On the Mechanism of Evaporation in Vacuum. I. Evaporation of Silica Gel(1)

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The replica methods are usually used to observe the solid surfaces by the electron microscope. Among these, the polystyrene-silica replica method(2),(3),(4) is generally accepted as the method of the best reliability. The cause of the high reliability of silica replica is, as Heidenreich and Peck(2) suggested, due to the high mobility of silica on the polystyrene surface. It is supposed from these facts that silica may evaporate in the form of very low molecular weight, such as a single molecule SiO_2, and deposit and migrate freely on the polystyrene surface, and then polymerize to form a glass-like film. The polystyrene-silica method, however, has some defects. Above all, the evaporation of silica needs a fairly difficult technique. Wyckoff(5) and some others entertained some doubts on the propagation of such a difficult method. Baker and Nicoll(6) tried to obtain the silica film by blowing $SiCl_4$ against the surface of specimen and hydrolysing it on the surface. No satisfactory result was, however, obtained.

The present author used silica gel instead of quartz, and was able to evaporate it very easily. Silica gel was prepared as follows: Dilute commercial water glass to 10 times, add the excess of hydrochloric acid of 1 N drop by drop to form jelly, filter by suction, wash with water, adjust it in a rod-like shape, and heat in a crucible. Silica gel was, thus, obtained in a rod shape, the diameter of which was 4 mm. The apparatus used for evaporation was an ordinary one, as shown in Fig. 1. B is a bell jar and G. P. is a rubber packing.

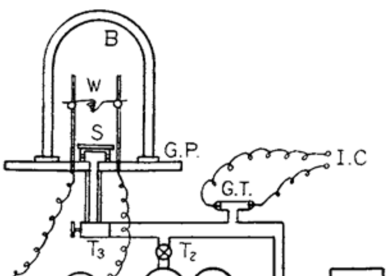

Fig. 1.—Apparatus for evaporation.

Specimen, that is, the polystyrene film, the slide glass, and so forth, are placed at S, and a piece of silica gel is put in the tungsten basket W. A bell jar is evacuated by a rotary pump R and two oil diffusion pumps D_1 and D_2. A tungsten filament W is made of wire

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(1) These results were presented before the Meeting of Colloid Chemistry held by the Chemical Society of Japan at Osaka, November 1950.

(2) R. D. Heidenreich and V. G. Peck, *J. Appl. Phys.*, **14**, 23 (1943).

(3) C. H. Gerould, *J. Appl. Phys.*, **18**, 333 (1947).

(4) R. B. Barnes, C. J. Burton and R. G. Scott, *J. Appl. Phys.*, **16**, 730 (1945).

(5) R. W. G. Wyckoff, "Electron Microscopy," New York, 1949, pp. 71 and 93.

(6) R. F. Baker and F. H. Nicoll, *J. Appl. Phys.*, **15**, 803 (1944).

of 0.5 mm. in diameter, which is coiled about 6 times in corn of 8 mm. in hight and 30° in the vertical angle. Various voltages are applied on the filament by a transformer T and current is read by the ammeter A. G.T. is a Geisler's tube and I. C. is an induction coil, by which vacuum in the bell jar is known.

Heating silica gel in a crucible does not seem to be sufficient to dehydrate it. By a rapid evaporation of water contained in the gel, it bursts and splashes, if much current is hastily applied. In order to avoid such trouble, and to keep vacuum in the bell jar better, preheating of the filament for 15 or 30 sec., with 150 watts or so, is desirable. Some examples of data are shown in Table 1. In this table, w_0 is the weight of silica gel evaporated, V and A are voltage and current applied to the tungsten basket, respectively, t is the time in which current is closed, W is the product of V and A, that is the power supplied, and Wt/w_0 corresponds to the energy provided for the evaporation of 1 mg. of silica gel. The most part of this energy is emitted away as radiation, and only a very small part of it is used to evaporate the gel. Wt/w_0 may have, therefore, no theoretical meaning. If the experiments are done, however, under a definite condition, Wt/w_0 may be used as a practical measure of the easiness of evaporation. From Table 1, it is seen that

$$Wt/w_0=1{,}000\sim1{,}500 \text{ joule/mg.}$$

In the case of quartz, data of Heidenreich and Peck⁽²⁾ and Gerould⁽³⁾ shows that

$$Wt/w_0=3{,}800\sim14{,}000 \text{ joule/mg.}$$

which is 3∼9 times greater than the value for silica gel. It is recognized from these values that silica gel evaporates much more easily than quartz. It is experienced that silica gel evaporats as easily as chromium.

