attendant will be necessary to see that the solution is not too acid or too alkaline after precipitation.

The further drying of the precipitates preliminary to the distillation of the sulfur must be effected by steam coils or by a special type of drying furnace in which there would be no danger of overheating, with attendant loss of sulfur.

In the distillation operations, it was found that the sulfur began to distil rapidly at 180° C. and from that temperature up to 450° C., the boiling point of sulfur, the rate of distillation would depend upon the rapidity with which the vapors were removed from the retort as well as the temperature.

In all cases, whether the precipitate consisted of $2BaS_2O_3 + S$ or whether a considerable proportion of the precipitate $2BaSO_3 + 3S$ was also present, the sulfur was completely distilled at 450° C. The distilled and condensed sulfur was practically pure. The residual product from the distillation was barium sulfite and sulfate.

In the reduction of the barium sulfite or sulfate, by mixing the residue with carbon, coke or coal and heating to a temperature between 750 and 1200° C., there was some tendency for the formation of small amounts of the oxides and carbonates of barium. When the reduced material was used as a precipitate these reacted very slowly with the SO_2 in the dilute solutions from the absorption towers. Therefore, they became "inert" substance, diluting the active BaS, and increasing in amount in each cycle of operations.

If the reduction was effected in a direct fired furnace where the products of combustion passed over the material, the proportion of these inert compounds was greater than if the reduction was brought about by carbon of high purity, quickly, at a high temperature, and in a furnace externally heated.

The use of a coal containing a high percentage of ash also adds "inert" substances to the reduced material in each cycle, and therefore as pure carbon as possible is desirable as reducing agent.

The oxide or carbonate can be connected to the sulfite by agitation with a strong sulfur dioxide solution, or to the sulfate by treatment with sulfuric acid. When reductions are effected in a direct fired furnace, probably 10 per cent of the material would have to be treated with strong sulfur dioxide solution or sulfuric acid in each cycle to keep the barium as sulfite in sulfate to be reduced again to the sulfide.

If coal, high in ash, is used as reducing agent, and the amount of insoluble matter increases to a certain amount, it will be necessary to leach the entire amount of reduced material, getting the BaS into reduction and discarding the insoluble material.

With the addition of these supplementary operations, it is believed that the technical operation of the process can be carried out successfully for the recovery of sulfur from sulfur dioxide in waste smelter gases. The indications are that, at least in some localities, the process can be applied on a commercial scale which will allow the production of sulfur at a cost of about $12 per ton.
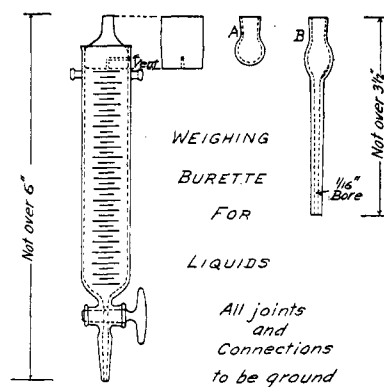

WEIGHING BURETTE FOR LIQUIDS

By W. Ed. Burkhard
Received July 9, 1917

The weighing burette illustrated below has been found very valuable.

The capacity which determines the diameter of the burette is governed by the material to be analyzed.

WEIGHING BURETTE FOR LIQUIDS
All joints and Connections to be ground

The cup *A* is used to prevent fuming while weighing, etc. *B* is made preferably for oleum or other material that would cause spattering. In case of "oleum over 20 per cent" the water into which the acid is to be run has a layer of neutral fine Glauber's salt crystals. By keeping the tip of *B* in the crystals all spattering is avoided. The attachment is left in the solution while titrating.

General Chemical Company
Bayonne Works, Bayonne, N. J.

ADDRESSES

THE VAPOR PRESSURE AND VOLATILITY OF SEVERAL HIGH-BOILING METALS—A REVIEW[1]

By John Johnston
Received July 19, 1917

The question as to the vapor pressure of a metal at a given temperature—or its boiling point at a particular pressure—often arises, as a knowledge of this property is valuable in connection with a number of problems. But the somewhat scanty data to be found in the literature refer, for any one metal, to a small

[1] Presented at the Symposium on the Chemistry and Metallurgy of Zinc, 54th Meeting American Chemical Society, Kansas City, April 10 to 14, 1917.

number of pressures, and in many cases, to a single vapor pressure only—that of one atmosphere; therefore in order to ascertain the vapor pressure at any particular temperature one must in general plot the curve and extrapolate. This procedure takes time and trouble and is moreover not feasible when only one point on the curve has been determined by experiment; more can be learned, as we shall see, by plotting at one time the available data for all the metals hitherto investigated, for by so doing we can set up equations which enable us to calculate the vapor pressure at any temperature with as much certainty as is inherent in the experimental results. On account of the greatly increased availability and usefulness of the data as

rearranged in this way, in comparison with their present form, it seemed worth while to publish a brief note on the matter. More accurate experimental data than we now possess would be highly desirable; but the figures presented in the table, which at least give the order of magnitude of the vapor pressure at the several temperatures, will suffice for many purposes.

