causes the electrons to emit light and causes a current (which is small compared to that of the electron beam) to be picked up by the grating. This small required movement shows the sharp definition of the edges of the electron beam.

Adjustment of the grating position showed that some electrons must strike the grating in order to produce light. This was investigated by means of an electrode introduced above the beam to catch electrons which ricochet from the grating at near-grazing incidence. Measurements of the current of reflected electrons showed that some reflected current was required to produce light and that the light intensity is proportional to this current. Measurements of the electron current passing the grating in a straight line show that the light intensity is proportional to this current also. The light intensity is thus proportional to the product of the current reflected from the grating and the undeflected current passing the grating. This proportionality has been tested for total currents of a fraction of a microampere, where the light is just visible, through the range of a few tens of microamperes, where light is visible in a well-lit room, up to about 10 ma where the light seems very bright.

Many different grating profiles and grating spacings were used in various observations. Grating line densities ranging from 4000 to 30,000 per centimeter were used.

The principal significant effect of the grating profile used is that light generated with a grating having flats between the rulings is rich in harmonics. A photograph made with a simple spectroscope, consisting of an auxiliary transmission grating, shows the fourth, fifth, sixth, and seventh harmonic of a fundamental which is in the far infrared. The four harmonics shown are in the visual portion of the spectrum (Fig. 3).

A simple explanation of this radiation is proposed here. As is well known, periodic acceleration of electrons produces electromagnetic radiation. The electrons reflected from the grating are believed to form sheets of space-charge having the same periodicity as the grating. Other electrons passing through these sheets of space-charge are alternately accelerated and decelerated by the electrostatic forces between them and the electrons in space-charge sheets. This periodic acceleration causes radiation from electrons that may be far from the grating surface (Fig. 4). This radiation in no way depends on surface currents in the grating. Low-density carbon deposits on the grating which are opaque to light will have no appreciable effect on high-energy electrons passing through them, because of the thinness and low density of the deposits.

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Pressure-Induced Dehydration Reactions and Transitions in Inorganic Hydrates

Abstract. *Application of high pressure at 25°C irreversibly dehydrated five inorganic compounds containing molecular water to lower hydrates or to anhydrous forms. Compression at 25°C also lead to ten new reversible phase transformations in another group of nine hydrates. Maximum pressure applied was 22.6 kilobars.*

There has been no concerted attempt so far to dehydrate inorganic compounds containing molecular water by compression alone. Bridgman *et al.* (*1*), while trying to produce stress minerals, accidentally dehydrated gypsum and opal. Kiyama and Yanagimoto (*2*) dehydrated $CuSO_4 \cdot 5H_2O$, and Levshists *et al.* (*3*) removed water from $MgSO_4 \cdot 7H_2O$ by applying high pressures and temperatures. We compressed inorganic hydrates to a maximum pressure of 22.6 kb at 25°C and found complete dehydration in $Na_2SO_3 \cdot 7H_2O$ at 8.9 kb, $ThCl_4 \cdot 8H_2O$ over a range of 2.2 to 4.6 kb, and partial dehydration of $ZnSO_4 \cdot 7H_2O$ to $ZnSO_4 \cdot 6H_2O$ at 4.6 kb. Dehydrations of indeterminate character also occurred in $Ca(CNS)_2 \cdot 4H_2O$ at 0.5 kb, and $Zr(SO_4)_2 \cdot 4H_2O$ over a broad range of pressure.

While none of the other nine compounds showed any degree of dehydration, they underwent first-order reversible volumetric transitions. Zinc sulfate heptahydrate and $ZnSO_4 \cdot 6H_2O$ undergo phase transitions at 2.2 kb and $ZnSO_4 \cdot 6H_2O$ has another one at 16.2 kb. Sodium thiosulfate pentahydrate changes reversibly into a new phase at 18.5 kb. Magnesium thiosulfate hexahydrate at 7.7 kb, $K_2(MoO_4) \cdot 5H_2O$ at 10.3 kb, $BeSO_4 \cdot 4H_2O$ at 10.3 kb, $ZrOCl \cdot 8H_2O$ at 5.6 kb, $Mg(SCN)_2 \cdot 4H_2O$ at 5.8 kb and $Th(SO_4)_2 \cdot 8H_2O$ at 9.8 kb have similar phase transformations.