Table 1

Evaporation of Silica Gel

Exper. No.	w_0, mg.	V, volt	A, amp.	t, sec.	W, watt	Wt/w_0
1	4	10	14	15	140	(preheating)
		15	18	20	270	= 1350
2	6	10	15	60	150	(preheating)
		13	18	30	234	= 1170
3	8	10	20	15	200	(preheating)
		15	24	30	360	= 1350
4	8	8	12.5	180	100	(preheating)
		15	17	30	255	= 1339
		17	18	10	306	
5	18	5	10	15	50	(preheating)
		10	14.5	15	145	
		13	17	60	221	= 1186
		15	18	30	270	
6	20	5	10	15	50	(preheating)
		10	13	30	130	
		15	18	110	270	= 1485

Polystyrene silica replica is made as follows. Polystyrene replica is made by the low pressure method or the lacquer method. In the low pressure method, 1 cm.^{2} of the polystyrene film, 0.02 mm. in thickness, is placed on a slide glass, and heated on a metal plate to 150∼200°C. The specimen, another silde glass, and a weight of 1 kg. are put on the film and cooled below 80°. Specimen is splitted from the film, and silica gel is evaporated on the film according to the method described above. In the lacquer method, one drop of polystyrene lacquer, that contains 1 g. of polystyrene in 15 cc. of benzene, is placed on the specimen and dried. The replica film is stripped after 2 days, and placed on a slide-glass and silica is evaporated to it. The thickness of silica film deposited is calculated by the equation:

$$d=\frac{h\ w_0}{4\pi\ (h^2+r^2)^{3/2}\ \rho} \qquad (1)$$

where h is the height of tungsten basket above the polystyrene replica, 6∼7 cm., r is the horizontal distance of the basket from the film, 4∼5 cm., and w_0 is the weight of silica gel used, 4∼5 mg. ρ is the density of silica film. A reliable value of ρ is not known. The value of bulk quartz $\rho=2.22$ is used. The thickness calculated was usually 200∼300 Å. Williams and Backus⁽⁷⁾ asserted that the value of d of equation (1) should be multiplied by an "efficiency factor" 3/4. The foundation of their opinion is somewhat uncertain, and a preliminary experiment by the present author to determine the thickness of the silica film directly from the interference color for somewhat thicker one seemed to show that such a factor is rather unnecessary. No efficiency factor is, therefore, used. The polystyrene-silica replica film thus obtained is cut off in pieces of 3∼5 mm. square. One of the pieces is pasted on a holder for the electron microscopy, facing the silica surface downward and the polystyrene surface upward. The difficulty of "Fishing" is thus avoided. Paste used must be insoluble in benzene. Usual starch paste is available. These holders are laid in benzene for 1∼2 days and put out carefully, holding the replica film vertically, from benzene and laid on a filter paper and dried. Some electron micrographs obtained are shown in Fig. 2. (a) is the surface

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(7) R. C. Williams and R. C. Backus, *J. Appl. Phys.*, **20**, 98 (1949).

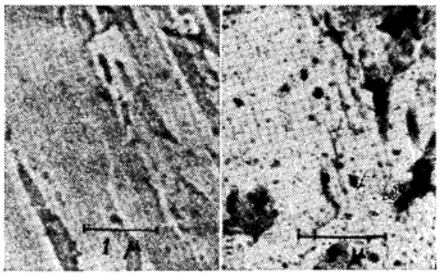
(a) (b)

Fig. 2.—Electron micrograph.

of a brass polished by sandpaper. The lacquer method is used and silica film is 250 Å. thick. (b) is the surface of a carbon brush. The low pressure method and silica film of 200 Å. are used. Reliability of these replica method is not yet tested, but, at least, the granular structure of silica film is not found. In Fig. 2 the applicability of this replica method for electron micrography are shown.

