axis S-Py between 53% and 54% $AgClO_4$. It is evidently the compound, $4AgClO_4.9C_5H_5N$, which contains 53.81% of silver perchlorate.

At temperatures higher than 30° conjugate solutions appear in the ternary system, but the study of isotherms above 25° was not attempted, and these solutions were not studied.

Summary

It has been shown that the formation of water-insoluble compounds such as those of silver perchlorate with aniline is not general for silver perchlorate with other aromatic amines. Pyridine, however, is precipitated quantitatively by silver perchlorate.

The solubility of silver perchlorate in pyridine has been measured from —40.3° to a temperature of 110°. The 25° isotherm of the system, silver perchlorate, water, pyridine, has also been determined. Three compounds isolated are $AgClO_4.4C_5H_5N$, unstable, m. p. 68°; $4AgClO_4.$-$9C_5H_5N$, unstable, m. p. 95.6°; and $AgClO_4.2C_5H_5N$, stable, m. p. 144–147°. The composition of the intermediate compound was established by a phase-rule method; of the others, by direct analysis.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

THE ENTROPIES OF THE VAPORS OF ZINC AND LEAD

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In a recent publication[2] a description was given of the measurement of the vapor pressure of cadmium by a direct method. In this method the cadmium was boiled under reduced pressure in an inert atmosphere and the temperature read by a platinum-platinrhodium thermocouple. This method with some modifications has been used in the measurements of the vapor pressures of zinc and lead.

On account of the higher temperature it was impossible to use Pyrex glass either for a container for the metal or to enclose the thermocouple. The metals were boiled in a porcelain test-tube and the thermocouple was enclosed in a quartz tube. For zinc the porcelain test-tube was mounted as described in the previous article in a large Pyrex tube. The porcelain test-tube was heated electrically and the walls of the enclosing Pyrex tube were shielded from radiation by silver foil. Since the temperature of the zinc vapor is just high enough to heat the walls of the containing tube to a visible red it was possible to see the exact height to which the zinc vapor rose.

In the measurements on lead it was not feasible to provide sufficient

[1] Research Fellow of the Chas. A. Coffin Foundation.

[2] Fogler and Rodebush, THIS JOURNAL, **45**, 2080 (1923).

energy input by electrical heating. Accordingly, the lead was placed in a porcelain tube 50 cm. long. The lower end of this tube was heated directly in a gas-fired furnace. The connections to pump, pressure gage, etc., were attached to the top of the porcelain tube with de Khotinsky cement. No difficulty was found in maintaining reduced pressure in the porcelain tube at high temperatures. The pressures were read directly with a cathetometer from a U-tube manometer of large bore containing mercury. A high vacuum was maintained in one limb of the manometer by continuous pumping. Nitrogen was used as the inert gas in the measurements for both metals.

The thermocouple was calibrated frequently against the boiling point of sulfur and the melting points of potassium chloride, potassium sulfate and copper. It did not show any variations in e.m.f. The metals used were purchased as C. P. and did not show qualitative tests for any impurities likely to be present. The other sources of error are undoubtedly more important than the amount of impurities that might be present in the metals. Enough metal was placed in the tube to fill it to a depth of about 5 cm. The thermocouple was mounted so that the tip was about 3 cm. above the surface of the metal.

The chief source of error is in the temperature reading. The vapor may be superheated or the thermocouple may lose heat by radiation and be colder than the vapor. In the case of zinc where the height to which the vapor rose could be readily controlled it is not likely that either of these effects was serious and the errors were probably as often positive as negative. It is more difficult to estimate the errors due to this source for lead.

The Vapor Pressure of Zinc

As was stated above, no difficulty was experienced in measuring the vapor pressure of zinc. When the depth of immersion of the thermocouple in the vapor was varied by several centimeters no appreciable variation of the temperature was observed. When the pressure was varied slightly the temperature responded instantly. The measurements, when plotted in the customary manner (that is, log p against $1/T$), gave a smooth curve which was almost a straight line. It was found possible to represent these data very satisfactorily by the following equation.

$$\log p_{\text{mm.}} = -\frac{6967}{T} - 2.162 \log T + 2.298 \times 10^{4}\, T + 15.1817 \qquad (1)$$

The comparison of experimental values with those given by the foregoing equation is given in Table I.

