

## COMMUNICATIONS TO THE EDITOR

### AN EQUATION OF STATE FOR SATURATED FLUIDS

Sir:

During a search for an equation of state for saturated fluids a simple relationship between pressure, temperature and specific volumes was found which seemingly is of general validity. In fact out of 59 substances tested only one, acetic acid, showed anomalous behavior. In this case the admittance of association, that is, double molecules, will explain the discrepancies. The test substances have molecular weights from 2 to 260, critical pressures from 2.3 to 218 atm., critical temperatures from  $-268$  to  $+448^\circ$  and critical densities from 0.03 to 1.15 g./cc.

Upon separating the roots of a more general, three constant, quadratic equation the following expression was arrived at:

$$P = \frac{CT}{v_g + v_e + 2B}$$

where  $C = R/M$  and  $B = (CT_c/2P_c) - v_c$ .

The symbols denote:  $p$ , the saturation pressure in atm.;  $T$ , the saturation temperature in  $^\circ\text{K}$ . (ice point  $273.16^\circ\text{K}$ .);  $v_g$  and  $v_e$  the specific volume of saturated vapor and saturated liquid, respectively, in l. per gram;  $R$ , the gas constant (0.08206 for l., atm., g.-moles) and  $M$ , the molecular weight in grams (based on atomic weights of 1942). Subscripts  $c$ , indicate critical values.

The pressures calculated by the equation from corresponding  $v_g$ ,  $v_e$  and  $T$  values are given for water from melting point to critical point. The critical data and constants for water are:  $T_c = 374.11^\circ\text{C}$ .,  $p_c = 218.167$  atm.,  $v_c = 3.1975$  cc./g.,  $C = 0.0045548$  and  $B = 0.0035593$ .

TABLE I

$T$ , $^\circ\text{C}$ .	$p$ , atm.		$T$ , $^\circ\text{C}$ .	$p$ , atm.	
	calcd.	lit. <sup>1</sup>		calcd.	lit. <sup>1</sup>
0	0.0060307	0.0060273	200	15.910	15.332
20	.023089	.023042	220	23.800	22.897
40	.073126	.072748	240	34.356	33.044
60	.19742	.19656	260	48.049	46.322
80	.47070	.46740	280	65.290	63.343
100	1.0109	1.0000	300	86.583	84.776
120	1.9901	1.9595	320	112.34	111.40
140	3.6419	3.5669	340	143.09	144.14
160	6.2638	6.1032	360	180.59	184.26
180	10.216	9.896	374.11	(218.167)	218.167

Evidently the equation does not compare with the high accuracy afforded by several vapor pressure equations; however, the wide range of application, the great simplicity and the ease of calculation will render it useful for checking and

(1) Fales and Shapiro, *THIS JOURNAL*, **58**, 2418 (1936); "Int. Crit. Tables," Vol. III, 1928.

supplementing experimental data. The agreement is considerably better for many of the substances tested and especially for the simpler gases such as helium, hydrogen, neon, nitrogen.

A complete report will be published later.

COMMONWEALTH COLOR AND CHEMICAL CO.  
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RECEIVED JANUARY 3, 1944

### ELECTRON MICROSCOPE OBSERVATIONS OF CLAM MUSCLE FIBRILS

Sir:

Submicroscopic fibrils have been obtained from the adductor muscles of marine and fresh-water clams (*Mya*, *Venus*, *Anodonta*). In the dark-field microscope they appear as long, slender, needle-like fibrils. This fibrous protein has the solubility properties of myosin; it dissolves in 0.6 *M* potassium chloride to form a solution showing high viscosity and stream birefringence. Dilution with water produces a flocculent precipitate which can be redissolved in potassium chloride and which is apparently devoid of fibrils.

Electron micrographs show the fibrils to be very long and evenly contoured, having widths usually between 200 and 1000  $\text{\AA}$ ., though sometimes less. In fibrils treated with osmic acid the density along the axis is not uniform but shows a periodic variation, producing a cross-striated appearance (Fig. 1). From measurements of 100 fibrils a distribution curve of "spacings" of this fiber axis repeat pattern was constructed. All the values lay between 290 and 470  $\text{\AA}$ ., a surprisingly small range in view of the mechanical lability usually associated with muscle fibers. The most frequently occurring spacings were between 330 and 390  $\text{\AA}$ ., the average value of all spacings being 360  $\text{\AA}$ .

