

mechanical strength must be attributed to solution forces, the system being physically homogeneous down to molecular and submolecular dimensions. A more complete survey of the elastic constants, particularly of the time of relaxation, in relation to composition and treatment, is now in progress, both mechanical and optical methods being used. It is believed that the comparison of mechanical and optical methods will permit a more definite allocation of the respective types of structure.

Summary.

1. Measurements of the rigidity of gelatin jellies are given, showing that the jellies follow Hooke's law nearly up to the breaking point.
2. The relation of the modulus of elasticity to the concentration of gelatin is discussed; it is found that a function of the type $E = kc^n$ is valid for a certain range, but the constants k and n may vary from one grade of gelatin to another.
3. The influence of acidity and alkalinity on the elasticity has been followed quantitatively. P_H measurements show that the observed variations of elasticity are not a simple function of the actual hydrogen-ion concentration.
4. The influence of alcohol and glycerin in different concentrations on the coefficient of rigidity has been measured.

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[CONTRIBUTION FROM RESEARCH LABORATORY OF WESTINGHOUSE LAMP COMPANY.]

VAPOR PRESSURE OF WHITE PHOSPHORUS FROM 44° TO 150°.

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1. **Purpose.**—In connection with another investigation in this Laboratory, measurements on the vapor pressure of white phosphorus between 50° and 150° having an error of not over 2 or 3% were desired.

2. **Previous Measurements.**—Measurements have been made on the vapor pressure of phosphorus by the following investigators: Schroetter,¹ from 165° to 287.3°; Hittorf,² from 230° to 530°; Troost and Hautefeuille,³ from 360° to 550°; Joubert,⁴ from 5° to 40°; Jolibois,⁵ from 145° to 312°; Centnerszwer,⁶ from 20° to 40°; Smits and Bokhorst,⁷ from 169° to 409°.

The results of these measurements together with our own are given

¹ Schroetter, *Wien. Ber.*, **1**, 130 (1848).

² Hittorf, *Pogg. Ann.*, **126**, 193-228 (1865).

³ Troost and Hautefeuille, *Ann. chim. phys.*, **2**, 145 (1874).

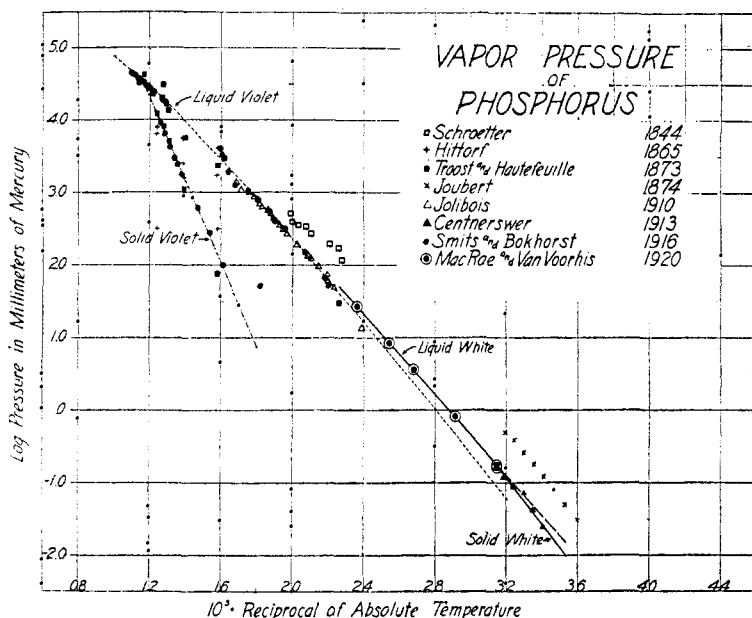
⁴ Joubert, *Compt. rend.*, **78**, 1853-5 (1874).

⁵ Jolibois, *ibid.*, **149**, 287 (1909); **151**, 382 (1910).

⁶ Centnerszwer, *Z. physik. Chem.*, **85**, 99-112 (1913).

