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THE RATES OF EVAPORATION AND THE VAPOR PRESSURES OF TUNGSTEN, MOLYBDENUM, PLATINUM, NICKEL, IRON, COPPER AND SILVER

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Abstract

Langmuir and Mackay's data on the rates of evaporation of tungsten, molybdenum and platinum have been corrected to the tungsten temperature scale of Forsythe and Worthing. Similar data on nickel, iron, copper and silver are published for the first time on the same temperature scale. The third law of thermodynamics has been assumed in all calculations and the vapor pressures are calculated from the rates of evaporation. The experimental data check the third law as shown by the constancy of the calculated values of λ_0, the latent heat of evaporation at the absolute zero. Tables are given of the rates of evaporation and the vapor pressures up to the boiling points. The data are compared with those of other investigators. The evaporation of metals heated in an atomic hydrogen flame was very rapid and gave results which confirmed the data on evaporation in vacuum. The values of λ_0 expressed in cal. gm. (atom)$^{-1}$ and the boiling points in degrees Kelvin are

	W	Mo	Pt	Ni	Fe	Cu	Ag
λ_0	191880	146000	127500	89440	89025	82060	71320
B.P.	6970	5960	4800	3650	3475	3110	2740

DATA have been published by Langmuir[1] on the rate of evaporation of tungsten as measured by the loss in weight of tungsten filaments. Langmuir and Mackay[2] have also published similar data for molybdenum and platinum. These measurements were based upon a temperature scale for tungsten filaments which has recently been revised.[3,4,5,6] For this reason we have recalculated the old measurements on the basis of the new temperature scale. We also have data taken in 1915, but not previously published, on the rate of evaporation of nickel, iron, copper and silver filaments. We now have recalculated all these data using the new temperature scale, assuming the validity of the third law of thermodynamics in all calculations.

A further discussion of the method which we have used will be given in a subsequent paper by S. Dushman and H. A. Jones in which also a comparison will be made with the results calculated by means of a semi-empirical equation developed by Dushman for the velocity of a unimolecular reaction.[7]

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[1] Langmuir, Phys. Rev. **2**, 450 (1913).

[2] Langmuir and Mackay, Phys. Rev. **4**, 377 (1914).

[3] Forsythe and Worthing, Astrophys. J. **61**, 126 (1925).

[4] Zwikker, Physica. **5**, 249 (1925) and Proc. Roy. Acad. Amsterdam, **34**, No. 5.

[5] Jones, Phys. Rev. **28**, 202 (1926).

[6] Jones and Langmuir, G. E. Rev. **30**, 310 (1927).

[7] Dushman, Jour. Amer. Chem. Soc. **43**, 397 (1921).

Variation of the Rate of Evaporation with the Temperature. The relation between the vapor pressure, p, of any substance and the temperature is given by the Clausius-Clapeyron formula

$$\lambda_T = T(V - v_0)\, dp/dT \tag{1}$$

In general the volume of the metal is entirely negligible as compared with the volume of the vapor produced by its evaporation, so we may place $v_0 = 0$. If we consider λ to be the latent heat of evaporation per gram atom of metal, then since $pV = RT$, we have

$$d \ln p/dT = \lambda/RT^2 \tag{2}$$

which result can also be obtained directly from Van't Hoff's equation.

The latent heat of evaporation λ_T is a function of the temperature such that

$$\lambda_T = \lambda_0 + \int_0^T C_p dT - \int_0^T c_p dT \tag{3}$$

where λ_0 is the latent heat of evaporation per gram atom of metal at the absolute zero, C_p is the specific heat of the vapor, and c_p the specific heat of the solid metal, both measured at constant pressure.

The atomic heat of a metallic vapor, which obeys the gas law at constant pressure, is constant down to absolute zero and equal to $(5/2)R$ calories per gm atom.

Substituting in (3) we have

$$\lambda_T = \lambda_0 + (5/2)RT - \int_0^T c_p dT \tag{4}$$

Substituting (4) in (2) we obtain

$$d \ln p/dT = \lambda_0/RT^2 - (5/2)T - (1/RT^2) \int_0^T c_p dT \tag{5}$$

and integration gives

$$\ln p = -\lambda_0/RT + (5/2) \ln T - H/R + i \tag{6}$$

where i is a constant of integration, the so-called "chemical constant," and

$$H = \int_0^T (dT/T^2) \int_0^T c_p dT$$

It has been shown by Sackur[8] and Tetrode[9] that for monatomic vapors

$$i = i_0 + (3/2) \ln M \tag{7}$$

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[8] Sackur, Ann. d. Physik. **40,** 67 (1913).