Search of the literature has revealed very few investigators who have made direct observations of the vapor pressure of metals of high boiling point. The earliest of these is Barus,[1] who worked with zinc, cadmium and bismuth (as well as some other substances). He heated the metal in a closed crucible provided with a connection to a vacuum pump and with a reëntrant tube in which the thermoelement to measure the temperature was placed; his criterion of boiling was that the temperature observed should vary with variations in pressure. Barus realized clearly that his results leave something to be desired, and considered that his boiling temperature would tend to be too high, particularly at the lower pressures. His original data follow:

TABLE I—BOILING POINTS OF ZINC, CADMIUM AND BISMUTH AS GIVEN BY BARUS; PRESSURE IN MM., TEMPERATURE IN DEGREES CENTIGRADE

ZINC		CADMIUM			BISMUTH*
p t	p t	p t	p t	p t	p t
10 582	42 710	26 675	22 549	63 606 ·	32 1199
40 710	35 699	67 731	25 552	84 622	32 1206
65 732	28 684	158 792	26 565	226 686	37 1222
96 757	62 736	264 833	32 574	274 704	42 1215
101 772	99 758	375 864	75 620	342 722	39 1213
156 785	166 802	473 884	105 639	510 752	34 1204
271 837	264 838	570 904	157 667	563 760	34 1207
345 857	368 863	654 916	189 681	636 770	40 1217
425 873	477 884	771 933	262 702	656 772	34 1206
535 897	557 900	... ...	292 706	755 785	39 1221
764 933	653 914	... ...	355 724	... ...	.. ..
... ...	773 925	... ...	381 729	... ...	
... ...	... ...	... ...	489 745	... ...	33 1215
... ...	... ...	... ...	517 750	... ...	
... ...	... ...	... ...	624 760	... ...	42 1233
... ...	... ...	... ...	644 766	... ...	.. ..
... ...	... ...	... ...	656 766	... ...	.. ..
... ...	... ...	... ...	756 772	... ...	... ...

*The values for pressures of about 90 mm. given in the original have been omitted because Barus considered that these values were lower than the corresponding boiling points.

Berthelot[2] made a series of determinations of the boiling point at atmospheric pressure of zinc and cadmium by a method similar to that used by Barus; the individual determinations differ by several degrees, the mean result being 920° for zinc and 778° for cadmium. The method followed by Féry[3] was such that accurate results could hardly be expected; he gives 1040° for the boiling point of zinc and 2100° for that of copper.

The procedure adopted by Greenwood[4] is in principle the same as that followed by Barus. The metal was confined in a long graphite crucible, lined where necessary with pure magnesia; the temperature was taken as that of the wall of the crucible, as measured on an optical pyrometer.

"The measurements of the boiling points were carried out by slowly raising the temperature of the crucible and observing the surface of the metal from above through an absorbing glass. At first the surface of the molten metal remains perfectly still, but as the boiling point is approached a slight agitation of the surface is observed which soon becomes vigorous. In the case of the metals studied, the difference between the temperature indicated when a gentle agitation is first apparent and that at which the ebullition has become so violent that globules of metal are being ejected from the top of the tall crucible does not exceed 100°. By taking the boiling point as the temperature at which ebullition becomes decided, quite concordant results were obtained in different experiments............From a study of a large number of metals in this manner, it appears probable that the temperature at which the vaporization becomes sufficiently rapid to cause a decided projection of drops

from the surface may be taken with fair approximation as the boiling point."

A current of gas, either hydrogen or nitrogen, was passed through the apparatus; when nitrogen was employed, the temperature readings, though concordant in similar experiments, were always considerably higher (50 to 100°) than those obtained in a hydrogen atmosphere. Greenwood attributes this effect to the ease with which hydrogen permeates the crucible walls, removing and diluting the column of heavy vapor; but considers "that the values observed in hydrogen approximate more closely to the boiling points of the metals at atmospheric pressure."

In a later paper Greenwood[1] describes similar experiments at pressures less than one atmosphere. At these low pressures, there were no noteworthy differences between the results obtained in hydrogen and in nitrogen; ebullition was quite sharply defined (in general more clearly than at atmospheric pressure) and the results of individual experiments showed a very satisfactory concordance. He also made a few observations, following

TABLE II—GREENWOOD'S RESULTS ON THE BOILING POINTS OF METALS; PRESSURE IN ATMOSPHERES, TEMPERATURE CENTIGRADE

METAL	p	t	METAL	p	t	METAL	p	t
Zinc..........	6.3	1120	Lead.....	0.14	1320	Chromium	1	2200
	11.7	1230		0.35	1420	Tin.......	0.13	1970
	21.5	1280		1.0	1525		0.35	2100
	53	1510		6.3	1870		1.0	2270
Magnesium...	1	1120		11.7	2100	Copper....	0.13	1980
Bismuth......	0.13	1200	Aluminum	1	1800		0.34	2180
	0.34	1310					1.0	2310
	1.0	1420	Manganese	1	1900			
	6.3	1740						
	11.7	1950	Silver.....	0.14	1660	Nickel.....	1	2400
	16.5	2060		0.35	1780			
Antimony.....	1	1440		1.0	1955	Iron.......	1	2450

essentially the same procedure, at higher pressures where the boiling temperatures were low enough to admit of this. Greenwood's original data, most of which represent the mean of several observations, are brought together in Table II.

Heycock and Lamplough[2] record the following observations, but give no description of the procedure adopted:

BOILING POINT	Cadmium	Zinc
At 1 atmosphere pressure....................	765.9	905.7° C.
Change per mm. at 760 mm................	0.12	0.133° C.

