

## THERMAL DESORPTION ANALYSIS:

DSC curves of H<sub>2</sub>O desorption from silicate glass in the multilayer coverage range

*H. Wittkopf, H. –J. Flammersheim and L. Herlitze*

DEPARTMENT OF CHEMISTRY, FRIEDRICH-SCHILLER-UNIVERSITY, JENA 6900, G.D.R.

Experiments on water desorption from silicate glass powders of different chemical compositions were carried out by means of DSC. In order to establish the desorption energy distributions, a model of the heterogeneous surface was applied to the thermoanalytical desorption curves, and the results are discussed together with contact angle measurements on flat polished glass samples.

The maxima in the desorption curves shift to lower temperature with increasing hydrophobic character; this is caused by divalent cations such as Pb<sup>2+</sup>, Ca<sup>2+</sup> and Zn<sup>2+</sup>, while alkali metal ions are responsible for an increase in the hydrophilic behaviour.

The reaction of water with silicate glass is one of the most interesting topics in research on glass reactivity [1]. Corrosion of glasses in a wet atmosphere occurs even at room temperature, and often limits the application of special glasses in optical instruments. The adsorption of water from the atmosphere is the first step of such a reaction. This paper presents results on water desorption from silicate glasses with different chemical compositions, investigated by means of DSC measurements and analysed by the theory of thermal desorption. The Perkin-Elmer DSC 2c was found to be sensitive enough to detect the heat flux due to the desorption of H<sub>2</sub>O multilayers from several silicate glass powders.

### Theoretical

In general, the heat flux  $dq/dt$  of a desorption process from homogeneous surface sites in a DSC spectrometer working in linear temperature rise mode ( $T = T_0 + \beta \cdot t$ ) can be correlated with the common desorption rate  $R_d$  ( $R_d = -\frac{dn}{dt}$ ) by the following relation:

$$\frac{1}{E} \frac{dq}{dt} = -\frac{dn}{dt} = -\frac{1}{\beta} \frac{dn}{dT} = R_d \quad (1)$$

where  $E$  is the molar energy of desorption (desorption energy),  $\beta$  is the

heating rate,  $n$  is the amount of adsorbed water molecules, and  $q = n \cdot E$ . The desorption rate can be described by the Polanyi-Wigner equation [2]:

$$R_d = n \cdot \gamma \cdot e^{-E/RT(t)} \quad (2)$$

for first-order desorption.

In the case of desorption from a heterogeneous surface, for the overall heat flux  $dQ/dt$  we have

$$\frac{dQ}{dt} = \sum_{i=1}^k \frac{dq_i}{dt} \quad (3)$$

where  $dq_i/dt$  is the heat flux, from the homogeneous surface sites, with activation energy  $E_i$ .  $k$  is the number of energetically different surface sites.

The desorption flux from the homogeneous surface sites can be described by

$$\frac{dq_i}{dt} = \gamma \cdot E_i \cdot n_{o_i} \cdot \exp\left(-\int \gamma e^{-E_i/R \cdot T} \cdot dt\right) \exp(-E_i/R \cdot T) \quad (4)$$

Equation (4) was obtained by integration of Eq. (2).  $n_{o_i}$  is the initial population of the surface sites with desorption energy  $E_i$  and  $\gamma$  is a measure of the frequency of surface sites with desorption energy  $E_i$ .

By providing  $k$  equidistant  $E_i$  values in the energy range  $E_1 - E_k$ , the corresponding initial coverage vectors  $n_{o_1} - n_{o_k}$  can be calculated by an iteration process which fits Eq. (3) to an experimental thermoanalytical desorption curve, as discussed in [3]. The relative frequency of an adsorption site  $H_j$  with desorption energy  $E_j$  is given by

$$H_j = \frac{n_{o_j}}{\sum_{i=1}^k n_{o_i}} \quad (5)$$

## Experimental

Glass samples with different chemical compositions, as given in Table 1, were ground in an agate mortar and sieved to a fraction 40–45  $\mu\text{m}$  in diameter. The glass powders were stored in saturated water vapour atmo-

Table 1 Characteristics of glass samples.  $T_M$  is the temperature of the desorption peak maximum