To detect dehydration we used visual evidence of leakage of water from our apparatus, and whenever possible we compared the curves for longitudinal strain versus pressure for the dehydrated compound with the same curves for the actual lower hydrate or anhydrous form. We define ℓ_0 as the length of the sample at atmospheric pressure and ℓ as the length of the sample at pressure P; $-\Delta\ell = -(\ell - \ell_0)$ and $\Delta\ell/\ell_0$ is the longitudinal strain. Thus similarities in the longitudinal strain–pressure curves (Fig. 1) for $Na_2SO_3 \cdot 7H_2O$ and Na_2SO_3, $ZnSO_4 \cdot 7H_2O$ and $ZnSO_4 \cdot 6H_2O$, and $ThCl_4 \cdot 8H_2O$ and $ThCl_4$ confirmed the dehydration of these compounds, whereas the oozing of moisture from the pressure cylinder during the compression of $Ca(SCN)_2 \cdot 4H_2O$ and $Zr(SO_4) \cdot 4H_2O$ was the only evidence for loss of water in these two compounds. We could not obtain $Ca(SCN)_2$ and $Zr(SO_4)_2$ for reference. The first drift of displacement with time and first deviation from continuity on a graph indicated the onset of a reversible phase transformation.

We used a piston cylinder–type assembly for subjecting our material to pressure. A General Electric carboloy 55A cylinder, 1.257 inches in outer diameter, 0.250 inch inner diameter, and 1 inch (2.54 cm) long, reinforced by three shrink-fitted Alco S steel rings, acted as a container for approximately 0.2 g of powdery sample. Two General Electric carboloy grade 883 pistons, 0.249 inch in diameter and 1 inch long, transmitted the pressure from a 200-ton hydraulic ram to the compound in the carbide cylinder. Alco S steel sleeves, 1 inch outer diameter, 0.247 inch inner diameter, and ½ inch long, press-fitted on the external part of these pistons, provided support for stress transmission. An automatic temperature controller connected to an electrically heated oil bath maintained the sample at 25°C. A dial indicator gauge with 0.0001-inch graduations measured the axial decrease in length of the sample due to compression.

Because of the nonhydrostatic nature of the applied pressure we calibrated the pressure cylinder to 37 kb using well-known (*4*) volumetric transitions as our reference points. By compressing to 0.01 kb about 0.2 g of the crystalline material held in place by two soft steel gaskets and two pistons, we obtained a pellet of the test compound. By subtracting the length of the pistons and gaskets from the overall length we found the length of the pellet in the cylinder. We applied pressure at a rate of 0.3 kb/sec, and kept the sample at each pressure for 2 minutes. Occasionally we increased the 2-minute sitting period to study the time-dependent aspects of the transformations. Bridgman's procedure (*5*) was used to obtain data relating longitudinal strain and pressure to a pressure of 22.6 kb.

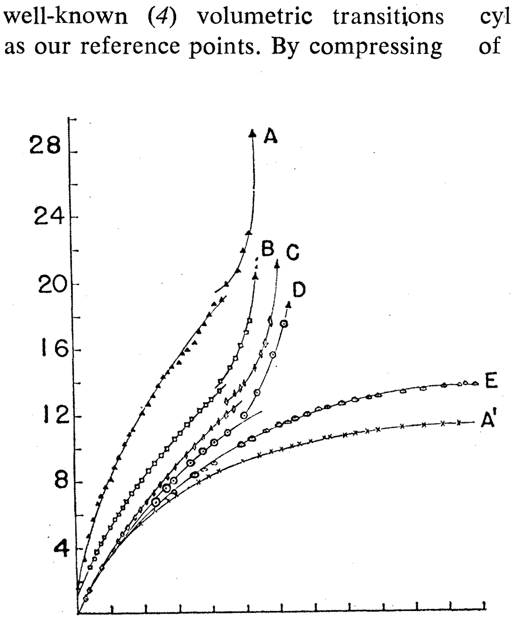

Fig. 1 (left). Dehydration of $Na_2SO_3 \cdot 7H_2O$ at 25°C and 8.9 kb. Curves A, B, C, D, and E show the progressive dehydration of the compound in five different cylinders. Curve A′ shows the compression of the anhydrous Na_2SO_3 in cylinder No. 5.