The irregularities in the measurements are greatest at the lower pressures, as might be expected. At higher pressures the results are very consistent. The measurements coincide almost exactly with those of Braune.[3]

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[3] Braune, *Z. anorg. Chem.*, **111**, 109 (1920).

TABLE I

VAPOR PRESSURES OF ZINC

T. °K.	P obs. Mm.	P calc. Mm.	P Obs.-calc. Mm.	Error %
857.1	8.35	8.19	+0.16	1.90
860.1	8.74	8.60	+ .14	1.60
863.3	9.18	9.16	+ .02	.22
868.3	10.23	10.10	+ .13	1.30
873.5	11.17	11.16	+ .01	.09
878.4	12.05	12.24	− .19	1.50
881.3	13.35	12.93	+ .42	3.20
882.3	13.20	13.17	+ .03	.23
890.7	15.33	15.39	− .06	.39
890.7	15.37	15.39	− .02	.13
900.6	18.51	18.41	+ .10	.54
903.8	19.45	19.49	− .04	.21
906.3	20.41	20.38	+ .03	.15
914.7	23.75	23.60	+ .15	.64
918.1	24.93	25.03	− .10	.40
923.9	27.55	27.64	− .09	.32
924.7	27.94	28.02	− .08	.31
926.9	29.15	29.09	+ .06	.21
927.2	29.15	29.23	− .08	.27
934.2	32.75	32.86	− .11	.33
934.9	33.04	33.24	− .20	.60
938.8	35.38	35.44	− .06	.17
938.9	35.38	35.51	− .13	.37
948.5	41.41	41.50	− .09	.22
948.7	41.59	41.63	− .04	.10
948.9	41.70	41.76	− .06	.14
955.6	46.64	46.48	+ .16	.35
956.5	47.22	47.15	+ .07	.15
958.9	49.00	48.96	+ .04	.08
959.7	49.52	49.57	− .05	.10

In setting up Equation 1 we have used the heat capacity data of Wüst[4] for molten zinc which varies with the temperature. Braune, on the other hand, made some determinations which led him to believe that the heat capacity of molten zinc is independent of the temperature. As a result of the different values used for heat capacity our equation has a different curvature from Braune's and while the observed data agree closely the results obtained by extrapolation differ somewhat. At the melting point of zinc, 692°K., we obtain 0.138 mm., while Braune's equation gives a value of 0.145 mm. At 1178.8°K. which is given by Heycock and Lamplough[5] as the boiling point under 760 mm., we find 785 mm. while Braune found 764 mm. at 1180.3°K. Since we are interested mainly in the lower pressures the value to be obtained depends entirely on the heat-capacity data

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[4] Wüst, *Verh. deut. Ing., Forsch.-arb.* **204** (1918).

[5] Heycock and Lamplough, *Proc. Chem. Soc.*, **28,** 4 (1912).

used. The very extensive data of Wüst appear to be often in disagreement with those of other observers. These discrepancies we believe to be due to inherent defects in the method used rather than to faulty work on the part of the experimenters. Wüst's data for molten zinc lie between those of Braune and Iitaka[6] and we shall accept them. While the equation obtained leads to results in error at the boiling point by several degrees, it gives a value at the melting point which lies between that of Braune's equation and that obtained by extrapolation of Egerton's[7] results on solid zinc.

The Vapor Pressure of Lead

The higher temperatures necessary to vaporize lead introduce considerable difficulty in the way of temperature measurement. When the tube is heated above the molten metal there is great danger of superheating. On the other hand, if the tube is not heated around the thermocouple, then it seems likely that heat losses by radiation and conduction will cause the thermocouple to register too low a temperature. In all of our work the heat was applied in such a way that the flame did not strike the tube above the liquid. Above the liquid the porcelain tube was surrounded by a heavy magnesia insulation which, of course, received considerable heat from the flame on the outside.

