken all the data as given in Gurvich et al. [1].

2.5 GeO$_2$−SiO$_2$ (glass-liquid)

From high-temperature drop-solution calorimetric data, Huffman et al. [33] obtained an enthalpy of mixing of (−12.8±1.5) kJ mol^{-1} at the 50 mol% composition for SiO$_2$−GeO$_2$ glasses, suggesting nonideal mixing. The Knudsen effusion-mass spectrometry data on GeO$_2$−SiO$_2$ (glass-liquid) at 1373 to 1453 K by Shul'ts et al. [34] was interpreted to reflect a positive deviation from ideality. Subsequently, Stolyarova [35] interpreted the same data as

showing a nearly ideal behavior. Maniar et al. [36] reinvestigated the enthalpies of mixing across the GeO_2-SiO_2 glass composition range because they suspected the presence of a trace crystalline phase in the sample measured by Huffman et al. The calorimetric data at 973 K obtained by Maniar et al. yielded ideal (zero) enthalpy of mixing. Thus, it is concluded that the GeO_2-SiO_2 (glass-liquid) can be treated as an ideal solution.

Shul'ts et al. [34] reported the only data on the partial pressures of GeO(g) over glass and liquid across the GeO_2-SiO_2 composition range. Unfortunately, their vapor pressure data for pure GeO_2 are an order of magnitude lower than the other published data (see below), suggesting that there is a systematic error in their values. We have not, therefore, considered their data in our analysis of vapor pressure measurements in a later section.

2.6 GeCl(g), $GeCl_2$(g), $GeCl_3$(g), $GeCl_4$(g), and $GeCl_4$ (liquid)

The thermodynamic data for the germanium chloride gases were taken from [1]. Validation of these data in terms of their ability to reproduce the available experimental vapor pressure measurements will be presented in a later section.

For $GeCl_4$ (liquid), the thermodynamic data from Barin et al. [37] were used with a slight modification to the enthalpy of formation. This modification was necessary in order to calculate the 1 bar boiling point correctly (at 356 K), using the modified $GeCl_4$((g) data (see below). The modified enthalpy of formation, -530.38 kJ mol^{-1} at 298.15 K, is close to that listed in [15] (-531.8 kJ mol^{-1}). The calculated standard enthalpy of vaporization at 356 K is 32.255 kJ mol^{-1}, which may be compared to the values of 32.04 kJ mol^{-1} [37], ≈ 30 kJ mol^{-1} (estimate in [38]), and 33.878 kJ mol^{-1} at 298 K derived from membrane method measurements by Golubenko et al. [39].

2.7 Other gaseous species

We use the FactSage™ database [2] for Ge_3(g), Ge_4(g), and GeH_4(g). We have incorporated the thermodynamic data for Ge_2Cl_6(g), GeH_3Cl(g), GeH_2Cl_2(g), and $GeHCl_3$(g) from the tabulation of Chang et al. [40] (see table 1). Reliable thermodynamic data could not be obtained for other possible species such as Ge_2OCl_6(g) (see [41]).

3. GeO_2-SiO_2 and $GeCl_4-SiCl_4$ phase diagrams

The GeO_2-SiO_2 and $GeCl_4-SiCl_4$ joins are the two most important binaries relevant for chemical vapor deposition. The most recent phase diagram of the GeO_2-SiO_2 binary is due to Baret et al. [21], who combined differential thermal analysis, X-ray diffraction, and thermodynamic modeling to describe the system. Complete solid solution exists between the quartz forms of SiO_2 and GeO_2. The high-temperature forms of SiO_2 (tridymite and cristobalite) and GeO_2 (rutile) do not show significant solid solubility. The liquid phase is completely miscible.
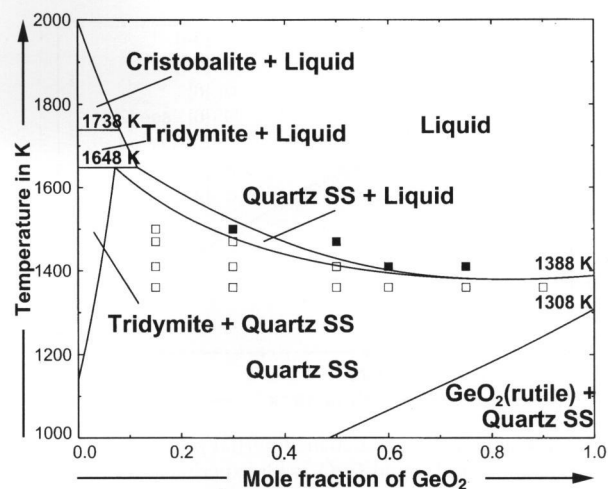

