[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MANITOBA, WINNIPEG]

The Viscosity of Liquid Phosphorus

BY ALAN NEWTON CAMPBELL AND SIDNEY KATZ

This work was undertaken, firstly as an application of Smits' theory of allotropy and, secondly, to evaluate a physical constant which had not been determined at the time this work was commenced (September, 1934). Smits[1] draws attention to the abnormally low viscosity of liquid phosphorus in the neighborhood of the melting point of the α-white (ordinary yellow) form. The viscosity is abnormally low in the sense that the molten form is supercooled by 550° with respect to the stable violet form, and Tammann[2] has shown that there is usually a sudden and large increase of viscosity with increasing supercooling. Smits, however, quotes no figures and presumably his statement is based on visual observation of the mobility of phosphorus.

The first part of our work consisted in raising molten phosphorus to a fairly high temperature in the viscometer, chilling as rapidly as possible to the solid state and determining the viscosity just above the melting point. Such treatment has been found slightly to alter the melting point of substances, even in the absence of intensive drying, and might be expected to show an effect on the viscosity, particularly if the internal equilibrium is one between simple and associated molecules. On the latter assumption the viscosity of a rapidly chilled liquid would be less than normal, since there would be a deficiency of polymerized particles.

Toward the conclusion of this work, an abstract was received of work on the viscosity of phosphorus carried out by Dobinski[3] in the previous year. His measurements give the viscosity of phosphorus over the temperature range, 17.5–79.9°. As the original paper[4] is somewhat inaccessible, we reproduce his figures here.

DATA OF DOBINSKI

Temp., °C.	Viscosity in poises	Temp., °C.	Viscosity in poises
17.5	0.02515	47.75	0.01648
21.5	.02342	48.1	.01640
25.15	.02197	49.6	.01612
27.95	.02094	50.5	.01595
31.2	.02021	53.65	.01549
34.15	.01929	60.2	.01446
37.5	.01849	65.6	.01377
43.2	.01728	69.7	.01323
45.05	.01695	74.8	.01260
46.4	.01671	79.9	.01209
47.05	.01659		

Dobinski plotted his results in accordance with the formula of Andrade[5] and, as the graph changes slope at low temperatures, he concluded that association becomes appreciable below 49°. He observed visual indications of an internal equilibrium but he did not investigate the equilibrium shift by chilling experiments.

Experimental

An Ostwald viscometer of the ordinary type was used in this work. The plan of procedure in all cases consisted in maintaining the temperature of the phosphorus at some initial temperature until internal equilibrium was presumably established. The viscometer was then plunged in ice water to "freeze" the equilibrium, and then placed in a thermostat just above the normal melting point. Times of flow were then read in rapid succession until a steady value was reached, or until experimental difficulties, such as the appearance of particles of a solid form, made further readings impossible.

The phosphorus used in these experiments had been in stock for many years and it is not possible to state its origin. It had been kept in a subdued light, and was only superficially coated with a more stable form. It was purified by the method of Cohen and Olie[6] and then stored under water in a dark cupboard. A fresh preparation was made every ten days.

To displace the liquid phosphorus in manipulation and purification, either nitrogen or carbon dioxide was used. To remove the residual oxygen and moisture, the gases passed through hot copper turnings, pyrogallol solution, spiral water condensers, sulfuric acid bubblers, calcium chloride towers and phosphorus pentoxide towers.

The thermostat used in the viscosity determinations had a variation of ±0.02° over the range 20–40°. From 40 to 60° the temperature variation was greater, about ±0.05°. For heating bath in the experiments on shift of internal equilibrium a glycerol bath was used, and this had no temperature regulation, the temperature being kept approximately constant by adjusting the heating flame.

It is well known that white phosphorus is photosensitive; the rate of transformation to more stable forms is greatly enhanced when the phosphorus is illuminated. To minimize this effect direct light was excluded from the labora-

---

[1] Smits, "Theory of Allotropy," p. 233.

[2] Tammann, *Z. physik. Chem.*, **28**, 17 (1899).

[3] Dobinski, *Sci. Abstracts, A*, Jan. 25, 1935, abs. no. 137.

[4] Dobinski, *Acad. Polonaise Sci. et Lettres*, Ser. A., p. 103, March-April, 1934.

[5] Andrade, *Nature*, **128**, 835 (1930).

[6] Cohen and Olie, *Chem. Weekbl.*, **6**, 821 (1909).

tory. Operations were carried out in a fume-cupboard whose walls were covered with black paper. The heating bulb of the thermostat was also covered with black paint. Observations were made by means of a ruby-colored photographic light.

