ϵ *ca.* 2.9 at 250 mμ, 4.2 at 210 mμ).[7] With pyridine–sulfur trioxide in pyridine overnight at room temperature, V furnished the tetraacetylglucotropaeolate ion VI, isolated as the monohydrated potassium salt, m.p. 186.5–187° dec. (lit.[8] 187–189° dec.), $[\alpha]^{32}\mathrm{D}$ $-22.6°$ (water), identified by infrared spectrum with specimens derived[8] from nature. The ion was also isolated, in 53% yield from V, as **tetramethylammonium tetraacetylglucotropaeolate,**[4] m.p. 182.5–183.5° (anhydrous form), $[\alpha]^{28}\mathrm{D}$ $-18.9°$ (water), converted in 94% yield by methanolic ammonia[8,9] to anhydrous **tetramethylammonium glucotropaeolate,**[4] the salt of I ($R = C_6H_5CH_2$), m.p. 188–189.2° dec., $[\alpha]^{28}\mathrm{D}$ $-16.7°$ (water). The glucotropaeolate was identical with a sample isolated from *Tropaeolum majus* seed by adsorption of an extract[8] on anion exchange resin and elution with tetramethylammonium hydroxide.[10] When the synthetic glucotropaeolate was treated with the usual protein fraction of yellow mustard, benzyl isothiocyanate (II, $R = C_6H_5CH_2$) was rapidly[11] formed in quantitative yield and was determined and isolated as benzylthiourea.

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[7] Ammonolysis of V afforded S-β-D-1-glucopyranosylphenylacetothiohydroximic acid, m.p. *ca.* 115° (hydrate), $[\alpha]^{28}\mathrm{D}$ $-44°$ (water), which was attacked by myrosin, if at all, with not more than one fiftieth of the rate of cleavage of the sulfated analog I ($R = C_6H_5CH_2$) and was not converted to benzyl isothiocyanate. The likelihood that rearrangement of I and departure of the sulfate and glucosyl groups are simultaneous renders dubious the accepted division of myrosin into thioglucosidase and sulfatase.

[8] O.-E. Schultz and W. Wagner, *Arch. Pharm.*, **288**, 525 (1955). Other monohydrated samples of natural or synthetic origin melted as low as 140–150° (dec.).

[9] A. Kjaer and R. Gmelin, *Acta Chem. Scand.*, **10**, 335 (1956).

[10] On isolation of amorphous potassium glucotropaeolate and hydrolysis to phenylacetic acid, see O.-E. Schultz and R. Gmelin, *Arch. Pharm.*, **287**, 342 (1954).

[11] The glucotropaeolate was cleaved to mustard oil approximately twice as fast as was natural glucosinalbate.

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RELAXATION PHENOMENA AND CONTACT ANGLE HYSTERESIS

Sir:

We wish to advance a kinetic mechanism for contact angle hysteresis as observed by Bartell and Bjorklund[1] on high energy smooth surfaces. Verwey[2] has presented evidence for the existence of an ice-like structure at the water–vacuum interface, and Grahame[3] has found evidence for a similar structure at the water–mercury interface. Recently Bockris, Mehl, Conway and Young[4] have proposed that water is oriented in an ice-like structure at the water–copper interface, and that its dielectric relaxation time there is about 10^{-6} sec. (as compared to 10^{-10} sec. for bulk water at room temperature).

These findings appear relevant to contact angle hysteresis on smooth surfaces. The measurement of a contact angle involves displacement of a periphery formed by the three-phase junction across one of the phases. There is a natural length associated with this process, namely, the peripheral thickness l. Just as the surface of discontinuity between two phases is not a mathematical surface, so the periphery is not a mathematical curve, but will have a thickness of the same order of magnitude as the surface of discontinuity. This latter thickness is normally taken as the distance over which concentration gradients are appreciable (at equilibrium), and is of the order of magnitude of molecular dimensions. A parallel definition of peripheral thickness can be made, and it should be of the same order of magnitude. There is a natural time associated with this process, namely, the relaxation time τ of the most slowly relaxing molecule at the periphery. There is therefore a natural displacement velocity $V_N = l/\tau$. Let V be the actual displacement velocity; then if $V << V_N$ the displacement should be quasistatic and all boundary tensions operating at the periphery should be equilibrium tensions, but if $V >> V_N$, then at least the most slowly relaxing molecule will be disoriented at the periphery, and boundary tensions at the periphery (which determine the contact angle) at interfaces involving this molecule will exceed their equilibrium values. On standing, the disoriented molecules will orient and the periphery will move, but at a velocity approximating V_N.

Now $l \sim 10^{-8}$ cm., and if we assume $\tau \sim 10^{-3}$ sec. it is possible to rationalize the experiment of Bartell and Bjorklund[1] involving substantial equality of contact angles formed by advanced and immediately (but slowly) receded water drops in the mercury–water–heptane system. Even more extreme time effects should be expected in systems such as water–heptane–silica, since adsorption at the water–silica boundary appears to involve formation of a surface silicic acid. If $\tau \sim 1$ sec. for this process, $V_N \sim 10^{-8}$ cm./sec. or about 0.01 mm./day. Most observers would consider such a drop motionless.

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[1] F. E. Bartell and C. W. Bjorklund, *J. Phys. Chem.*, **56**, 453 (1952).

[2] E. J. W. Verwey, *Rec. trav. chim.*, **61**, 564 (1942).

[3] D. C. Grahame, *J. Chem. Phys.*, **23**, 1725 (1955).

[4] J. O'M. Bockris, W. Mehl, B. E. Conway and L. Young, *ibid.*, **25**, 776 (1956).

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CRYSTALLINE PHOSPHORUS PENTANITRIDE, P_3N_5

Sir:

Phosphorus nitrides generally are reported to be amorphous. In one exception,[1,2] a crystalline

[1] H. Moureu and P. Rocquet, *Bull. soc. chim.*, [5] **3**, 1801 (1936).

[2] H. Moureu and G. Wetroff, *ibid.*, [5] **4**, 918 (1937).