The vapor pressure of arsenic has been determined recently by Gibson[3] and by Preuner and Brockmöller[4] by direct measurement by means of a quartz manometer constructed on the principle of the Bourdon gauge; their results, which agree satisfactorily, are given in Table III.

TABLE III—EXPERIMENTAL DATA ON THE VAPOR PRESSURE OF ARSENIC; PRESSURE IN MM., CENTIGRADE TEMPERATURE

GIBSON		PREUNER AND BROCKMÖLLER	
p	t	p	t
...	....	6................	.400
...	....	19................	.450
26.0	............469.4	28................	.470
31.6	............476.3	32................	.476
50.9	............488.3	42................	.488
67.4	............499.9	61................	.500
96.2	............512.3	90............	.512
131.6	............526.4	130................	.526
269.9	............557.4	268................	.557
334.1	............568.9	334................	.569
...	....	430................	.580
...	....	586................	.600

Von Wartenberg[5] has published observations, made by the dynamic method, on the vapor pressure of high-boiling metals at temperatures at which the vapor pressure of the metal is very small. The essential feature of this method is to pass a measured volume of gas over the metal, kept at the desired temperature, and determine the loss of weight of the metal. From these observations the vapor pressure at that temperature can readily be calculated on the basis that the actual partial

1 C. Barus, Bull. U. S. Geological Survey, 103, 1893; Phil. Mag., 29 (1890), 141.

2 D. Berthelot, Compt. rend., 131 (1900), 380. He also refers to several earlier determinations of these two boiling points, but these have now only historical interest.

3 Ann. chim. phys., [7] 28 (1903), 428. He also gives results for a brass containing 63 Cu : 37 Zn.

4 "An Approximate Determination of the Boiling Points of Metals," Proc. Roy. Soc. London (A), 82 (1909), 396.

1 "The Influence of Pressure on the Boiling Points of Metals," Proc. Roy. Soc. London (A), 83 (1910), 483. His other papers (Trans. Faraday Soc., 7 (1911), 151; Z. physik. Chem., 76 (1911), 484; Z. Elektrochem., 18 (1912), 319) merely recapitulate the results.

2 Proc. Chem. Soc., 28 (1912), 4; Chem. News, 105 (1912), 66.

3 Dissertation, Breslau, 1911.

4 Z. physik. Chem., 81 (1913), 167.

5 Z. Elektrochem., 19 (1913), 482.

pressure of the metal in the gas stream is equal to its vapor pressure, a basis which can be secured by proper experimentation, provided always that the vapor density is known. His mean results, expressed in atmospheres and degrees centigrade, follow:

LEAD		SILVER[1]		THALLIUM	
p	t	p	t	p	t
1.05×10^{-4}	808	1.90×10^{-4}	1178	7.40×10^{-5}	634
2.30×10^{-3}	996	1.08×10^{-3}	1316	1.75×10^{-3}	783
2.20×10^{-2}	1176	5.10×10^{-3}	1435	3.20×10^{-2}	970

[1] In another paper (Z. Elektrochem., 19 (1913), 489) Von Wartenberg points out that the vapor pressure of silver is twice as great in presence of oxygen as in an indifferent gas, and attributes this to the temporary formation of oxide which decomposes again at lower temperatures; by this means one may get a considerable sublimate of silver at 1300°. Similar effects have been observed with tungsten.

Moreover, he concluded that the vapor pressures of both copper and platinum are less than 10^{-5} atmosphere at 1360°, and found that of tin to be appreciable though he was unable to calculate it because the vapor density of tin is not known.

The vapor pressure of three high-boiling metals has been investigated recently by Langmuir[1] and by Langmuir and Mackay,[2] who measured the rate of loss of weight of a wire maintained at a definite temperature in an exceptionally good vacuum; from these results the vapor pressures were calculated by means of a formula derived on the basis of the kinetic theory of gases and the Clausius-Clapeyron equation. The metals studied were platinum, molybdenum and tungsten; the calculated boiling points at two pressures are subjoined.

BOILING TEMPERATURE—ABSOLUTE

Pressure, mm.	Platinum	Molybdenum	Tungsten
10^{-6}	1740	2020	2600
760	4180	3890	5100

Thus these three metals have boiling points at far higher temperatures than the more common metals which we are here considering, so in what follows we shall not deal further with them.[3]

Quite recently Egerton[4] has published determinations of the vapor pressures of zinc, cadmium (and mercury) at temperatures at which the vapor pressure is very small (0.01 mm. and smaller); the method, originally used by Knudsen[5] for mercury, depends upon the kinetic flow of molecules through small apertures.

TABLE IV—VAPOR PRESSURE IN MM. AND DEGREES CENTIGRADE OF CADMIUM AND ZINC, ACCORDING TO EGERTON

CADMIUM		ZINC	
t	p	t	p
169	1.9×10^{-5}	257	1.2×10^{-4}
178	3.6	268	1.7
189	8.5	280	4.2
198	2.7×10^{-4}	291	8.4
210	5.3	312	2.1×10^{-3}
222	1.0×10^{-3}	331	5.2
229	1.5	341	7.7
240	2.9	363	1.8×10^{-2}
250	4.7		
260	8.0		
272	1.3×10^{-2}		

The rate of flow, through an aperture of known "resistance," of the vapor of the metal, kept at constant temperature, was measured, whence, on the basis of the kinetic theory, the corresponding vapor pressure can be calculated. His mean results appear in Table IV.

