

(decahydronaphthalene).¹ Magnetic measurements on these substances were made by methods previously described.² The following data were obtained at 35°.

	Density, d_{25}	Susceptibility, $\chi \cdot 10^6$
<i>cis</i> decalin	0.8867	-0.774
<i>trans</i> decalin	.8607	-0.779

It is not surprising that the susceptibilities are almost exactly equal. The small difference is, however, believed to be significant. According to Van Vleck³ the susceptibility per gram mole of a polyatomic molecule without resultant spin is given by

$$\chi_{\text{mol}} = -\frac{Le^2}{6mc^2} \sum \bar{r}^2 + \frac{2}{3}L \sum_{n' \neq n} \frac{|m^0(n'; n)|^2}{h\nu(n'; n)}$$

where the symbols have their usual significance.

This expression consists of the familiar diamagnetic part and of a temperature-independent paramagnetic part. The latter term is generally believed to be negligible in most molecules. The present results suggest that the term may be detectable when, as in the case of *cis* and *trans* decalin, the only difference is one of symmetry. As anticipated, the paramagnetic term is larger for the *cis* form in which atomic orbits are probably slightly more distorted than in the *trans* form.

(1) Seyer and Walker, *THIS JOURNAL*, **60**, 2125 (1938).

(2) Selwood, *ibid.*, **61**, 3168 (1939); Preckel and Selwood, *ibid.*, **62**, 2765 (1940).

(3) Van Vleck, "The Theory of Electric and Magnetic Susceptibilities," Oxford University Press, New York, N. Y., 1932, p. 275.

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Preparation and Properties of Dimethylphosphine

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In the course of an investigation on the polymerization of some derivatives of trimethylaluminum,¹ a pure sample of dimethylphosphine was required. According to Hofmann,² pure dimethylphosphine can be obtained by (1) heating phosphonium iodide, methyl iodide and zinc oxide in a sealed tube in the molar ratio $2\text{PH}_4\text{I}:2\text{MeI}:1\text{ZnO}$, (2) treating the product with water whereby phosphine and monomethylphosphine are evolved, and (3) liberating the dimethylphosphine by addition of an alkali. We have found that the product thus obtained is contaminated with trimethylphosphine, which can be separated from the di-

methylphosphine by fractionation *in vacuo*. Hofmann's procedure for the preparation and isolation of dimethylphosphine is considerably simplified by the use of modern high vacuum techniques.

Nine grams of methyl iodide, 10.3 g. of phosphonium iodide and 2.6 g. zinc oxide were heated for eight hours at 100° in a bomb tube. The tube was opened, connected to a vacuum line, and water added to drive off the phosphine and monomethylphosphine. The addition of gaseous ammonia (in excess) to the residue liberated a mixture of dimethylphosphine and trimethylphosphine. This mixture was subjected to fractional distillation in a simple, partial reflux column (wire-spiral type) with the still head at -95 to -100° ("pumped down" carbon dioxide-ether) and the still pot at -80°. Under these conditions³ the distillate could be bled off as a vapor directly into the vacuum apparatus, in the absence of an inert atmosphere or a mercury bubbler. From 90 cc.⁴ of the mixture there was isolated 71 cc. of pure dimethylphosphine. The last fractions were shown to consist chiefly of trimethylphosphine by vapor tension measurements ($p = 14$ mm. at -46°).⁵

The purity of the sample of dimethylphosphine was established by several observations. Its molecular weight was 62.3 (a 25.5-cc. sample weighed 70.5 mg.) as compared with the calculated value of 62.0; it was tensimetrically homogeneous ($p = 30$ mm. at -47°); and the observed value of the vapor pressure with 99% of the total sample in the vapor phase agreed very well with that calculated from values obtained at lower temperatures. A series of vapor tension measurements from -47.0 to 15.0° were made; the data fit the equation, $\log p = -(1370/T) + 7.539$, as shown in the following table.

VAPOR TENSIONS OF DIMETHYLPHOSPHINE						
Temp., °C.	-47.0	-41.9	-30.9	-21.2	0	15.0
p in mm., obsd.	30	40.5	75	127	338	595
p in mm., calcd.	30	41	76	127	336	598

From these data, the boiling point is calculated to be 21.1°;⁶ ΔH (vap.), 6.27 kcal.; and Trouton's constant, 21.2.

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(3) The vapor tension of the dimethylphosphine is of the order of 2-3 mm. at -80° and several tenths of a mm. at -95 to -100°.

(4) Measured as a gas at standard conditions.

(5) Rosenbaum and Sandberg, *THIS JOURNAL*, **62**, 1622 (1940).

(6) Hofmann reports 25°. His value for the boiling point of trimethylphosphine is also high (see reference 5).

(1) Davidson and Brown, *THIS JOURNAL*, **64**, 316 (1942).

(2) Hofmann, *Ber.*, **4**, 605 (1871).