at liquid nitrogen temperature and a clear white or pale yellow liquid at −100°C. Similar samples have had a vapor pressure three- to fivefold greater than that of ClF_3. In sharp contrast with the behavior of ClF_3, ClF_5 reacts slowly, if it reacts at all, with water vapor.

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References and Notes

1. K. S. Pitzer [*Science* **139**, 414 (1963)], in discussing the bonding in the xenon fluorides and halogen fluorides, notes that detailed calculations indicate that the boundary of stability is essentially the same for the XF_4 units and XF_2 units where X represents, for example, xenon or ClF. He suggested that the F-F nonbonded exchange repulsions may account for the absence of a stable ClF_5.
2. The method was similar to that used in the preparation of XeF_6 by Dudley, Gard, and Cady [*Inorg. Chem.* **2**, 228 (1963)].

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Volume Changes of a Thixotropic, Sodium Bentonite Suspension during Sol-Gel-Sol Transition

Abstract. *Dilatometric measurements during the sol-gel-sol transition of an air-free, thixotropic, sodium bentonite suspension revealed a reversible change in volume of about* 2.4×10^{-4} *percent. The volume of the suspension increased during gelation and decreased when the gel was subsequently liquified. This is taken as evidence of a progressive building up, during gelation, of a water structure less dense than normal.*

Some colloidal systems stiffen to a gel on standing but become liquified again when disturbed by stirring or vibration; systems exhibiting this behavior in a reversible manner under virtually isothermal conditions are said to be thixotropic. There has been speculation and debate over the nature of the gel state and its source of strength. Most investigators now regard the gel as a more or less continuous framework made up of the solid phase, the interstices being passively occupied by the suspending liquid (*1*). But the extent, however small, to which the suspending fluid is affected by the solid phase during the gelation of colloidal suspensions is no doubt important in physical and biological systems (*2*, *3*).

In bentonite clay suspensions, for example, it is known that water in close proximity to the mineral surfaces is significantly influenced by the solid phase; its density is lower than that of normal water (*4*), its viscosity is higher (*5*), and the ionic mobilities and diffusion coefficients of solutes in it are lower (*6*) than in aqueous solution. Moreover, as thixotropic bentonite suspensions gel, all of the water is affected (*7–9*). The chemical potential of the water decreases gradually as gelation proceeds but is nearly restored to its initial value when, upon agitation, the suspension is reliquified (*9*).

One is thus led to visualize the sol state as a suspension of clay particles oscillating in Brownian motion, about which a water structure, less dense than normal but of limited extent, has been induced. As gelation proceeds the particles contact each other and orient themselves into a continuous network; as this happens their Brownian motion ceases or is greatly reduced, promoting a more extensive development of the water structure. If this is true and if the induced water structure is less dense than that of normal water, an increase in the volume of the suspension is to be expected upon gelation, followed by a decrease in volume on subsequent liquefaction of the gel.

To test this prediction we measured the volume changes accompanying the sol-gel-sol transformation of a thixotropic, sodium bentonite suspension by means of a sensitive dilatometer. The dilatometer was a U-tube made by fusing together two lengths of glass tubing. One arm was simply a length of glass capillary (0.6 mm inner diameter) and the other consisted of a length of glass tubing (15.0 mm inner diameter) with a glass stopcock at the top. The latter was cut so that its volume was about 75 cm^3. During the construction of the dilatometer, a stainless-steel ball measuring 12.8 mm in diameter was sealed in the large arm.

A sodium bentonite suspension was prepared by slowly passing a dilute (about 20 g clay per liter) suspension of Wyoming bentonite through a sodium-saturated, Rohm and Haas IR-120 cation-exchange resin (*10*). The resulting suspension was concentrated to 4.67 g per liter by evaporation and placed in a large vacuum erlenmeyer flask (*7*). Preliminary experiments showed that the presence of occluded air resulted in an initial irreversible volume change on gelation that appeared to depend upon the amount of air present and the method employed in filling the dilatometer. Apparently, this effect has not been recognized before (*11*). To remove as much occluded air as possible, the suspension was agitated for half an hour during which time it was exposed to the partial vacuum created by a water aspirator. The suspension was then drawn into the dilatometer and confined between the closed stopcock at the top of the large arm and a 10-cm thread of mercury in the capillary tube. Care was taken to insure that no air was entrained while the dilatometer was being filled. The height of the interface of the mercury and suspension was adjusted during filling so that a slight positive hydrostatic pressure was created throughout the suspension. The filled dilatometer was then put into a water bath maintained at constant temperature (30° ± 0.005°C); the steel ball was raised and kept in position at the top of the dilatometer with a magnet. The position of the interface was then observed periodically through the telescope of a cathetometer.

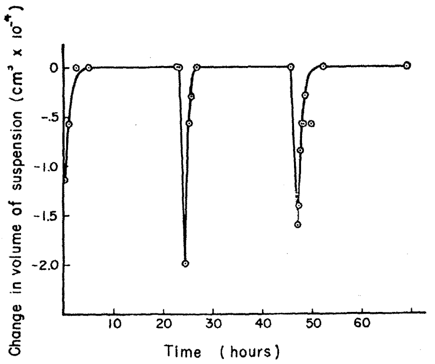

Fig. 1. The change in the volume of a suspension during three sol-gel transitions as a function of time.

