THE VAPOR TENSIONS OF THE METALS.*

BY

J. W. RICHARDS,

Professor of Metallurgy, Lehigh University.

Secretary of the American Electrochemical Society.

Member of the Institute.

It has been known for centuries that mercury could be boiled under atmospheric pressure, and it has been known for a long time that some other metals are volatile at high temperatures. We can at once state the general conclusion that all metals are volatile, or possess characteristic maximum vapor tensions at any given temperature.

Volatility, or exertion of vapor tension, is generally thought of in connection with liquids, and we speak of their normal boiling points as the temperature at which their vapor can exert 1 atmosphere pressure (760 mm. of mercury column). With many metals this single datum is the only one known; with a few, *e.g.*, mercury, cadmium, zinc, sodium, lead, thallium, bismuth, tin, silver and copper, several or many similar data have been determined, enabling us to plot to a greater or less extent their vapor tension curves.

Solids, however, can exert vapor tension, and the vapor tension of the solid at the melting point is the same as that of the liquid. The two curves, however, are not prolongations of each other; there is a cusp or bend in the curve at the melting point, the vapor tension of the solid being always *less* than the extrapolation of the curve for the liquid below the melting point. This behavior we know to be true of all materials (elements or compounds) whose vapor tensions in the solid and liquid states, below and above their melting points, have been determined, such as sulfur, iodine, bromine, water, and many inorganic and organic compounds.

* Presented at a meeting of the Section of Physics and Chemistry held Tuesday, December 10, 1918.

VAPOR TENSION CURVES.

(A) Vapor Tension Plotted Against Temperature.

This is the simplest and most natural chart to make. It means simply charting the observed maximum vapor tensions against determined temperatures. Figure I, line *A*, shows this for

FIG. I.

mercury. It will be noted that the curve is very flat at low temperatures and very steep at high temperatures. Such curves are difficult to draw, also difficult to interpolate accurately and almost impossible to extrapolate beyond observation points with any degree of probability. They are serviceable only within the limits covered by the experimental data, and even then are not very manageable. They cannot be expressed by any simple or convenient mathematical formula, although numerous attempts have been made to do it.

One valuable general deduction, however, has been made from a study of these curves, by Ramsay and Shields, *viz.*, that a nearly constant numerical relation subsists, for any two given elements or compounds, between the *absolute* temperatures at which they have the same vapor tension. Expressing this in mathematical language, if two substances *A* and *B* have the same tension *p* at *T_A* and *T_B*, and the tension *p'* at *T'_A* and *T'_B*, then

$$\frac{T_A}{T_B} = \frac{T'_A}{T'_B}$$

This relation is not exactly accurate, but approximately so. For instance, if *A* is mercury and *B* water, the value of the ratio is

$$\begin{array}{ll} p = 34.4 \text{ mm. Hg.} & T_A/T_B = 1.63 \\ p = 157.2 \text{ mm. Hg.} & T_A/T_B = 1.66 \\ p = 761. \text{ mm. Hg.} & T_A/T_B = 1.69 \\ p = 2905. \text{ mm. Hg.} & T_A/T_B = 1.74 \end{array}$$

If chemically like substances are compared, however, the rule seems to hold closer. It follows from the above relation, mathematically, that

$$\frac{T_A}{T'_A} = \frac{T_B}{T'_B}$$

which expresses the fact that the ratio of the absolute temperatures at which a given substance has the pressures *p* and *p'* is the same as the ratio of the absolute temperatures at which another substance has the same pressures *p* and *p'*. If the relation first given is true the other must be true, and *vice versa*. Nernst gives such a comparison for five methyl salts, in which the ratio was 1.115 to 1.113, and ten ethyl salts, in which it varied between 1.117 and 1.111. It therefore appears likely that when metals are similarly compared, a like uniformity of ratio may be found, reliable enough to serve as a guide towards a first approximation. Mercury, in fact, gives the ratio 1.117 for the same pressures used comparing the methyl and ethyl salts. We therefore feel considerable confidence in applying the same principle when comparing one metal with another metal.