⁷ Smits and Bokhorst, *ibid.*, **91**, 249-312 (1916).

in the accompanying plate in the form of a log p , reciprocal T plot. From this plate it will be seen that, previous to our own, there were no measurements on the vapor pressure of white phosphorus in the temperature range 40° to 145° ($10^3/T = 3.2$ to 2.4). Also the extrapolation of the equation representing the combined results of Smits and Bokhorst and of Jolibois, probably the most reliable above 150° , gives vapor pressures of



supercooled liquid white phosphorus very much lower than those obtained for solid white phosphorus by Centnerszwer¹ or Joubert.¹ Since at a given temperature a supercooled liquid cannot have a vapor pressure lower than that of its solid form, either the extrapolated values or the measurements on the solid must be in error. Consequently values obtained by the extrapolation of Smits and Bokhorst's equation would have been subject to uncertainty in the range desired.

3. Results.—The results of 4 series of measurements are given in Table I. The first 2 series are to be regarded as preliminary and are recorded merely to give an idea of the reliability of the method as applied to phosphorus. Neither the thermometry, the technique of measurement nor the purity of the materials was so good in these as in the third and fourth series. The fourth series of measurements was made on phosphorus from an entirely different source from that used in the other measurements, but in no case differs from Series III by more than 1%.

¹ *I. oc. cit.*

TABLE I.
 Vapor Pressure of White Phosphorus in Mm. of Hg At 0°.

Series I.		Series II.		Series III.		Series IV.		Selected values.	
Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.	Temp.	Press.
..	...	44.1°	0.169	44.13°	0.173	44.13°	0.173
50°	0.338	50°	0.260
59°	0.331	50°	0.259
..	...	69.7°	0.834	69.92°	0.823	69.92°	0.823
..	...	69.7°	0.822
100°	3.68	99.7°	3.70	100.11°	3.65	100.11°	3.67	100.11°	3.66
120°	8.74	119.3°	8.68	119.85°	8.57	119.85°	8.62	119.85°	8.60
150°	27.22	150.00°	27.19	150.00°	27.21	150.00°	27.20

Series I was made on once distilled white phosphorus, employing an isoteniscope U-tube 6 mm. in diameter. Series II was made on twice distilled white phosphorus, employing an isoteniscope U-tube 10 mm. in diameter. Series III was made on twice distilled white phosphorus and temperature was measured with a carefully calibrated thermocouple. Series IV was made on triply distilled white phosphorus obtained from red phosphorus and had as its object the detection of possible errors due to impurities in the phosphorus used in the first 3 series. The equation

$$\log_{10} P(\text{mm. Hg}) = 7.9515 - 2757.5/T \quad (1)$$

was derived to express the vapor pressure of white phosphorus as a function of the temperature. Table II shows the agreement between values calculated from this equation and the most reliable observed pressures at corresponding temperatures.

 TABLE II.
 Vapor Pressure of White Phosphorus Observed and Calculated from Equation 1.

Temp. ° C.	Pressure in mm. of Hg.		
	Obs.	Calc.	ΔP .
150.00	27.20	27.20°	0.00
119.85	8.60	8.60	0.00
100.11	3.66	3.66 ^a	0.00
69.92	0.823	0.819	+0.004
44.13	0.173	0.181	-0.008

^a Points used in deriving equation.

Table III gives values calculated at 10° intervals from 0° to 200°. Pressures obtained by extrapolation are given in italics.

4. **Method of Measurement.**—The method of measurement was essentially that described by Smith and Menzies¹ except that in order to make accurate measurements of the pressure at a given temperature, the temperature was held constant, until constant pressure readings were obtained, and that the pressure of the inert gas was adjusted to approximately that of the phosphorus, after which the slight difference in height of the levels of the phosphorus in the isoteniscope was measured with a micrometer microscope (or cathetometer). From this difference in levels and the densities of liquid phosphorus and mercury a correction to be applied to the manometer reading was cal

¹ Smith and Menzies, THIS JOURNAL, 32, 1412 (1910).

culated. The densities of phosphorus required were obtained from the equation $d = 1.786 - 9.06 \times 10^{-4}t$ which represents with sufficient accuracy the values given in the Landolt-Börnstein tables.

TABLE III.

