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.

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

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

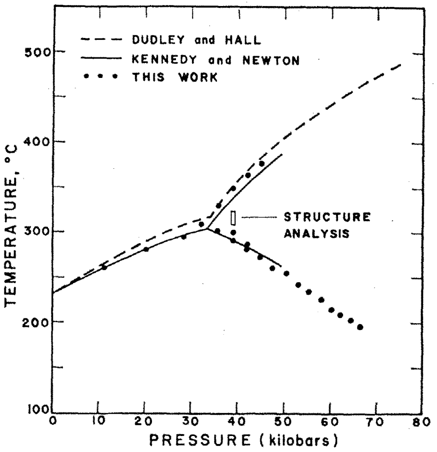

Fig. 1. Phase diagram for tin.

and considers the position of the atoms at the moment of maximum displacement. At this moment the atoms would have eight nearest neighbors. Musgrave then assumes that the more symmetrical bcc structure forms immediately from the bct structure.

This "virtual" bct structure would have lattice parameters of $a = 4.12$ Å and $c = 3.18$ Å, with $c/a = 0.77$ at 1 bar and 25°C. Our measurements indicate an incomplete movement of this virtual bct lattice toward the bcc lattice (the bcc lattice may be considered as a bct lattice with $c/a = 1.00$). Apparently at 39 kb and 314°C the bonds between second nearest neighbors located along the c axis are sufficiently important to prevent the complete movement to the bcc structure, as suggested by Musgrave.

In addition to the above elucidation of the tin II structure, we have used x-ray diffraction techniques to determine the phase diagram of tin. The melting curve was followed to 45 kb and the tin I-II phase boundary to 70 kb. Melting was followed to the triple point by observing the (200) and (101) lines of the tin I x-ray pattern as temperature was slowly increased at a fixed pressure. The temperature at which these lines disappeared into the background was taken to be the melting point. This temperature was reproducible to ± 4°C. Temperature was measured by a thermocouple located within an electrically heated graphite furnace used to heat the tin. The tin was centrally located within the furnace, and was surrounded by polyethylene. The x-ray beam was directed axially through the furnace. Melting beyond the triple point was similarly detected by observing the (110) and (101) lines of the tin II pattern.

The phase boundary between tin I-II was determined by the disappearance of the (200) and (101) lines of tin I and the appearance of the (110) and (101) lines of tin II. During temperature excursions of one particular sample, the presence of a small single crystal properly oriented for Bragg diffraction became evident in the form of a sharp, high-intensity peak. This peak, in a matter of seconds, would repeatedly disappear or reappear as the transition temperature was traversed. The rapidity of the transformation and the retention of the crystal orientation after passing to tin II and returning to tin I provide strong evidence for the nonreconstructive nature of this transition. It was possible to detect the occurrence of this transition within ± 2°C. A comparison of our determination of the tin phase diagram with that of Dudley and Hall and that of Kennedy and Newton is shown in Fig. 1 (*7*).

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Hydrated Electron: Production and Role in Photobiology

Abstract. *Many inorganic anions in aqueous solution either yield the hydrated electron on photolysis or they are strong scavengers. In neutral solution the hydrated electron is a primary photochemical product of aromatic amino acids.*

The hydrated electron is produced by ultraviolet-light flash photolysis of inorganic salts and aromatic compounds. Some anions that give the hydrated electron are Cl^-, Br^-, I^-, OH^-, $Fe(CN)_6^{4-}$, PO_4^{3-}, and CO_3^{2-} (*1, 2*). We obtained negative results with NO_3^-, BrO_3^-, and $CH_3CO_2^-$, although there was sufficient light absorption to induce photolysis. Figure 1 shows the hydrated-electron spectrum from Na_3PO_4 after correction for emulsion sensitivity. The fine structure on the uncorrected spectra obtained by Hart and Boag (*3*) with pulse radiolysis and by Grossweiner *et al.* (*2*) with flash photolysis is due to emulsion spectral sensitivity and nonlinearity; only a single broad band with a possible shoulder near 500 mμ is considered valid, in agreement with the work of Matheson *et al.* (*1*).

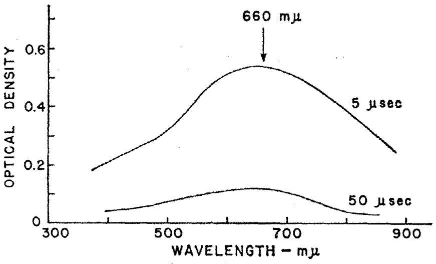

Fig. 1. Transient spectra from the flash photolysis of air-free 0.05*M* Na_3PO_4 at *p*H 11.8. The data were taken on Kodak 103-F and I-N plates and corrected for spectral sensitivity.

There is evidence that some of the anions that do not yield hydrated-electron spectra react rapidly with it, so that the hydrated electron could have been produced in those cases also. For example, the addition of 0.01*M* $NaNO_3$ or $KBrO_3$ to 0.001*M* *p*-cresol at *p*H 11.7 (Na_3PO_4 buffer) suppresses the hydrated electron, although the production of *p*-methylphenoxyl radical is not altered. Again, the photolysis of 0.0002*M* KI in 0.5*M* phosphate buffer at *p*H 9 gives the I_2^- absorption and only a very weak hydrated-electron band, indicating that $H_2PO_4^-$ or HPO_4^{2-} is a scavenger. However, $CH_3CO_2^-$ neither gives the hydrated electron on photolysis nor scavenges. The photochemical scavenging experiments are in agreement with rate constants, measured by pulse radiolysis, which show that NO_3^- reacts very rapidly with the hydrated electron and that $CH_3CO_2^-$ reacts very slowly (*4*).

Noting that hydrogen phosphate buffer scavenges the hydrated electron, we reinvestigated the photolysis of aromatic amino acids in air-free, neutral solution. Under such conditions, positive results were obtained with phenylalanine, tyrosine, and tryptophan. The earlier negative results at *p*H 4 to 5 were due to scavenging by buffer as well as hydrogen ion (*2*). Furthermore, the