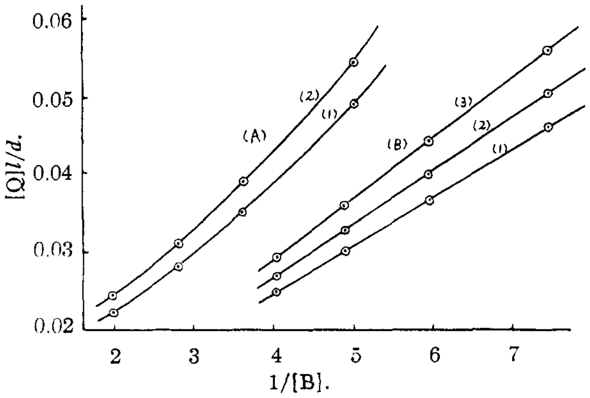

Fig. 1.—Electron donor, hydroquinone dimethyl ether: solvent, (A) carbon tetrachloride, (1) 15°, (2) 30°; (B) *n*-heptane, (1) 10°, (2) 20°, (3) 30°; wave length, 400 mμ.

their paper).[10] But it seems to be difficult to obtain the accurate value of the molar extinction coefficient ($\epsilon_{\max}$) of the absorption maximum characteristic for the molecular compound, while its product with K (equilibrium constant) can be obtained exactly from the tangent of the straight line[11] representing the relation between $[Q]l/d$ and $1/[B]$ where the meaning of each notation is the same as given in Benesi and Hildebrand's paper.[10] So we tried to obtain the binding energy by measuring the temperature dependence of $K\epsilon_{\max}$. Neglecting the temperature dependence of $\epsilon_{\max}$ the following equation can be derived

$$R \ln (K\epsilon_{\max}) = -\Delta H/T + (\Delta S + R \ln \epsilon_{\max})$$

Experimental results show that such a straight line relationship between $R \ln(K\epsilon_{\max})$ and $1/T$ as expected from the above equation is satisfied in most cases (for instance see Fig. 2). Consequently, the binding energy can be obtained from its tangent. One difficulty encountered in this case is that the absorption band of the component molecule overlaps with the characteristic one of the molecular compound. In the present study, the value of extinction properly due to the latter (d in the Hildebrand–Benesi equation) was obtained by the equation

$$d = d_{\text{obs}} - d'$$

where d_{obs} and d' are the observed extinction of the solution and the sum of the extinction of all the component molecules, respectively. Since, at the wave length in question, the extinction coefficients of the absorption bands due to the component molecules are always very small, and very little portions of the component molecules added in the solution are in the binding states, the above procedure seems to be reasonable.

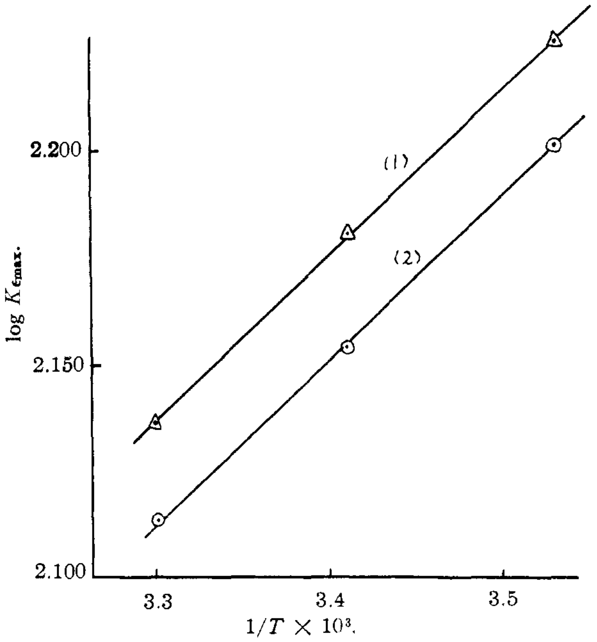

Fig. 2.—Electron donor, hydroquinone dimethyl ether; solvent, *n*-heptane; wave length (1) 413 mμ, (2) 400 mμ.