Vapor Pressure of White Phosphorus Calculated from Equation 1 between 0° and 200°

Temperature. C.	Pressure. mm. Hg at 0°.
0	0.007
10	0.016
20	0.035
30	0.071
40	0.139
50	0.262
60	0.472
70	0.823
80	1.39
90	2.28
100	3.63
110	5.69
120	8.66
130	12.9
140	18.9
150	27.2
160	38.5
170	53.6
180	73.5
190	99.4
200	132.8

At 100°, 120° and 150° the pressure of nitrogen (or nitrogen plus a small amount of phosphorus vapor) was measured with another micrometer microscope focused on the levels of a mercury manometer having a tube one inch in diameter. (This manometer was so arranged that both levels could be simultaneously raised or lowered before a measurement. Thus possible errors due to sticking of mercury to the glass and consequent different curvature of the mercury menisci were avoided.) Below 100° the nitrogen pressure was measured with a McLeod gage connected to the isoteniscope through a liquid-air trap which prevented passage of phosphorus into the gage.

The isoteniscope was surrounded by a stirred oil thermostat held at a constant temperature by adjusting a resistance in series with its electric heater. In Series I and II the temperature of this thermostat was measured with a mercurial thermometer good to $\pm 0.2^\circ$ and in Series III and IV, with a copper-constantan thermocouple which was calibrated before Series III and again before Series IV by means of the following standard temperatures:

- 0.00°, m. p. of ice.
- 32.38°, m. p. of sodium sulfate decahydrate.
- 100.00°, b. p. of water at 760 mm. Hg.
- 216.93°, b. p. of naphthalene at 742.2 mm. Hg.
- 231.9°, m. p. of tin (Bureau of Standards, Sample No. 42).

Both calibrations were in excellent agreement with previous calibrations of thermocouples made from the same materials in this laboratory. The 3 lower standard temperatures were checked within 0.02° by means of a mercurial thermometer calibrated

by the Bureau of Standards. The method of determining the temperature corresponding to a given electromotive force was that described by L. H. Adams.¹

5. Precision of Measurements.—In making measurements of temperature the e. m. f. was read to one microvolt with the aid of a Leeds and Northrup potentiometer. This corresponds to a precision of 0.023° at 44° and 0.020° at 150°. At 44° one microvolt corresponds to 0.14% error in the pressure measurement, at 150° to 0.08%. So it can be safely claimed that errors in temperature measurement in this investigation do not produce appreciable errors in the pressure values.

The nitrogen pressures used in determining the vapor pressures above 100° were measured with the aid of a Gaertner micrometer microscope which could hardly have been in error by more than 0.01 mm. Below 100° the nitrogen pressure were measured with a McLeod gage checked at its upper limit against the mercury manometer mentioned above. Measurements made with the McLeod gage should be reliable to 0.5%.

In order to retard evaporation of the phosphorus in the isoteniscope, the pressure of the inert gas was adjusted to a value slightly greater than the vapor pressure being measured.

Since the density of liquid phosphorus is about one-eighth that of mercury, and since the difference in levels in the isoteniscope was measured to the nearest 0.05 mm., the error from this source is assumed to be less than 0.01 mm. of Hg.

After completing the measurements in Series III and finding our own results to be 30 to 60% higher than the values calculated from the equation of Smits and Bokhorst² for liquid white phosphorus the discrepancy seemed so great that in spite of our faith in the purity of our own materials (as evidenced by a melting-point³ determination of 44.0° ± 0.1° and a Marsh test showing freedom from arsenic) we decided to make measurements on phosphorus from another source. Accordingly, red phosphorus of a good degree of purity was distilled *in vacuo* and the white phosphorus resulting condensed in a receiver adapted to reject the first portion of the distillate. The last portion of the red phosphorus was also rejected by stopping the distillation, when enough white had been obtained, and sealing off the red phosphorus container from the system. The white phosphorus was then triply distilled, each time rejecting a small part at the beginning and end of each distillation. A clear colorless liquid resulted from the final distillation into the isoteniscope. A portion of the final distillate into the isoteniscope was found to have a melting point of 44.10° ± 0.05°.

In Series II, III and IV, but particularly in Series IV, the isoteniscope

¹ Adams, "Pyrometry:" a symposium published by *Am. Inst. of Min. and Met. Eng.*, 1920.

² *Loc. cit.*

³ 44.1°. Hulett, 1899.

was repeatedly "boiled out" until no further decrease in pressure resulted and apparently all gases had been removed from the apparatus and the phosphorus.