[9] Tetrode, Ann. d. Physik. **38,** 434; **39,** 255 (1912).

where M is the atomic weight of the metal and i_0 is a universal constant given by

$$i_0 = \ln\left[(2\pi)^{3/2}k^{5/2}/N_0^{3/2}h^3\right] \tag{8}$$

where k is the molecular gas constant, N_0, is Avogadro's number and h is Planck's constant. Using the values for the constants adopted in the International Critical Tables, i.e., $k = 1.372 \times 10^{-16}$ erg deg.$^{-1}$; $N_0 = 6.061 \times 10^{23}$ mol.$^{-1}$; $h = 6.554 \times 10^{-27}$ erg sec. we find that

$$(2\pi)^{3/2}k^{5/2}/N_0^{3/2}h^3 = 26130 \text{ baryes}\cdot\text{deg.}^{-5/2}\,\text{gm.}^{-3/2}$$

Substituting equation (7) in equation (6) and converting to common logs we have

$$\log_{10}p = -\lambda_0/2.303RT + (5/2)\log_{10}T - H/2.303R + 4.417 + (3/2)\log_{10}M \tag{9}$$

The pressure p being expressed in baryes.

Langmuir has shown[10] that on the basis of the kinetic theory the rate at which vapor comes into contact with the metal is given by

$$m = p(M/2\pi RT)^{1/2} \tag{10}$$

where m is the rate in gm cm^{-2} sec.$^{-1}$, and R is the molecular gas constant (83.15×10^6 erg. deg.$^{-1}$ mol.$^{-1}$) Expressing equation (10) logarithmically and expressing p in baryes, we obtain

$$\log_{10}p = \log_{10}m - (1/2)\log_{10}M + (1/2)\log_{10}T + 4.359 \tag{11}$$

If we assume that every atom of the vapor which strikes the metal condenses, then equation (10) gives the desired relation between the vapor pressure and the rate of evaporation in vacuum. If, however, a certain proportion r, of the atoms of the vapor is reflected from the surface, then the vapor pressure will be greater than that calculated from (10) in the ratio $1:(1-r)$.

Langmuir[11] has presented a great deal of evidence in support of the assumption that the reflection of molecules from the surface of the metal takes place to a negligible degree only. Hence we substitute equation (11) in equation (9) and obtain

$$\log_{10}m = 2\log_{10}M + 2\log_{10}T + 0.058 - H/4.577 - \lambda_0/4.577T \tag{12}$$

Transposing, we have

$$\lambda_0/T = 4.577(2\log_{10}M + 2\log_{10}T + 0.058 - \log_{10}m) - H \tag{13}$$

Hence, accepting the third law of thermodynamics, we are enabled by means of equation (13) to calculate the latent heat of evaporation per gm atom of solid metal at the absolute zero from a single measurement of the rate of evaporation of the metal at a known temperature T in vacuum. With the value λ_0 determined, we may then calculate the complete curve for the

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[10] Langmuir, Phys. Rev. **2,** 331 (1913).

[11] Langmuir, Physical Review **2,** 332 (1913).

rate of evaporation as a function of temperature and may convert the rates of evaporation to vapor pressures by means of equation (10).

To evaluate the double integral, H, of equation (13) we proceed as follows: Debye's theory of the specific heat of solids at low temperatures gives us the curve for c_v, the specific heat of a solid at constant volume, as a function of θ/T, where θ is a characteristic temperature for the solid and is proportional to ν the vibrational frequency of the atoms of the solid. The values of θ for different elements are given by F. Simon[12] and the values of the Debye integral

$$F=\int_0^T (dT/T^2)\int_0^T c_v dT$$

are given as F/T in tables in volume 10 of the Handbuch der Physik by Julius Springer, Berlin (1926). Since we are interested, however, only in the value c_p, the atomic heat of the solid at constant pressure, we add a correction equal to the double integral of (c_p-c_v) which may be calculated from data on the linear expansion and the compressibility. It may be shown thermodynamically that

$$c_p-c_v=9\alpha^2VT/\beta \tag{14}$$

where α is the coefficient of linear expansion, V the atomic volume and β the compressibility. The quantities α and β have been measured for most substances at room temperature, but they are functions of the temperature and there is considerable uncertainty in making the calculation at low temperatures. Lindemann and Magnus[13] have proposed the empirical equation

$$c_p-c_v=aT^{3/2} \tag{15}$$

where a is calculated at ordinary temperatures from the measured values of α and β. Equation 15 is a very rough approximation, but the total value of the correction term is usually about one percent and is nearly negligible in all cases.

Hence we may write

$$H=F+(4/15)aT^{3/2} \tag{16}$$

The Debye theory leads to a limiting value of $c_v=3R$ cal. (gm. atom)$^{-1}$ degree^{-1}. It has been shown experimentally, however, that $c_p>3R$ for nearly all metals at high temperatures and is approximately a linear function of the temperature. We therefore plot all the experimental data on the specific heat c_p of the solid and obtain the equation of the straight line which best fits the data. The temperature at which c_v (Debye) plus (c_p-c_v) meets the curve through the experimental data on specific heats we call T_0. Values of the double integral, H, in equation (13) for temperatures less than T_0 are evaluated from the tables plus the double integral of the correction term (c_p-c_v).

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[12] F. Simon, Zeits. f. Phys. Chem. **109**, 138 (1924).

