

ion decreases. The solid phase present in solutions containing less than 31% HF has been shown by Kurternacker, Finger, and Hey (10) to be $\text{Ni}(\text{H}_2\text{O})_4\text{F}_2$. This observation was confirmed in this work by use of the Schreinemaker technique.

Results represent a typical phase diagram for a mixed solvent system. The major difficulties arise from problems of handling and transferring the solvent. Problems of this kind have made relatively simple operations formidable obstacles in the progress of this work.

ACKNOWLEDGMENT

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Vapor Pressures of Zinc, Cadmium, Antimony, and Thallium

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The vapor pressures of solid zinc, cadmium, antimony, and liquid thallium in the range of 10^{-1} to 10^{-4} mm. of Hg have been remeasured using the torsion-effusion technique. The following standard latent heats of vaporization have been calculated: Zn, $\Delta H_{298}^{\circ} = 31.01 \pm 0.20$ kcal. per mole; Cd, $\Delta H_{298}^{\circ} = 26.64 \pm 0.11$ kcal. per mole; Sb, $\Delta H_{298}^{\circ} = 49.21 \pm 0.16$ kcal. per mole; Tl, $\Delta H_{298}^{\circ} = 42.85 \pm 0.20$ kcal. per mole.

DURING THE COURSE of a general series of measurements of vapor pressures over alloys, the vapor pressures of solid zinc, cadmium, antimony, and liquid thallium have been redetermined using the torsion-effusion technique (12). The materials used were spectroscopically pure zinc and cadmium supplied by the Imperial Smelting Co., Ltd. and spectroscopically pure antimony and thallium obtained from Johnson Matthey Ltd. The experimental method has been described in detail previously (1, 8) and consists basically of measuring the force exerted by vapor effusing from an orifice. A graphite effusion cell is suspended from a fine wire, and the vapor effuses in a horizontal direction from two eccentrically placed orifices thus exerting a torque.

The angle through which the cell deflects is a measure of the vapor pressure.

RESULTS

Zinc. The results obtained for zinc are given in Table I. In addition, an average value of the standard latent heat of vaporization, $\Delta H_{298}^{\circ} = 31.01 \pm 0.20$ kcal. per mole, has been calculated by the third law method using relevant thermodynamic information given by Stull and Sinke (10). The vapor pressure data are compared graphically with previous results in the same pressure range in Figure 1. The values agree well with those of Vance and Whitman (11) but indicate somewhat higher vapor pressures than determined by Egerton (3) and McKinley and Vance (5). The average value of ΔH_{298}° for the present results agrees

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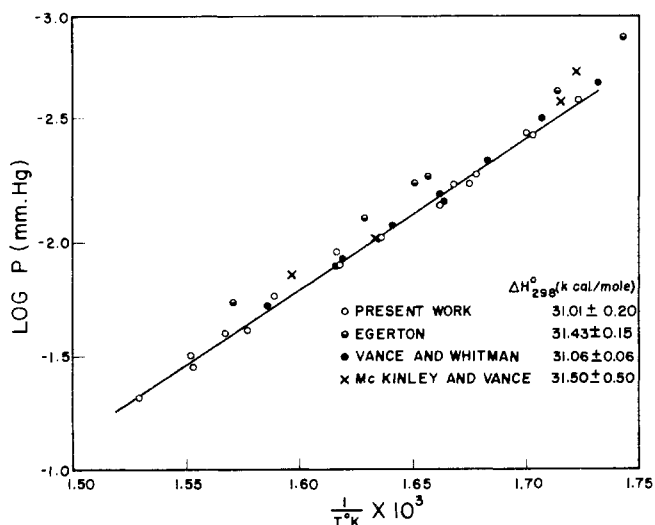


Figure 1. Comparison of reported vapor pressure values for zinc. Full line is least squares fit to present data

Table I. Experimentally Determined Vapor Pressures of Zinc

| $T, ^\circ\text{K.}$ | $P, \text{mm. of Hg,} \times 10^4$ |
|----------------------|------------------------------------|
| 580.5 | 23.07 |
| 587.2 | 33.19 |
| 588.3 | 32.66 |
| 596.0 | 49.77 |
| 597.0 | 54.58 |
| 599.3 | 54.83 |
| 601.6 | 68.23 |
| 611.1 | 94.41 |
| 618.1 | 124.2 |
| 619.1 | 109.1 |
| 629.5 | 169.8 |
| 634.0 | 240.4 |
| 638.0 | 250.6 |
| 643.7 | 354.8 |
| 644.2 | 310.5 |
| 653.9 | 482.0 |

The data are represented by the equation $\log_{10} P(\text{mm. of Hg}) = 8.843 - (6651/T)$.

well with a value of $\Delta H_{298}^{\circ} = 31.25 \pm 0.05$ kcal./gram atom selected by Hultgren (4) after consideration of all existing measurements.