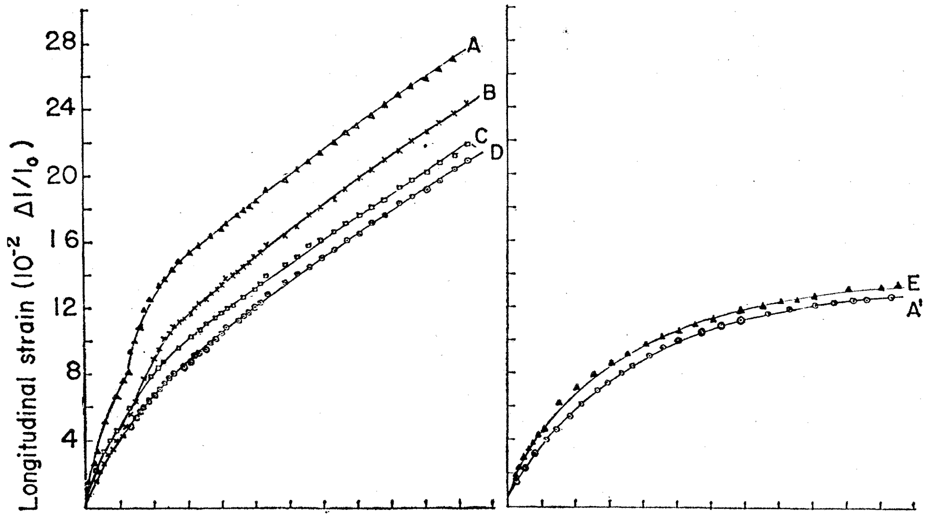

Fig. 2 (center). Dehydration of $ThCl_4 \cdot 8H_2O$ at 25°C and from 2.2 to 4.6 kb. Curves A, B, C, D (all left), and E (right) show progressive dehydration of the compound. Curve A′ (right) shows the compression of the anhydrous $ThCl_4$.

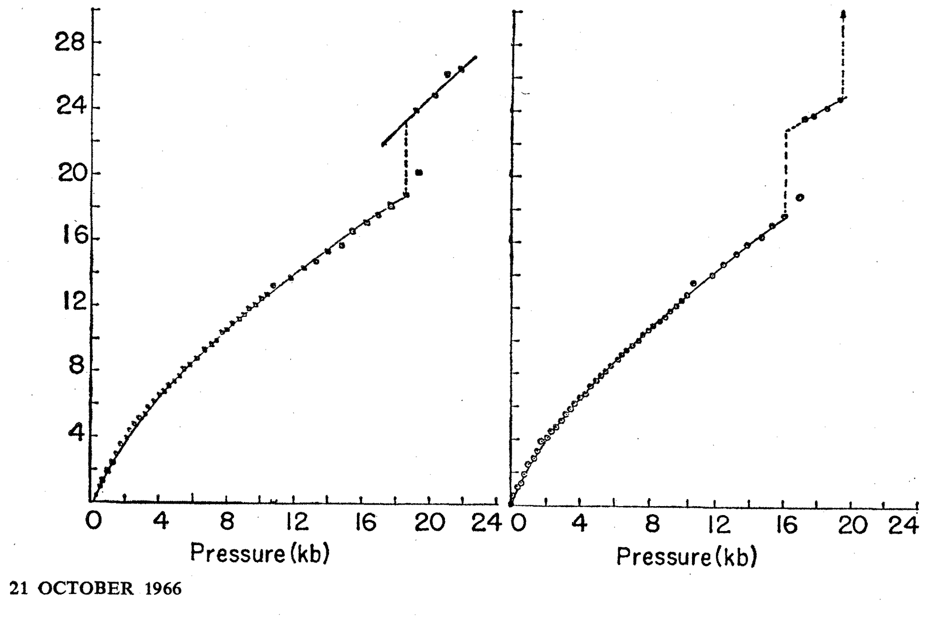

Fig. 3 (bottom). Phase transitions in $Na_2S_2O_3 \cdot 5H_2O$ at 18.5 kb and 25°C (left) and in $Na_2S_2O_3 \cdot 5H_2O$ at 16.0 kb and 43.3°C (right). The arrow pointing upward indicates an explosion at 19.3 kb.