It will be shown in the next section that the vapor tensions of most of the metals can be fairly accurately represented by the formula

$$\log p = -\frac{A}{T} + B.$$

For a second metal we would have

$$\log p = -\frac{A'}{T} + B'$$

The above discussed relations are accurately true if the two metals have the same values of B , that is, if $B = B'$. If B is not equal to B' , the above relations will not be constant; conversely, if the above discussed relations are constant, then the B 's are all alike. This is strikingly true of the esters discussed by Nernst; it is only approximately true for water and mercury; it is probably nearly true for comparisons of the metals with each other.

(B) *Logarithm of Pressure Plotted Against Temperature.*

The form of the curve showing variation of vapor tension against temperature suggests investigating the variation of the logarithm of pressure against temperature, because of the asymptotic approach of the plain pressure curve towards zero at low temperatures and towards the vertical at high temperatures. In fact, an arithmetical analysis of the pressure curve confirms this by showing practically equal percentage (geometric) increases of the tensions for equal arithmetic increases of temperature. On plotting $\log. p$ for mercury against temperatures, the curve marked B in Fig. 1 is obtained. This is a slightly convex curve, with nearly equal curvature throughout, and therefore much better adapted for interpolation and extrapolation. These curves were used for some time, for plotting the vapor tensions of the metals, until a still more satisfactory relation was found.

(C) *Logarithm of Pressure Plotted Against Reciprocal of Temperature.*

A further study of the subject of pressures of liquids other than metals showed that when the logarithms of pressures were plotted against the reciprocals of the absolute temperatures, curves were obtained, with but slight curvature, approximating straight lines (see Curve C, Fig. 1). This is true of all such liquids and solids whose vapor tensions have been accurately determined. The curves are not straight lines, but only approximately so. A straight line relation would require $\log. p. = -\frac{A}{T} + B$ and this does not accurately fit the tabulated values; but the formula of

Nernst ($\log. p = \frac{A}{T} + 1.75 \log. T - CT + D$), with three constants instead of two, correlates the observed pressures and temperatures satisfactorily.

The vapor tension data for the metals, with the single exception of mercury, are not accurately known, and we may say of these experimental data that the formula $\log. p = -\frac{A}{T} + B$ (wherein A and B are constants, and T the absolute temperature) fits them in general within the experimental errors of the determinations. In short, while a Nernst formula with three constants may be constructed for mercury, the simpler straight line formula is all that we are justified in constructing for the other metals. This simplifies very much the discussion of the vapor tensions of the metals, and enables us to make generalizations from very scanty data.

DISCUSSION OF THE STRAIGHT-LINE EQUATION.

Plotting as accurately as we can the logarithms of the known vapor tensions of the metals against the reciprocals of the absolute temperatures, we obtain practically straight lines in all cases, within the experimental errors, as shown for iodine, mercury and zinc in Fig. 2. The right hand vertical line, representing $\frac{1}{T} = 0$, really stands for infinite temperature, while absolute zero, $T = 0$, would lie at an infinite distance to the left. In all cases, the vapor tension line, if prolonged beyond the observations, is seen to cut the right hand vertical, $T = \infty$, at a finite distance, which represents the value B in the straight-line equation. This, if exactly true, would indicate an absolute maximum pressure ($\log. p_{max} = B$), which the substance could not exceed even with $T = \infty$. This is an interesting speculation, pointing to the conception of an absolute maximum of vapor pressure, the antithesis of the absolute zero of temperature.

Another interesting generalization is that for the different metals the values of B appear to be approximately alike. Where we have sufficient data to draw the line (at least two observations of tensions at two different temperatures) the indicated values of B appear to be as follows:

Sodium	6.85
Copper	8.75
Zinc	8.17

Arsenic	8.65
Selenium	8.10
Silver	7.90
Cadmium	8.74
Mercury	7.73
Lead	8.00
Bismuth	7.45
<hr/>	
Average	8.03

FIG. 2.