As a further check on the reliability of our measurements, the apparatus of Series IV was used to determine the vapor pressure of water at 25.4°. Our value was 24.35 mm. Hg which is in surprisingly good agreement with the value 24.34 mm. Hg given in Smithsonian Physical Tables, 6th Edition, 1918.

In view of the above considerations in regard to the precision of our measurements we are led to the conclusion that values obtained by extrapolating the equation of Smits and Bokhorst are 25 to 40% too low between 150° and 44° and that our own equation is not in error by more than 0.5% between 150° to 100° although below this range it may become less reliable with decreasing temperature, not however attaining an error as great as 5% above 44°.

6. Discussion.—Having concluded that Equation 1 represents sufficiently accurately the true vapor pressure of liquid white phosphorus between 150° and 44°, the immediate object of this investigation is attained. However, certain other results are suggested by, or follow from it.

Choosing the value determined from Equation 1 at the melting point of white phosphorus, 44.10°, as more reliable than the measurements at this point, we obtain 0.181 mm. of Hg. With this point and the most careful measurement of Centnerszwer,¹ namely 0.02530 mm. of Hg at 20°, we have derived the equation

$$\log_{10} P(\text{mm. Hg}) = 9.6511 - 3297.1/T \quad (2)$$

for the vapor pressure of solid phosphorus near its melting point. Values calculated from this equation are compared with the measurements by Centnerszwer¹ in Table IV.

TABLE IV.
Vapor Pressure of White Phosphorus Observed by Centnerszwer and Calculated from Equation (2).

<i>T</i> ,	<i>P</i> (calc.) in mm. Hg.	<i>P</i> (obs.) in mm. Hg.	ΔP .	$\frac{\Delta P \times 100}{P}$
44.1°	0.1810 ^a	(0.1810)	0.0000	0.00
40	0.1317	0.1221	−0.0096	−7.29
35	0.0893	0.0889	−0.0004	−0.45
30	0.0595	0.0724	+0.0129	+22.2
25	0.0391	0.0426	+0.0035	+9.05
20	0.0253 ^a	0.0253	0.0000	0.00
10	0.0101
0	0.0038

^a Used in deriving equation.

Further, if we assume with Smits and Bokhorst that supercooled violet

¹ *Loc. cit.*

phosphorus and liquid white phosphorus are identical, we can change the single equation of these investigators for the vapor pressure of both liquid violet and liquid white phosphorus over the range 145° to 634° from

$$\log_{10} P(\text{mm. Hg}) = 19.2189 - 3585.96/T - 3.59 \log_{10} T$$

to

$$\log_{10} P(\text{mm. Hg}) = 11.5694 - 2898.1/T - 1.2566 \log_{10} T \quad (3)$$

which represents all the data on liquid violet and liquid white phosphorus (except those of Schroetter) from 44° to 634° with deviations seldom greater than 5%. However a plot of the deviations of these data from the equation showed, in each set of measurements, decided trends that would be difficult to eliminate by a single smooth curve. It does however appear that the vapor pressure of liquid violet and liquid white phosphorus can be represented approximately by a single smooth curve.

Summary.

1. The vapor pressure of liquid white phosphorus has been measured in the range 44° to 150° by the static isotenscope method of Smith and Menzies.

2. The relation between temperature and vapor pressure in this range is given by equation

$$\log_{10} P(\text{mm. Hg}) = 7.9542 - 2757.5/T$$

with maximum error probably as small as 0.5% from 100° to 150° and probably increasing below this temperature to a value not greater than 5% at 44.0°.

3. The measurements reported in this paper are not inconsistent with the measurements of Centnerszwer on the solid and are from 30 to 60% higher than values obtained by extrapolating the equation of Smits and Bokhorst to temperatures between 150° and 44°.

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA.]

ARISTOL.

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Little is known concerning the chemistry of aristol,¹ although the substance has been on the market for about 30 years.

It is an amorphous powder made by the action, at ordinary temperature, of an excess of a solution of iodine and potassium iodide on a solution of thymol and approximately 4 equivalents of alkali. When fresh it has a dark red color but soon fades to a buff or brown, a change which is hastened by light.

The red variety is capable of producing, more or less slowly, about 2

¹ Other names for this substance are annidalin, thymotol and diiododithymol.