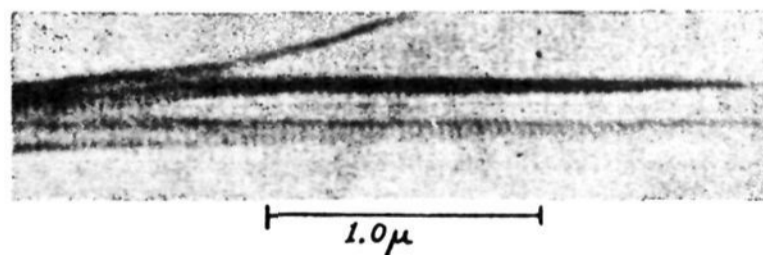


Fig. 1.—Electron micrograph of clam muscle fibrils, magnification  $\times 27,000$ .

Subsequently Dr. R. S. Bear examined these muscles with X-rays and obtained diffraction evidence that the fiber-axis period in the intact dried muscle is 720  $\text{\AA}$ . It is improbable that this apparent difference is due to alterations produced in isolating the fibrils and preparing them for elec-

tron microscope examinations. More likely, the larger X-ray period reflects density differences not yet resolved with the electron microscope but which may become apparent when special methods are applied. The structural problem, which is of great interest in connection with the mechanism of contractility, is one which requires for its solution both electron microscope and X-ray diffraction data. Details of the analysis will be reported in due course.

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RECEIVED JANUARY 8, 1944

### SPIROPENTANE

Sir:

The authors have made a Raman spectroscopic study of the low-boiling products obtained in the debromination of pentaerythrityl bromide by zinc. The first reduction was carried out in aqueous methanol.<sup>1</sup> In addition to lines assignable to methylenecyclobutane (I) and to 2-methyl-1-butene (II) the Raman spectrum of the product showed lines at 581 and 1033  $\text{cm}^{-1}$  which arose from about 1-5% of a third component (III). Examination of the spectra of various fractions obtained in the distillation of the reduction mixture indicated that the boiling point of III should be near 37°. By means of this information and the known Raman spectra and generalizations therefrom it was possible, at least tentatively, to conclude that III did not correspond to any compound known to the authors. It seemed quite probable that the lines belong to spiro-pentane.

It was reasoned that if this were spiro-pentane and if it could be formed at all by zinc in aqueous methanol, in spite of the preponderance toward rearrangement, there should be other conditions, under which III would form in larger proportion. This proved to be the case. When the reduction was carried out by zinc in molten acetamide in the presence of sodium iodide and sodium carbonate<sup>2</sup> the product showed the same low-boiling

(1) A report on this part of the work was presented before the Organic Division of the Pittsburgh Meeting of the American Chemical Society, September, 1943.

(2) Hass, McBee, Hinds and Gluesenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

substances but the compound responsible for the 581 and 1033  $\text{cm}^{-1}$  lines was now a major component—approximately 40%.

Isolation of the pure compound involved removal of the accompanying olefins, first by repeated extraction with saturated aqueous silver nitrate, then with saturated aqueous silver per-

TABLE I

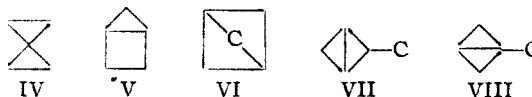
RAMAN SPECTRUM OF SPIROPENTANE			
$\Delta\nu$ , $\text{cm}^{-1}$	$I^a$	$\Delta\nu$ , $\text{cm}^{-1}$	$I^a$
305	4	1397	5
581	16	1426	10
613	4	2836	0.4
779	4	2881 <sup>b</sup>	
872	30	2991	100
1033	50	3065	30
1150	1		

<sup>a</sup> Intensities measured on Gaertner microdensitometer.

<sup>b</sup> Intensity too low to measure.

chlorate and finally by reaction with bromine. None of these reagents noticeably affected the new compound. The final, purified product has an odor similar to chloroform; b. p. 38.3-38.5°;  $n_D^{20}$  1.4117. *Anal.*<sup>3</sup> Calcd. for  $\text{C}_5\text{H}_8$ : C, 88.17; H, 11.83. Found: C, 87.91; H, 11.53. Its spectrum is given in Table I.

Raman spectra considerations, boiling point, and non-reactivity with bromine conclusively eliminated acetylenes, diolefins and monocyclic olefins and left only the possibility that the compound was one of the following dicyclic hydrocarbons



The authors favor formula IV because, 1, the product is formed in greater amount when conditions are less favorable to rearrangement and 2, the Raman pattern in the 2800-3100  $\text{cm}^{-1}$  region indicates that all the hydrogens present are attached to cyclopropane rings and none either to cyclobutane rings (V, VI) nor to carbon in a methyl group (VII, VIII).

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(3) Micro-analysis by Dr. T. S. Ma, University of Chicago.