

The present experimentation is an example. The results are offered as further clarification of the problem and as new proof that the α and β' forms of tristearin do melt at approximately 55 and 64°, respectively.

Tristearin made by hydrogenation of linseed oil and recrystallization from hexane to an iodine value of 0.1 and having capillary m.p. of 54.2, 64 and 72.5° for lowest, next lowest and highest melting forms was formed into a flake in the following manner. In a flat can-lid of 5 cm. diam., 1 g. of tristearin was melted and chilled on ice-water. A 2-cm. flake of about 0.5 mm. thickness was cut from the pan. It was X-rayed at room temperature, with the beam passing perpendicularly through the middle of the stationary flake to give a typical α pattern having a single strong short spacing corresponding to 4.14 Å. and with a full complement of long spacings, d equal 50.2 Å. This alpha flake after X-ray was divided into 3 nearly equal portions.

A 3-liter beaker was thermostated to hold temperature within $\pm 0.10^\circ$. In the beaker was located a test-tube of 1-inch diameter containing water which was within 0.2° of the bath temperature during observations. The test-tube was closed with a cork except as necessary to admit samples. Both ordinary, -15 to 250° , and precise, 0 to 65° titer-type, thermometers were kept in the bath; they were in agreement as closely as they could be read. The -15 to 250° thermometer was put at a position such that the top of its mercury column (more readily photographed than the column of the precise thermometer) was about even with the top of the water in the test-tube so they would appear together on a photograph.

The left-hand piece of the X-rayed flake was dropped into the test-tube at 53.0° and was photographed floating on water after 0 and 80 sec. and showed, as expected, no change.

On Plate A⁶ are shown the X-ray pattern of the flake—typical α with 1st, 2nd, 3rd, 5th and 6th orders of long spacings visible; the appearance of the whole flake after X-ray; the divided flake; the left-hand third of the flake after 80 sec. at 53° where it remained entirely solid.

The mid-portion of the flake was dropped into the test-tube at 60.0° and was photographed at 0, 10, 20, 40 and 80 sec. during which time it obviously melted and resolidified. On Plate B⁶ the results appear and may be described as follows: after 0 sec., flake solid; 10 sec., edges of flake melted; 20 sec., flake $\frac{2}{3}$ melted; 40 sec., flake entirely melted; 80 sec., flake resolidified.

It is clear that the X-rayed flake contains a large proportion of a phase which exhibits long spacings, *i.e.*, α , and it is equally clear that the X-rayed portion of this flake melts completely or very nearly completely below 60° , although Malkin's position is that no tristearin phase with long spacings melts below 64 – 65° . The present author's 1945 conclusion,⁴ that the α form of tristearin melts at 54 – 55° , still holds.

It was little more difficult to give a simple pictorial demonstration of the β' melting level. In this case a similar flake was formed by crystallizing well-melted tristearin at 54.5° , close to the lowest melting point—at such a temperature that visible clouding occurred in 5 min. but not in 1 minute. Total time for crystallization was 20 minutes. This intermediately melting flake was X-rayed in the same way as the α flake to give, in this case, a typical β' pattern with two strong short spacing lines corresponding to 4.20 and 3.81 Å. and with a simple set of sharp long spacings, d equal 46.5 Å.

After X-ray this β' flake was divided into 3 parts. The left-hand portion was photographed in the previously described apparatus at 60° after 0 and 80 sec. and showed no change. The middle portion was photographed at 67° after 0, 20, 40, 80, 120 sec. and 20 min., during which time it melted and resolidified. Essential results shown in Plate C⁶ are as follows: top of plate, β' pattern of whole

(6) At the suggestion of the editor, the full-page plates prepared for this article have been deposited as Document number 4460 with the ADI Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the Document number and by remitting \$1.25 for photoprints, or \$1.25 for 35 mm. microfilm, in advance by check or money order payable to: Chief, Photoduplication Service, Library of Congress.

flake; mid-portion flake after 20 sec. edges melted; 120 sec., flake entirely melted; 20 min., flake resolidified. It follows then, as was also stated before by the present author,⁴ that it is the β' form, not the α form, whose m.p. is at 64° .

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The Preparation and Some Properties of Magnesium Hydride¹

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The optimum conditions for the preparation of MgH_2 by the reaction of hydrogen on magnesium metal have been investigated.