All the measurements of absorption spectra were made with a Beckman quartz spectrophotometer model DU. The temperature of the cell compartment was kept constant by the thermospacer during the measurement.

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[10] H. A. Benesi and J. H. Hildebrand, THIS JOURNAL, **71**, 2703 (1949).

[11] The straight line relationship between $[Q]l/d$ and $1/[B]$ was exactly satisfied in most cases (see Fig. 1) with the exception of system containing phenol, anisole and hydroquinone dimethyl ether as electron donor in carbon tetrachloride and phenol in *n*-heptane. In the latter cases, the binding energies were obtained by determining $K\epsilon_{\max}$ from the values of $[Q]l/d$ measured at only two different values of $[B]$. The binding energy thus obtained with each molecular compound was almost constant for the various sets of $[B]$.

Pictorial Proof of α (55°) and β' (64°) M.P. Levels for Tristearin

BY E. S. LUTTON

RECEIVED AUGUST 23, 1954

Twenty years ago Clarkson and Malkin[1] elucidated the general character of triglyceride polymorphism and showed the power of X-ray diffraction in dealing with the problem. But Malkin firmly adheres[2] to details of his position which others have criticized independently after re-examining tristearin, in particular, also with the help of X-rays.[3–5] The principal points of difference are indicated in Table I.

TABLE I

COMPARISON OF DESCRIPTIONS OF TRISTEARIN POLYMORPHISM

	B, L, F[a]			M		
Melting level	Name	Approx. m.p., °C.	Approx. L.S. (Å.)	Name	Approx. m.p., °C.	Approx L.S.. (Å.)
Lowest	α	55	50.5	Vitreous	55	None
Intermediate	β'	64	47	α	64	50.5
				β'	70	47
Highest	β	73	45	β	73	45

[a] One laboratory did not investigate intermediate melting levels of tristearin.

All would seem to agree that the differences in viewpoint have arisen from differences in experimental technique. The original difficulty is thought to lie in Malkin's use of one procedure for treating X-ray samples and another for m.p. samples; the present author has commonly used the same procedure for each and has frequently submitted a given sample to both X-ray and m.p. observation.

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[1] C. E. Clarkson and T. Malkin, *J. Chem. Soc.*, 666 (1934).

[2] T. Malkin, Chapter on "Glyceride Polymorphism" in R. T. Holman, W. O. Lundberg and T. Malkin, "Progress in the Chemistry of Fats and Other Lipids," Vol. II, Academic Press, Inc., New York, N. Y., 1954.

[3] A. E. Bailey, M. E. Jefferson, F. B. Krieger and S. T. Bauer, *J. Am. Oil Chem. Soc.*, **22**, 10 (1945).

[4] E. S. Lutton, THIS JOURNAL, **67**, 524 (1945).

[5] L. J. Filer, Jr., S. S. Sidhu, B. F. Daubert and H. E. Longenecker, *ibid.*, **68**, 167 (1946).

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 ±0.10°. 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 A[6] 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 B[6] the results appear and may be described as follows: after 0 sec., flake solid; 10 sec., edges of flake melted; 20 sec., flake $^2/_3$ 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 C[6] are as follows: top of plate, β' pattern of whole 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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(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.

The Preparation and Some Properties of Magnesium Hydride[1]

BY F. H. ELLINGER, C. E. HOLLEY, JR., B. B. MCINTEER, D. PAVONE, R. M. POTTER, E. STARITZKY AND W. H ZACHARIASEN

RECEIVED DECEMBER 2, 1954

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

$$\frac{1}{m}\frac{\mathrm{d}m}{\mathrm{d}t} = -K(T)\frac{p - p_D}{P_0} \qquad (1)$$

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 $\mathrm{d}m/\mathrm{d}t$, 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.

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(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).