THERMOGRAVIMETRIC INVESTIGATION OF THE KINETICS AND THERMODYNAMICS OF DEHYDRATION OF AMORPHOUS SILICA

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Several commercial and laboratory-synthesized specimens of silica gel have been studied, using thermogravimetry. Two forms of adsorbed water have been found: the first form, which evaporates in the temperature range 100—200°, is polymolecular water layer in open pores and loosely-bonded molecules on the surface and in the bulk of the globules; the second form, which evaporates in the temperature range 200—700°, comprises water molecules hydrogen-bonded to silanol groups, and evidently coordinated to silicon atoms. The dehydration heat of the first form, determined from the DTA curves, depends on the ratio of the two forms, and varies from 3.7 ± 0.6 kcal/mole H_2O for coarse-grain silica gel produced at pH = 7 to 12 ± 1 kcal/mole H_2O for fine-grain silica gel of commercial "chromatography" grade.

The activation energy of evaporation of water determined from the TG curves is about 10 kcal/mole in the temperature range 150—200°.

Silicon dioxide is a commonly-used compound of great commercial importance. Both crystallyne and amorphous silicon dioxides are produced on an industrial scale, mainly from aqueous solutions by polycondensation of silicic acid. Hydration of silicic acid in solution and the kinetics of removal of water molecules formed during polycondensation determine the structure of the silicon-oxygen skeleton, and numbers of hydroxyl groups and water molecules bonded on the silica surface and in the bulk of the particles formed [1]. Investigation of water in amorphous silica facilitated an understanding of the formation of the silicon-oxygen structure and determination of the conditions for production of silica-based materials possessing the necessary properties.

The present paper deals with the nature of water in amorphous silica, based on an investigation of the thermodynamics and kinetics of silica dehydration, using a thermogravimetric method which permits the determination of thermal effects, as well as the determination of the enthalpy and activation energy. Published data on silica gel dehydration by a thermogravimetric method mainly deal with the detection of one [2—4] or several [5] thermal effects associated with the loss of water, no attempts being made to determine the quantitative thermodynamic characteristics.

We have studied silica gels of "chromatography" grade commercial silicic acid of "analytical" grade and silica gels produced by neutralization of aqueous solu-

Table 1

No.	Silica gel grade or method of its production	Surface, m^2/g	Pore volume, cm^3/g	Pore mean radius, Å	Porosity, %
1	2	3	4	5	6
1	KCK No. 2 for chromatography	338	1.19	70	72.7
2	KCK No. 2.5 for chromatography	376	0.971	51.6	67.4
3	KCK No. 3 for chromatography	522	0.925	35.4	67.4
4	KCM 14 for chromatography	650	0.760	23.4	62.8
5	KCM No. 5 for chromatography	715	0.575	16.1	56.4
6	KCM No. 6 for chromatography	527	0.296	11.2	40
7	Na_2SiO_3 + HCl, pH ≈ 1	—	—	—	—
8	Na_2SiO_3 + HCl, pH ≈ 1, kept outdoors for eight months	800	—	—	—
9	Na_2SiO_3 + HCl, pH ≈ 2—3, passed through ion-exchange resin KY-2	—	—	—	—
10	Na_2SiO_3 + C_2H_5OH neutralized by CH_3COOH to pH ≈ 6	—	—	—	—
11	Na_2SiO_3 + HCl, to pH = 7	—	—	—	—
12	$SiO_2 \cdot nH\,O$, commercial "analytical" grade	—	—	—	—
13	Commercial $SiO_2 \cdot nH_2O$, dissolved in water at 80°, evaporated in the air	—	—	—	—
14	Solution Na_2SiO_3 (pH = 10), saturated with CO_2	—	—	—	—
15	Solution Na_2SiO_3 (pH = 10), saturated with CO_2, with addition of NaCl	—	—	—	—
16	Solution $SiO_2 \cdot nH_2O$ passed through KY-2 + NH_4OH to pH = 9	—	—	—	—
17	Solution $SiO_2 \cdot nH_2O$ passed through KY-2 + Cs_2CO_3 to pH = 9—10	—	—	—	—
18	Solution $SiO_2 \cdot nH_2O$ passed through KY-2 + K_2CO_3 to pH = 9—10	—	—	—	—

tions of various silicates. Preparation conditions and properties of specimens are listed in Table 1.