Figure 2. Calculated SiO_2-GeO_2 phase diagram; experimental data from [21], open squares == quartz solid solution (SS), solid squares ==liquid.
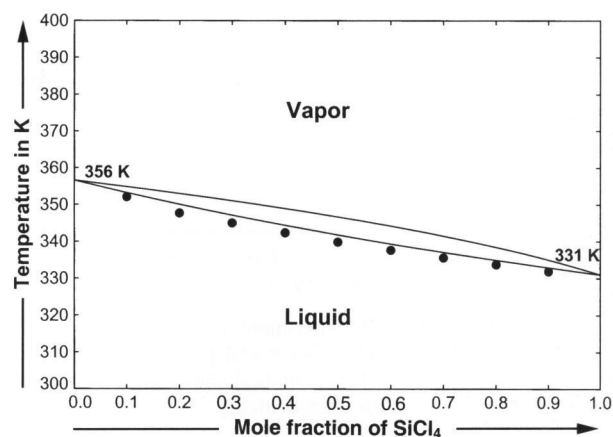

Figure 3. Calculated $GeCl_4-SiCl_4$ liquid vapor phase diagram; experimental liquid compositions [42] are shown.

The thermodynamically optimized SiO_2-GeO_2 phase diagram is shown in figure 2. The thermodynamic data for the pure SiO_2 phases were taken from the FactSage™ database [2]. The liquid solution was assumed to mix ideally, while the SiO_2-GeO_2 quartz solution was described using a regular solution parameter (3.694 kJ mol^{-1}).

Mikhailin et al. [42] measured liquid vapor equilibria of the pure components and mixtures in the $GeCl_4-SiCl_4$ system using an ebulliometer. Figure 3 shows the calculated $GeCl_4-SiCl_4$ liquid vapor equilibrium diagram and the experimental data from Mikhailin et al. The $GeCl_4-SiCl_4$ liquid was assumed to be an ideal mixture.

4. Vapor pressure calculations

4.1 Ge–O system

As mentioned earlier, experimental vapor pressure measurements suggested that the major gaseous species in the system is GeO. In fact, the evaporation of GeO from amorphous $(Si,Ge)O_2$ is a problem in the manufacturing of glass
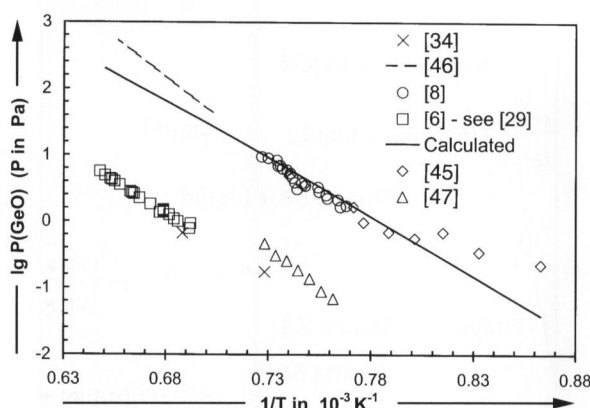
Figure 4. Comparison of calculated partial pressures of GeO(g) over crystalline and liquid GeO_2 with experimental data.
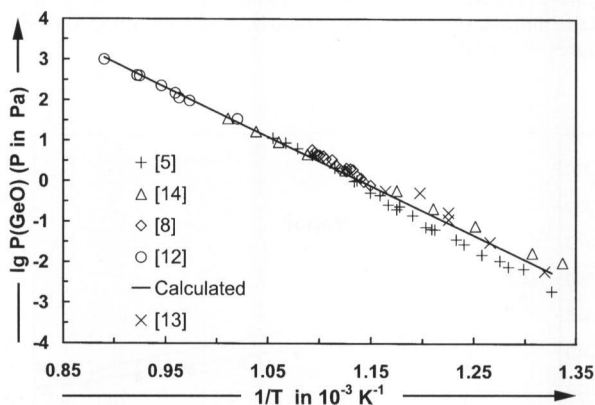