According to this observation, we may as a first approximation to a vapor tension curve write

$$\log. p = -\frac{A}{T} + 8.00$$

and if we have only one determination of vapor tension, at some temperature, we can determine A . If we have T for $p = 760$ mm. (1 atmosphere), as is often the case, then $A = 5.22 T$. This is

frankly an approximate formula, since B is not properly a definite constant, but it is quite satisfactory to get a working formula which is approximately true, when only one value for the vapor tension is known.

The thermodynamics of this straight-line formula is interesting. The Clapeyron-Clausius equation gives the relation

$$L = RT^2 \frac{dp}{dT}$$

where L is the molecular latent heat of vaporization, T the absolute temperature, and R the gas constant, in calories.

Differentiating the straight-line equation for p and t we have

$$\frac{dp}{dT} = \frac{A}{mT^2}$$

where m is the modulus of the ordinary system of logarithms (0.4243).

Combining these, we have

$$\begin{aligned} L &= \frac{R}{m} A \\ &= 4.57 A \end{aligned}$$

It follows, that A furnishes us with the latent heat of vaporization, and that the straight-line equation makes this quantity a constant, at all temperatures. This is not a fact of nature, since we know that the latent heat of vaporization changes with the temperature, because of the difference of specific heats of the gaseous and liquid material, that it increases slowly going towards low pressures, and decreases fast at high pressures, becoming zero at the critical point. The straight line is therefore only a sector of a curve, drawn through two points of a curve which is convex towards the axis T , and which gives the average value of the latent heat of vaporization ($4.57A$), for the temperature range between the points which have been used to determine the equation.

Since, however, the straight line does fit quite satisfactorily most of the actual determinations of vapor tensions of the metals which have been made, it follows that at these comparatively low pressures, far removed from the critical temperature, the latent heat of vaporization does not vary very much, is approximately constant, and can be derived from the vapor tension equation.

TROUTON'S RULE.

Trouton found that the molecular latent heat of vaporization at normal atmospheric pressure was a function of the absolute temperature of the normal boiling point. Numerically it averages $23\ T$. Nernst maintains that the 23 is not a constant, but varies somewhat with the temperature, being as low as 15 for substances boiling at very low temperatures and as high as 29 for those boiling at very high temperatures. It seems to be true, however, that for many substances boiling between 0°C. and 500°C. , the constant is between 20 and 25 , and averages 23 . Substituting normal atmospheric pressure in the straight-line equation, and $23\ T$ for $4.57\ A$, we would find that B was fixed, since

$$B = \log. p + \frac{A}{T} = 2.88 + \frac{23\ T}{4.57\ T} = 7.90$$

This is in pretty good agreement with the average value of B , 8.03 , derived directly from the actual straight-line equation for ten different metals, on a previous page, using the experimental values. If we assume $B = 8.03$, and work the equation backwards, Trouton's constant would figure out 23.85 . I have concluded to use the values 23 and 7.90 for low boiling-point metals ($500^\circ\text{--}1500^\circ\text{C.}$), and 25 and 8.4 for high boiling-point metals (over 1500°C.).

RICHARDS' RULE.

A rule similar to Trouton's was discovered by the writer concerning the latent heat of fusion, *viz.*, the molecular latent heat of fusion is approximately $2.1\ T$, where T is the absolute melting point. This observation is useful in deriving the straight-line relation for the sublimation of a solid metal below its melting point.

$$\log. p = \frac{A'}{T} + B'$$

In this equation, $4.57\ A'$ is the latent heat of sublimation, and a study of the rather scanty data on the vapor tension of solid substances shows that such an equation fits satisfactorily the experimental data. Fig. 3 shows this for ice, iodine and arsenic.

Since the latent heat of sublimation equals the sum of the latent heat of vaporization of the liquid and the latent heat of fusion, then

$$4.57 A' = 4.57 A + L_{\text{fusion}}$$

$$A' = A + \frac{L_{\text{fusion}}}{4.57}$$

If the latent heat of fusion of a metal is known, we express

FIG. 3.

it per molecular (= atomic) weight, divide by 4.57 and add the quotient to A to get A' .

