

Brèves communications – Kurze Mitteilungen – Brevi comunicazioni – Brief Reports

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Discontinuous Nature of Stress-Strain Relationship

Two 0.0138 in. dia. piano wires ($E = 28.65 \times 10^6$ lb/in² at 200,000 lb/in², ultimate stress = 320,000 lb/in²) are pre-stressed, then clamped with specially hardened and serrated grips in a stressing bed 2 feet long, made of 4 × 2 in. channel sections. While one wire is sufficient for the experiment, the second one served for measuring the relaxation of the stress. If a small weight is placed at the middle of the span the wire will deflect assuming a triangular shape. The major load, causing a deflection, $\delta \approx 20 \times 10^{-3}$ in., was followed by minor loads of 100, 50, 20 and 10 mg. An increase in δ was observed upon applying the first two minor riders, but none for 20 or 10 mg. This meant that an increase in the wire stress was not followed by an appropriate increase in strain. The calculated deflection for a 20 mg increment was 9.3×10^{-6} in. which, due to the geometry of the wire (25.92 in. long), meant 10×10^{-10} strain with a corresponding stress of 28×10^{-3} lb/in². This stress, which is of the order of 0.1 lb/in², will be referred to as the entry stress and is defined as the tension below which stress is not followed by strain.

The basic difficulty in finding the entry stress lies in the limited accuracy of micrometers for measuring travel. A large drum micrometer with 10^{-4} in. graduations was used, with an accuracy of 5×10^{-6} in. The electronic contact indicator will register a maximum gap between wire and micrometer shaft of the order of 10^{-6} in. but the exact magnitude of this gap is impossible to find by a mechanical measuring device and recourse has to be made to the differential thermal expansion that exists between the wire and the stressing bed.

Let ϵ_s and ϵ_w be these expansion coefficients of the steel frame and of the wire respectively and let $\epsilon_w = \epsilon_s + \Delta\epsilon$. It may be shown that the following relationship exists between ϵ_s and $\Delta\epsilon$:

$$\varphi \Delta\epsilon (1 - \varphi \Delta\epsilon) + \frac{\alpha^2}{2} = \frac{\delta_\varphi^2}{2 l^2} (1 - 2 \varphi \epsilon_s) \quad (1)$$

where φ is the temperature change, α is the angle between the horizontal and the slope of the wire before φ takes place, and δ_φ is the deflection of the centre of the span after the temperature increase. From equation 1 $\Delta\epsilon$ can be found if ϵ_s is known; however, it may be shown that even if the large error of 1×10^{-6} in ϵ_s is assumed the error in $\Delta\epsilon$ is of the order of 10^{-10} , hence $\epsilon_s = 6 \times 10^{-6}$ was adopted for the mild steel frame.

Having found $\Delta\epsilon$ to be 4.4×10^{-7} per F the exact magnitude of the sensitivity gap between wire and micrometer

need not be known as contact can be achieved by lifting the wire slowly during decreasing temperature. It may be shown that

$$d \delta_\varphi / dt = \Delta\epsilon (l^2 / \delta_\varphi) d\varphi / dt \quad (2)$$

where the left-hand derivative is the rate of the rise of the wire, while the right-hand derivative is the rate of change of the temperature (cooling is positive).

The cooling down process took place in a windowless room, free of draught, during the evening hours when the temperature decrease was fairly uniform. Three experiments have been carried out on different days when the temperature drop was 0.8 F per hour and the speed of the ascending wire was calculated as 5.5×10^{-5} in./min.

When, now, while the wire was ascending and the contact indicator arc began to vibrate, a load of 20 mg was added to the load the contact should have immediately been broken because this load increment, as mentioned before, should have caused a deflection of 9.3×10^{-6} in., a distance the wire takes more than 10 sec to travel. Failure of breaking the contact means that 20 mg was insufficient to cause a change of strain.