[1] Phys. Rev., 2 (1913), 329.

[2] Ibid., 4 (1914), 377.

[3] The equations to the respective vapor-pressure curves, as given in the original, follow:

For Pt : $\log p = -27800/T - 1.26 \log T + 14.09$
Mo : $\log p = -38600/T - 1.26 \log T + 17.354$
W : $\log p = -47440/T - 0.9 \log T + 15.502$

[4] Phil. Mag., 33 (1917), 33.

[5] Ann. Physik., 29 (1909), 179.

REDUCTION OF THE DATA

The experimental results as a whole are not so accurate as one would wish to have them, and it is difficult to estimate the uncertainty which attaches to them. Von Wartenberg considers that Greenwood erred in choosing as his final values those observed in hydrogen, and that the true boiling point, i. e., the temperature at which the liquid is in equilibrium with a pressure of one atmosphere of its own vapor should lie higher even than that observed in nitrogen. In any case we must take the results as they are, remembering merely that they are approximate; but for many purposes this is ample. The experimental data, if they are to be useful, must be reduced; this was accomplished in the following way:

The slope of the vapor-pressure curve at any point is given by the relation $\dfrac{d \ln p}{dT} = \dfrac{\Delta H}{RT^2}$ where ΔH is the heat of vaporization per mole at the absolute temperature T. If we integrate this on the assumption[1] that ΔH is independent of T (an assumption which in many cases is not seriously in error) we obtain as the equation to the curve, $\ln p = \dfrac{-\Delta H}{RT} + \text{constant}$ (1)

which is of the form, $\log p = -A(1/T) + B$ (2)

or, $1000/T = -A' \log p + B'$ (3)

where $A' = 1000/A$, and $B' = A'B = 1000B/A$.

Accordingly, if we plot values of $\log p$ against the corresponding values of $1/T$, the graph will be a straight line if the above assumption holds, and nearly linear, although the assumption does not hold rigorously; in any case the curve thus obtained is such that we may interpolate readily and even extrapolate with some degree of safety.

The actual data for each metal were plotted on a large scale in this way, and the points were found to lie as close to a straight line as would be expected; accordingly, the best straight line was drawn through each series of points. The graphs are reproduced in Fig. I, from which it is manifest that the inclination (and hence A' in Equation 3) decreases regularly as we pass from metals of lower to metals of higher boiling point. We are therefore justified in assuming, for the purpose of the present approximation, that the A' values for those metals for which only a single determination was made, would follow the same regular sequence. The values of A' derived from the curves were plotted against the respective boiling points, and by interpolation at the appropriate temperatures, values of A' for the other metals were deduced and the corresponding lines drawn (not reproduced in Fig. I). From the curves values of $1/T$ for a series of rounded values of p were read by inspection, whence the corresponding values of t (i. e., the boiling temperature centigrade) are readily derived; the latter are tabulated in Table V for all of the metals.

As regards the accuracy of these figures little can be stated, except that they are probably as good as the original data. The extrapolation which we have made implies that there is no melting nor inversion within the temperature range, but the error caused by the fact that other forms do appear is not serious,

[1] It would undoubtedly be theoretically more correct to assume that $\Delta H = \Delta H_0 + aT$, an assumption which leads to the equation $\log p = -A_1/T + B_1 + C \log T$. The use of this equation, which is much more troublesome to work with than the simpler one, is here hardly warranted by reason of the uncertainty of the data; moreover, it can readily be shown that C is less than unity for the metals which give monoatomic vapors, as a consequence of which the term $C \log T$ would vary but little throughout the range of temperatures and therefore the results would differ very little from those derived from the simpler equation. For example, Egerton expresses his results for cadmium and zinc respectively by the equations

$\log p = -6060/T + 10.598 - 0.5 \log T$
$\log p = -7176/T + 10.944 - 0.5 \log T$

but they are reproduced equally well by the simpler form of equation.

because for a metal the heat of fusion or of inversion is very small compared to the heat of vaporization. In any case the figures tell us the order of magnitude of the vapor pressure of the pure

point at one atmosphere. The position of arsenic is anomalous, presumably because of the fact that its vapor is at these temperatures polyatomic, wherefore ΔH is not constant and conse-

TABLE V—APPROXIMATE BOILING TEMPERATURES* (CENTIGRADE) OF METALS AT VARIOUS PRESSURES

METAL	Melting Tempera- ture	10^{-3}	10^{-2}	10^{-1}	1	10	50	100	760
Cadmium..........	321	220	270	330	410	500	590	630	780
Zinc...............	419	290	350	420	500	610	700	750	920
Magnesium........	651	380	440	520	620	750	860	920	1120
Thallium..........	302	500	570	660	770	910	1030	1090	1300
Bismuth..........	271	540	620	720	840	990	1130	1200	1440
Antimony.........	630	540	620	720	840	990	1130	1200	1440
Lead..............	327	620	710	820	960	1130	1290	1360	1640
Aluminum........	630	730	830	950	1090	1280	1440	1520	1800
Manganese........	1225	790	890	1020	1170	1360	1530	1610	1900
Silver............	960	920	1030	1160	1320	1520	1700	1780	2090
Chromium	1510	980	1090	1230	1400	1610	1800	1890	2200
Tin...............	232	1010	1130	1270	1440	1660	1850	1940	2260
Copper...........	1083	1080	1200	1340	1520	1740	1930	2030	2350
Nickel...........	1452	1100	1220	1370	1550	1780	1970	2070	2400
Iron.............	1520	1130	1250	1400	1590	1820	2010	2110	2450
Arsenic...........	830	220	260	310	360	430	490	510	610

p in mm. mercury

* *i. e.*, the temperature at which the vapor pressure is 10^{-3} mm., etc.