Since at the melting point the vapor tensions of the solid and the liquid are alike, if we substitute $T_{m.p.}$ in the two equations under consideration, we have

$$\log. p_{m.p.} = -\frac{A'}{T_{m.p.}} + B' = -\frac{A}{T_{m.p.}} + B$$

Whence

$$B' = \frac{A' - A}{T_{m.p.}} + B$$

$$= B + \frac{L_{\text{fusion}}}{4.57 T_{m.p.}}$$

If the latent heat of fusion is known, B' can thus be calculated, and we have the complete vapor tension line for the solid state.

If the latent heat of fusion is not known, we may put it, as a first approximation, as equal to 2.1 $T_{m.p.}$. We then have

$$A' = A + \frac{2.1 T_{m.p.}}{4.57} = A + 0.46 T_{m.p.}$$

$$B' = B + \frac{2.1 T_{m.p.}}{4.57 T_{m.p.}} = B + 0.46$$

Richards' rule would therefore enable us to pass from the vapor tension equation for the liquid state to that for the solid state, and *vice versa*, if merely the melting point is known, without knowing experimentally the latent heat of fusion. In a few cases, *e.g.*, arsenic, both equations can be determined from experimental data. Taking these empirical equations for arsenic, we have

$$\begin{aligned} A' - A &= 5610 - 5115 = 495 = 0.45 T_{m.p.} \\ B' - B &= 9.10 - 8.65 = 0.45 \end{aligned}$$

which is a striking confirmation of the approximate accuracy of the $0.46 T_{m.p.}$ and 0.46 deduced by applying Richards' rule.

It results, therefore, from the above discussions, that given two determinations of vapor tension and temperature, we can determine a straight-line relation between them; if this is for the liquid state we can pass over to the similar equation for the solid state if we know the melting point and latent heat of fusion, and *vice versa*. If we have only one such determination, in either the liquid or solid state, we can assume B or B' , and then work out A or A' and thence the whole of both equations. If we do not know the latent heat of fusion, it may be assumed as equal to $2.1 T_{m.p.}$, and then the complete scheme worked out. Finally, if we do not have a single vapor tension determination, but know the latent heat of vaporization (of the liquid) or the latent heat of sublimation (of the solid) we could work out a first approximation to the vapor tension equation for the liquid or the solid state; if we know the melting point, we can pass from one to the calculation of the other.

Table I gives the vapor tensions of the metals, and a few non-metals, as far as their straight-line equations can be determined, either from the experimental data, or by assumption of values of the constant B . These data are in many cases only first approximations, but they are also, in not a few cases, the first attempts to get an idea of the order of magnitude of these vapor tensions, and therefore deserve some serious consideration even if they cannot be considered as accurate.

Table II gives several estimated and a few observed values of the latent heats of vaporization of some elements, mostly metals. Since the experimental values are mostly lacking for the metals, the calculated, or estimated values, using Trouton's rule, are of considerable value as first approximations, even though we know they cannot be strictly accurate.

THE TRUE VAPOR TENSION CURVE.

From the experimental data regarding the vapor pressures of the metals we are not justified in deducing formulas of more than two terms—the straight-line formulas already discussed (with the single exception of mercury, whose vapor tension has been minutely studied)—yet for mercury and some non-metals, whose vapor tensions are more accurately known, the true vapor tension curve, as developed by Nernst, may be constructed.

It is therefore *apropos* to state this true curve, in order that it may be used for mercury and for any other metal for which the experimental data are sufficiently accurate.

The more accurate relationship is

$$\log. p = -\frac{A}{T} + 1.75 \log. T - C T + D$$

The three constants of this equation A , C and D are not the same as A and B of the straight-line formula above discussed, but $4.57 A$ of this equation represents the latent heat of vaporization of the substance for $T = 0$; a wholly theoretical quantity.

The formula requires for its determination only three observations of vapor tensions at three different temperatures. They must be accurate enough to fix the form of the curve and the three constants.

