of a variety of natural products, some of which, such as ellagic acid and its derivatives, are contained in vegetable foods (*5*). A search for carcinogenicity among isocoumarins thus seems to be indicated.

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6. Supported by grants from the Institut National de la Santé et de la Recherche Médicale and from the French National Tobacco Authority (SEITA).

14 August 1967

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Enthalpy of Transformation of a High-Pressure Polymorph of Titanium Dioxide to the Rutile Modification

Abstract. *The enthalpy of transformation of a high-pressure form of titanium dioxide, which has the alpha lead dioxide structure, to the rutile modification was measured by the method of "transposed temperature-drop calorimetry." For the reaction, titanium dioxide (alpha lead dioxide form) transforming to rutile, the change in the heat content is* -0.76 ± 0.17 *kilocalorie per mole. From this value and the volume change (+ 2.8 percent) associated with the transformation, we estimate the equilibrium pressure at 294°K to be* 60 ± 20 *kilobars.*

High-pressure studies (*1, 2*) have shown the existence of a new high-pressure polymorph of titanium dioxide (TiO_2) which possesses the orthorhombic alpha PbO_2 structure and has a density about 2.8 percent greater than that of rutile. This material has been recovered as a metastable product from rutile single crystals shocked to pressures greater than 330 kb (*1*). It also has been synthesized directly from rutile at pressures of 40 to 120 kb and temperatures of 400° to 1500°C (*2*). This is not in contradiction to the x-ray studies to 150 kb (*1*) in which no conversion was found, in that for kinetic reasons the reaction probably does not occur at room temperature. Similarly, the α-PbO_2 transformation is bypassed under explosive loading on compression. At atmospheric pressure, this metastable form of TiO_2 transforms rapidly to rutile at temperatures above about 450°C (*1*).

To elucidate the stability of this phase, we have measured its enthalpy of transformation to rutile by means of a novel technique, "transposed temperature-drop calorimetry." This method was used in this laboratory in order to determine the enthalpy of transformation of stishovite to silica glass (*3*).

In this calorimetric technique, a sample of the metastable high-pressure polymorph, contained in a thin-walled platinum capsule, is dropped from room temperature into a calorimeter maintained at a temperature high enough for rapid transformation to the low-pressure form. The observed heat effect in the calorimeter represents the algebraic sum of the heat content of the sample and its enthalpy of transformation to the low-pressure form at the calorimetric temperature. In a second calorimetric experiment on the same capsule, which now contains transformed material, the heat content of the transformed sample is obtained at the same temperature. The difference between the heat effects measured in the first and second experiments yields the enthalpy of transformation at room temperature.

The specimen of TiO_2 in the α-PbO_2 modification used in this work had been recovered from the single-crystal shock experiments of McQueen, Jamieson, and Marsh (*1*). It consisted of a coarse, crystalline, grayish powder with particles ranging in size from about 0.1 to 2 mm. The x-ray diffraction patterns of this sample indicated the presence of 5 to 10 percent of untransformed rutile as a second phase. Four separate, clean, dry, platinum capsules, each weighing about 120 mg, were filled with about 150 mg of sample which had been dried for 1 hour at 120°C with no observable loss in weight. The capsules were crimped shut by means of a three-jaw chuck.

The calorimeter and the experimental arrangements have been described (*3*). As before, calibration of the calorimeter (at 692°C) was achieved by dropping 2-mm wire platinum pieces into it from room temperature (21.0°C). The calibrating heat effects were calculated from the known weight of platinum and the equation for heat content of platinum given by Kelley (*4*). This equation was also used to calculate the heat content of the platinum capsules used. The total heat effect involved in each experiment was about 20 to 25 calories. Of this amount, about 3 calories, or some 15 percent, was due to the heat content of the platinum capsules. The enthalpy of transformation represented about 5 percent of the total heat effect.

The results obtained in the two sets of drop experiments are given in Table 1. Our mean value for the heat content (H) of rutile at 965°K is in agreement with the value (11.090 kcal/mole) calculated from the data of Kelley and Mah (*5*). From the difference in the mean heat effects observed in the two types of experiments, for the reaction

$$TiO_2\ (\alpha\text{-}PbO_2\ \text{form}) = TiO_2\ (\text{rutile}) \qquad (1)$$

we calculate

$$\Delta H^\circ_{294} = -0.76 \pm 0.17\ \text{kcal/mole}$$

This value is subject to two main uncertainties. We noted above that the available sample contains 5 to 10 percent rutile as a second phase. Correction of the calorimetric data for the presence of rutile would make the enthalpy of transformation according to reaction 1 more exothermic by some 0.04 to 0.08 kcal/mole. The second uncertainty arises from the strain energy stored in the shocked specimens. The broadened lines and the absence of back reflections in the x-ray diffraction patterns indicate that the specimens were in a highly strained condition. When the specimens transform spontaneously to rutile at high temperature, the major part of this strain energy is released along with the enthalpy

Table 1. Apparent heat content of titanium dioxide samples in four capsules. Drop 1, α-PbO_2 plus transformation; drop 2, rutile. The average for drop 1 was 10.29 ± 0.07 kcal per mole; that for drop 2 was 11.05 ± 0.16.