TABLE VI—VALUES, FOR THE SEVERAL METALS, OF THE COEFFICIENTS IN THE FORMULAE AND OF THE HEAT OF VAPORIZATION ΔH PER MOLE

$$\log p = -A/T + B \quad 1000/T = A' \log p + B'$$

METAL†	A	B	A'	B'	$\Delta H = 4.579A$
Arsenic..........	6670	10.47	0.150	1.570	30500
Cadmium........	5460	8.04	0.183	1.473	25000
Zinc.............	6290	8.14	0.159	1.294	28800
Magnesium.......	7250	8.09	0.138	1.116	33200
Thallium........	8850	8.50	0.113	0.961	40500
Bismuth.........	9010	8.12	0.111	0.902	41300
Antimony........	9010	8.12	0.111	0.902	41300
Lead.............	9900	8.05	0.101	0.813	45400
Aluminum.......	11500	8.41	0.087	0.732	52600
Manganese.......	12300	8.55	0.081	0.694	56300
Silver...........	14300	8.97	0.070	0.628	65500
Chromium	14900	8.91	0.067	0.597	68200
Tin..............	15100	8.83	0.066	0.583	69000
Copper..........	16400	9.14	0.061	0.557	75000
Nickel..........	16700	9.12	0.060	0.547	76500
Iron.............	17000	9.10	0.059	0.537	77800

† The figures for the metals named in italics are derived from a single observation only.

metal, and suffice for many practical purposes; it is probable that the boiling temperatures given are minimum values; conversely that the vapor pressures as calculated from the formulae are maximum values.

quently the simple equation does not apply so well. Attention is drawn to the constancy of the values of B (which, however, show an undoubted trend); from which it is evident that one could get a fair idea of the vapor pressure of a metal at any
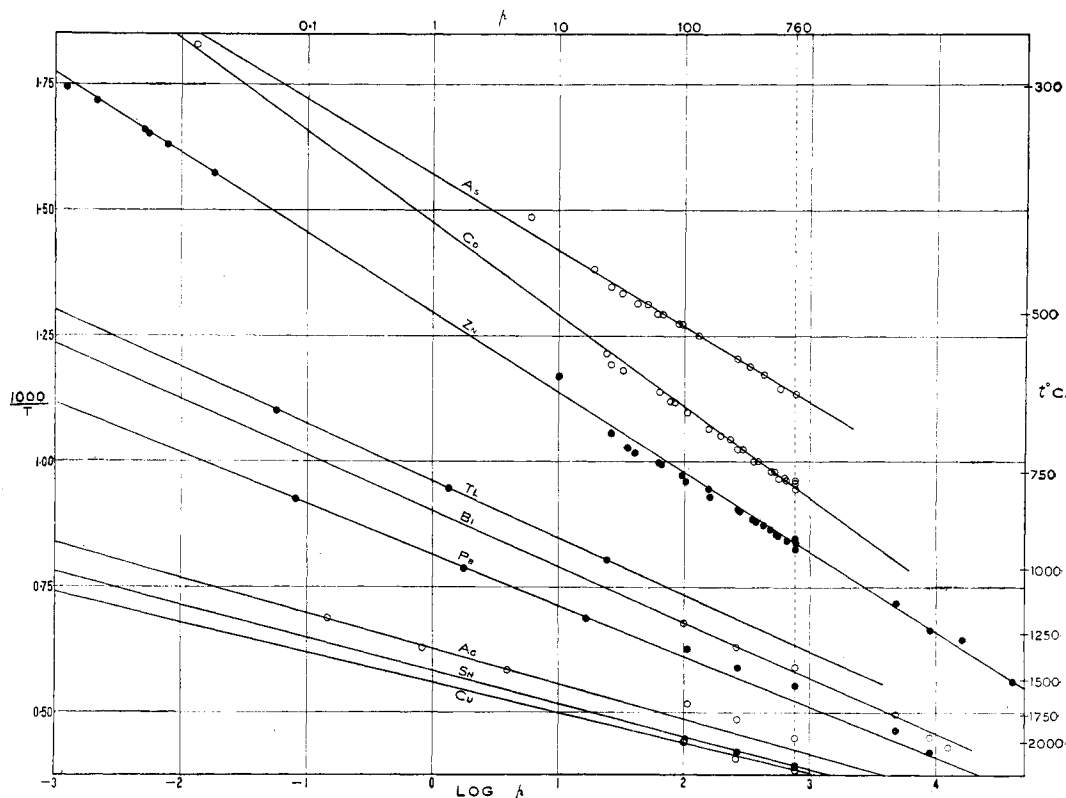

FIG. I—THE VAPOR PRESSURE OF THE SEVERAL METALS; GRAPHS OF LOG p AGAINST $1000/T$
THE CIRCLES REPRESENT THE POINTS DETERMINED EXPERIMENTALLY

In Table VI are brought together the respective values of A, B (Equation 2), A' and B' (Equation 3) as derived from the graphs, for each of the metals; by means of these one can readily calculate the vapor pressure at any desired temperature or the boiling temperature under any specified pressure. This table also gives approximate values of the molar heat of vaporization, derived from A; for, by comparison of Equations (1) and (2), it is obvious that $\Delta H = 2.303 \ RA = 4.579A$ calories. Here again therefore, we observe that the values of A are such that there is a parallelism between heat of vaporization and boiling

temperature if it has been determined at a single temperature.