Figure 5. Calculated and experimental partial pressure of GeO(g) over [GeO_2(quartz) + Ge(crystal)] as a function of reciprocal temperature. The data from [12] and [13] are according to the interpretation by Drowart et al. [5].

Figure 6. Calculated and experimental partial pressures of GeO_2(g) and O_2(g) over GeO_2 (crystal, liquid) as a function of reciprocal temperature. The data from [45] and [47] are according to the interpretation by Drowart et al. [5].

Figure 7. Calculated and experimental partial pressures of Ge_2O_2(g) and Ge_3O_3(g) over [GeO_2 (quartz) + Ge (crystal)] as a function of reciprocal temperature.

fiber. In order to assess the influence of this and other gaseous species and also to verify the ability of the selected thermodynamic data to describe published vapor pressure data, we present in this section the results of vapor pressure calculations.

Calculations of equilibria involving GeO(g) indicated that better agreement between computed and experimental GeO(g) partial pressures could be achieved if the recommended thermodynamic data of GeO(g) were modified. The largest uncertainty in the GeO(g) data is related to the standard enthalpy of formation. Gurvich et al. [1] considered the literature up to 1973 in evaluating the enthalpy of formation for this species. Other values have appeared in the literature since then [11, 43 and 44]. Rau and Schnedler [43], using a flow method, studied the reactions of Ge (crystal) and GeO_2 (rutile) with a CO/CO_2 gas mixture and obtained a standard enthalpy of formation of GeO(g) at 298.15 K of (−41.4±2.8) kJ mol^{-1}. The values obtained by Pedley and Marshall [44] and Lamoreaux et al. [11] by analyzing earlier experimental and molecular constant data are (−36±13) kJ mol^{-1} and (−37.415±4.16) kJ mol^{-1}, respectively. These latter values are in good agreement with the value from Gurvich et al. [1] of −37.694 kJ mol^{-1}. In our calculations discussed below, a more negative enthalpy of formation of −41 kJ mol^{-1}, which is close to the value of [43], yielded better agreement (within 0.05 lg units) with the
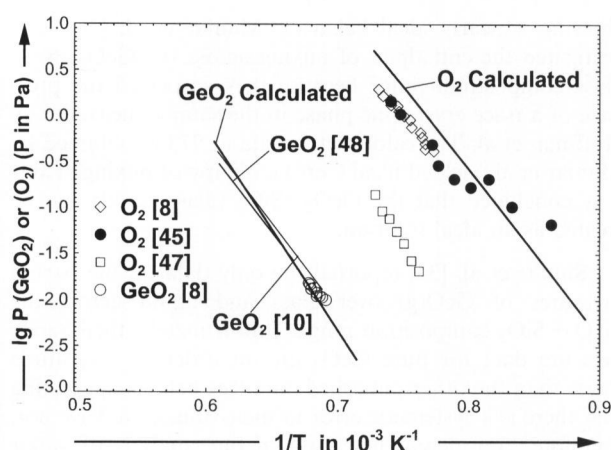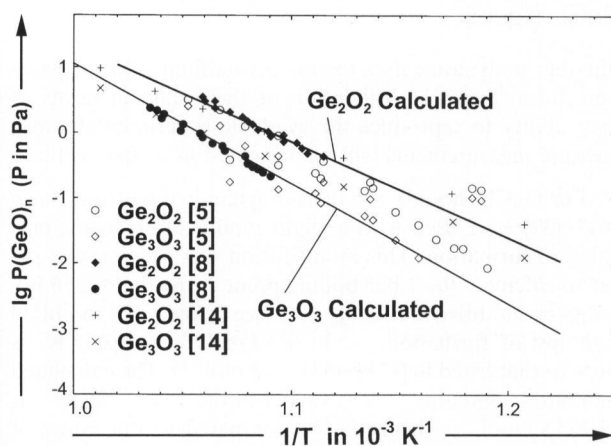
experimental partial pressure data of GeO(g) over GeO_2 and over [GeO_2+Ge] mixtures.