Experiments were carried out with a derivatograph (MOM, Hungary) in the temperature range from 20 to 1500° in corundum crucibles. The heating rate varied from 3 to 10° per min. The time-dependence of the specimen temperature was almost linear, and therefore it was possible to determine the kinetic characteristics of the studied processes from the thermogravimetric curves.

Our previous mass-spectrometric results show that up to 1500° no volatile products other than water are liberated from silica gel, so that the entire mass loss is associated with dehydration of the specimen [6].

Evaporation temperature of 1st form of water, °C	Amount of 1st form of water, % by weight	Amount of 2nd form of water, % by weight	Total amount of water, % by weight	Other effects on heating curve, °C		Evaporation heat of 1st form of water, Kcal/mole H_2O
				endo-therm	exo-therm	
7	8	9	10	11	12	13
110—120	3.4	3.8	7.2	—	—	8 $\pm$1
100—130	3.7	2.0	5.7			8 $\pm$1
110—130	5.3	5.1	10.4			9 $\pm$1
120—130	6.1	2.5	8.6	—	—	9.9$\pm$0.3
125—130	9.0	3.3	12.3	—	—	12 $\pm$1
130—150	7.6	3.2	10.8	—	—	11.4$\pm$0.1
140—160	6.8	6.2	13	—	930	8.7$\pm$0.6
100—130	11.4	4.6	16	—	—	8.4$\pm$0.7
120—130	6.9	4.9	11.8	1060	1240	8.9$\pm$0.4
100—110	6.6	6.6	13.2	—	—	
120—130	4.2	3.5	7.7	—	880	3.7$\pm$0.6
100—130	5.0	3.8	8.8	1020	1070	9.2$\pm$0.5
100—110	2.4	5	7.4	—	825	
100—130	5.7	5.4	11.1	—	1040	
110—130	3.6	5.0	8.6	—	—	
120—140	2.8	4.2	7.0			6.8$\pm$0.6
120—150	8.2	5.7	13.9			8.0$\pm$2
100—130	3.1	3.6	6.7		1000	6.1$\pm$0.7

The thermoanalytical curves of silica gel produced in acid medium are shown in Fig. 1 (Table 1). The DTA curve displays a distinct endothermal peak at 150°, due to water loss. The TG and DTG curves in this temperature range show a mass loss, which is described by the S-shaped arm of high slope. With increasing temperature, the DTA curve does not indicate any other thermal effect up to about 900°. In this temperature range an exothermal peak due to partial crystallization of silica gel is observed. An X-ray powdergram of silica gel recorded after thermogravimetric measurements reveals a mixture of quartz and cristobalite in the specimen. In the range from 150 to 1200° the TG curve shows a gradual mass loss. The curve has a constant slope up to 800°, but then the slope

begins to decrease, becoming almost parallel to the X-axis at 1200°. No effects (except partial crystallization) are observed in the DTA and DTG curves in this temperature range.

A pronounced endothermal peak at $100-160°$ has made it possible to determine dehydration thermal effects by the method of Berg and Anosov [7]. In this method, the thermal effect is determined by comparing the peak area in the DTA curve with the area of the peak due to the thermal effect of decomposition of the reference specimen. Reference specimens used were $CaCO_3$ and $CdCO_3$ of "analytical" grade, their decomposition temperatures being 910 and 430°, respectively.
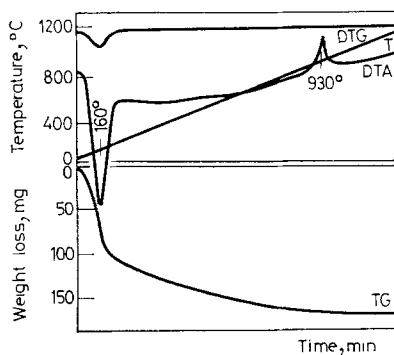
Fig. 1. Thermal curves of silica gel produced in acid medium

Silica gel was mixed in a certain definite proportion with the reference specimen and was placed in the crucible, alumina being in the other crucible.