The viscometers were of a 5-cc. lower bulb capacity and had a water run time of about eighty seconds or more at room temperature. The stems were calibrated for five different volumes as shown in Fig. 1. A complete series of run times was taken for each of the five volumes over the temperature range in which the phosphorus was to be investigated. As standardizing liquid water was used for the range 20 to 80°. The water used was laboratory distilled water, redistilled from potassium hydroxide and potassium permanganate through a block tin condenser; it was collected and stored in a silica flask. For standardization at the higher temperatures, monobromobenzene was used. It was purified by dehydration over calcium chloride and redistilling the fraction with the correct boiling point being collected. After the conclusion of a series of runs with phosphorus, the apparatus was dismembered, and the viscometer restandardized. No appreciable variation was ever observed.

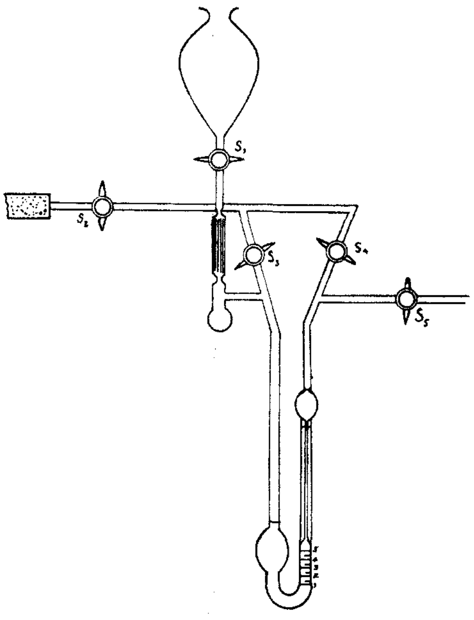

Fig. 1.

The very simple apparatus of Fig. 1 was used. The viscometer proper was wired to a wooden mount, to which were attached small spirit levels. The preliminary work had shown that molten phosphorus rapidly develops a thin yellowish scum,[7] and eventually particles of the stable violet form. As soon as particles commenced to deposit on the walls the apparatus had to be cleaned. Hence, after a day's running the apparatus was completely dismembered and the viscometer cleaned. After rebuilding, the apparatus was again cleaned. It was then thoroughly flushed for at least two hours with nitrogen or carbon dioxide.

The mode of operation was as follows. The reservoir of the apparatus was half filled with hot water and a few cc. of the purified liquid phosphorus then forced into it. The apparatus was full of inert gas and stopcocks, S_2, S_3, S_4 and S_5, being open, inert gas was streaming through the apparatus. Stopcock S_1 was then cautiously opened and phosphorus allowed to enter the capillary filled tube, drop by drop. The capillaries served to filter off any scum which might be formed at the phosphorus-water interface. The small round bulb below was intended to trap any impurities heavier than liquid phosphorus, but none were detected. The phosphorus was then allowed to run very slowly into the viscometer till the large lower bulb was approximately full. S_1 was closed and the phosphorus in the upper part of the system frozen by chilling the upper tube. From this point on work was performed as rapidly as possible to obtain the maximum number of runs before the accumulation of red phosphorus rendered the readings unreliable. By opening and closing suitable cocks, the phosphorus was brought to the level, O, in the bulb of the viscometer and the volume read from the level attained in the calibrated limb. Application of pressure then drove the phosphorus through the capillary of the viscometer, to the graduation mark above the bulb. With stopcocks S_1, S_2, and S_5 closed, and S_3 and S_4 open, the phosphorus was then under uniform gas pressure in both limbs.

Our first experiments dealt with the effect of rapid chilling from a high temperature on the viscosity at a fixed temperature. The viscometer and its contents were kept in the high temperature glycerol bath for from one-half to one hour. It was removed and plunged into ice water to "freeze" the equilibrium. It was then immersed in the thermostat which was set at a temperature slightly above the melting point of α-white phosphorus. Run times were taken in rapid succession as soon as the phosphorus was sufficiently liquid. At the same time, the time interval from the moment of placing the viscometer in the thermostat to the beginning of each run was noted. The results of a set of determinations are given below. In several cases, runs were begun before the phosphorus in the lower bulb had completely melted. The presence of unmelted phosphorus during a run is indicated by an (x). Data for runs so marked are, of course, meaningless. The thermostat temperature was 45.0°.