This result was obtained for $\sigma \approx 200,000$ lb/in² prestress (less relaxation). Similar experiments were carried out for 65,000, 100,000 and 150,000 lb/in² prestress with no significant change in the entry stress. The ratio of the stresses in the wire as against those in the stressing bed and contacts is of the order of 10^4 . It follows that effects due to the entry stress are restricted solely to the wire.

It is emphasized that 200,000 lb/in² stress is not high enough for the load to be carried by the skin as against the core. Hence, even if crystals begin to slip dislocations moving towards the free surface will not have to travel through many atomic spacings as this would involve an appreciable plastic strain in the core. The dislocation theory cannot, therefore, explain the entry stress.

Zusammenfassung. Wird ein vorgespannter, dünner Draht mit zunehmender Kraft in der Mitte belastet, so ist jeder Lastzuwachs mit einer Zunahme der Durchbiegung verbunden. Dies trifft nicht mehr zu, falls der Lastzuwachs einen gewissen Wert unterschreitet, was bedeuten würde, dass für kleine Spannungsänderungen unterhalb der Grössenordnung 0,1 lb/in² das Hooksche Gesetz ungültig ist.

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Preparation of 5,6-o-Isopropylidene-L-ascorbic Acid¹

It has been found that, while L-ascorbic acid is sparingly soluble in acetone, it is very soluble in acetone saturated with hydrogen chloride. However, 5,6-o-isopropylidene-L-ascorbic acid exhibits the opposite characteristics, being poorly soluble in acetone saturated with hydrogen chloride and readily soluble in acetone. It is

possible to take advantage of these solubility properties to prepare the isopropylidene derivative in high yield. The condensation can also be accomplished in lower yields by shaking with anhydrous copper sulfate for 24 h or treatment with sulfuric acid overnight². The product is

¹ Supported by PHS Research Grant CA-03994-06.

² L. V. VARGHA, *Nature* 130, 847 (1932).

a convenient source for the synthesis of potassium 3,4-*o*-isopropylidene-L-threonate³ and of threonic acid, although L-threonic acid can also be obtained in equimolecular mixture with oxalic acid from the direct oxidation of L-ascorbic acid^{4,5}. There is increasing interest in L-threonic acid, because it is a possible intermediate in the catabolism of L-ascorbic acid *in vivo*.

	Num- ber	mg sub- stance	mg H ₂ O	mg CO ₂	% H	% C
Ascorbic acid	1C 6	5.861	2.360	8.810	4.51	41.02
Small-scale run	1C 9S	4.619	2.340	8.500	5.67	50.21
Large-scale run	2C 9L	4.940	2.505	9.070	5.68	50.10
Large-scale run, recrystallized	3C 9R	5.176	2.655	9.530	5.74	50.24

Dry hydrogen chloride is rapidly bubbled through glass tubing of 8 mm I.D. for 5 min into a 200 ml centrifuge flask containing 10 g (0.057 mole) of powdered L-ascorbic acid and 100 ml of dry, redistilled acetone. After addition of 80 ml *n*-hexane, stirring, cooling in ice water and centrifuging, the supernate is decanted. The precipitate is washed four times with 140 ml of acetone-hexane mixture 4:7 (v/v), with stirring, cooling, centrifuging and removal of supernate after each addition. The flask is closed with a rubber cap, and opened only for minimal periods required for the operations. The yield of 5,6-*o*-isopropylidene-L-ascorbic acid, dried *in vacuo* over sodium hydroxide, is 85–90%, m.p. 219–222° (cor., dec.). Less than 2 h are required for all steps up to the drying process. Thoroughly powdered starting material is essential, because admixture of fairly large crystals sometimes gives

product having depressed melting point, i.e. presumably contains unreacted L-ascorbic acid. The unrecrystallized material is substantially pure, judged by its melting point, mixed melting point with isopropylidene derivative prepared by use of anhydrous copper sulfate² and analysis. It may be recrystallized from acetone-hexane mixture. Alternatively, it may be washed with peroxide-free diethyl ether, dried *in vacuo* and then continuously extracted with dry, peroxide-free diethyl ether to yield crystalline 5,6-*o*-isopropylidene-L-ascorbic acid in the receiving flask, with a melting point at 223–224° (cor., dec.), slightly higher and better defined than that reported by v. VARGHA². Using glass-stoppered test tubes and appropriate quantities of solvents and reagents, similar yields may be obtained from 1 mmole of L-ascorbic acid. The procedure is thus also useful for preparing labelled threonic acid³.