The thermal effect was calculated via the formula:

$$\Delta H_{deh} = \Delta H_{ref} \cdot \frac{S_{sp}}{S_{ref} X}$$

where ΔH is the heat of decomposition of the tested or the reference specimen;

S is the area of the peak in the DTA curve (corresponding to this effect) expressed for 1 mole of the reference specimen and 1 mole of evaporated water for the tested specimen;

X is a factor which depends on the difference in the temperatures of the compared effects. It is given by the formula: $X = 0.98 + 0.00057\Delta t$.

The ratio of peak areas was determined as the ratio of the weights of photographic paper cut along the profiles of the thermal peaks in the DTA curves (Fig. 2) of the tested and the reference specimens. The thermal effect due to dehydration of silica gel was determined as the mean of three measurements under identical conditions with various reference specimens. This measurement method yields an accuracy of the order of 10% of the thermal effect, which is quite satisfactory.

Sections corresponding to evaporation of two different forms of water may be distinguished in the TG curves. In the temperature range 100−200° the first form of water is evaporated, which is described by the S-shaped TG curve. Its amount may be calculated by means of the point in the TG curve which corresponds to termination of the thermal effect in the DTA curve. Evaporation of the second form of water takes place in the range 200−700°, and is described by the line inclined at a certain angle to the X-axis. This evaporation is not accompanied by a perceptible thermal effect.
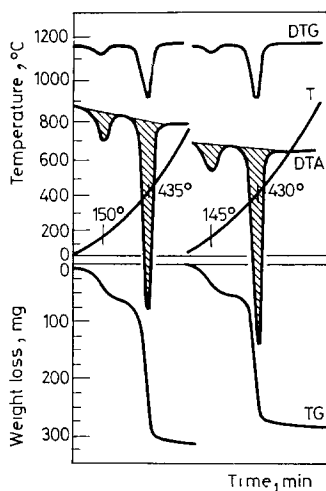

Fig. 2. Determination of dehydration heat from DTA curves; reference specimen − CdCO₃

Since the loss of specimen mass in this temperature range proceeds at a constant rate, the absence of a perceptible thermal effect is evidenced that the properties of the evaporating water are constant and the thermal conditions of the specimen are stationary. Under such conditions, the divergence of the thermal flux is evidently constant, and only the shift of the DTA curve relative to the X-axis may result. We did not observe any such shift in our experiments. Probably, the flow of heat to the specimen far exceeds the absorption of heat due to dehydration, which is indicative of the low heat of evaporation of the second form of water. Termination of evaporation of this water form, and hence its content, may be determined by the point where the line becomes parallel to the X-axis.

The conditions of thermal measurements (linear dependence between temperature and time) have made it possible to determine the activation energy of the first form of water from TG curves by a non-isothermal kinetic method. The calculation procedure is given in detail in [8].

According to the general equation of non-isothermal kinetics, the activation energy E may be determined by the segment cut on the Y-axis by a line expressed in the following coordinates:

$$\Delta \log \frac{\mathrm{d}W}{\mathrm{d}t} \ vs. \ \Delta \log W$$

where W is the loss of specimen mass in the reaction, and t is the time.

Figure 3 shows the results of such an analysis of TG curves for silica gel produced in acid medium. The activation energy was found to be 10 ± 1 kcal/mole.
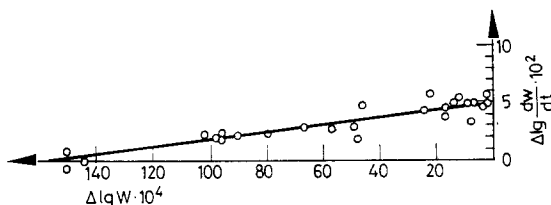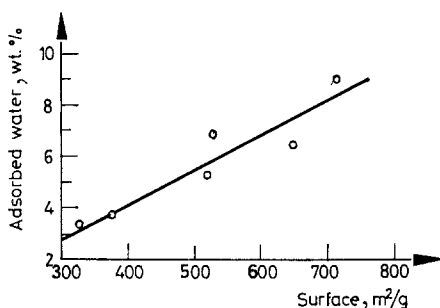