It is apparent that chilling from 80° has produced no effect on the viscosity. Considering the 100 and 120° figures, and discounting the asterisked figures, where unmelted phosphorus was present, there is some indication of a decrease in run-time with time. One would expect, however, if the pseudo-components of phosphorus stand in the relation of simple and associated molecules that chilling from a high temperature

---

[7] Mellor, "Comprehensive Treatise on Inorganic Chemistry," Longmans, Green and Co., New York City, Vol. VIII, p. 747.

TABLE II

EFFECT OF SUDDEN CHILLING ON VISCOSITY OF PHOSPHORUS

Run	Total time, min.	Run time, sec.	Run	Total time, min.	Run time, sec.
A. Viscometer No. 1. Heated to 80° for 60 minutes					
1	6	106.5	3	14	106.3
2	9.5	106.4	4	18.5	106.6
B. Viscometer No. 1. Heated to 100° for 30 minutes					
x1	13	110.8	8	32.5	103.4
x2	15.5	107.0	9	37.5	103.3
x3	18.5	106.0	10	40.5	103.9
4	21	104.9	11	42.5	103.4
5	23.5	103.8	12	45.0	103.4
6	26.5	104.0	13	47.0	103.4
7	29.5	103.8			
C. Viscometer No. 1. Heated to 120° for 30 minutes					
1	10.5	104.7	3	17.0	103.8
2	14	104.3	4	19	103.8
D. Viscometer No. 1. Heated to 120° for 30 minutes					
x1	5.5	103.9	5	31	104.3
x2	9	104.4	6	34	104.3
x3	13	104.5	7	36	104.4
4	28.5	104.4			

would give rise to a solid, and eventually to a melt, abnormally high in simple molecules, and therefore having a viscosity lower, not higher, than normal. The only conclusion we feel justified in drawing is that the effect, if it be real, is very slight; in other words, the internal equilibrium in liquid phosphorus is very rapidly established.

The normal viscosities of phosphorus were determined in the same way, except, of course, that the prior heating and chilling were omitted. At 140°, in spite of the rapidity of working, the viscometer became badly clogged with red phosphorus in a very short time, but below this temperature no difficulty was experienced from this cause. In the supercooled region, little difficulty due to solidification was experienced above 25°. At 25° spontaneous crystallization occurred once, and at 20° three or four times. It is well known that the velocity of crystallization of phosphorus is very great[8] and once nuclei are developed, crystallization is almost instantaneous. By slowing the stirrer somewhat to minimize vibration, a satisfactory set of readings was obtained at 20°. The effect of shock on initiating spontaneous crystallization has been demonstrated.[9] Attempts at 17.5° invariably resulted in solidification half way through the runs, and it was found impossible to supercool to 15° without spontaneous crystallization occurring immediately.

Calculations and Results

In the determination of the viscosity of phosphorus about two hundred runs were made.

The density and viscosity of water were obtained from the "International Critical Tables." The figures of Meyer and Mylius[10] were used for the density and viscosity of bromobenzene. The data for the density of phosphorus were taken from a paper by Pisati and De Franchis and from Dobinski.[11] The former made dilatometric measurements over the range 20–280°. Dobinski developed an empirical formula

$$D = 1.76705 - 0.0009222(t - 20)$$

which shows good agreement with the figures of Pisati and De Franchis, especially up to about 60°. The density figures of both Pisati and De Franchis and of Dobinski were used in a series of preliminary calculations of viscosity. Determinations to four figures, of which only three are probably significant, gave the same results for both sets of densities.

The data for the standardizing fluid were determined at very nearly the same temperature as the corresponding phosphorus run. The greatest difference was at 48°, where the nearest water determination was at 50°. In order that the volume of standardizing fluid and of phosphorus might be the same, time of flow of standardizing fluid was determined for each volume graduation of the viscometer. Where the value of phosphorus did not exactly coincide with a calibrated volume, half-interval interpolation was employed. It was found that intervals of less than half a scale division gave rise to variations less than the working limits of the stopwatch.

Dobinski plotted the logarithm (Napierian) of viscosity against the reciprocal of the absolute temperature, in accordance with the method of Andrade (*loc. cit.*) and, as he obtained a change of slope toward lower temperatures, he deduced that association was setting in. We, therefore, repeated our determinations twice, over the range of 25 to 60°, where the highest accuracy is obtainable, using fresh preparations, fresh apparatus

---

(8) Gernez, *Compt. rend.*, **95**, 1278 (1882); **97**, 1298, 1366, 1433 (1883).

(9) Young and Van Sicklen, THIS JOURNAL, **35**, 1067 (1913).