Our first run was made with the thermocouple inserted loosely in a silica tube and we obtained results agreeing with those of Ingold[8] obtained by a similar method. We found, however, when the thermocouple was raised by the slightest amount so that the junction did not rest on the bottom of the enclosing quartz tube, that the temperature dropped 20–30°. It was apparent that the contact of the thermocouple with the tube was not sufficient to overcome the effect of conduction along the wires. Accordingly we drew the quartz tube down to a thin tip and fused this tip down onto the wires of the thermocouple for about 3 cm. above the junction in order to insure intimate contact between the thermocouple and the tube.

The results obtained in this way showed temperatures about 30° higher than the first observations at the corresponding pressures. When these results were plotted on the log p, $1/T$ diagram, they were found to be grouped in such a way that a straight line could be drawn through them in a satisfactory manner.

It must be recognized, of course, that the temperature of a vapor above a boiling liquid depends upon the rate of boiling and the height to which the vapor rises. There is a tendency for the thermocouple to lose heat by radiation and read too low. On the other hand, if the boiling is very rapid the vapor becomes superheated. At lower temperatures, the rate

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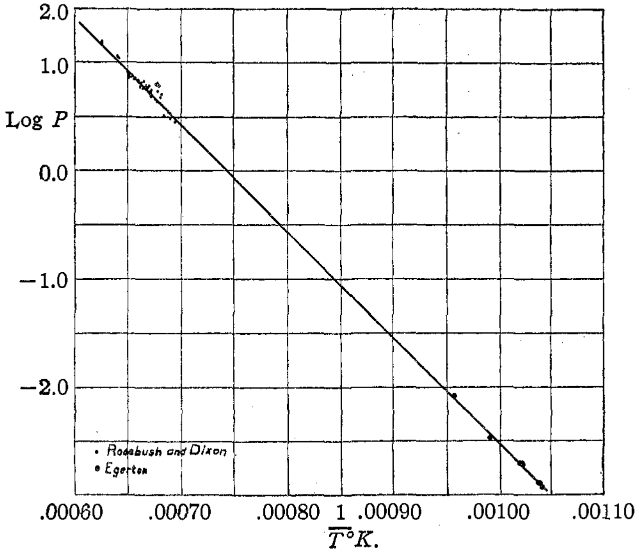
[6] Iitaka, *Sci. Repts., Tokohu Imp. Univ.*, **8**, 99 (1919).

[7] Egerton, *Phil. Mag.*, **33**, 33 (1917).

[8] Ingold, *J. Chem. Soc.*, **121**, 2419 (1922).

of boiling may be varied greatly without producing noticeable changes in the temperature observed, but at 1300°C. any change in the rate of boiling becomes noticeable and the best that we can do is to measure a temperature range the upper and lower limits of which represent conditions of superheating and underheating, respectively. The average deviation of the forty observed points from the straight line was only 7° but it must not be assumed that this is the limit of error. We believe that the general tendency is toward underheating rather than superheating and that our temperatures as read may be too low. Since Ingold's results agree with those we obtained when the thermocouple was in poor contact with the enclosing tube, we are convinced that his results are in error by a corresponding amount.



The other data of importance are those of Egerton[9] obtained in the range 800–1000°K. Egerton fitted his data to a straight line equation (on the log p, $1/T$ diagram) which appears justifiable, but from Egerton's data alone the slope of the line seems uncertain, since it is possible to fit the data equally well by lines of different slopes. If we plot both our data and Egerton's on a large plot, however, it is possible to draw a straight line through both in a very satisfactory manner. The line so drawn differs slightly from Egerton's. Since the data of Wüst indicate too slight differences between the heat capacities of liquid and vapor to cause an appreciable curvature, the use of a straight line appears justifiable. It may be remarked that the data of Ingold cannot be made to agree with those of Egerton.

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[9] Egerton, *Proc. Roy. Soc.*, **103**, 469 (1923).

The equation thus obtained was the following.

$$\log_{\text{mm.}} = -\frac{9854}{T} + 7.822 \qquad (2)$$

It is believed that the heat and entropy of vaporization can be calculated from this equation with considerable accuracy.