In order to comprehend the easiness of the evaporation of silica gel, it is necessary to know the vapor pressure of it. The estimation of vapor pressure is tried. Clapeyron-Clausius' equation, usually used to describe the vapor pressure curve, is written under some approximation as:

$$\frac{\mathrm{d}\ln P}{\mathrm{d}T}=\frac{L}{RT^2}, \qquad (2)$$

where P is vapor pressure, T is absolute temperature, R is gas constant, and L is heat of sublimation or evaporation. Using Nernst's assumption:

$$L=L_0+1.5\,T-\mathcal{E}T^2+RT \qquad (3)$$

Eq (1) is integrated to

$$\log P(\text{atm.})=-L_0/2.303\,RT+1.75\log T-\mathcal{E}T/2.303\,R+\kappa, \qquad (4)$$

where P (atm.) is the pressure expressed in atmosphere, and κ is the conventional chemical constant and $\mathcal{E}$ is a parameter determined from experimental data, *e. g.*, boiling point.

It is known(8) that the boiling point, Tv, of rock crystal or quartz is 2590°. It is assumed that silica evaporates as SiO_2, which is thought to be a linear molecule. The conventional chemical constant(9) κ is, then,

$$\kappa=-3.273+1.5\log M+\log(N_A\,A\times10^{16}) \qquad (5)$$

where M is molecular weight, 60.06, N_A is Avogadro's number, and A is the moment of inertia of the molecule. Assuming the Si=O distance to be 1.62 Å., the value of κ of Eq. (5) is obtained as 1.319. If the value of L_0 is obtained, vapor pressure P is calculated from Eq. (4), with the estimated value of $\mathcal{E}$ by the use of T_v.

The heat of sublimation of quartz $L_0^{(A)}$ is approximately equal to twice the bond energy of Si-O,

$$L_0^{(A)}\simeq 2D(\text{Si-O}) \qquad (6)$$

This is easily seen from Fig. 3 (a), because four bonds should be broken to produce a molecule of SiO_2, and each bond is held in common with two SiO_2 molecules. The bond energy D(Si-O) is calculated by Pauling(10) from the data of the heat of generation of quartz as:

$$D(\text{Si-O})=89.3\ \text{kcal./mol.} \qquad (7)$$

Seitz(11) cited the cohesive energy of quartz E as

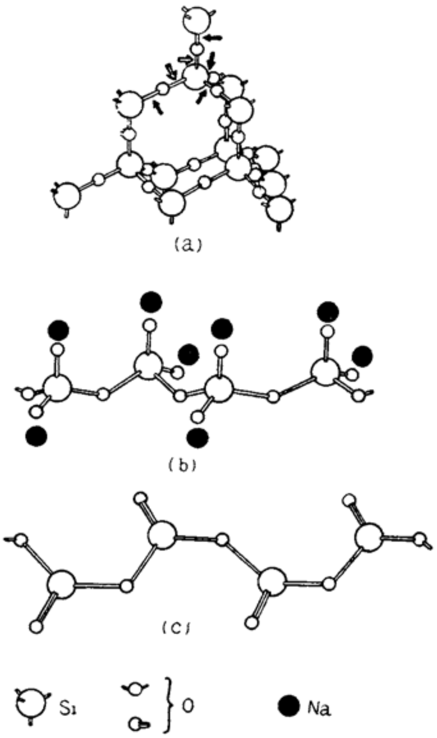

Fig. 3.—Molecular structure of silica.

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(8) Edited by Tokyo Astronomical Observatory, "Rika-Nenpyo", Tokyo, 1950.