REMARKS ON VAPOR PRESSURE AND VOLATILITY OF METALS

The values given in Table V or calculable from the appropriate formula, refer only to the pure metal. The vapor pressure of a metal in solution will always be smaller, depending upon its actual concentration, or better its effective mole fraction, in the solution. When $1/n$ of the total moles present are moles of X, the mole fraction of X is $1/n$, and its partial vapor pressure is

$1/n$ of that of pure X at the same temperature;[1] but it is to be borne in mind that the mole fraction is not necessarily given by the gross molecular proportion of X in the mixture, for part of it may be present in other molecular species, *e. g.*, as a compound.

It has been argued that a better separation of two metals (*e. g.*, of zinc and cadmium) by distillation could be achieved by regulating the pressure;[2] but within the practicable range of temperature there is little advantage to be gained in this way unless it should happen that there is a change in constitution of the mixture (*e. g.*, the formation of a compound, the unmixing of a solution, or *vice versa*) within this range, for, when a mixture of a specified composition and constitution is distilled at a series of temperatures, the degree of separation achieved in each case depends upon the ratio of the vapor pressure of zinc to that of cadmium; but between 500 and 1000° this ratio ranges only from about $1/7$ to $1/4$, so that there would be no substantial advantage in conducting the distillation of mixtures of these two metals at one temperature rather than at another. On the other hand, in cases where the metals form a compound, a much better separation would be possible by distilling at a temperature below the dissociation point of this compound than at a higher temperature; nevertheless such a course may not be practicable because of the slowness of distillation at the low temperature requisite.

For a given temperature the amount of material volatilized and carried by a current of indifferent gas can be calculated very easily from the vapor pressure; but this estimate will usually exceed the actual amount because (1) of lack of purity, (2) of incomplete saturation. Both these factors are likely to be met with in practice; thus Welch and Duschak[3] found the vapor pressure of As_2O_3 in a typical flue dust to be only about one-half of that of pure As_2O_3 at the same temperature, and that the flue gas was not even saturated with respect to the flue dust which it carried. The completeness of saturation depends, other things being equal, upon the rate of volatilization under the particular conditions; this rate is very much greater in a very good vacuum that it is in an atmosphere of indifferent gas,[4] and depends very markedly upon the excellence of the vacuum maintained.[5] There have been numerous experiments on the volatilization of metals in a vacuum;[6] these we shall briefly review.

[1] This is absolutely true in many cases, and is true as a first approximation in all cases. With respect to this whole question see papers on the vapor pressures of amalgams by J. H. Hildebrand, *J. Am. Chem. Soc.*, **35** (1913), 501; by Hildebrand and Eastman, *Ibid.*, **36** (1914), 2020; **37** (1915), 2452; also Hildebrand, *Ibid.*, **38** (1916), 1452. In how far the above considerations apply to solid solutions is open to question; there is reason for believing that the above rule does not apply to X when the proportion of X present in a solid solution is very small.

[2] And it has been implied that this could be done by regulating the pressure of some indifferent gas.

[3] "The Vapor Pressure of Arsenic Trioxide," Bureau of Mines, *Technical Paper*, **81**, 1915.

[4] The fact that the rate of volatilization is much less in an atmosphere of indifferent gas than *in vacuo* is the basis of the nitrogen-filled tungsten lamp, for by this means the filament may be run at a higher temperature and consequently with increased efficiency, without unduly shortening its life.

[5] Nair and Turner, *J. Chem. Soc.*, **103** (1913), 1524, observing that the amount of zinc volatilized is much diminished by imperfection of the vacuum, determined the amounts of zinc (and cadmium) volatilized in 30 minutes under various pressures of air, hydrogen and carbon monoxide, and ascertained in each case the temperature required under their conditions for complete volatilization of a given amount of metal in 30 min. As one would expect, this temperature is lowest in a vacuum, successively higher for hydrogen, carbon monoxide, air, and for any one gas increases with the pressure. Their observations for zinc in air at several pressures, follow:

p	0	3	20	50	80	200	600 mm.
Temp. required	460	500	620	660	680	720	840° C.

Incidentally they observed that at 800° zinc oxidizes very slowly in quiescent air, probably because the air is displaced by the heavier zinc vapor; in moving air oxidation is rapid.

[6] With respect to this whole question, particularly on its theoretical side, see recent papers by Langmuir, *e. g., J. Am. Chem. Soc.*, **38** (1916), 2249, where numerous references are given.

Demarçay[1] observed the occurrence of vaporization *in vacuo* in periods of 24 to 48 hours as follows: Cd at 160°, Zn at 184°, Sb and Bi at 293°, Pb and Sn at 360°; and similar observations were recorded by Krafft.[2] Later Krafft and Bergfeld[3] investigated the lowest temperature at which they could observe metal to vaporize in a cathode-ray vacuum in the course of a few hours, with the following results: Cd,[4] 150°; Zn, 180°; Bi, 270°; Pb, 335°; Ag, 680°; Au, 1070°. Reference to the several formulae as given above shows that at the above temperatures the vapor pressure of each metal was of the order 10^{-5} mm., thus adding another instance of the actuality of such very small vapor pressures.