After a certain time the steel ball was released, and the time taken for it to fall through the suspension was measured. The ball was raised immediately afterwards and was allowed to fall again; this was repeated 25 or 30 times until the time being taken for it to fall through the suspension was constant. Timing the falling steel ball gave an index of the strength of the gel and the repeated passage of the ball through the tube provided a means of liquifying the gel at will. The gel strength, as inferred from the initial falling time of the steel ball, increased noticeably as the time interval between the initiation of gelation and release of the ball was progressively lengthened, increasing more than threefold during the first hour. After an interval of 24 hours, the times taken for the first and second falls were, respectively, about 4 and 2 times that taken for the ball to drop through the thoroughly liquified suspension.

The gel was thoroughly liquified after standing undisturbed for 24 hours. As shown in Fig. 1, this was accompanied by an immediate decrease in volume of about 1.8×10^{-4} cm^3, corresponding to a change of about 2.4×10^{-4} percent of the volume of the suspension. The effect was shown to be nearly reversible by permitting the suspension to re-gel and observing essentially the same effect upon liquefaction.

An estimate of the reliability of the results may be obtained from the dimensions of the dilatometer and the fact that calibration tests proved the cathetometer readings to be accurate to within ± 0.1 mm. From this, a maximum possible error of 5×10^{-5} cm^3 in determining a change in the volume of the suspension may be computed. The data presented in Fig. 1 suggest that the error was actually much less. Observation showed that small fluctuations in the temperature (± 0.005°C) of the water bath were damped sufficiently in the dilatometer fluid that they did not confuse the results.

It has been pointed out (*2*) that the partial-specific-volume data of Anderson and Low (*4*) indicate that the volume of their sodium bentonite suspension was greater by at least 0.045 cm^3 per gram of clay than would have been the case if the water in the suspension had everywhere its normal density. If it had been possible in this study to completely break down the water structure on liquifying the gel, a volume change of the order of 0.15 cm^3 evidently could have been expected. The observed change in volume, however, was of the order of 1.8×10^{-4} cm^3, indicating that the water structure nearest the clay particles was left relatively undisturbed by the passage of the steel ball up and down the column.

The reversible expansion and contraction in volume of the bentonite suspension in undergoing the sol-gel-sol transition is good evidence that the structure induced in the surrounding water by suspended clay particles in the sol state is further developed on gelation, and that it is less dense than normal water (*12*).

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X-ray Diffraction Studies on Tin at High Pressure and High Temperature

Abstract. *Tin at a pressure of 39 kb and at 314°C has tetragonal symmetry with an atom at each point of a body-centered tetragonal lattice. The unit cell dimensions are* a *equal to 3.81 Å,* c *equal to 3.48 Å, and* c/a = *0.91. The melting curve of tin was observed up to 45 kb and the boundary line between the tin I and tin II phases was observed to 70 kb by x-ray diffraction techniques.*

The fusion curve of tin (*1*) indicated a phase transition with a triple point at 34 kb (corrected to the volume scale) and 318°C. The resistance measurements in this region failed to establish the phase line (the boundary line between tin I and tin II) extending from the triple point, and it was suggested that other techniques would be necessary for its determination.

Kennedy and Newton by means of differential thermal analysis succeeded in finding and following this phase line to 50 kb (*2*). Stager, Balchan, and Drickamer (*3*) detected a small rise in the resistance curve of tin at 113 to 115 kb, which they correlated to an extrapolation of the tin I-II phase line described by Kennedy and Newton. Stager *et al.* suggested a cubic structure for the tin II phase. The crystal structure of the tin II phase was postulated to be face-centered cubic (fcc) by Kaufman (*4*), and Jamieson has indicated that a body-centered cubic (bcc) phase exists at the 113- to 115-kb transition reported by Drickamer (*5*).

By means of a tetrahedral, high pressure and high temperature, x-ray diffraction apparatus, we have obtained the standard Debye-Scherrer pattern for tin II at 39 kb and 308° to 320°C (data were obtained from an overnight experiment in which the temperature fluctuated between 308° and 320°C). The data (Table 1) indicate a simple body-centered tetragonal (bct) structure with two atoms per unit cell located at 000 and ½½½. Unit-cell parameters are: a = 3.81 Å, c = 3.48 Å, and c/a = 0.91. A calculation of the volume yields a compression ($\Delta V/V_0$) of 0.65 relative to 1 bar at 25°C.

The tin I structure is tetragonal with four atoms per unit cell located at 000, ½0¼, ½½½, and 0½¾. A possible (nonreconstructive) mechanism for the tin I-II transition involving a simple shifting of atoms in the tin I structure has been considered from the standpoint of lattice vibrations (*6*). According to Musgrave (*6*), the atoms will be located at the lattice points of a bct lattice if one selects appropriate vibrational modes of the tin I structure

Table 1. X-ray diffraction data for tin II at 39 kb and 308° to 320°C. The observed interplanar spacing corresponding to the indexes *hkl* is $d_{\text{exp.}}$. The corresponding calculated spacing, $d_{\text{calc.}}$, is based on a bct lattice with $a = 3.811$ Å, $c = 3.483$ Å, and $c/a = 0.914$. The calculated intensity, $I_{\text{calc.}}$, includes multiplicity, structure, and Lorentz polarization factors but does not include absorption or temperature factors. $I_{\text{exp.}}$ is the observed, integrated intensity of the diffracted x-ray beam.

(*hkl*)	$d_{\text{calc.}}$	$d_{\text{exp.}}$	$I_{\text{calc.}}$	$I_{\text{exp.}}$
110	2.688	2.695	58	50
101	2.571	2.571	100	100
200	1.915	1.906	26	40
002	1.747	1.741	7	9
211	1.534	1.531	38	30
112	1.463	1.463	17	4
220	1.341	1.347	7	4