The differentiation of this formula for dp , and substitution of this in the Clausius expression for L , the latent heat of vaporization, gives

$$L = 4.57 [A + 0.743 T - C T^2]$$

This formula is true only for moderate pressures, far removed from the critical temperature, where the volume of the liquid is negligible in comparison with the volume of the gas which it forms. At high pressures, where the volume (and density) of the vapor approximates the volume (and density) of the liquid, the formula is not accurate for two reasons: (1) The density of

TABLE I.

Vapor Tensions of the Metals.

*In the Solid and Liquid States, at Their Melting Points, and at 0° C. p = mm. Hg.,
 T = Degrees Absolute = °K.*

	Solid		At 0° C. mm. Hg.	At M. P. mm. Hg.	Liquid	
	$\log. p = -\frac{A'}{T} + B'$				$\log. p = -\frac{A}{T} + B$	
	A'	B'			A	B
H ₂					51.5	5.4
Br ₂			66	45	1635	7.8
I ₃	3458	10.43	2×10^{-2}	89	2390	8.1
P ₃	2260	7.34	0.115	1.63	2160	7.0
Hg.....	3170	8.26	0.0002	5.13×10^{-6}	3069	7.75
S ₈	4140	9.15	1×10^{-6}	0.028	3745	8.1
As ₃	5610	9.10	2.8×10^{-21}	10,000	5115	8.65
Se ₃	5250	8.56	2.1×10^{-11}	0.71	5025	8.1
Cs.....	4900	8.35	2.5×10^{-10}	1.2×10^{-8}	4760	7.92
K.....	5300	8.26	7.1×10^{-12}	2.25×10^{-8}	5190	7.92
Rb.....	5040	8.28	6.7×10^{-11}	1.5×10^{-8}	4890	7.90
Cd.....	6470	9.28	3.8×10^{-15}	2.6×10^{-2}	6151	8.74
Na.....	4700	7.30	8.1×10^{-9}	3.55×10^{-6}	4565	6.85
Zn.....	6685	8.63	1.03×10^{-16}	9.3×10^{-2}	6365	8.17
Mg.....	8060	8.81	5.25×10^{-20}	1.15	7690	8.4
Te ₂	10,230	9.84	8.1×10^{-32}	6.3×10^{-5}	9180	8.4
Bi.....	10,000	8.45	6.6×10^{-29}	$1. \times 10^{-10}$	9460	7.45
Sb ₃	10,850	9.58	6.5×10^{-31}	3.55×10^{-3}	9790	8.4
Tl.....	10,260	8.5	8.3×10^{-30}	4.7×10^{-10}	9940	7.92
Li.....	8900	8.38	$6. \times 10^{-25}$	4.9×10^{-12}	8690	7.92
Pb.....	9744	8.41	4.9×10^{-28}	1.5×10^{-8}	9500	8.0
Mn.....	12,650	8.85	3.2×10^{-38}	1.98	11,195	8.4
Ag.....	12,180	8.36	5.6×10^{-37}	3.2×10^{-2}	11,600	7.9
Ni.....	14,245	8.90	5.25×10^{-44}	4.36	13,375	8.4
Al.....	14,190	8.98	1.0×10^{-43}	5.25×10^{-7}	13,650	8.4
Si ₂	15,530	9.0	8.0×10^{-47}	1.32	14,200	8.4
Cr.....	14,460	8.86	7.8×10^{-45}	4.47	13,650	8.4
Sn.....	14,420	9.1	5.6×10^{-44}	6.3×10^{-20}	13,930	8.4
Cu.....	15,765	9.17	2.6×10^{-49}	3.5×10^{-3}	15,160	8.75
Fe.....	15,840	8.84	6.9×10^{-50}	1.20	15,030	8.4
Pt.....	16,250	9.0	3.0×10^{-51}	9.55	15,040	8.4
Ti.....	16,090	8.85	8.3×10^{-49}	11.75	15,170	8.4
Rh.....	16,500	8.94	3.2×10^{-52}	38	15,300	8.4
Ru.....	16,450	8.86	4.0×10^{-52}	28.8	15,420	8.4
Au.....	16,175	8.93	4.8×10^{-51}	6.8×10^{-4}	15,470	8.4
Pd.....	16,340	8.85	1.4×10^{-60}	0.78	15,500	8.4
Ir.....	16,670	8.81	5.6×10^{-53}	302	15,580	8.4
Os.....	16,880	8.81	9.6×10^{-54}	97.7	15,870	8.4
U.....	17,975	8.85	1.0×10^{-57}	5.5×10^{-6}	17,400	8.4
Mo.....	22,650	8.85	7.6×10^{-75}	4.9	21,380	8.4
B ₂	21,230	8.36	3.9×10^{-70}	5.0	19,950	7.92
C ₂	24,300	9.0	1.0×10^{-80}	6,310	22,195	8.5
W.....	31,670	8.86	7.4×10^{-108}	1.3	30,000	8.4