The rate of a metal-gas reaction in a system of working pressure, p , may be influenced by the temperature in two opposing ways: (1) the intrinsic reaction rate constant, $K(T)$, increases strongly with temperature; (2) the decomposition pressure, $p_D(T)$, of the reaction product increases similarly. However, for the reaction to proceed at all the condition $p > p_D$ must be satisfied. Hence the choice of temperature may be rather critical. These principles have been applied to the magnesium-hydrogen reaction using a system with a maximum working pressure of 70 atmospheres. The measured decomposition pressure is shown by curve a of Fig. 1. Points were obtained approaching equilibrium from each direction. The rate constant, $K(T)$, is defined by the assumed rate law

$$\frac{1}{m} \frac{dm}{dt} = -K(T) \frac{p - p_D}{P_0} \quad (1)$$

where m is the mass of unreacted magnesium metal and P_0 is a constant chosen as 68 atm. (1000 p.s.i.). In the closed system employed, the hydrogen uptake by the magnesium is proportional to the pressure change, and measurement of the pressure change as a function of time, together with m_0 , the initial mass of magnesium, allows calculation of m and dm/dt , and therefore of $K(T)$. Such measurements and calculations, over a wide range of pressures, were made at several temperatures, and the resulting values of $K(T)$ are plotted against $1/T$, in curve b of Fig. 1.

The slopes of the curves of Fig. 1 indicates a heat of formation of 16 kcal./mole at 450° , provided that no solid solution is formed, and an activation energy of 53 kcal./mole.

The direct synthesis of magnesium hydride from its elements has been reported previously by Wiberg, Goeltzer and Bauer.² The conditions given by them were 200 atmospheres hydrogen pressure and 570° with magnesium iodide as a catalyst, resulting in a 60% yield of magnesium hydride. This pressure and temperature are represented by point c in Fig. 1.

(1) This work was performed under the auspices of the A. E. C.
(2) E. Wiberg, H. Goeltzer and R. Bauer, *Z. Naturforsch.*, **6b**, 394 (1951).

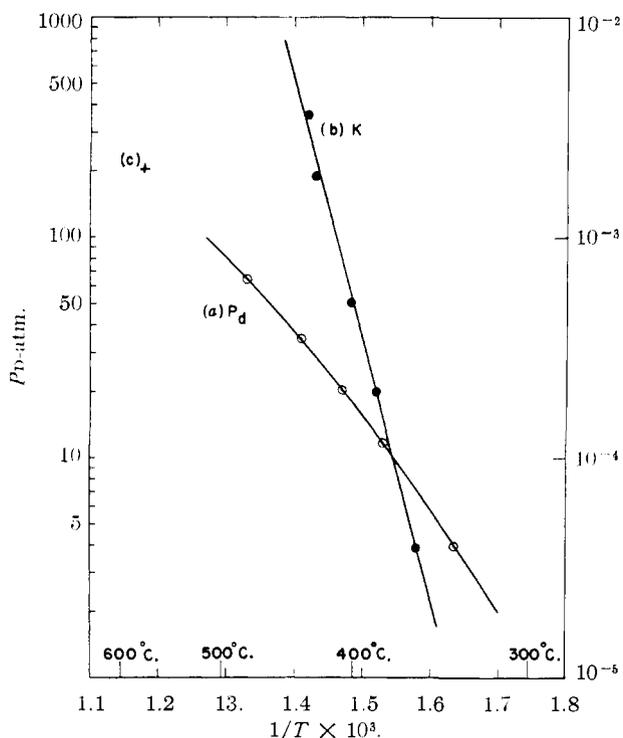


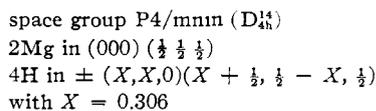
Fig. 1.—a, decomp. pressure of MgH_2 ; b, reaction rate constant for formation of MgH_2 ; c, Wiberg, Goeltzer and Bauer.²

The results here presented indicate that no catalyst is necessary.

Magnesium hydride prepared from fine turnings of high purity, doubly distilled magnesium by direct synthesis is a very light gray in color, is sensibly inert to laboratory air, and reacts slowly with water giving off bubbles of hydrogen. This behavior is in contrast to the high reactivity observed by Wiberg and Bauer for magnesium hydride prepared by the pyrolysis of diethylmagnesium.³ The difference is probably due to the difference in particle size.