By taking advantage of these differences one may achieve a more or less complete separation of two metals; the completeness of the separation depends upon the ratio of the partial vapor pressures of the two metals in the mixture, a ratio which, as we have seen, does not vary markedly with change of the pressure (or, of course, temperature) at which distillation is performed. Tiede and Fischer[5] showed that lead could be separated from tin by heating in a vacuum. Berry,[6] on heating mixtures of zinc and magnesium in a well evacuated bent glass tube, found that both zinc and magnesium distil off, leaving the compound $MgZn_2$; and also, at a somewhat higher temperature, that this compound distils unchanged. In another paper[7] he states that copper and cadmium heated in vacuum at 600° can be separated quantitatively; that cadmium and magnesium volatilize together; and that the distillate from mixtures of magnesium and lead at 680° contains only traces of lead. Vialay has patented[8] a process of separating zinc and aluminum from their alloys by heating the alloy slowly to 1200°, in a thin layer, preferably in a vacuum.

Groves and Turner[9] record a series of experiments, the main results of which follow. Zinc when heated *in vacuo* begins to volatilize appreciably at 375°; from 60:40 brass volatilization of zinc is appreciable at 520°, from 70:30 brass at 550°. When brass is heated *in vacuo* at 1080° the zinc is quantitatively removed in half an hour. An alloy of zinc and iron at 500° loses only zinc, and that very slowly; at 600° some iron comes over with the zinc. Their further observations on volatilization *in vacuo* can be summarized as follows:

I—No appreciable loss of weight occurs after heating at 1100° *in vacuo* for half an hour with Cu-Al, Cu-Ni, Cu-Sn, Cu-Fe.

II—Quantitatively separable: Cu-Bi, Cu-Pb in 45 min. at 1100°; Cu-Zn in 30 min. at 1100°; Fe-Zn at 500°, but at 1000° more than half the iron had volatilized; Pb-Sn.

III—Excess of more volatile metal removed, leaving a compound; Au-Zn, leaving AuZn; Cu-Sb, leaving Cu_3Sb; Au-Cd, leaving AuCd; Mg-Zn, leaving $MgZn_2$.

IV—More volatile metal is completely removed: Cu-As.

V—Two (or more) metals volatilize together: from Ag-Zn mixtures little silver comes over at 600°, but more and more at higher temperatures; Ag-Pb; Pb-Zn; Zn-Cd.

In a later paper[10] Thorneycroft and Turner present results on the rate of volatilization in a vacuum of copper-zinc alloys ranging from 75-10 per cent Cu. They found that alloys containing more than 40 per cent are quantitatively separable by this means, but that a little copper is also volatilized from the

[1] *Compt. rend.*, **95**, 183.

[2] *Ber.*, **36** (1903), 1690.

[3] *Ibid.*, **38** (1905), 254.

[4] Langmuir, *Proc. Nat. Acad.*, **3** (1917), 141, was able to observe vaporization of Cd at 60°.

[5] Tiede and Fischer, *Ber.*, **44** (1911), 1711.

[6] A. J. Berry, *Proc. Roy. Soc. London (A)*, **86** (1912), 67.

[7] A. J. Berry, *Proc. Camb. Phil. Soc.*, **17** (1912), 31.

[8] A. D. Vialay, French pat. 458,189, July 31, 1912; *C. A.*, **8**, 2868.

[9] Groves and Turner, *J. Chem. Soc.*, **101** (1912), 585; also Turner, *J. Inst. Metals*, **7** (1912), 105.

[10] *J. Inst. Metals*, **12** (1913), which I have been able to see only in abstract (*C. A.*, **8**, 3548).

alloys carrying less than 40 per cent Cu. Some work on the vapor pressure of zinc from brass was done by Hansen[1] and by others,[2] the several results being tolerably concordant.

There are, moreover, scattered observations on volatilization of metals at atmospheric pressure. Bengaugh and Hudson[3] and Bassett[4] present results on the rate of loss of zinc from brass at various temperatures. Rose[5] made experiments on the estimation of zinc in coinage bronze by volatilization; he found that, though only 0.1 per cent of the zinc volatilized at 1200° in two hours, a period of two hours at 1375° sufficed to remove all but 0.3 per cent of the zinc, this volatilization being accompanied by a loss of about 0.2 per cent of the tin and copper. Again, in the process of refining zinc by distillation it has been observed, that other metals, notably lead,[6] tend to come over with the zinc unless the distillation is conducted slowly.

Butts[7] has discussed the vaporization of copper in wire-bar furnaces, and cites data which indicate that this occurs to an appreciable extent at 1120°. Mostowitsch and Pletneff[8] made experiments on the volatility of gold in atmospheres of various gases, and state that it is not appreciably volatile at 1400° in an atmosphere of oxygen, nitrogen, carbon monoxide or carbon dioxide but that in hydrogen volatility is noticeable at 1250°; the latter effect they attribute to the formation of an unstable compound, but an alternative explanation may be that offered by Greenwood[9] to account for the lower boiling points in hydrogen observed by him.