TABLE II

VAPOR PRESSURES OF LEAD

T °K.	P obs. Mm.	P calc. Mm.	P Obs.-calc. Mm.	T °K.	P obs. Mm.	P calc. Mm.	P Obs.-calc. Mm.
1432.9	9.80	8.74	+1.06	1505.6	18.26	18.96	−0.70
1440.0	8.76	9.50	−0.74	1509.1	20.63	19.68	+0.95
1448.0	9.68	10.35	−0.67	1512.4	18.80	20.29	−1.49
1453.8	11.00	11.04	−0.04	1514.1	21.09	20.62	+0.47
1462.2	10.36	12.10	−1.74	1514.2	21.22	20.65	+0.57
1466.7	16.07	12.64	+3.43	1520.8	22.32	22.11	+0.21
1469.5	14.94	13.07	+1.87	1521.6	21.88	22.27	−0.39
1475.6	16.83	13.92	+2.91	1524.1	21.94	22.80	−0.86
1476.7	13.79	14.05	−0.26	1527.5	24.01	23.60	+0.41
1480.2	14.58	14.58	0.00	1530.8	23.27	24.27	−1.00
1485.8	15.58	15.49	+0.11	1533.3	23.77	24.86	−1.09
1486.8	17.69	15.66	+2.03	1534.1	22.76	25.10	−2.34
1487.9	15.08	15.80	−0.72	1535.0	24.52	25.28	−0.76
1489.1	16.51	16.07	+0.44	1536.7	25.81	25.77	+0.04
1490.4	17.31	16.25	+1.06	1540.1	25.76	26.60	−0.84
1491.8	16.85	16.50	+0.35	1557.8	34.91	31.46	+3.45
1492.0	19.30	16.52	+2.78	1559.5	35.03	32.02	+3.01
1495.5	18.70	17.10	+1.60	1562.0	35.41	32.80	+2.61
1497.9	19.26	17.52	+1.74	1596.2	48.96	45.05	+3.91
1504.2	21.05	18.70	+2.35	1597.0	48.51	45.25	+3.26

The Entropies of the Vapors at 298°K.

According to the calculations of Lewis, Gibson and Latimer[10] the entropy of solid zinc is 9.83 at 298°K. Using the data of Eastman, Williams and Young[11] for the specific heat of solid zinc, we find the entropy of zinc at its melting point 692°K. to be 15.23. The entropy of fusion as given by the concordant data of Wüst and Iitaka is 2.18. If the vapor pressure is represented by an equation of the form $\log p_{\text{mm.}} = -\frac{A}{T} + B \log T + CT + D$, then the entropy of vaporization to a hypothetical pressure of one atmosphere is given by the relation, $\Delta S_v = RB(1 + lnT) + 9.152CT + 4.576D - R\ ln\ 760$. For zinc using Equation 1 we find $\Delta S_v = 25.2$. Finally, we have the term, $-4.97\ ln\ \frac{Tf}{298}$ to correct the entropy of the vapor to 298°K.

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[10] Lewis, Gibson and Latimer, THIS JOURNAL, **44**, 1008 (1922).

[11] Eastman, Williams and Young, *ibid.*, **46**, 1178 (1924).

For lead we have the values $S_{298} = 15.53$ from Lewis, Gibson and Latimer. The data of the various observers for the heat capacity of lead between 298° and the melting point are so discordant that it is impossible to decide on an exact value. We shall take as an average $C_p = 6.70$ which should not lead to serious error.[12] This gives a value at the melting point 600°K. of $S = 20.2$. Again Wüst and Iitaka agree on the entropy of fusion, $\Delta S_f = 1.90$.

Equation 2 can be assumed to give the vapor pressures only in the region 900–1600°K. Between 900°K. and the melting point there is no doubt that the heat capacity of the liquid is greater than that of the vapor. The data of Wüst and Iitaka are so discordant here that we shall be obliged to assume an average value again of $C_p = 6.3$. It now becomes necessary to set up a new vapor-pressure equation for the region 600–900°K. which will merge with the straight line equation at 900°K.