Figure 4 shows the calculated and experimental equilibrium partial pressure of GeO(g) over GeO_2(crystal, liquid). The calculated curve is in good agreement with the Knudsen-mass spectrometric data of Kazenas et al. [8], Davydov [45], and Kato et al. [46]. The experimental (Knudsen) data of Shul'ts et al. [6 and 34] and Shimazaki et al. [47] differ by about an order of magnitude from the other experimental data as well as from the calculated curve. Better agreement is seen among the various experimental determinations of partial pressures of GeO(g) over [GeO_2 (quartz) + Ge(crystal)] (figure 5). The calculated data also agree well with these data, especially those of Bues and von Wartenberg [12], Jolly and Latimer [13] (as reinterpreted by Drowart et al. [5]), and Kazenas et al. [8].

The equilibrium partial pressures of O_2(g) and GeO_2(g) over GeO_2 (crystal, liquid) versus reciprocal temperature are plotted in figure 6 along with available experimental data [8, 10, 45, 47 and 48]. The agreement in the case of GeO_2(g) is excellent among the experiments and the calculation. The agreement between the calculated and experimental partial pressures of O_2(g) is slightly worse.
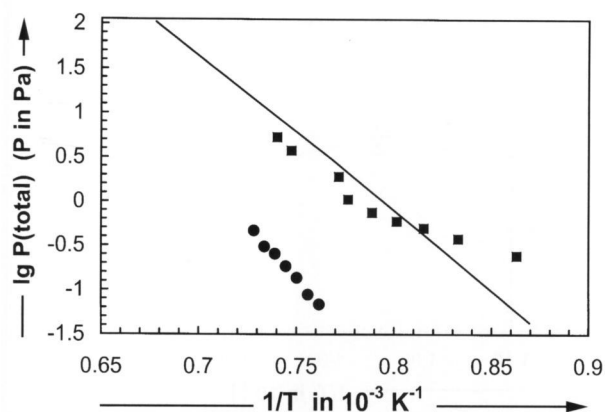
Figure 8. Experimental and calculated total vapor pressure over GeO$_2$ as a function of reciprocal temperature. The curve is calculated, while solid squares and solid circles represent data from [45] and [47] respectively.

Figure 9. Calculated and experimental total pressure over [GeO$_2$ (quartz) + Ge (crystal)] as a function of reciprocal temperature. The curve is calculated. Experimental data: solid circles from [12] and solid square from [13].

In figure 7, the calculated equilibrium partial pressures of the polymeric species Ge$_2$O$_2$(g) and Ge$_3$O$_3$(g) are plotted against reciprocal temperature along with corresponding experimental data. 15.7 kJ mol^{-1} were added to the standard enthalpy of formation of Ge$_3$O$_3$(g) given in [11], in order to give better agreement with the mass spectrometric data in [8], which has the least scatter. For Ge$_2$O$_2$(g) also, a minor adjustment to the standard enthalpy of formation (addition of 5.425 kJ mol^{-1}) resulted in better agreement with the mass spectrometric data in [8]. The modifications made to the enthalpy of formation values (see table 1) are within the error margins quoted in [11] (for Ge$_2$O$_2$(g): (-274.375 ± 16.63) kJ mol^{-1}, and for Ge$_3$O$_3$(g): (-495.538 ± 16.63) kJ mol^{-1}).