Fig. 3. Scheme for calculation of activation energy

Fig. 4. Relationship between first form of water and specific surface of silica gel

Table 1 lists the results of thermogravimetric investigation of silica gel: thermal effects, total and relative contents of various forms of water, heat of dehydration for the first form of water.

The heats of dehydration of industrial silica gels of "chromatography" grade vary from 7 to 12 kcal/mole of evaporated water. The minimum dehydration heat (about 4 kcal/mole) is exhibited by silica gel produced in neutral medium, whereas for other specimens it varies from 7 to 9 kcal/mole. Silica gel specimens were prepared several times in neutral medium and the dehydration heats were reproduced with satisfactory accuracy.

For most of the silica gel specimens studied, the dehydration heat is about $1 - 3$ kcal/mole less than the heat of evaporation (10 kcal/mole) which makes it possible to identify the first form of water as a polymolecular water layer located in the open pores of the silica gel. This is confirmed by the linear relationship between

the content of the first form of water and the specific surface area (Fig. 4). Besides, this is proved by the coincidence of the magnitudes of the dehydration heat and activation energy during evaporation of water from silica gel. A slightly lower dehydration heat as compared to the heat of evaporation of water is caused by the decreased evaporation heat due to the small dimensions of water particles in vapour from silica gel.

Calculations by means of the Gibbs–Thomson formula:

$$\log \frac{P_r}{P_\infty} = \frac{2\sigma V}{r} = \frac{\Delta\lambda}{2.3RT}$$

(where σ is the surface tension of water, V is the molecular volume, and P is the pressure of saturated water vapour over a drop of radius r) show that the evaporation heat decreases by 1.5 kcal/mole when the drop radius is of the order of 50 Å.

With decreasing pore radius, the number of water molecules hydrogen-bonded to surface hydroxyl groups increases, and consequently the dehydration heat exceeds the heat of evaporation of water. Thus, for silica gels of "chromatography" grade having dehydration heats of 12 and 11.4 kcal/mole, the mean pore radius is 16 and 11 Å. The dehydration heats of specimens 3 and 4, having the same specific surface but larger pore diameters, are 8.9 – 9.9 kcal/mole, close to the heat of evaporation of water.

These results permit identification of two forms of water in amorphous silica:

1. A polymolecular water layer in open pores and loosely-bonded molecules on the surface and in the bulk of the globules.

2. Water molecules hydrogen-bonded to silanol groups, as well as water molecules bonded to silicon atoms. Probably, the water-to-silicon bonding is coordination due to the vacant d-orbitals of silicon.

The integral thermal effect of dehydration varies, depending on the ratio of the different forms of water in the silica gel. Thus, for fine-grain silica gel produced in acid medium, the polymolecular layer in the inter-grain space ($\Delta H_{deh} = 10$ kcal/mole) makes the main contribution to the flow of evaporating water. In silica gel produced in neutral medium the grains are of much greater size [1], and hence the gel has fewer silanol bonds and more siloxane bonds. In this case, the main contribution to the flow of evaporating water is made by the molecules bonded to silicon, which reduces the integral thermal effect down to 4 kcal/mole.

It is not possible to separate the coordinated or hydrogen-bonded forms of water but their total thermal effect of evaporation is much less than the heat of evaporation of water.

References

1. N. E. NEIMARK, The structure and properties of silica gels, Nauka, Moscow, 1962.
2. I. A. LEONTYEVA, I. A. SHEVCHENKO and M. V. KIREEVA, Neorgan. Materialy, Dep. No. 4060–72.
3. J. M. BERAK and W. CELLER, Przem. Chem., 43 (1964) 311.