Cadmium. Table II lists the vapor pressures determined for cadmium. In a previous paper (1), the authors have considered the vapor pressure of solid cadmium in detail, and have derived, on consideration of all the results, an equation to express the vapor pressures over solid cadmium: $\log_{10} P(\text{mm. of Hg}) = 8.818 - 5808/T$. The present data are in better agreement with this equation than the originally published experimental values (1), and the average value of $\Delta H_{298}^{\circ} = 26.64 \pm 0.11$ kcal. per mole compares more favorably with Hultgren's (4) selected value of 26.77 ± 0.15 kcal. per mole.

Antimony. The results are shown in Table III and compared with previous measurements in Figure 2. The values agree well with those of Niwa and Yosiyama (7) and Rosenblatt and Birchenall (9), both determined by the torsion-effusion method. These authors also ascertained that in the temperature range investigated antimony vapor consisted of 100% Sb_4 molecules within experimental error.

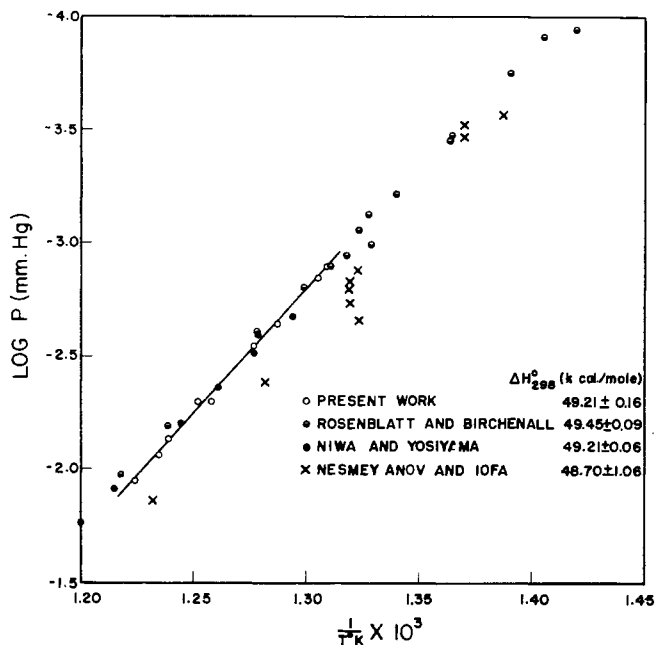


Figure 2. Comparison of reported vapor pressure values for antimony. Full line is least squares fit to present data

Table II. Experimentally Determined Vapor Pressures of Cadmium

| $T, ^\circ\text{K.}$ | $P, \text{mm. of Hg,} \times 10^4$ |
|----------------------|------------------------------------|
| 480.7 | 5.728 |
| 497.5 | 16.75 |
| 500.1 | 16.79 |
| 513.3 | 38.82 |
| 513.7 | 35.08 |
| 529.5 | 72.61 |
| 537.0 | 113.2 |
| 544.8 | 152.1 |
| 554.5 | 241.0 |
| 555.4 | 267.9 |
| 559.0 | 325.1 |

The data are represented by the equation $\log_{10} P(\text{mm. of Hg}) = 9.00 - (5879/T)$.

Vapor pressures measured by Nesmeyanov and Iofa (6) using the Knudsen effusion technique and assuming that the vapor contained 100% Sb_4 molecules are considerably higher. An average value of $\Delta H_{298}^{\circ} = 49.21 \pm 0.16$ kcal. per mole determined from the present results assuming 100% Sb_4 molecules in the vapor again agrees well with the work of Niwa and Yosiyama and Rosenblatt and Birchenall but not the work of Nesmeyanov and Iofa.

Thallium. Vapor pressures measured over liquid thallium are presented in Table IV and compared in Figure 3 with the only previous determination in this temperature range, the work of Coleman and Egerton (2). The present results appear to be about 40% higher than the earlier ones, although a value of $\Delta H_{298}^{\circ} = 42.85 \pm 0.20$ kcal. per mole calculated from the present data agrees reasonably well with a value of 43.49 ± 0.06 kcal. per mole deduced from Coleman and Egerton's results.