[13] Lindemann and Magnus, Zeits. f. Electrochem. **16**, 269 (1910).

To obtain the value of H in equation (13) for temperatures greater than T_0, we add to the value determined up to T_0, i.e., $T=T_0$ in equation (16), the value of the double integral of the specific heat curve between the limits T_0 and T_2, i. e.,

$$\int_{T_0}^{T_2}(dT/T^2)\int_0^{T_2}c_p dT=G$$

Since all values of m, the rate of evaporation in gm cm^{-2} sec^{-1} have been measured at temperatures T_2 greater than T_0 in the cases which we are considering equation (13) may be written

$$(\lambda_0/T)=4.577(2\log_{10}M+2\log_{10}T+0.058-\log_{10}m)-F-(4/15)aT_0^{3/2}-G \qquad (17)$$

Specific heats. The specific heats of solid tungsten,[14] molybdenum,[15] platinum,[16] nickel,[17] iron,[18] copper[19] and silver[20] at constant pressure have been measured by a number of investigators.

If we express the atomic heats of the solids by a general equation of the form

$$c_p=N+ZT \qquad (18)$$

where T is the absolute temperature we find from the plots of the experimental data that the values of the constants for the various metals are those given in Table I.

For tungsten, the value of c_v (Debye) plus (c_p-c_v) equals 6.05 at 900°K and c_p calculated by equation (18) equals 6.05 at 900°K so that T_0 equals 900°K. For tungsten Simon gives $\theta=306$°K.

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[14] Tungsten: Pirani, Verh. d. Phys. Ges. **14,** 1037 (1912); Corbino, Phys. Zeits. **13,** 375 (1912); Worthing, Phys. Rev. **12,** 199 (1918); Smith and Bigler, Phys. Rev. **19,** 268 (1922); Smith and Bockstahler, Proc. Nat. Acad. Sci. **10,** 386 (1914); Phys. Rev. **25,** 677 (1925); Gaehr, Phys. Rev. **12,** 396 (1918).

[15] Molybdenum: Stücker, Wien. Ber. **114** (2a) 657 (1905); Richards and Jackson, Zeits. f. Phys. Chem. **70,** 414 (1910); Wüst, Verh. Deutsch. Ing. Forschungsarb No. 204 (1918).

[16] Platinum: White, Phys. Rev. **12,** 438 (1918); see also Wüst, loc. cit. 15.

[17] Nickel: Wüst, loc. cit. 15; Schübel, Z. Anorg. Chem. **87,** 81 (1914); Schimpf, Z. Phys. Chem. **71,** 257 (1910); Weiss and Beck, J. Physique **7,** 299 (1908); Pionchon, Comptes rendus. **103,** 1122 (1886); **106,** 1344 (1888); Richards and Jackson: loc. cit. 15; Tilden, Proc. Roy. Soc. **71,** 220 (1903); Phil. Trans. **A201,** 37 (1903); Schlett, Ann. d. Physik. **26,** 201 (1908).

[18] Iron: Wüst, loc. cit. 15; Griffiths and Griffiths, Trans. Roy. Soc. London **214A,** 319 (1914); Schübel, loc. cit. 17; Weiss and Beck, J. Physique **7,** 299 (1908); Dürrer, 17 S. Diss. Aachen (1915).

[19] Copper: Wüst, loc. cit. 15; Griffiths and Griffiths, loc. cit. 18; Schübel, loc. cit. 18; Naccarri, Atti di Torino **23,** 107 (1887–8); Nernst and Lindemann, Berl. Sitzber 1160 (1912); J. W. Richards, Chem. New. **68,** 58, 69, 82, 93 (1893); Le Verrier, Comptes rendus. **114,** 907 (1892); Harper, Bull. Bur. Stds. **11,** 259 (1915); Magnus, Ann. d. Physik. (4) **31,** 597 (1910).

[20] Silver: Wüst, loc. cit. 15; Griffiths and Griffiths, Proc. Roy. Soc. **A88,** 549 (1913); Phil. Trans. **213A,** 119 (1913); Schübel, loc. cit. 17; Eastman, Williams and Young, J. Amer. Chem. Soc. **46,** 1178 (1924); Le Verrier, loc. cit. 19; Pionchon, Ann. Chim. Phys. (6) **11,** 33 (1887); Comptes rendus. **102,** 675, 1454 (1886); **103,** 1122 (1886); Tilden, loc. cit. 17; Nernst and Lindemann, loc. cit. 19.

The values of T_0 and θ for the other metals obtained in a similar manner are given in Table I.

TABLE I

Constants in Equation (18) for c_p.

	N	Z	T_0	θ
Tungsten	4.70	0.0015	900	306
Molybdenum	4.88	0.00248	360	360
Platinum	5.40	0.0017	220	220
Nickel	4.39	0.00411	300	375
Iron	4.39	0.00405	300	390
Copper	5.33	0.0016	300	315
Silver	5.44	0.00194	300	390

We may write equation (17) in the general form

$$\lambda_0/T = A - B\log_{10}T - C\log_{10}m - DT - E/T \tag{19}$$

Using the data from Table I, we have tabulated the values of the constants for the different metals in Table II.