(10) Meyer and Mylius, *Z. physik. Chem.*, **95**, 349 (1920).

(11) Pisati and De Franchis, *Gazz. chim. ital.*, **4**, 497 (1874); Dobinski, *Z. Physik*, **83**, 129 (1933).

TABLE III

THE ABSOLUTE VISCOSITY OF PHOSPHORUS

Temperature °C.	Temperature variation °C., ±	n poise	Log₁₀n
	1st Series		
20.0	0.02	0.0231	−1.6366
24.9	.02	.0221	−1.6562
29.9	.02	.0202	−1.6562
35.5	.02	.0190	−1.7222
40.05	.04	.0177	−1.7513
42.05	.04	.0173	−1.7612
44.1	.04	.0169	−1.7734
44.6	.05	.0167	−1.7762
45.1	.05	.0167	−1.7783
45.2	.05	.0167	−1.7783
46.1	.05	.0165	−1.7825
47.1	.05	.0163	−1.7889
48.1	.05	.0168	−1.7951
49.1	.05	.0158	−1.8005
50.1	.05	.0157	−1.8049
60.3	.05	.0132	−1.8794
70.35	.1	.0124	−1.9083
80.55	.1	.0114	−1.9423
90.85	.5	.0104	−1.9834
100.9	.5	.0095	−2.0214
120.0	.5	.0080	−2.0953
140.0	1.0	.0071	−2.1481
	Second and Third Series		
25.1		0.0218	−1.6617
30.2		.0205	−1.6897
35.2		.0191	−1.7183
40.25		.0179	−1.7467
45.3		.0169	−1.7719
50.3		.0160	−1.7959
55.4		.0153	−1.8176
60.5		.0145	−1.8392

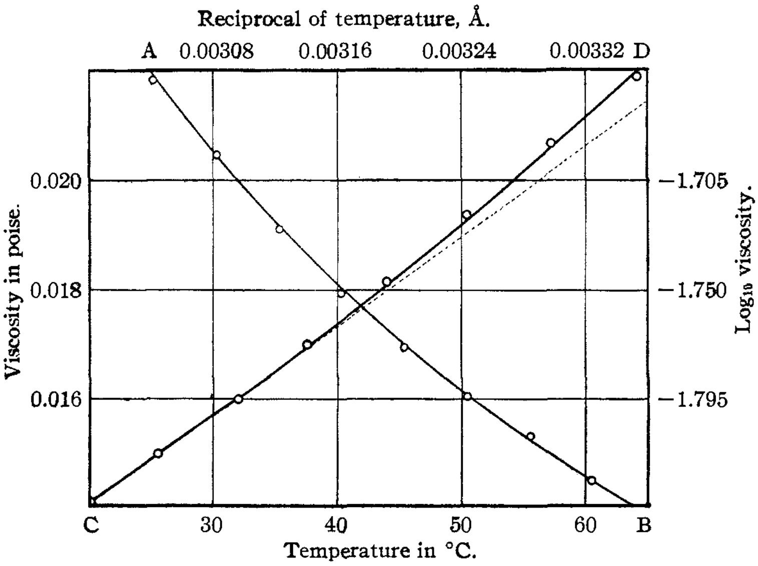

Fig. 2.—Curve AB, temperature–viscosity; Curve CD, reciprocal of temperature—log of viscosity.

and fresh calibrations. The two sets of observations were practically identical. They were therefore averaged and these results are appended to our previous results in Table III. Viscosities are given to three significant places. The common logarithms of the viscosities and the variation in temperature of the thermostat, as measured with a Beckmann thermometer, are also given. The repeat figures differ very slightly from our previous figures, with the exception of the figure for 60°, which the plot of our earlier figures showed to be discordant.

In Fig. 2, (a) viscosity is plotted against temperature for the range 25 to 60°; (b) the logarithm (common) of the viscosity is plotted against the reciprocal of absolute temperature, between the same temperature limits.

Discussion

There is no evidence of a change of viscosity when heated phosphorus is suddenly chilled, under our experimental conditions. There are logically four explanations of this, of unequal probability.

1. Smits' theory is incorrect.

2. The equilibrium displacement on cooling is so rapid that it is complete before solidification takes place. This is in agreement with Smits' own belief. He comments on the rapidity with which the inner equilibrium of liquid phosphorus is established just above the melting point of the α-white form.[12] We were not able to apply the anti-catalytic effect of intensive drying.

3. The temperature–composition curve of the inner equilibrium of liquid phosphorus is practically vertical, that is, the temperature change of internal equilibrium is too small to be detectable.

