Note

The Validity of Raoult's Law in Molten Solutions of Lead Chloride and Lead Bromide

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The work of Salstrom and Hildebrand[1] on the thermodynamic properties of molten solutions of lead chloride and lead bromide indicates that over the temperature range 440 to 550° the mixtures do not follow Raoult's law. To quote these authors: "this result does not accord with the measurements of Jellinek and Bolubowski,[2] who found Raoult's law obeyed by the vapor pressures at temperatures from 660 to 780°. We are at a loss to explain the discrepancy, as neither the difference in the temperature range nor the departure of the vapors from the gas laws would seem to be sufficient to account for it." It is the purpose of this note to show that the conclusions of the latter authors are open to serious objections.

Jellinek and Bolubowski measured the partial pressures of the components in the 50–50 and the two possible 75–25 mole per cent. mixtures at the temperatures 660, 700, 740 and 780°. No measurements were made to determine the vapor pressures of the pure components. Their conclusion that Raoult's law is valid over the temperature range indicated depends upon the following points. (1) The partial pressures of the components as determined in the three mixtures, when plotted as isotherms on vapor pressure–composition diagrams, lie on a line which deviates from the linear only within the limits of experimental error. (2) The linear extension of this line to the pure component axes gives values for the vapor pressure of the pure components which seem to be substantiated by conclusions to be drawn from data in the literature. It is this point which is open to particular question.

For the vapor pressure of pure lead chloride Jellinek and Bolubowski refer to the work of Wartenburg and Bosse[3] which gives the vapor pressure over the temperature interval 770 to 950°, and to Eastman and Duschak as quoted in the Landolt and Börnstein Tables.[4] The use of these data required an extrapolation to give the vapor pressures at the four specified temperatures, but had the original work of Eastman and Duschak[5] been consulted the desired values could have been obtained by interpolation on a smooth curve. Moreover, the pressures thus obtained would not have compared so favorably with those obtained by extrapolation. The latter values were obtained by plotting log p against $1/T \times 10^4$ using a straight line extrapolation. Eastman and Duschak[5] have shown that plotting log p

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[1] Salstrom and Hildebrand, THIS JOURNAL, **52**, 4641 (1930).

[2] Jellinek and Bolubowski, *Z. physik. Chem.*, **A147**, 461 (1930).

[3] Wartenburg and Bosse, *Z. Elektrochem.*, **28**, 384 (1922).

[4] Bd. II, S. 1348.

[5] U. S. Bureau of Mines, Technical Paper No. 225 (1919).

against $1/T$ does not give a straight line and they attribute the curvature which they obtain to rather rapidly changing values for the heat of vaporization. Using an independent method Maier[6] has confirmed the curvature found by Eastman and Duschak and has obtained values for the vapor pressure of molten lead chloride which, while slightly higher than those of the earlier workers, compare favorably throughout. On the other hand, Jellinek and Bolubowski state that the heat of vaporization appears to be constant over the temperature range in question.

Table I gives values for the vapor pressure of pure lead chloride as given by the investigators mentioned, along with the partial pressure of lead chloride in a mixture containing 75 mole per cent. of lead chloride and 25 mole per cent. of lead bromide according to the data of Jellinek and Bolubowski. All pressures are recorded in millimeters of mercury.

TABLE I

THE VAPOR PRESSURE OF LEAD CHLORIDE

t, °C.	Pure $PbCl_2$ Eastman and Duschak	Maier	Jellinek and Bolubowski	75–25 mixture Jellinek and Bolubowski
660	10.6	12.1	20.5	15.2
700	22.4	26.9	38.5	26.3
740	45.0	53.7	68.0	51.5
780	87.0	100.0	120.0	91.9

It will be observed that the partial pressure of lead chloride in the 75–25 mixture exceeds, in certain cases, the vapor pressure of the pure substance as given by Eastman and Duschak and by Maier. The extrapolated values for the pure substance as obtained by Jellinek and Bolubowski appear to be very high. One explanation for these discrepancies lies in the use of linear functions in the extrapolation. Were it not for changing values of the heat of vaporization a linear relationship between logarithm of vapor pressure and reciprocal temperature would be expected on the basis of the Clausius equation

$$\log p_1 - \log p_2 = \frac{Q}{4.57}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

The presence of these inconsistencies in the vapor pressure data would seem to strengthen the case for the more accurate methods of electromotive force measurements, *i. e.*, the conclusion of Salstrom and Hildebrand that Raoult's law is not obeyed in these mixtures.

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[6] U. S. Bureau of Mines, Technical Paper No. 360, 28 (1925).