TABLE II

Constants in Equation (19) for λ_0/T.

Metal	A	B	C	D	E	K	λ_0	λ_l	λ_F	T_m	$B.P.$
W	44.510	1.666	4.577	0.00075	80	3.227	191880	180680	11200	3655	6970
Mo	44.719	2.076	4.577	0.00124	457	3.368	146000	137620	8380	2895	5960
Pt	48.023	3.276	4.577	0.00085	340	3.214	124750	119490	5260	2045	4800
Ni	40.218	0.971	4.577	0.00206	400	3.475	89440	85100	4340	1725	3650
Fe	40.231	0.971	4.577	0.00203	240	3.486	89025	86350	2675	1808	3475
Cu	44.638	3.126	4.577	0.00080	370	3.458	82060	79310	2750	1356	3110
Ag	45.836	3.396	4.577	0.00097	382	3.343	71320	68690	2630	1234	2740

Langmuir[1] and Zwikker[4] have measured the rate of evaporation of tungsten filaments in vacuum.

Langmuir's temperature data were based upon the candle power relation previously given by him, i.e.,

$$T = \frac{11230}{7.029 - \log_{10}C'} \tag{20}$$

We find that these data come into agreement with Zwikker's more recent data when the Langmuir temperatures are corrected by means of the equation which expresses the latest data on the candle power of tungsten as a function of temperature,[6] i.e.,

$$T = \frac{10957}{6.797 - \log_{10}C'} \tag{21}$$

Langmuir and Mackay[2] have measured the rate of evaporation of molybdenum and platinum filaments in vacuum. The platinum temperatures were based upon equation (20) so that these temperatures may be corrected by means of equation (21).

They actually photometered molybdenum filaments and multiplied the observed values by the ratio of the assumed emissivities (0.514/0.529) to obtain the candle power of tungsten, the curve of which furnished the temperature. Hence their temperatures are corrected by calculating the candle power for tungsten from Langmuir's old relation, i.e., equation (20) for the temperatures given in their paper. These calculated candle powers for tungsten are then multiplied by (0.529/0.514) to obtain the candle power of molybdenum actually observed. These observed values of candle power are then substituted in the equation expressing the candle power of molybdenum as a function of temperature which we have derived from Worthing's[21] measurements. The nickel and iron data are based solely upon the unpublished measurements made by Langmuir and Mackay on the rate of evaporation of filaments in vacuum.

They determined the temperatures of nickel and iron filaments by an optical pyrometer which was calibrated against a tungsten standard in the red ($\lambda = 0.665\mu$). The nickel and iron temperatures were calculated by means of Wien's equation from the known relation between the emissivities of the two metals for $\lambda = 0.665\mu$. They assumed the emissivities to be constant for $\lambda = 0.665\mu$ and equal to 0.46, 0.36, and 0.36 for tungsten, nickel and iron[22] respectively.

Worthing and Forsythe[3] have shown that the emissivity of tungsten is not constant in the red so that the temperatures calculated have been corrected for the latest data on the emissive power of tungsten in the red ($\lambda = 0.665\mu$).

TABLE III

Values of λ_0 calculated from the data for tungsten.

		Langmuir				Zwikker	
1 Old temp. of fil.	2 Corr. temp. of fil.	3 $m \times 10^6$	4 λ_0	5 Method	6 Temp. of fil.	7 $m \times 10^6$	8 λ_0
2440°K	2518°K	0.0020	193000	Weight	2389°K	0.000115	197200
2522	2610	0.0059	191900	"	2510	0.00099	196100
2800	2913	0.39	189000	Resistance	2614	0.00525	196400
3136	3300	30.0	187700	"	2637	0.00621	198700
2738	2852	0.151	193300	"	2657	0.00969	195200
2825	2950	0.52	192400	"	2759	0.0427	194300
2825	2950	0.59	191800	Weight	2887	0.293	192000
2875	3000	1.01	191800	Resistance	2889	0.275	192300
2875	3000	1.14	191000	Weight	3017	1.28	191400
2925	3060	1.73	191900	Resistance	3108	3.47	190700
2925	3060	2.33	190200	Weight	3124	3.82	190800
2930	3066	1.84	191900	Resistance	3129	4.69	189800
2930	3066	2.45	189800	Weight	3132	4.69	190000
					3137	4.95	190300
				Average = 191,880			

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[21] Worthing, Phys. Rev. **28**, 190 (1926).

[22] Burgess and Waltenburg, Bul. Bur. Stds. **11**, 591 (1915).