Constituent Sample No	SiO <sub>2</sub>	B <sub>2</sub> O <sub>3</sub>	BaO	PbO mol %	Na <sub>2</sub> O/K <sub>2</sub> O	other	H <sub>2</sub> O coverage mol/g	$T_M$ , K	Contact angle, deg
I	78	—	—	9.5	11.5	(Al <sub>2</sub> O <sub>3</sub> ) 1	$1.5 \cdot 10^{-2}$	361	$55 \pm 15$
II	74	9.5	1	—	15.5	—	$7.2 \cdot 10^{-3}$	356	$43 \pm 5$
III	69	—	—	23	8	—	$4.4 \cdot 10^{-3}$	354	$45 \pm 8$
IV	60.5	—	—	34.5	5	—	$8.3 \cdot 10^{-4}$	315	$56 \pm 4$
V	64	6.5	10	0.5	9	(ZnO) 10	$7.2 \cdot 10^{-4}$	311	$58 \pm 4$

sphere in a desiccator at room temperature for 3 months. The small alumina DSC pans were filled with 10–20 mg of the glass powder and covered with a perforated lid to avoid the squirting out of the sample material. On removal of the samples from the wet atmosphere, they were immediately put into the DSC 2c (Perkin-Elmer) and cooled down to 250 K. As thermal equilibrium appeared, the samples were heated with a linear temperature rise of 10 deg min<sup>-1</sup> up to 400 K. The second run was taken as reference.

The DSC curves in Fig. 1 show only the influence of the adsorbed water

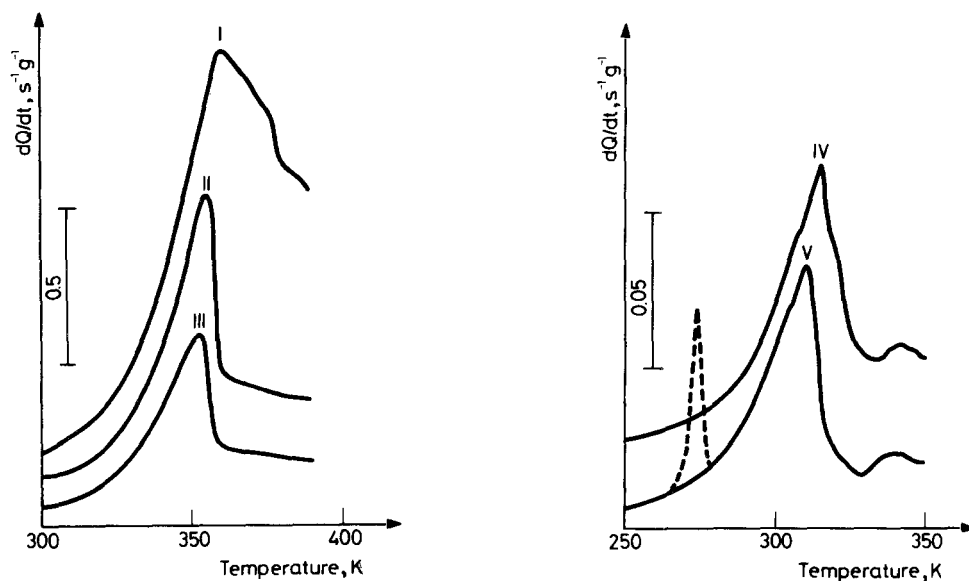


Fig. 1 DSC desorption curves

The sensitivity range is marked as bars in both diagrams, the melting peak (dashed line) is only shown in curve V.

layer. The curves in general exhibit two peaks, the melting peak of the adsorbed water layer at about 274 K, and the desorption peak at different temperatures. For simplification, the melting peak is only demonstrated in curve *V*. All measurements were carried out under  $N_2$  flow conditions. The flow rate was about 20 ml/min.

## Discussion

The  $H_2O$  coverage varies by two orders of magnitude from sample *I* to sample *V*, which indicates the large difference in the hydrophilic characters of the glass samples investigated. Similarly, the desorption peak maximum temperature  $T_M$  shifts to lower values, as indicated in Table 1. The hydrophilic character decreases with increasing lead content (*III* and *IV*). In the case of sample *V*, ZnO and BaO may be responsible for the corresponding behaviour, while alkali metal ions relate to a higher  $H_2O$  coverage.

The shape of the desorption peak appears to be caused by more than one binding state of  $H_2O$  in the multilayer. This is confirmed by the energy distribution in Figure 2. The main desorption energy contribution varies from 102 to 88 kJ/mol with decreasing  $H_2O$  coverage. This is always more than twice the condensation energy of liquid water.

Another interesting feature is the conformity of the  $H_2O$  coverage, the desorption energy, and the  $H_2O$  contact angle measured on flat polished glass samples. The highest desorption energy corresponds to the lowest contact angle, except for glass sample *I*.