4. V. V. MORARIU and R. Z. MILLS, Phys. Chem., 78 (1972) 298.
5. SEIICHI KONDO and MASA-AKI MUROYA, Bull. Chem. Soc. Japan, 43 (1970) 2657.
6. M. N. DANCHEVSKAYA, G. P. PANASYUK, et al., Proceedings of the 7th International Conference on Mass spectrometry, Florence, 1976.
7. L. G. BERG and V. YA. ANOSOV, Zh. Obsch. Khim., 12 (1942) 31.
8. New Methods of Polymer Research, Mir, Moscow, 1968, p. 148.

RÉSUMÉ — Plusieurs échantillons de gels de silice commerciaux et synthétisés au laboratoire ont été étudiés par TG. Deux formes d'eau adsorbée ont été mises en évidence: la première s'évapore entre 100 et 200° et consiste en une couche d'eau polymoléculaire dans les pores ouverts et à l'intérieur des globules; la seconde forme s'évapore entre 200 et 700° consiste en molécules d'eau liées par ponts d'hydrogène à des groupes silanol et, évidemment, par des liaisons de coordination aux atomes de silice. La chaleur de déshydratation de la première forme, déterminée à partir des courbes ATD, dépend de la proportion des deux formes et varie depuis 3.7 ± 0.6 kcal/mole pour le gel de silice à gros grains produit à pH-7 jusqu'à 12 ± 1 kcal/mole H_2O pour le gel de silice à grains fins de qualité commerciale «pour chromatographie».

L'énergie d'activation de l'évaporation de l'eau, calculée à partir des courbes TG, est d'environ 10 kcal/mole dans l'intervalle de température compris entre 150 et 200°.

ZUSAMMENFASSUNG — Verschiedene handelsüblich und im Laboratorium synthetisierte Proben von Kieselgel wurden durch Thermogravimetrie untersucht. Zwei Formen von adsorbiertem Wasser wurden gefunden: die erste im Temperaturbereich von 100 bis 200° entweichende, ist eine polymolekulare Wasserschicht in offenen Poren und lose gebundenen Molekülen an der Oberfläche und in der Masse der kugelförmigen Teilchen; die andere Form, welche im Temperaturbereich von 200 bis 700° verflüchtigt wird, besteht aus Wassermolekülen, die durch Stickstoffbindungen an Silanolgruppen und offensichtlich koordinativ an Siliziumatome gebunden sind. Die aus den DTA-Kurven ermittelte Dehydratisierungswärme der ersten Gruppe hängt vom Verhältnis der beiden Formen ab und variiert von 3.7 ± 0.6 kcal/Mol H_2O für grobkörniges Kieselgel, das bei pH = 7 hergestellt wird, bis zu 12 ± 1 kcal/Mol H_2O für feinkörniges Kieselgel der handelsüblichen »chromatographischen« Qualität.

Die aus den TG-Kurven ermittelte Aktivierungsenergie der Verflüchtigung des Wassers beträgt im Temperaturbereich von 150 bis 200° etwa 10 kcal/Mol.

Резюме — Используя термогравиметрию изучено несколько образцов силикагеля, выпускаемых промышленностью и синтезированных в лаборатории. Было установлено две формы адсорбированной воды, первая из которых испаряется в области температур 100—200° и представляет собой полимолекулярный слой воды в открытых порах и слабосвязанные молекулы воды на поверхности и в объеме гранул. Вторая форма, испаряющаяся при температуре 200—700°, представляет собой молекулы воды, связанные водородными связями с силанольными группам и, очевидно, координационно-связанные с атомами кремния. Теплота дегидратации первой формы, определенная из кривых ДТА, зависит от соотношения двух форм и изменяется от 3.7 + 0.6 ккал/моль H_2O в случае крупнозернистого силикагеля, получаемого при pH = 7 до 12 ± 1 ккал/моль H_2O в случае мелкозернистого силикагеля, выпускаемого промышленностью марки "хроматографический". Энергия активации испарения воды, определенная из кривых ТГ, составляет около 10 ккал/моль в области температур 150—200°.