The copper and silver data are based upon the measurements by Langmuir and Mackay together with several measurements by Rosenhain and Ewen[23] of the loss in weight of copper and silver rods in a high vacuum electric furnace. We have used the values given by Forsythe and Worthing for the emissivity of tungsten in the red and the values [24] $E_\lambda=0.11$ and 0.07 for copper and silver respectively (for $\lambda=0.665\mu$) to calculate the true temperatures. Rosenhain and Ewen used a platinum, platinum-rhodium thermocouple imbedded in the copper or silver rods for temperature determinations and in this way probably attained a high order of accuracy.

The values of λ_0 calculated from the data for tungsten are given in Table III. Col. 1 gives Langmuir's original temperatures calculated by equation (20); col. 2, the corrected temperatures calculated by equation (21); col. 3, the experimental rates of evaporation in gm cm^{-2} sec $^{-1}$; col. 4, the values of λ_0 calculated by means of equation (19) while col. 5 gives the method used in the determination of (m).

Column 6 and column 7 give Zwikker's experimental values of temperature and the rate of evaporation respectively, while column 8 gives the values of λ_0 which we have calculated from his data by means of equation (19).

The values of λ_0 calculated from the data of Langmuir and Mackay for molybdenum are given in Table IV. Column 1 gives their original temperatures; column 2, the temperatures corrected in the manner described above; column 3, the experimental rates of evaporation in gm cm^{-2} sec^{-1} while column 4 gives the values of λ_0 calculated by means of equation (19).

TABLE IV

Values of λ_0 calculated from the data for molybdenum and platinum.

Molybdenum				Platinum			
1 Old temp. of fil.	2 Corr. temp. of fil.	3 $m\times10^6$	4 λ_0	5 Old temp. of fil.	6 Corr. temp. of fil.	7 $m\times10^6$	8 λ_0
1994°K	2070°K	0.00766	149,200	1682°K	1697°K	0.00617	124,400
2040	2118	0.0305	146,700	1710	1728	0.0052	125,200
2112	2200	0.124	146,500	1800	1823	0.0695	124,500
2121	2215	0.111	146,400	1890	1918	0.373	124,500
2220	2325	0.630	146,600	1912	1942	0.503	124,700
2287	2388	1.74	145,500	1982	2016	1.32	125,200
2312	2430	3.29	145,000	2000	2035	1.88	124,800
2326	2455	3.65	145,800				
2350	2480	6.49	144,300			Average	124,750
2373	2504	8.47	144,200				
		Average	146,000				

The values of λ_0 calculated from the data of Langmuir and Mackay for platinum are also given in Table IV. Column 5 gives their original temperatures; column 6, the corrected temperatures; column 7, the experimental rates of evaporation in gm cm^{-2} sec^{-1} while column 8 gives the values of λ_0 calculated by means of equation (19).

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[23] Rosenhain and Ewen, Journ. Inst. of Metals **2**, 8, 149 (1912).

[24] Foote and Fairchild, Trans. Amer. Inst. of Min. & Met. Engrs., pp. 1404 (1919).

The values of λ_0 calculated from the data of Langmuir and Mackay for nickel and iron are given in Table V. Column 1 gives the true temperature of the nickel in degrees Kelvin; column 2, the experimental rates of evaporation in gm cm^{-2} sec^{-1}, while column 3 gives the values of λ_0 for nickel calculated by means of equation (19). Column 4 gives the true temperature of the iron in degrees Kelvin; column 5 the experimental rates of evaporation in gm cm^{-2} sec^{-1}, while column 6 gives the values of λ_0 for iron calculated by means of equation (19). These data for nickel and iron were obtained by the loss in weight method only.

TABLE V

Values of λ_0 calculated from the data for nickel and iron.

	Nickel			Iron	
1 True temp. of fil.	2 $m \times 10^6$	3 λ_0	4 True temp. of fil.	5 $m \times 10^6$	6 λ_0
1318°K	0.03	90,400	1270°K	0.013	89,800
1409	0.604	88,000	1438	0.852	89,100
1532	3.77	89,600	1562	9.66	88,600
1544	4.38	89,700	1580	13.4	88,600
1602	14.2	89,500			
				Average	89,025
	Average	89,440			

The values of λ_0 calculated from the data on copper and silver are given in Table VI. Column 1 gives the author; column 2, the true temperature of the copper in degrees Kelvin; column 3, the experimental rates of evaporation in gm cm^{-2} sec^{-1}, while col. 4 gives the values of λ_0 for copper calculated by means of equation (19). Column 5 gives the author; column 6 the true temperature of the silver in degrees Kelvin; column 7, the experimental rates

TABLE VI

Values of λ_0 calculated from the data for copper and silver.