(9) R. H. Fowler and E. A. Guggenheim, "Statistical Thermodynamics", Cambridge, 1939, p. 171.

(10) L. Pauling, "The Nature of the Chemical Bond," New York, 1940, p. 53.

(11) F. Seitz, "The Modern Theory of Solid", New York, 1940, p. 61.

$$E = 405.7 \text{ kcal./mol.} \qquad (8)$$

E is the energy necessary to produce one gram atom of Si and two gram atom of O from quartz, and equals to the sum of $L_0^{(A)}$ and $2D(\text{Si-O})$, as shown in Fig. 3 (a). Therefore,

$$E \simeq L_0^{(A)} + 2D(\text{Si-O}) \simeq 4D(\text{Si-O}) \qquad (9)$$

From Eqs. (8) and (9),

$$D(\text{Si-O}) \simeq 101.4 \text{ kcal./mol.} \qquad (10)$$

This is the same order of magnitude with Pauling's value, Eq. (7), but is not exactly equal. The mean value

$$D(\text{Si-O}) = 95.4 \text{ kcal./mol.} \qquad (11)$$

is used in the following estimations. From Eq. (6),

$$L_0^{(A)} = 190.8 \text{ kcal./mol.} \qquad (12)$$

Silica gel is prepared from water glass, $(Na_2SiO_3)_n$, which is considered as a chain polymer as shown in Fig. 3 (b). The idealized structure of silica gel, therefore, will be also a chain polymer. The heat of sublimation of idealized silica gel, $L_0^{(B)}$, will be, as explained easily from Fig. 3 (c),

$$L_0^{(B)} \simeq D(\text{Si-O}) = 95.4 \text{ kcal./mol.} \qquad (13)$$

As for actual silica gel, the probability of dehydration from two hydroxyl groups of adjacent molecules forming an oxygen bridge should be taken into account, beside with the probability of dehydration from two hydroxyl groups belonging to the same silica atom in meta-silicic acid molecule. Uuder the somewhat arbitrary assumption that the latter probability is twice as large as the former probability, the heat of sublimation of real silica gel $L_0^{(C)}$ becomes:

$$L_0^{(C)} = \frac{2L_0^{(B)} + L_0^{(A)}}{3} = \frac{4}{3} D(\text{Si-O})$$
$$= 127.2 \text{ kcal./mol.} \qquad (14)$$

Using these values of the heat of sublimation L_0, vapor pressure is calculated for various temperatures, using $\kappa = 1.319$ and $\mathcal{E} = -0.01145$, the latter is obtained from boiling point for quartz. For some metals, vapor pressure curves are estimated in an analogous way, and temperature corresponding to some vapor pressure are cited in Table 2. In this table, SiO_2(A) means quartz, SiO_2 (B) means idealized silica gel and SiO_2 (C) means actual silica gel. It is seen that the evaporation of quartz is almost as difficult as platinum, while silica gel, SiO_2 (C), evaporates as easily as gold or chromium. These agree well with the results described above.

Table 2

Calculated Vapor Pressure—Temperature Relations

Substances	Temperature corresponding to the vapor pressure, °K.			
	10 mm.Hg	10^{-1} mm.Hg	10^{-3} mm.Hg	10^{-5} mm.Hg
Pt	3300	2600	2200	1900
SiO_2 (A)	2650	2450	2250	2050
Au	2200	1850	1550	1350
SiO_2 (C)	2000	1800	1650	1500
Cr	2050	1750	1500	1300
SiO_2 (B)	1650	1450	1300	1150
Al	1700	1400	1200	1050

Summary

The evaporation of silica is facillitated by the use of silica gel, instead of quartz. The silica film thus obtained is available as replica for the electron microscopy. The difference of the easiness of evaporation between quartz and silica gel is atributed to molecular constitutions. Under the assumption that quartz consists of three dimensional net work of covalent linkage, while silica gel is constructed by linear chain having some oxygen bridges between chains, vapor pressure is calculated, and the ease of evaporation is accounted for by the comparison to some usual metals.

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