Table III. Experimentally Determined Vapor Pressures of Antimony

| T, ° K. | P, mm. of Hg, × 10 ⁴ |
|---------|---------------------------------|
| 763.7 | 12.69 |
| 766.2 | 14.17 |
| 777.0 | 22.66 |
| 782.6 | 28.72 |
| 794.8 | 50.21 |
| 798.8 | 50.65 |
| 807.0 | 73.58 |
| 809.6 | 86.90 |
| 817.0 | 111.9 |

The data are represented by the equation $\log_{10} P(\text{mm. of Hg}) = 11.539 - (11025/T)$.

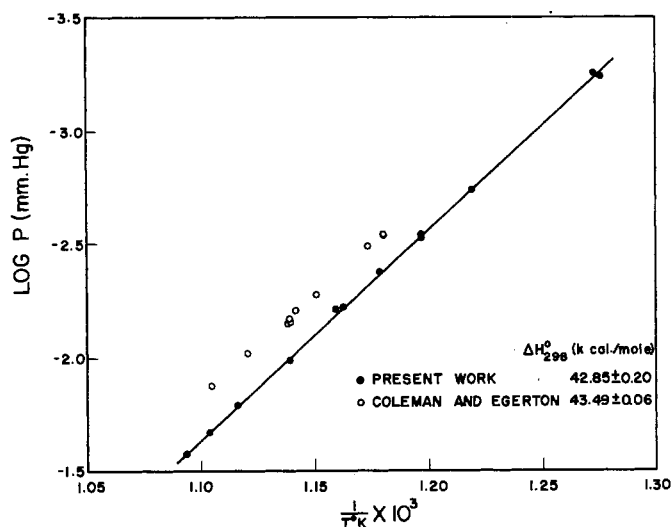


Figure 3. Comparison of reported vapor pressure values for thallium. Full line is least squares fit to present data

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CORRECTION:

In the Article "Physical Properties of Diarylkanes" by Richard J. Best [J. CHEM. ENG. DATA 8, 267(1963)] the second and third paragraphs on page 270 should have read.

Dixon and Clark (5) reported correlation of the physical properties of high molecular weight alkylbenzenes and alkylcyclohexanes with their structure and showed that methyl groups attached to the benzene ring increased the density and viscosity of the compound. The fusing of rings causes the same effects. The interpretation proposed is that the rigidity of a molecule is increased by the fusing of rings or by the addition of methyl groups to a phenyl ring. They suggested that hyperconjugation of the methyl groups attached to the ring created a significant double bond character in the C—C bond between the ring and methyl group and raised the barrier to wagging of the methyl group. Hydrogenation of the ring eliminated this hyperconjugation, and the anomalous density, viscosity and molecular attraction disappeared. Steric hindrance of the substituents did not seem to be the cause of the anomalous properties in their series.

Table IV. Experimentally Determined Vapor Pressures of Thallium

| T, ° K. | P, mm. of Hg, × 10 ⁴ |
|---------|---------------------------------|
| 783.4 | 5.768 |
| 785.6 | 5.585 |
| 820.0 | 18.20 |
| 835.4 | 29.85 |
| 835.8 | 28.91 |
| 848.1 | 41.98 |
| 860.1 | 60.26 |
| 862.2 | 61.52 |
| 878.3 | 103.0 |
| 896.0 | 162.2 |
| 906.0 | 216.3 |
| 914.3 | 263.6 |

The data are represented by the equation $\log_{10} P(\text{mm. of Hg}) = 8.536 - (9247/T)$.

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CONCLUSIONS

For the physical properties of the six isomers—density, refractive index, surface tension, and viscosity—there is a continuous change as a function of the structure. The order of the properties is as follows: $pp' < mp' < mm' < op' < om' < oo'$. The least compact structure, pp' -DTE, has the lowest values of these properties, and oo' -DTE, the most compact structure—i.e., the methyl groups are in as close to the ethane chain as possible—has the highest values. In addition it was not known *a priori* whether mm' -DTE or op' -DTE would be the denser, optically or by weight, but the measurements definitely establish that op' -DTE is the more dense. Figure 2 shows the variation of the physical properties on an arbitrary scale, which, however, is proportional to the true values for each property.