	Copper				Silver		
1 Author	2 True temp. of fil.	3 $m \times 10^6$	4 λ_0	5 Author	6 True temp. of fil.	7 $m \times 10^6$	8 λ_0
L and M	1186°K	0.0292	80900	L and M	1167°K	1.54	70600
"	1298	0.426	81600	"	1198	2.11	71800
Rosenhain	1288	0.236	82350	"	1234	3.81	72300
and Ewen	1288	0.293	81600	Rosenhain	1143	0.82	70750
"	1288	0.151	83500	and Ewen	1143	0.569	71600
"	1288	0.229	82400	"	1143	0.75	70900
				"	1143	0.639	71300
		Average	82060	"	1143	1.06	70200
				"	1143	0.472	72000
				"	1143	0.476	72000
				"	1143	0.60	71500
				"	1143	0.521	71750
				"	1143	0.919	70500
						Average	71320

of evaporation in gm $\mathrm{cm}^{-2}\ \mathrm{sec}^{-1}$; while column 8 gives the value of λ_0 for silver calculated by means of equation (19). These data for copper and silver were obtained by the loss in weight method only.

Substituting the average value of λ_0 for the metal in equation (19) the equation expressing the rate of evaporation of the solid in gm $\mathrm{cm}^{-2}\ \mathrm{sec}^{-1}$ in vacuum becomes in general form

$$\log_{10}m=\frac{A}{C}-\frac{\lambda_0+E}{CT}-\frac{B}{C}\log_{10}T-\frac{DT}{C} \tag{22}$$

From equation (10), it follows that

$$\log_{10}m=\log_{10}p-K-0.5\log_{10}T \tag{23}$$

where K is a constant depending on the metal and the units in which p is expressed. Expressing p in baryes, the values of K for the various metals are those given in Table II.

Substituting equation (23) in equation (22) we obtain for the equation expressing the vapor pressure of a metal in baryes

$$\log_{10}p=\frac{A}{C}+K-\frac{\lambda_0+E}{CT}-\left(\frac{B}{C}-0.5\right)\log_{10}T-\frac{DT}{C} \tag{24}$$

Tables, VII and VIII contain the calculated values of m, the rate of evaporation in gm $\mathrm{cm}^{-2}\ \mathrm{sec}^{-1}$ and p, the vapor pressure of these metals in baryes at 100° intervals.

Since $\lambda_0=\lambda_l+\lambda_F$ where λ_l is the latent heat of evaporation per gm atom of the liquid and assuming that the equation which expresses the atomic heat of the solid as a function of temperature applies also to the liquid, we may write the equation expressing the rate of evaporation of the liquid in gm $\mathrm{cm}^{-2}\ \mathrm{sec.}^{-1}$ in general form

$$\log_{10}m_l=\frac{A}{C}-\frac{\lambda_l+E}{CT}-\frac{B}{C}\log_{10}T-\frac{DT}{C}-\frac{\lambda_F}{CT_m} \tag{25}$$

Similarly we may write the equation expressing the vapor pressure of the metal over the liquid in baryes in the general form

$$\log_{10}p_l=\frac{A}{C}+K-\frac{\lambda_F}{CT_m}-\frac{\lambda_l+E}{CT}-(B-0.5)\log_{10}T-\frac{DT}{C} \tag{26}$$

The values of λ_0, λ_l, λ_F and T_m used to calculate the rates of evaporation and the vapor pressures of the liquids are given in Table II.

It was found by plotting the latent heats of fusion λ_F of metals as given by the International Critical Tables against the melting point in degrees Kelvin that the heat of fusion is roughly proportional to the melting point. We have, therefore, used this method to estimate the heats of fusion for tungsten and molybdenum. Experimental data are lacking on these metals, but we believe that the values 11200 and 8380 cal. gm atom^{-1} for tungsten and molybdenum are probably within ten percent of the true values.

TABLE VII

Values of the rate of evaporation m and the vapor pressure p of tungsten, molybdenum and platinum.