The total pressure of GeO$_2$ contained in quartz cells was determined by Davydov [45] in the temperature range 1159 to 1351 K and by Shimazaki et al. [47] in the range 1313 to 1373 K with the Knudsen method. Davydov attributed the temperature trend shown by his data to the quartz rutile transition in the GeO$_2$ sample. Drowart et al. [5], however, believed that the data correspond indeed to the quartz form. The calculated total pressures for GeO$_2$ are in good agreement with the data of Davydov, but differ considerably from the data of Shimazaki et al. (figure 8). Interaction between the GeO$_2$ sample and the quartz container has been suggested as the reason for the high values reported by Shimazaki et al. [47] (see [5]).

The total pressure over a mixture of [GeO$_2$ (quartz) + Ge (crystal)] was determined by Bues and von Wartenberg [12] using manometric and transport methods and by Jolly and Latimer [13] with the Knudsen technique (the latter on amorphous GeO, which disproportionated to the above mixture on heating). These experimental data are plotted along with the calculated total pressure over [GeO$_2$ (quartz) + Ge (crystal)] in figure 9. The calculated data are in close agreement with the experimental measurements.

4.2 Ge–Cl, Ge–Cl–H, and Ge–O–Cl systems

It is critically important to know the behavior of germanium chloride gas species in the reaction environment in order to control the glass-forming process. Reliable thermo-
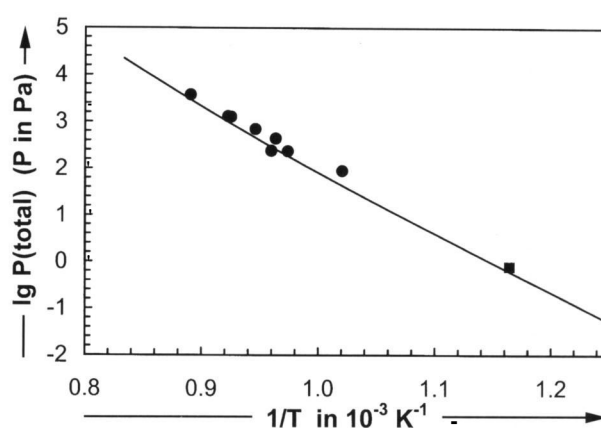
dynamic calculations to this end require accurate thermodynamic data for the germanium chloride species, in addition to those for the oxide species discussed thus far. In this section we discuss vapor pressure calculations involving germanium chlorides with the data from [1] in order to assess the reliability of the thermodynamic data.

Experimental vapor pressure studies on germanium chlorides include those of Sedgwick [49], Uy et al. [50], Van Hai et al. [51], Vavilov et al. [52], and Rau [41]. Sedgwick studied equilibria in the Ge-Cl$_2$ system using Bourdon gauge (static pressure) measurements in the temperature range 300 to 1300 K. From the pressure-temperature relation obtained for pure GeCl$_4$(g) up to 1300 K, he concluded that GeCl$_4$(g) does not dissociate significantly in this temperature range. From two temperature regimes (one less than 570 K and the other greater than 950 K) marked by an approximate doubling of the pressure temperature slope for the [Ge(crystal) + GeCl$_4$(g)] system, he inferred the reaction Ge(crystal) + GeCl$_4$(g) $\rightleftharpoons$ 2 GeCl$_2$(g) and presented the corresponding lg K_{eq} versus reciprocal temperature data.

Uy et al. [50] conducted a Knudsen-mass spectrometric study of the equilibrium vapor species in the [Ge(crystal) + GeCl$_4$g)] system. They confirmed Sedgwick's [49] inference that Ge(crystal) + GeCl$_4$(g) = 2 GeCl$_2$(g) is the only reaction involved, meaning that no polymeric species are present in significant amounts. They presented equilibrium constant data for the temperature range of 659 to 774 K.

The equilibria in the Ge(crystal)–Cl$_2$–H$_2$ and GeCl$_4$–H$_2$ systems were investigated by Van Hai et al. [51] in the temperature range of 900 to 1200 K using a transpiration technique. They have reported equilibrium constant versus reciprocal temperature data for the reactions GeCl$_2$(g) + H$_2$(g) = Ge(crystal) + 2 HCl(g) and GeCl$_4$(g) + H$_2$(g) = GeCl$_2$(g) + 2 HCl(g).