TABLE II.
Latent Heats of Vaporization.

	B. P.		Trouton's Rule 23 T (Molecular)	Calc. by Trouton's Rule (per Kg.)	Observed (per Kg.)	Calc. from Vapor Tension Curve (per Kg.)
	C.°	K.°				
H ₂	—253	20	460	230		118
N ₂	—196	77	1771	63	50	54
O ₂	—188	85	1955	61	58	52
Cl ₂	—22	251	5773	81	67	72
Br ₂	58	331	7613	48	46	
I ₃	174	447	10,280	27	24	
P ₃	287	560	12,880	138	130	
Hg.....	357	630	14,490	72	68	67
S ₈	444	717	16,390	64	72	
As ₃	450	723	16,625	74		
As ₃	616	889	[22,225]	99		114
Se ₃	690	963	22,150	94		97
K.....	757	1030	23,690	607		
Cd.....	778	1051	24,170	216	181?	251
Na.....	877	1150	26,450	1150		905
Zn.....	930	1203	27,670	426	366?	446
Mg.....	1120	1393	32,040	1335	1700?	1443
Te ₂	1390	1663	38,250	151		166
Bi.....	1435	1708	39,280	189	162?	208
Sb ₃	1500	1773	41,480	115		124
Tl.....	1700	1973	45,380	222		
Li.....	1450	1723	39,630	5,660		
Pb.....	1580	1853	41,820	202		209
Mn.....	1900	2173	49,980	909		995
Ag.....	2040	2313	53,200	493		490
Ni.....	2150	2423	55,730	953		1042
Al.....	2200	2473	56,880	2107		2305
Si ₂	2200	2473	56,880	1015	1262	1153
Cr.....	2200	2473	56,880	1094		1197
Sn.....	2250	2523	58,030	492		538
Cu.....	2310	2583	59,410*	934		1087
Fe.....	2450	2723	62,630	1118		1224
Pt.....	2450	2723	62,630	318		351
Ti.....	2475	2748	63,200	1317		1431
Rh.....	2500	2773	63,780	619		677
Ru.....	2515	2788	64,120	629		689
Au.....	2530	2803	64,470	327		358
Pd.....	2535	2808	64,580	606		667
Ir.....	2545	2818	64,810	336		368
Os.....	2600	2873	66,080	346		379
U.....	2900	3173	72,980	305		333
Mo.....	3600	3873	89,780	935		1015
B ₂	3700	3973	91,380	4155		
C ₂	3700	3973	99,325	4140		
W.....	5200	5473	125,880	684		

the gas no longer obeys Boyle's law; (2) the density of the liquid increases because of the great pressure. The formula is very applicable, however, to all ordinary temperatures and pressures. Worked out for mercury, at 760 mm. pressure, it gives 66.8 calories per gram, whereas experiment shows 67.8 cal.; for 0° C. it gives 77.1 cal.

PRACTICAL APPLICATIONS.