4. The shifting internal equilibrium does not reflect itself in viscosity change. In other words, the pseudo-components are isomers and not polymers.

Considering the viscosity figures as such, it is apparent that the agreement with Dobinski's figures is good, being well within 1%, below 60°. Above this temperature, the error probably increases with rising temperature, but it cannot be great, since, when all our figures,

---

(12) "Theory of Allotropy," p. 233.

including the figure for 140° and eliminating our first figure for 60°, which is obviously discrepant, are plotted against temperature, a smooth curve is obtained. Dobinski's figures do not extend above 80°. When our figures are plotted by the method of Andrade, the same change in slope is observed as with Dobinski's figures. If, therefore, Andrade's theory is sound, so is Dobinski's deduction, *viz.*, association of liquid phosphorus becomes appreciable below about 45°. If this is so, possibilities 3 and 4 (above) are ruled out. It is very probable that 2 contains the real explanation of our failure to observe positive results.

Summary

1. Experiments have been carried out on the effect of rapid chilling on the viscosity of phosphorus.

2. The viscosity of liquid phosphorus has been determined between the temperature limits 20–140°. The agreement with the prior figures of Dobinski (range 17.5–79.9°) is very good. As most of our work was carried out in ignorance of the very recent work of Dobinski, it appears that the viscosity of phosphorus is now known with a satisfactory degree of accuracy, at least over the temperature range common to both.

3. Association becomes appreciable in liquid phosphorus below 45°. The bearing of this and of the chilling experiments on Smits' theory is discussed.

WINNIPEG, CANADA RECEIVED JUNE 24, 1935

[CONTRIBUTION FROM GATES CHEMICAL LABORATORY, CALIFORNIA INSTITUTE OF TECHNOLOGY, NO. 487]

The Potentials of Cells in Liquid Ammonia Solutions. The Thermodynamic Constants of the Ammino Cadmium Chlorides and of Cadmium Chloride

BY CLIFFORD S. GARNER, EMERSON W. GREEN AND DON M. YOST

Introduction

The present investigation was undertaken to determine the suitability of the cadmium amalgam–hexammino cadmium chloride half-cell as a reference electrode for electromotive force measurements in liquid ammonia, and to evaluate the thermodynamic constants of the ammino cadmium chlorides and cadmium chloride.

For the purpose of establishing an electromotive series in the ammonia system it is desirable to refer all half-cells to some half-cell whose potential is taken arbitrarily as zero. Such a half-cell in the aqueous system is the hydrogen electrode. The same half-cell is here adopted for the liquid ammonia system in which the ammonium ion corresponds to the hydrogen ion of the aqueous system.

In this paper are presented the results of measurements on cells of the type Zn(amalg., N_2), $ZnCl_2 \cdot 6NH_3(s)$, NH_4Cl(in NH_3(l), f.), $CdCl_2 \cdot 6NH_3(s)$, Cd(amalg., N_1) together with the thermodynamic constants for the ammino cadmium chlorides and cadmium chloride. Provisional values of known potentials in terms of the standard hydrogen half-cell in liquid ammonia are also presented.

Preparation of Materials and Experimental Procedure

Ammonia.—The gas from a tank was passed over solid potassium hydroxide, condensed into a trap containing metallic sodium, and then fractionated over into an auxiliary vessel.

Mercury.—Mercury was repeatedly sprayed through nitric acid, and washed and dried. It was then redistilled five times in a current of air.

Zinc.—C. P. zinc sticks were scraped free from an oxide coating, placed in a sectioned Pyrex tube and distilled in four fractions in a current of pure dry hydrogen. It was then stored in weighing bottles filled with hydrogen.

Cadmium.—C. P. cadmium sticks were purified and stored in the same manner as for zinc.

Hydrogen.—The gas from a tank was passed through platinized asbestos at 350° to remove oxygen, and then through anhydrous phosphorus pentoxide to dry it.

Zinc Chloride.—Analytical reagent zinc chloride was fused, and immediately upon solidifying it was placed on the zinc amalgam in the cell. A stream of pure hydrogen was passed through the cell during this operation.

Cadmium Chloride.—A nearly saturated solution of recrystallized cadmium chloride (C. P.) was prepared containing a very small amount of hydrochloric acid to prevent hydrolysis. The solution was placed in a desiccator containing sulfuric acid, and the crystals resulting were filtered, pressed dry, and then placed in a flask. The flask was evacuated and at the same time heated to nearly the melting point of the cadmium chloride. Portions of the purified cadmium chloride were then placed on the cad-