The chlorination of condensed GeO$_2$ phases was investigated by Rau [41] and Vavilov et al. [52]. Vavilov and coworkers did not mention which form of GeO$_2$ was used in their flow study, although Gurvich et al. [1] report it as the quartz form. Rau equilibrated the rutile, quartz, and glassy forms of GeO$_2$ with pure chlorine gas in a glass vessel from room temperature to 1225 K. Because of the low reaction rate, equilibrium data could not be obtained at temperatures be-
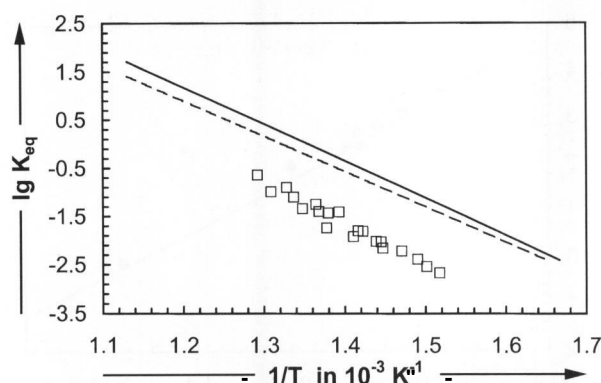
Figure 10. Comparison of the calculated and experimental equilibrium constant versus $1/T$ for the reaction $GeCl_4(g) + Ge(crystal) = 2\,GeCl_2(g)$. The solid curve is calculated. The dashed line represents experimental determination of [49] and the open squares, experimental data from [50].

Figure 11. Calculated equilibrium constant versus reciprocal temperature for the reaction $GeCl_2(g) + H_2(g) = Ge(crystal) + 2\,HCl(g)$. The diamonds and triangles represent two different $H_2/GeCl_4$ ratios in Van Hai et al.'s [51] experiment.

low 1000 K from the rutile and quartz forms; the glassy form reacted fast enough with chlorine even at 835 K. Equilibrium constant versus reciprocal temperature data are given for the chlorination reactions of the three GeO_2 forms in [41].

The equilibrium constant, calculated with the thermodynamic data for germanium chloride species listed in [1] for the reaction $Ge(crystal) + GeCl_4(g) = 2\,GeCl_2(g)$, agreed rather closely with the experimental data of Sedgwick [47], which are somewhat different from the results of Uy et al. [50]. For the reaction $GeCl_2(g) + H_2(g) = Ge(crystal) + 2\,HCl(g)$, the calculated equilibrium constant agreed well with that given by the equation in [51]. However, the equilibrium constants for the chlorination equilibria of the condensed GeO_2 forms calculated with the data in [1] showed poor agreement with the experimental data from Rau [41]. It may be mentioned here that Gurvich et al. [1] did not list Rau's work among their experimental data sources. Because of the importance of GeO_2 chlorination equilibria to the current work, especially that of the glassy GeO_2, we decided to modify the thermodynamic properties of germanium chlorides so that a better overall agreement is achieved with all the experimental data mentioned.