Distillation of Metals.—Some metals are obtained entirely by distillation from their ores, escaping from the reduction furnaces entirely as vapor. Such is the case with mercury, cadmium and zinc. In these cases, the useful work performed by the furnace is not entirely known until the heat in the vapor of the metals is known. For mercury this item is not large, but it is considerable for cadmium and still greater for zinc. In fact, for zinc it forms a material part, some 25 per cent., of the total thermal work done in the furnace. It is only recently that the latent heat of vaporization of zinc has been experimentally determined; up to that time we could use only the value derived from the vapor tension curve or by use of Trouton's rule. In electric furnaces large quantities of high boiling-point metals are volatilized, and thus consume a large proportion of the expensive electric power required to run them; a silicon furnace is a good example of this, where as much as 25 per cent. of the reduced silicon may be vaporized out of the furnace. We can get a first approximation to these losses of power by studying the vapor pressures of these metals and thus their latent heats of vaporization.

According to the principle of partial pressures of the constituent gases in mixtures, the metallic vapors may be at small fractions of atmospheric pressure when mixed with other inert gases. The problem of condensing these vapors is then complicated by the fact that they do not commence to condense at their normal boiling points, but only at much lower temperatures corresponding to their partial pressures in the gas mixture. This dew point, as it may be properly called (since the principle involved is exactly similar to the deposition of water as condensed moisture, or dew, from moist air) is often at unexpectedly low temperatures, and the more dilute the gas mixture the lower the condensing temperature. Gases from the mercury furnace are sometimes only 1 per cent. mercury vapor, and their dew point may be 150° to 200° C. instead of 357°, the condensing point of pure

mercury vapor. The whole phenomena of condensation of metallic vapors, including the heat liberated in the condensation as well as the per cent. of the metallic vapor condensed, depend for their study and investigation on the correct use of vapor tension data.

When zinc-lead-silver-gold skums from the Parkes process are distilled, the first zinc coming off is nearly pure, but as the zinc present in the alloy decreases a higher and higher temperature is required to drive it off, at atmospheric pressure, until the last part of the zinc comes off only at the maximum temperature of the furnace, some 1300° C. Successively larger amounts of lead, silver and gold come over the higher the temperature and the lower the proportion of zinc in the alloy. All these phenomena are governed by the vapor tensions of the respective metals, and the principle that they exert fractions of their maximum tensions proportional to the relative *molecular* proportions of each present in the alloy. Interesting and practically valuable calculations can thus be made. The temperature necessary to reach in order to attain any given purity of the residual alloy or metal can be thus calculated, as also the composition of the condensed vapors. The composition of the condensate is very different from that of the residuum; the former approximates to equal molecular weights (atomic weights) of the metals present; the latter to one single metal (the least volatile), almost pure, with decreasing amounts of the impurities according to their greater volatilities.

Zinc Losses in Brass Melting.—Considerable zinc is lost in making and melting brass. The normal boiling point of zinc is 930° C., yet brass is usually made and cast at 1000° to 1200° C. We are spared the loss of all the zinc by two facts: (1) The molecular (atomic) proportion of the zinc present is 15 to 30 per cent., which means that at any given temperature the zinc in this alloy can exert only 15 to 30 per cent. of the maximum vapor tension of pure zinc at that temperature; (2) the copper and zinc unite with some energy, and the energy of that combination also retards the volatilization of the zinc and lowers still more its vapor pressure. Owing to these two circumstances, the vapor tension of zinc from brass is usually less than atmospheric tension at operating temperatures, and therefore the losses are not excessive.

If the vapor tension of pure zinc is

$$\log. p = - \frac{6365}{T} + 8.17$$

then if the atomic fraction of zinc present in the alloy is f , the vapor tension relation becomes

$$\log. p + \log. f = -\frac{6375}{T} + 8.17$$

Further, if the zinc atom unites with copper with evolution of the energy Q ($Cu_x, Zn=Q$), this energy must be added to the work done in the vaporization of the zinc, and we have

$$\log. p + \log. f = -\frac{6365 + Q/4.57}{T} + 8.17$$

as the complete expression for the vapor tension of zinc from brass.

This equation, if Q were known for different grades of brass, would be of considerable use in the scientific development of the brass industry (Fig. 4).