T^0K	Tungsten		Molybdenum		Platinum	
	m	p	m	p	m	p
500						
600						
700						
800					1.29×10^{-26}	5.99×10^{-22}
900					7.21×10^{-23}	3.55×10^{-18}
1000			1.37×10^{-24}	1.01×10^{-19}	6.70×10^{-20}	3.47×10^{-15}
1100			9.77×10^{-22}	7.57×10^{-17}	1.81×10^{-17}	9.80×10^{-13}
1200	3.22×10^{-27}	1.88×10^{-22}	2.44×10^{-19}	1.97×10^{-14}	2.06×10^{-15}	1.17×10^{-10}
1300	1.34×10^{-24}	8.13×10^{-20}	2.53×10^{-17}	2.13×10^{-12}	9.73×10^{-14}	5.74×10^{-9}
1400	2.50×10^{-22}	1.57×10^{-17}	1.29×10^{-15}	1.13×10^{-10}	2.92×10^{-12}	1.79×10^{-7}
1500	2.36×10^{-20}	2.86×10^{-15}	3.81×10^{-14}	3.44×10^{-9}	5.23×10^{-11}	3.31×10^{-6}
1600	1.24×10^{-18}	8.61×10^{-14}	7.60×10^{-13}	7.09×10^{-8}	6.56×10^{-10}	4.24×10^{-5}
1700	4.16×10^{-17}	2.89×10^{-12}	1.05×10^{-11}	1.01×10^{-7}	6.18×10^{-9}	4.18×10^{-4}
1800	9.46×10^{-16}	6.75×10^{-11}	1.06×10^{-10}	1.05×10^{-6}	4.42×10^{-8}	3.07×10^{-3}
1900	1.47×10^{-14}	1.18×10^{-9}	7.52×10^{-10}	7.64×10^{-5}	2.57×10^{-7}	1.83×10^{-2}
2000	1.75×10^{-13}	1.32×10^{-8}	5.34×10^{-9}	5.58×10^{-4}	1.24×10^{-6}	9.07×10^{-2}
2100	1.58×10^{-12}	1.22×10^{-7}	2.82×10^{-8}	3.01×10^{-3}		
2200	1.25×10^{-11}	9.89×10^{-7}	1.30×10^{-7}	1.43×10^{-2}	1.7×10^{-5}	1.3
2300	7.82×10^{-11}	6.32×10^{-6}	5.00×10^{-7}	5.60×10^{-2}		
2400	4.36×10^{-10}	3.52×10^{-5}	1.80×10^{-6}	2.05×10^{-1}	1.5×10^{-4}	1.2×10^{1}
2500	2.03×10^{-9}	1.71×10^{-4}	5.62×10^{-6}	6.58×10^{-1}		
2600	8.79×10^{-9}	7.57×10^{-4}	1.57×10^{-5}	1.87	8.5×10^{-4}	7.1×10^{1}
2700	3.17×10^{-8}	2.77×10^{-3}	4.18×10^{-5}	5.07		
2800	1.12×10^{-7}	9.99×10^{-3}	1.04×10^{-4}	12.8	4.0×10^{-3}	3.4×10^{2}
2900	3.45×10^{-7}	3.18×10^{-2}	2.35×10^{-4}	29.5		
3000	9.69×10^{-7}	9.09×10^{-2}	5.0×10^{-4}	64.	1.5×10^{-2}	1.3×10^{8}
3100	2.66×10^{-6}	2.51×10^{-1}				
3200	6.67×10^{-6}	8.06×10^{-1}	1.8×10^{-3}	2.4×10^{2}	4.5×10^{-2}	4.2×10^{3}
3300	1.60×10^{-5}	1.55				
3400	3.55×10^{-5}	3.49	5.6×10^{-3}	7.7×10^{2}	1.2×10^{-1}	1.1×10^{4}
3500	7.57×10^{-5}	7.55				
3600	1.55×10^{-4}	15.7	1.5×10^{-2}	2.1×10^{3}	2.8×10^{-1}	2.7×10^{4}
3655	2.28×10^{-4}	23.3				
3800	5.6×10^{-4}	58.	3.5×10^{-2}	5.1×10^{3}	5.9×10^{-1}	5.9×10^{4}
4000	1.7×10^{-3}	1.8×10^{2}	7.7×10^{-2}	1.1×10^{4}	1.2	1.2×10^{5}
4200	4.7×10^{-3}	5.1×10^{2}	1.5×10^{-1}	2.3×10^{4}	2.1	2.2×10^{5}
4400	1.1×10^{-2}	1.3×10^{3}	2.8×10^{-1}	4.3×10^{4}	3.6	3.9×10^{5}
4600	2.6×10^{-2}	2.9×10^{3}	4.7×10^{-1}	7.5×10^{4}	5.8	6.4×10^{5}
4800	5.2×10^{-2}	6.1×10^{3}	7.7×10^{-1}	1.3×10^{5}	8.9B. P.	1.0×10^{6}
5000	1.0×10^{-1}	1.2×10^{4}	1.2	2.0×10^{5}	B. P. =4800°K	
5200	1.8×10^{-1}	2.2×10^{4}	1.8	3.0×10^{5}		
5400	3.2×10^{-1}	3.9×10^{4}	2.5	4.3×10^{5}		
5600	5.4×10^{-1}	6.8×10^{4}	3.5	6.1×10^{5}		
5800	8.6×10^{-1}	1.1×10^{5}	4.6	8.2×10^{5}		
6000	1.3	1.7×10^{5}	5.6 B. P.	1.0×10^{6}		
6200	2.0	2.6×10^{5}	B. P. =5960°K			
6400	2.8	3.8×10^{5}				
6600	4.0	5.5×10^{5}				
6800	5.6	8.8×10^{5}				
6970	7.1 B. P.	1.0×10^{6}				
	B. P. =6970 °K					

For example, if the value chosen for the heat of fusion of tungsten is high by ten percent, the calculated values of m_l and p_l will be correct at the melting point, but would be high by about 8 percent at the boiling point.

In view of the assumption that the atomic heat of the liquid is the same function of the temperature as that of the solid, we have calculated the possible error if the atomic heat of the liquid remains constant up to the boiling point. For example if the atomic heat of liquid tungsten remains constant between the melting and boiling points, the values of m_l and p_l which we have calculated would be low by about 13 percent at the boiling point (6970°K). Hence the data for the liquid metals are probably correct at the melting points and have a probable error of 10–15 percent at the boiling points. For this reason, the calculated values are tabulated at 200° intervals and are given to two significant figures. The differences between values of m_l or p_l for adjacent temperature points are usually known more accurately than the absolute value at one point.