We found some new data about the compression behavior of $ThCl_4 \cdot 8H_2O$ and $Na_2SO_3 \cdot 7H_2O$ at 25°C and $Na_2S_2O_3 \cdot 5H_2O$ at 43°C. The process of dehydration of $ThCl_4 \cdot 8H_2O$ starts at 2.2 kb and stops at 4.6 kb. Above 4.6 kb and below 2.2 kb there is no dehydration. Water oozed out of a given sample in the pressure range over a number of successive runs on the same cylindrical pellet until dehydration was complete. This dehydrated compound and the commercially obtained anhydrous $ThCl_4$ had similar curves (Fig. 2). We found that the range of dehydration for $ThCl_4 \cdot 8H_2O$ was independent, not only of the rate at which the pressure was applied, but also of the time for which the apparatus sat at each pressure.

Compression of $Na_2SO_3 \cdot 7H_2O$ beyond 8.9 kb (25°C) was not possible in our apparatus. At this pressure water started oozing out, a crunching noise was heard, and then an explosion invariably damaged the high-pressure cylinder. The dehydrated material resembled the anhydrous salt in its compression behavior. Figure 1 shows the effects of successive compression on the same cylindrical pellet examined over five runs.

Sodium thiosulfate pentahydrate has an isobaric transition (*6*) at 48°C and atmospheric pressure. We found an irreversible transition at 19.3 kb and 43.3°C (Fig. 3). This transition occurred with a distinctly audible explosion that always caused circumferential cracks in the carbide cylinder. We think that these explosions, observed during compression of $Na_2S_2O_3 \cdot 5H_2O$ and $Na_2SO_3 \cdot 7H_2O$, are due to appearances of new phases whose molar volumes are considerably less than molar volumes of lower pressure phases. The resulting sudden contraction thus caused would produce a shock wave sufficient to damage the cylinder.

The dehydration of $ThCl_4 \cdot 8H_2O$ over the 2.2- to 4.6-kb range of pressure can be explained as due to the appearance of two new phases, one at 2.2 kb downward and another at 4.6 kb upward. The 2.2- to 4.6-kb phase most probably holds the water of crystallization loosely, whereas water is tightly bound in the phases existing above 4.6 kb and below 2.2 kb.

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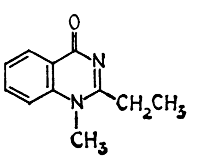
19 August 1966

1,2-Dialkyl-4(3H)-Quinazolinones in the Defensive Secretion of a Millipede (Glomeris marginata)

Abstract. *Two crystalline components isolated from the defensive secretion of the glomerid millipede,* Glomeris marginata, *are identified as 1-methyl-2-ethyl-4(3*H*)-quinazolinone and 1,2-dimethyl-4(3*H*)-quinazolinone. These heterocyclic compounds bear a close structural resemblance to arborine, the chief alkaloid of the Indian medicinal plant,* Glycomis arborea *Correa.*

Many millipedes, in common with a diversity of insects, phalangids, and other terrestrial arthropods, respond to disturbance by ejecting a noxious fluid from special glands. These defensive secretions have recently been investigated intensively, and in a variety of millipedes the active principles of the discharge have been identified (*1*). Species of the orders Julida, Spirobolida, and Spirostreptida produce *p*-benzoquinones and, in one exceptional case, 2-dodecenal. Members of Polydesmida produce hydrogen cyanide and benzaldehyde. The single species of Chordeumida that has been studied secretes *p*-cresol. Several orders remained to be investigated. One of these, the Glomerida, includes an interesting European species, *Glomeris marginata*, the anomalous secretion of which is the subject of this report (see *2*).



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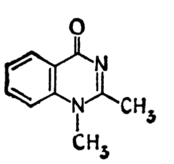

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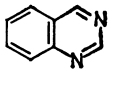

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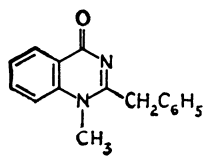

IV

Glomeris is a small millipede, about 1.5 cm long when fully grown. It bears a striking resemblance to the familiar isopod crustaceans called "sow bugs" and shares with some of these animals the characteristic habit of coiling into a tight sphere when disturbed. *Glomeris* discharges its secretion in response to pinching, tapping, or, on occasion, even mere prodding. The liquid oozes as single droplets from eight pores spaced evenly in a row along the dorsal midline of the animal (Fig. 1).