FIG. 4.

Loss of Metals as Fume.—This subject is of great importance with metals of high value, such as silver, gold and platinum, where comparatively small losses in weight represent large losses

in value. Even in such a simple operation as melting silver, if the heating is done by a flame coming in contact with the metal, the vaporization losses even from the *solid* metal, before it melts, may be considerable. This is a phenomenon strictly analogous to the vaporization (sublimation) of ice in a current of dry air at temperatures below the freezing point. To estimate its amount, we must know the vapor tension of solid silver below its melting point. While melting, and at higher temperatures, considerably more silver is volatilized, and the vapor tension curve enables us to calculate the amounts for different temperatures of the gases in contact with it.

One firm, using the tabulated vapor tensions, and measuring carefully the temperatures and amounts of the gases going through its furnaces, calculated that it was vaporizing about \$30,000 worth of silver per year. On the strength of this calculation they put in a Cottrell electrostatic precipitation plant (costing \$25,000), and in the first year of its operation collected just \$30,000 worth of silver from the fume.

Sherardizing and Calorizing.—These are processes which coat iron or other metals with zinc or aluminum respectively, by heating the iron objects to a moderate temperature, below the respective melting points of zinc and aluminum, until their surface has absorbed the desired amount of coating.

Sherardizing was invented first, and has already come into large use as a competitor of ordinary galvanizing. The zinc soaks into the surface of the iron like ink into blotting paper, adding to the weight of the object but not to its external dimensions, and leaving perfectly sharp and unchanged screw threads or other superficial characteristics. The whole operation depends on the formation of zinc vapor from the solid zinc dust and its absorption by the iron. The vapor tension curve of solid zinc, at the temperatures used, gives a quantitative explanation of the rate of absorption with change of temperature, and therefore serves as a practical guide in studying and operating the process.

Calorizing is operated at still lower metallic vapor pressures, because of the high normal boiling point of aluminum, yet while about 0.1 mm. (Hg) pressure of zinc vapor effects Sherardizing, not over 0.000001 mm. (Hg) of aluminum vapor effects calorizing.

A study of the vapor tensions of metals at their melting points

will show which are best able to act like zinc and aluminum in a similar manner, for metal plating purposes.

Vapor Losses During Electrolysis.—We will consider finally the question of losses of metal at the cathode during electrolysis of melted salts, using melted metal as cathode. The production of aluminum is a good example. Here, the ampere efficiency of metal obtained is 75 to 90 per cent. of the metal actually deposited; the loss is due to the phenomenon of metallic mist or fog or vapor, called *metallische Schleier* by Lorenz, of Zurich, who investigated it most fully.

There seems to be strong evidence for believing that these large percentage losses are connected directly with the vapor tension of the molten metal. Lorenz was handicapped in his discussion by very inadequate data as to the vapor tensions of these metals at the temperatures in question, which are not far above their melting points.

We may indulge the hope that the approximate values of the vapor tensions deduced by us may be of use also in this field, in helping to a better understanding of these losses and possibly in helping to reduce or to obviate them.

"Vest-pocket" Camera for Commercial Photography. ANON. (*British Journal of Photography*, vol. lxvi, No. 3070, p. 109, March 7, 1919.)—There are occasions when a high-grade small camera, far from being a toy, may be of very real service to the photographer placed in exceptional circumstances. The fact that these instruments are fitted with lenses of short focus and wide aperture, and thus give good definition over many varied planes of distance without recourse to stopping down may often be of real service. A case in illustration of this point was told some time ago by a commercial worker. He was commissioned to make a series of pictures of certain pieces of machinery in a factory which was rather poorly lighted. As the work would have necessitated the use of a lens well stopped down in order to gain the required definition, and as the stoppage of the machinery was an important factor, the operator took with him a vest-pocket camera. This he found gave all the definition required, and fine definition without stopping down the lens. The result was that the pictures were taken in a very short time, as the worker was enabled to use the lens working at $f/6$ instead of one stopped down to $f/22$. Enlarged prints were made that gave the customer entire satisfaction.