The equation obtained is

$$\log p_{\text{mm.}} = -\frac{10100}{T} - 0.65 \log T + 10.05 \qquad (3)$$

The entropy of vaporization obtained from this equation is 23.2 at the melting point. The entropy of the vapor at 298°K. is then calculated assuming $C_p = 4.97$. The experimental values for the two metals are compared with the values predicted by the Tetrode[13] equation in Table III.

TABLE III

ENTROPY OF VAPOR AT 298°K. AND ONE ATMOSPHERE

	Exptl.	Predicted
Zn	38.4	38.5
Pb	41.8	41.9

The Kinetic Theory of Evaporation

The equation obtained by one of the authors[14] for the relation between vapor pressure and heat of vaporization may be written in the form,

$$p_{\text{mm.}} = 0.131 \frac{d^{2/3}}{M^{1/6}} T \sqrt{\Delta H}\, e^{-\frac{\Delta H}{RT}} \qquad (4)$$

where d is the density and M the atomic weight, the other letters having their usual significance. Table IV shows the experimental and calculated values for the vapor pressure at the melting points of the metals. The agreement is well within the experimental error.

TABLE IV

	ΔH	$P_{mm.}$ obs.	p calcd.	T °K.
Zn	29465	0.138	0.0910	692
Pb	45500	2.6×10^{-9}	6.00×10^{-9}	600

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[12] See Ref. 11, p. 1185.

[13] Tetrode, *Ann. Physik*, **38**, 434 (1912).

[14] Rodebush, THIS JOURNAL, **45**, 606 (1923).

Summary

The vapor pressures of zinc and lead have been determined by a direct method and from the values obtained together with those of other observers, satisfactory vapor-pressure equations have been set up.

The heats of vaporization and the entropy of the vapors have been calculated. The values for the entropies are in satisfactory agreement with the predicted values for the entropies of monatomic vapors.

URBANA, ILLINOIS

NOTES

The Dehydration of Ammonium Nitrate.—In the present note we wish (1) to direct attention to certain experiments of Pelouze which seem, for more than eighty years, to have escaped the attention of writers of textbooks and handbooks of inorganic chemistry, (2) to point out the necessary implications of his facts, (3) to show that they make clear the mechanism of the best known of the several modes of decomposition of ammonium nitrate, namely, of the decomposition into water and nitrous oxide, (4) and lastly to report experiments in which we have heated ammonium nitrate with concd. sulfuric, orthophosphoric, and metaphosphoric acid and have obtained nitrous oxide and nitrogen, the presence of which latter gas may be accounted for by a reaction reported by Pelouze and also not reported in the textbooks. The several reactions show much about the several modes of decomposition of ammonium nitrate.

When ammonium nitrate is heated with a large excess of concd. sulfuric acid, about 85% of all of its nitrogen is given off as nitrous oxide and a large part of the remaining nitrogen is evolved in the elementary state. When ortho- or metaphosphoric acid is used, the yield of nitrous oxide is much less and a large part of the total nitrogen is retained in non-volatile combination.

In 1841 Pelouze[1] reported (*a*) that ammonium nitrate heated with two equivalents of concd. sulfuric acid behaves in the normal manner and yields nitric acid, (*b*) that it gives off nitrous oxide (*protoxyde d'azote*) at about 150° when heated with 50 times its weight of concd. sulfuric acid, (*c*) that with a smaller amount of sulfuric acid it yields less nitrous oxide

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[1] Pelouze, *Ann. chim. phys.*, [3] II, 47 (1841). Abegg's "Handbuch der Anorganischen Chemie," Hirzel, Leipzig, 1907, vol. III, p. 314, cites the article but reports it wrongly to the effect that "beim Erwärmen auf 150° treten als Nebenprodukte N_2 und NO_2 auf." Pelouze also reported the abnormal behavior of ammonium nitrite, that it yields nitrogen when warmed with a large excess of concd. sulfuric acid, a reaction which suggests the existence of *nitroso-amide,* at present unknown. His observations on the conduct of ammonium nitrate with sulfuric acid explain the fact that the Kjeldahl method for the determination of nitrogen is not accurate in the presence of nitrates and in the case of certain nitro compounds.