X-Ray examination of magnesium hydride shows that it crystallizes in the tetragonal system with $a_0 = 4.5168 \text{ \AA}$. and $c_0 = 3.0205 \text{ \AA}$. The measured density of $1.45 \pm 0.03 \text{ g./cm.}^3$ shows that there are two molecules in the unit cell. The calculated X-ray density is 1.419 g./cm.^3 .

The X-ray powder pattern shows that the two magnesium atoms in the unit cell are in a body-centered configuration, *i.e.*, 2Mg in $(000) (\frac{1}{2} \frac{1}{2} \frac{1}{2})$. A consideration of all tetragonal space groups shows that there is one and only one possible choice of positions for the four hydrogen atoms leading to a plausible structure. This is



In this structure (rutile type) each magnesium is coordinated to six hydrogens at a distance of 1.95 \AA ., and each hydrogen is coordinated to three magnesiums. One H-H distance is 2.49 \AA . and the

(3) E. Wiberg and R. Bauer, *Chem. Ber.*, **85**, 593 (1952).

others are 2.76 \AA .. The distance of 2.76 \AA . compares favorably with the diameter of the H^- ion (2.72 \AA .) as found in LiH. The one short H-H distance is characteristic of one anion-anion distance of the rutile type structure.

Magnesium hydride is optically uniaxial positive with refractive indices 1.95 for the ordinary ray and 1.96 for the extraordinary ray at the wave length 5893 \AA ..

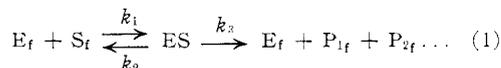
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The Evaluation of Enzyme-Substrate Dissociation Constants¹

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For an enzyme-catalyzed reaction that can be described in terms of the steady-state process depicted in equation 1



it is generally recognized that when $d[\text{ES}]/dt = 0$ and $[\text{S}_f] \doteq [\text{S}]$ the rate of disappearance of the specific substrate with respect to time is given by equation 2.

$$-d[\text{S}]/dt = k_3[\text{E}][\text{S}]/(k_2 + k_3)/k_1 + [\text{S}] \quad (2)$$

Briggs and Haldane³ were the first to call attention to the fact that although the ratio $(k_2 + k_3)/k_1$ can be evaluated, and is numerically equal to the so-called Michaelis constant derived from the earlier equilibrium treatment of Michaelis and Menten,⁴ knowledge of the value of this ratio for a particular system does not lead to an unambiguous estimate of the enzyme-substrate dissociation constant k_2/k_1 of that system. Because of many unsuccessful attempts to evaluate the ratio k_2/k_1 , or the rate constants k_1 and k_2 , from conventional kinetic data based upon the determination of the rate of disappearance of a specific substrate, or the rate of appearance of a reaction product, under the conditions specified above, we were surprised to find in a recent review⁵ the statement that this goal had been achieved by Slater and Bonner⁶ for the system succinic dehydrogenase-succinate. In view of the unquestioned acceptance of the treatment of Slater and Bonner⁶ by Thorn,⁷ by Dixon⁸ and by Lindley⁹ it appears worthwhile to call attention to the fact that the argument of Slater and Bonner⁶ contains a tacit assumption which is not immediately apparent and which weakens, if it does not invalidate, their principal conclusion, *i.e.*, that k_1 and k_2 have

(1) Supported in part by a grant from the National Institutes of Health, Public Health Service.

(2) To whom inquiries regarding this article should be sent.

(3) G. E. Briggs and J. B. S. Haldane, *Biochem. J.*, **19**, 338 (1925).

(4) L. Michaelis and M. L. Menten, *Biochem. Z.*, **49**, 333 (1913).

(5) E. C. Slater, *Ann. Rev. Biochem.*, **22**, 17 (1953).

(6) E. C. Slater and W. D. Bonner, *Biochem. J.*, **52**, 185 (1952).

(7) M. B. Thorn, *ibid.*, **53**, 540 (1953).

(8) M. Dixon, *ibid.*, **55**, 161 (1953).

(9) H. Lindley, *Adv. Enzymology*, **15**, 271 (1954).