Glass *I* forms a much thicker corrosion layer than other glasses. This can be concluded from surface area measurement after several corrosion times [4, 5]. On storage in the wet atmosphere, the surface area of sample *I* increases much more than those of the other glass samples. This increase in specific surface area can be explained by the formation of a porous corrosion layer.

The energy distribution can be used to predict the adsorption behaviour of investigated glasses, e.g. to calculate adsorption isotherms or surface pressures of  $H_2O$ .

More detailed research is necessary on this subject.

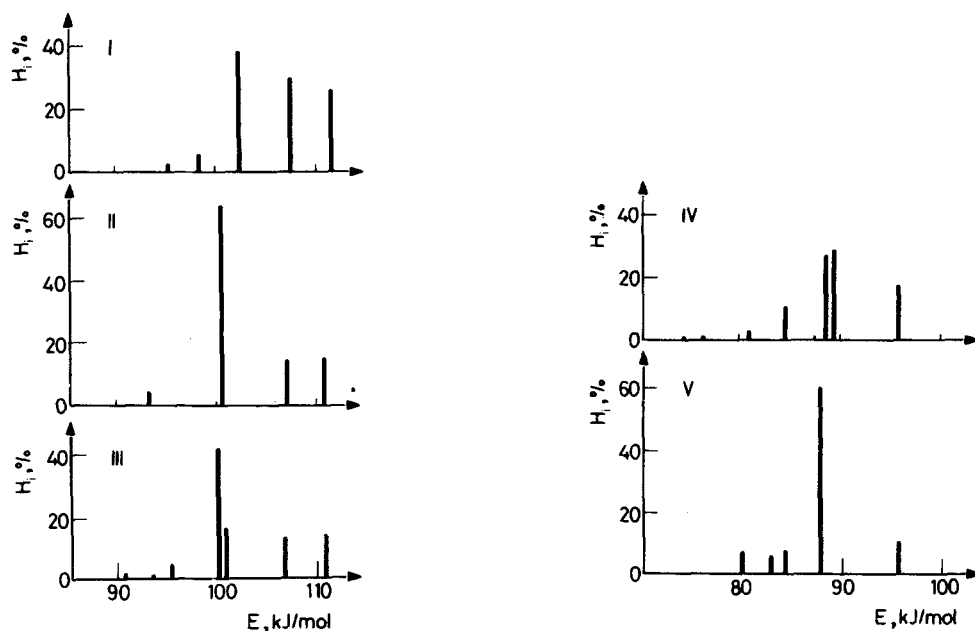


Fig. 2 Energy distributions calculated from the DSC desorption curve shown in Fig. 1.

## References

- 1 R. H. Doremus, *Treatise on Materials Sci. and Technol.*, 17 (1979) 41.; H. Dunken, *Physikalische Chemie der Glasoberfläche*, Leipzig, 1981.
- 2 P. A. Redhead, *Vacuum*, 12 (1962) 203.
- 3 H. Wittkopf, *Vacuum*, to be published in 1987
- 4 H. Wittkopf and M. Bösel, *Glass Technology*, to be published in 1987
- 5 H. Wittkopf and B. Müller, *Silicates Industriels*, to be published in 1987

**Zusammenfassung** – Wasserdesorptionsexperimente an Silikatglaspulvern unterschiedlicher Zusammensetzung wurden mittels DSC ausgeführt. Für die Berechnung von Desorptionsenergieverteilungen wurde ein Modell der heterogenen Oberfläche genutzt und zusammen mit Randwinkelmessungen an glatten, polierten Glasoberflächen diskutiert. Das Maximum der Desorptionskurven verschiebt sich mit wachsendem hydrophoben Verhalten nach tieferen Temperaturen, wofür divalente Kationen wie  $Pb^{2+}$   $Ca^{2+}$   $Zn^{2+}$  verantwortlich sind, während Alkaliionen das hydrophile Verhalten begünstigen.

**РЕЗЮМЕ** — Методом ДСК изучена десорбция воды на порошкообразных силикатных стеклах с различным химическим составом. С целью получения распределений энергий десорбции к термическим аналитическим кривым десорбции была применена модель гетерогенной поверхности и полученные результаты были обсуждены совместно с измерениями углов контакта на поверхности полированных образцов стекла. Максимум кривых десорбции сдвигается в сторону более низких температур с увеличением гидрофобного характера стекол, обусловленного наличием ионов свинца, кальция и цинка, тогда как ионы щелочных металлов ответственны за увеличение гидрофильности стекол.