The various observations summarized above are in general harmony with what one would expect from the vapor pressure, although they could not have been predicted precisely from a knowledge of the vapor pressure alone. There are two observations to which I wish to revert for a moment—those namely of Groves and Turner and of Thorneycroft and Turner, who found that some iron or copper came over with the zinc when the respective binary alloys were distilled under certain circumstances, the temperature, however, corresponding to a very small vapor pressure of the less volatile metal. This may be accounted for in two ways,[10] which in essence do not differ materially: (1) that the particles of vapor of the less volatile metal are entrained by the blast of zinc vapor just as the gas from the vessel to be exhausted is entrained by the blast of mercury vapor in the condensation pump;[11] (2) that when all the zinc particles surrounding a given iron (or copper) particle have vaporized, the iron particle is left unattached, and so is carried over into the distillate. This question could readily be elucidated by making series of experiments with mixtures containing different (small) proportions of iron (or other metal) in which the rate of distillation is varied within wide limits. In any case this observation shows that one cannot with safety deduce, from the calculated partial pressure of the components, the composition of the distillate except when the rate of distillation is very small—in other words, the theory applies strictly only to static conditions. Nevertheless a knowledge of the vapor pressure of metals is à prerequisite to any intelligent treatment of the volatility of metals.

SUMMARY

The data in the literature on the vapor pressure and volatility of metals have been reviewed and collated, and thus made more readily available. Formulae are given by means of which the vapor pressure at any temperature can be calculated with an accuracy in the result not inferior to that of the original data; and the temperatures corresponding to a series of pressures are tabulated.

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DISCUSSION

N. T. BACON criticized the statement that every substance has some vapor pressure at any temperature. This is the theory on which Nernst has built much of his work, but Mr. Bacon's study has led him to believe it false. Instead, he believed that each substance had a critical temperature, below which it could not exist in gaseous form, being the counterpart of the temperature above which it cannot exist in liquid form.

In conversation a few months ago, Dr. Irving Langmuir had at first denied this, but when asked what the concentration of platinum vapor would be at 0° C., he calculated it out by extrapolation and found, as a result, a value so small that several hundred thousand worlds would have been required as the space proportion for a single molecule.

As, to maintain a vapor pressure in any space, enough molecules must be present to maintain equal pressure in all dimensions, theoretically a minimum of three is required for the unit of space under consideration. Any smaller number could be looked upon as merely sporadic particles, like particles of dust, of which it would be difficult to postulate whether they were in solid, liquid, or gaseous condition.

Either would necessarily acquire something like gaseous velocity by contact with other molecules in any atmosphere, until they finally dropped under gravity or adhered to the walls by adsorption. This theory is built on the idea that the old assumption is false, that all molecules are perfectly elastic. Now that we recognize atoms as having a multiplicity of parts, it is easy to see how by distortion of these, from a normal form by collision with some other particle, the kinetic energy of a molecule might be transformed into heat. We know very little of the temperature of gaseous molecules, except as manifested by their kinetic energy, but if heat is being continuously withdrawn through the walls of a system, the higher temperatures resulting from collisions with the wall will be cut down first, and thus the secondary equilibrium disturbed, which might have resulted in throwing back the molecule by local overheating.

Some of Dr. Langmuir's experiments seem to indicate this, though he has not interpreted them so, for he has noted that as the temperature approaches that of liquid air, molecules of one kind after another cease to be reflected from the walls and form adsorption films on the walls.

This is just what should happen by the theory of a critical temperature of each gas. This does not mean that there would be no molecules of each kind left in the atmosphere, but rather that no vapor saturation pressure remains.

A new definition of saturated vapor tension seems called for. It has been defined as the condition of equilibrium between the gaseous and liquid phases, so that for each molecule impinging on the liquid surface and condensing there, a fresh one is driven off by the resulting latent heat. This postulates a liquid phase, whereas, in many cases, when saturation is produced by condensation or cooling, the saturation must result solely from an oversupply of gaseous molecules. As, for many substances, the vapor tension as calculated by extrapolation would not be sufficient to maintain a single molecule in the volume of the apparatus employed, is it not obvious that this cannot serve as a satisfactory hypothesis to explain chemical phenomena even though the system based on it agrees pretty well with observed phenomena?

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[1] *Proc. Am. Inst. Metals,* **1912,** 111.

[2] Collated by Gillett: "Brass Furnace Practice," Bur. of Mines, *Bull.* **73** (1914), 126.

[3] *J. Inst. Metals,* **4** (1910), 101.   [4] THIS JOURNAL, **4** (1912), 164.

[5] T. K. Rose, *J. Soc. Chem. Ind.,* **33** (1914), 170; *C. A.,* **8,** 1722.

[6] See German patent No. 286,557, Aug. 12, 1915; *Metall and Erz,* **12** (1915), 350, where means to obviate this in a process of electrothermic distillation are described.

[7] A. Butts, *Met. and Chem. Eng.,* **16** (1917), 84.

[8] Mostowitsch and Pletneff, *J. Russ. Met. Soc.,* **1915,** 410; through *Met. and Chem. Eng.,* **16** (1917), 153.

[9] See supra, p. 874.

[10] It is, of course, possible that the compound of zinc with copper or iron has an appreciable vapor pressure and distils as such.

[11] See Langmuir, "The Condensation Pump; an Improved Form of High Vacuum Pump," *Gen. Elec. Review,* **1916,** 1060.