We collected the secretion for chemical analysis by seizing individual millipedes with forceps and aspirating their secretion into capillary tubing. The tubing was pulverized under methylene chloride, and the insoluble residue was separated by centrifugation. The residue was extracted repeatedly with methylene chloride to ensure complete extraction of the soluble components. Careful evaporation of the solvent under nitrogen gave a crystalline residue (40 mg from approximately 1000 animals), melting point 140° to 160°C, resolved into two chief zones by thin-layer chromatography on silica gel (5 percent methanol in methylene chloride). The infrared spectrum of the mixture showed intense maxima at 6.05 and 6.24 μ; these maxima are indicative of conjugated carbonyl and imine groups. In the ultraviolet region, the mixture showed absorptions at 230, 265, 275, 305, and 315 mμ (ethanol), which are suggestive of a bicyclic aromatic nucleus (*3*).

Preparative thin-layer chromatography separated this mixture into its two main constituents, the less polar compound A (23 mg, mp 145° to 147°C) and the more polar compound B (16 mg, mp 198° to 200°C). Sublimation at 120° to 140°C at 0.1 mm gave, for A, mp 146° to 147°C, and for B, mp 200° to 201°C. The infrared and ultraviolet spectra of the separate constituents were very similar to those of the original mixture.

Table 1. High-resolution mass spectra.

Nominal (*m/e*)*	Mass Measured	 Calculated	Composition
	Compound A		
188	188.094803	188.094958	$C_{11}H_{12}N_2O$
160	160.063766	160.063659	$C_9H_8N_2O$
133	133.052463	133.052761	C_8H_7NO
105	105.033888	105.034037	C_7H_5O(10%)
	105.057786	105.057846	C_7H_7N(90%)
	Compound B		
174	174.079270	174.079308	$C_{10}H_{10}N_2O$
146	146.084385	146.084394	$C_9H_{10}N_2$
145	145.076795	145.076569	$C_9H_9N_2$
133	133.052907	133.052761	C_8H_7NO
105	105.033888	105.034037	C_7H_5O(10%)
	105.057686	105.057846	C_7H_7N(90%)
104	104.049951	104.050022	C_7H_6N

* Mass/charge

Nuclear magnetic resonance spectra of both compounds showed the presence of four aromatic protons, three as a complex multiplet centered at τ 2.5, and one as a doublet (9 cy/sec) of closely spaced doublets at τ 1.8. Methyl groups appeared as singlets at τ 6.25 in both compounds, but B showed an additional methyl singlet at τ 7.35, and A showed a typical ethyl group pattern at τ 7.11 (quartet) and τ 8.61 (triplet).

The high-resolution mass spectra of A and B establish the molecular formula

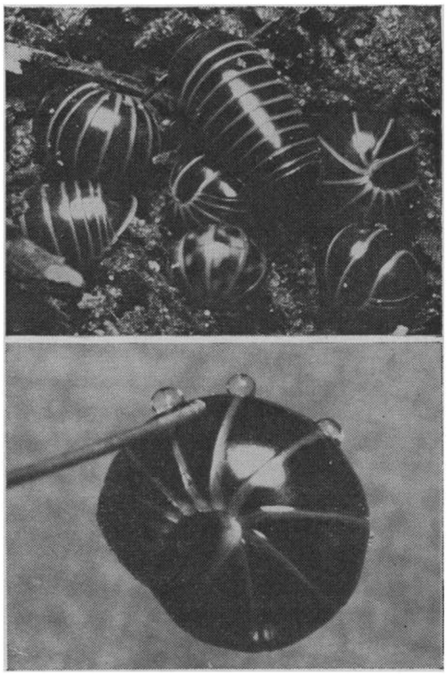

Fig. 1. (Top) *Glomeris marginata* on soil. Several of the millipedes are seen in the typical coiled defensive posture which they assume when disturbed. (Bottom) A coiled *Glomeris* discharging secretion from three of its eight glandular pores in response to prodding with a warm needle.