While the standard entropy and heat capacity data are reasonably well constrained from vibrational spectra and molecular constant data for all the germanium gas species under consideration (see [1 and 41]), the enthalpy of formation values have relatively larger associated errors. For example, the standard enthalpy of formation value for $GeCl_4(g)$ reported in [1] is $(-500\pm10)\,kJ\,mol^{-1}$. Rau's [41] analysis of his measured chlorination equilibrium data together with selected thermochemical values from the literature yielded a value of $(-494.8\pm2.7)\,kJ\,mol^{-1}$. We have modified the recommended enthalpy of formation value of $GeCl_4(g)$ to $-495\,kJ\,mol^{-1}$ in order to obtain better agreement with Rau's chlorination data. Similarly, the enthalpy of formation of $GeCl_2(g)$ was adjusted by a small amount (by $200\,J\,mol^{-1}$; the value given in [1] is $(-171.0 \pm 5.0)\,kJ\,mol^{-1}$) so that good agreement with the Van Hai et al. [51] data is maintained while bringing the equilibrium constant of the reaction $Ge(crystal) + GeCl_4(g) = 2\,GeCl_2(g)$ closer to the data from Sedgwick [49]. It is not possible to obtain good agreement with the data of Uy et
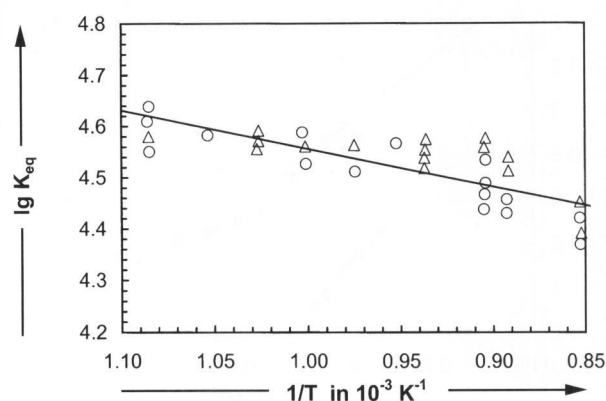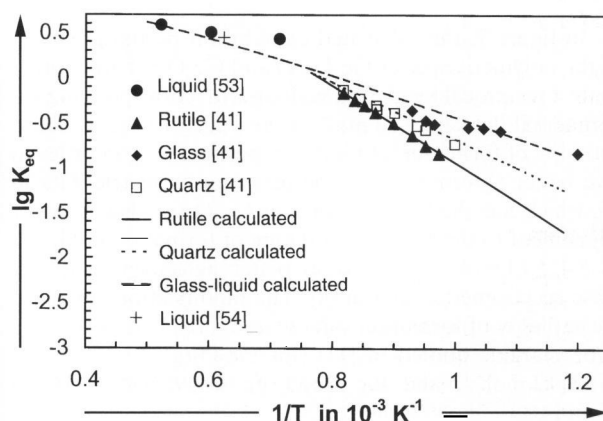

Figure 12. The equilibrium constants for the chlorination reactions of rutile, quartz, and glass liquid forms of GeO_2.

al. [50] without substantial changes to the enthalpy of formation values of the germanium chloride gas species involved in the reaction.

In figure 10, the $\lg K_{eq}$ versus reciprocal temperature relation calculated using the revised data for the reaction $Ge(crystal) + GeCl_4(g) = 2\,GeCl_2(g)$ is shown against experimental determinations from [49] and [50]. The $\lg K_{eq}$ versus $1/T$ data for the reaction $GeCl_2(g) + H_2(g) = Ge(crystal) + 2\,HCl(g)$ from [51] are shown along with the calculated data in figure 11. The calculated curve agrees with the experimental data quite well. Finally, the calculated equilibrium constant versus reciprocal temperature data for the chlorination equilibria of GeO_2 (rutile), GeO_2 (quartz), and GeO_2 (glass-liquid) are presented in figure 12 along with experimental data of Rau [41] for all the three GeO_2 phases, and of Kleinert et al. [53] and Wood et al. [54] for GeO_2 liquid. Satisfactory agreements of the calculated chlorination equilibria are obtained with the thermodynamic data.

5. Summary

We have presented an overview of the thermodynamic and phase equilibrium studies relevant to the GeO_2-SiO_2 con-

densed phase gas phase reactions in the Ge$-$Si$-$O$-$Cl$-$H system. The largest thermodynamic dataset for germanium-bearing species is that of Gurvich et al. [1]. We have adopted the data mainly from this source with modifications where needed. In order to evaluate the thermodynamic properties of the critical oxide and halide species, available data were reviewed and assessed through vapor pressure calculations in the Ge$-$O, Ge$-$Cl, Ge$-$Cl$-$H, and Ge$-$O$-$Cl systems. The current database can be used in conjunction with complementary data from the FactSage^{TM} database [2] to perform thermodynamic calculations involving glass/gas phase equilibria relevant to vapor deposition processes used in the glass fiber industry.

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6. References

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