Pt (mg)	TiO_2 (mg)	$(H^\circ_{965} - H^\circ_{294})$ kcal/mole	
		Drop 1	Drop 2
0.11940	0.11164	10.215	10.953
.13100	.13927	10.381	11.287
.12506	.15521	10.314	10.989
.14500	.16465	10.254	10.979

of transformation. This is indicated by the appearance of the powder diffraction pattern of the transformed sample, which shows sharp lines characteristic of rutile. Consequently, the enthalpy of transformation of the unstrained high-pressure polymorph to rutile would be somewhat less exothermic than that of the strained sample.

Gross (*6*) showed that the stored energy in heavily deformed calcite represents some 1 to 2 cal/g. If this value is typical of simple ionic crystals, we estimate that the contribution of strain energy to the observed enthalpy of transformation represents some 10 to 20 percent of the measured quantity. However, a significant fraction of this correction, perhaps more than one-half, would be compensated by the presence of 5 to 10 percent rutile in the untransformed sample. Because we lack more quantitative data on the magnitude of the stored energy, we shall not attempt to pin down this effect.

If information is available on the standard enthalpy, standard entropy, and standard volume change of a given transformation, we can estimate in principle the equilibrium pressure (P_{eq}) at a given temperature by means of well-known thermodynamic methods. Among the mentioned quantities, we do not now have any data on the entropy of transformation from rutile to the α-PbO_2 modification.

Because this transformation is accompanied by a relatively small volume (V) change ($\Delta V = -2.8$ percent), we estimate ΔS° to be small, probably of the order of ± 0.5 cal/deg^{-1} mole^{-1} or less. At room temperature (T) and below, the term $T\Delta S^\circ$ for reaction 1 presumably will be small compared to ΔH°. This provides a justification for making a very rough estimate, of the equilibrium pressure for the considered phase transformation, based on neglect of the entropy contribution and compressibility effects:

$$P_{eq} \simeq \Delta H^\circ_{298} / \Delta V^\circ_{298}$$

If we set $\Delta V^\circ_{298} = -0.028\ V^\circ_{\text{rutile}} = -0.0126$ cal/bar, this yields an estimated equilibrium pressure of 60 kbar at 298°K. It is difficult to ascertain the uncertainty in this figure, but it is probably less than ±20 kbar.

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28 August 1967

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Basilar Membrane Vibration Examined with the Mössbauer Technique

Abstract. *The tuning curve has been measured, in vivo, at a point approximately 1.5 millimeters from the stapes in the first turn of the guinea pig cochlea. Curves for constant stapes movement and constant sound pressure were obtained over the range 350 hertz to 30 kilohertz, with an amplitude peak at about 18 kilohertz.*

Bekesy (*1*) has published observations of the movement of the basilar membrane and has presented approximate drawings of the relative amplitude of vibration as a function of frequency, as determined at several points along the membrane. No absolute values of these amplitudes were presented, however, and all the observations were made on the apical coils, as the technique did not permit the observation of the higher frequencies associated with the basal turn. This was very unfortunate, since much of cochlear electrophysiology is based on recordings from the round window and the basal turn.

The Mössbauer effect permits the measurement of very small velocities, and this technique has been applied to the study of vibrations of the eardrum and of the ossicular chain (*2*). We have used the technique to measure, in vivo, the absolute amplitude of vibration of the basilar membrane in the first turn of the guinea pig cochlea. By simultaneous measurement of the stapes displacement, we were able to refer the basilar amplitude to a constant stapes amplitude, as well as to a roughly constant sound pressure.

The basilar membrane of the first turn was exposed by enlargement of the round window, and a source of Co^{57} in 5-μ-thick stainless steel foil (area, 0.008 mm^2; mass, 0.3 μg) was placed on the membrane about 1.5 mm from the stapes. A similar source (area, 0.014 mm^2) was placed on the incostapedial joint. A small, thin copper shield, sufficient to stop the 14-kev Mössbauer line, was arranged so that each source could be covered in turn. The absorber was a stainless steel foil enriched in Fe^{57}; this had a nominally zero isomer shift with respect to the source. Sound was turned on for 4 seconds every 8 seconds, and the output from the detection system was fed to two scalers gated to record for sound on and off, respectively. The sound pressure was adjusted, usually between 60 and 95 db SPL (that is, relative to 0.0002 dyne/cm^2), so as to give a count rate difference between the scalers of 10 to 30 percent; these differences correspond to velocities of 0.2 to 0.6 mm/sec. Thus, at 20 khz, a peak amplitude of 15 Å could be measured. The count rates were such that a statistical accuracy of 10 percent in each determination could be achieved in about 3 minutes. The difference in count rate in terms of velocity amplitude was calibrated with the sources mounted on a vibrator driven through an LV syn; the voltage output from this gave the velocity amplitude directly. Care was taken to duplicate the conditions of the actual experiment in which there is an increase of background in the counting channel over that from one source alone due to the presence of a background from the other shielded source.