Zusammenfassung. Die Synthese der 5,6-*o*-Isopropyliden-L-ascorbinsäure mit Hilfe von Chlorwasserstoffgas wird beschrieben.

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August 27, 1963.

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⁴ R. W. HERBERT, E. L. HIRST, E. G. V. PERCIVAL, R. J. W. REYNOLDS, and F. SMITH, *J. chem. Soc.* 1933, 1270.

⁵ P. KARRER, G. SCHWARZENBACH, and K. SCHÖPP, *Helv. chim. Acta* 16, 302 (1933).

The Nature of Carbonate Contents in Tooth Mineral¹

Precipitation experiments *in vitro* from aqueous solutions demonstrate that in the pure calcium phosphate system no ideal crystallization processes will arise, but we must consider these precipitations as agglomerations of calcium phosphate complexes (colloid clusters, 0.005–0.05 μ m, with positive excess charge).

This situation, found during development of teeth, is complicated by the presence of mucous substances as well as by additional carbonate, citrate and other ions. Hereby, the amorphous character of a precipitated matter would be likewise favoured and yields a matrix gel.

The regular formation of the apatitic enamel crystals will be performed by the combination of the following events: the fluoride content and the pattern of keratine. The one effect inducing the apatitic structure, even of small amounts of fluoride ions, will be caused by the primary formation of fluorapatite germs². The function of the keratine structure as epitactic matrix effects the parallel straightened inotrope texture and the longitudinal extension of the enamel crystals³.

The difference between the solubility of the crystallized apatite and the amorphical matrix gel enables a recrystallization of the enamel matter. In this gel the main part of the carbonate ions will be bound chemically and there deposited. The carbonate (fluoride etc.) is therefore available as ion only at the absolute extent of solubility—that

is at small concentrations—for combining with the crystal bindings of the enamel crystals. This slow building process determines an orderly separation of the crystalline phase⁴. At larger concentrations, carbonate and phosphate mutually disturb the regular crystallization of their low solubility calcium compounds⁵ and are not suited for the corresponding isomorphous substitution in their lattice formations. It is supposed that, in topochemical reactions, the apatite lattice will be able to take up a small percentage (< 2%) of carbonate ions⁶. Herewith vacancies occur, which must be neutralized in their charges. With regard to the structure of the lattice, the carbonate uptake is always followed by a contraction of the elementary unit along *a*. We can ascertain that the answer to the question on the nature of the carbonate in the tooth material cannot be given by deciding whether the carbonate is an integral part of the dental apatite structure or not.

¹ See preceding communication: H. NEWSELY and E. HAYEK, *Exper.* 19, 459 (1963).

² H. NEWSELY, *Proceed. ORCA* 8, 174 (1961) (Suppl. Arch. Oral Biol.).

³ W. G. PERDOK and G. GUSTAFSON, *Proceed. ORCA* 7, 70 (1960) (Suppl. Arch. Oral Biol.).

⁴ H. NEWSELY, *Proceed. ORCA* 9, 277 (1962) (Suppl. Arch. Oral Biol.).

⁵ O. R. TRAUTZ and R. R. ZAPANTA, *Proceed. ORCA* 7, 122 (1960) (Suppl. Arch. Oral Biol.).

⁶ H. NEWSELY, *Monatshfte für Chemie* 94, 270 (1963).