TABLE VIII

Values of the rate of evaporation m and vapor pressure p for nickel, iron, copper and silver.

T°K	Nickel		Iron		Copper		Silver	
	m	*p*	*m*	*p*	*m*	*p*	*m*	*p*
500					8.89×10^{-29}	5.71×10^{-24}	5.61×10^{-24}	2.77×10^{-19}
600	2.21×10^{-25}	1.62×10^{-20}	3.30×10^{-25}	2.48×10^{-20}	7.23×10^{-23}	5.08×10^{-18}	7.55×10^{-19}	4.07×10^{-14}
700	8.41×10^{-21}	6.65×10^{-16}	1.25×10^{-20}	1.01×10^{-15}	1.16×10^{-18}	8.81×10^{-14}	3.26×10^{-15}	1.90×10^{-10}
800	2.35×10^{-17}	1.99×10^{-12}	3.17×10^{-17}	2.75×10^{-13}	1.64×10^{-15}	1.33×10^{-10}	1.64×10^{-12}	1.03×10^{-7}
900	1.08×10^{-14}	9.68×10^{-9}	1.38×10^{-14}	1.27×10^{-9}	3.64×10^{-13}	3.13×10^{-8}	2.10×10^{-10}	1.39×10^{-5}
1000	1.42×10^{-12}	1.34×10^{-7}	1.82×10^{-12}	1.76×10^{-7}	3.96×10^{-11}	3.59×10^{-6}	9.97×10^{-9}	6.95×10^{-4}
1100	7.48×10^{-11}	7.41×10^{-6}	9.35×10^{-11}	9.48×10^{-6}	1.51×10^{-9}	1.44×10^{-4}	2.29×10^{-7}	1.67×10^{-2}
1200	2.00×10^{-9}	2.07×10^{-4}	2.43×10^{-9}	2.58×10^{-4}	3.11×10^{-8}	3.10×10^{-3}	3.13×10^{-6}	2.39×10^{-1}
1300	3.19×10^{-8}	3.43×10^{-3}	3.89×10^{-8}	4.29×10^{-3}	3.94×10^{-7}	4.08×10^{-2}		
1400	3.38×10^{-7}	3.77×10^{-2}	4.04×10^{-7}	4.63×10^{-2}	3.5×10^{-6}	3.6×10^{-1}	1.6×10^{-4}	1.3×10^{1}
1500	2.55×10^{-6}	2.94×10^{-1}	3.04×10^{-6}	3.60×10^{-1}				
1600	1.46×10^{-5}	1.74	1.74×10^{-5}	2.13	1.0×10^{-4}	1.2×10^{1}	2.9×10^{-3}	2.5×10^{2}
1700	6.82×10^{-5}	8.40	8.11×10^{-5}	1.02×10^{1}				
1800	2.5×10^{-4}	3.2×10^{1}	3.08×10^{-4}	4.00×10^{1}	1.4×10^{-3}	1.8×10^{2}	2.6×10^{-2}	2.5×10^{3}
2000	2.2×10^{-3}	2.9×10^{2}	2.9×10^{-3}	3.9×10^{2}	1.1×10^{-2}	1.4×10^{3}	1.5×10^{-1}	1.5×10^{4}
2200	1.2×10^{-2}	1.7×10^{3}	1.6×10^{-2}	2.4×10^{3}	5.9×10^{-1}	7.9×10^{3}	6.0×10^{-1}	6.2×10^{4}
2400	5.0×10^{-2}	7.3×10^{3}	6.9×10^{-2}	1.0×10^{4}	2.3×10^{-1}	3.2×10^{4}	1.9	2.1×10^{5}
2600	1.6×10^{-1}	2.4×10^{4}	2.2×10^{-1}	3.5×10^{4}	7.3×10^{-2}	1.1×10^{5}	5.0	5.6×10^{5}
2800	4.0×10^{-1}	6.3×10^{4}	6.5×10^{-1}	1.1×10^{5}	1.9	2.9×10^{5}	8.8 B.P.	1.0×10^{6}
3000	9.0×10^{-1}	1.6×10^{5}	1.3	2.2×10^{5}	4.3	6.8×10^{5}	B.P. =2740°K	
3200	1.8	3.0×10^{5}	2.6	4.6×10^{5}	6.4 B.P.	1.0×10^{6}		
3400	3.1	5.4×10^{5}	4.7	8.4×10^{5}	B.P.=3100°K			
3600	5.1	9.0×10^{5}	7.5 B.P.	1.0×10^{6}				
3650	5.5 B.P.	1.0×10^{6}	B.P.=3475°K					
	B.P.=3650°K.							

Table IX contains data on the vapor pressure of metals which have been published by other investigators. Column 1 gives the metal; column 2, the absolute temperature; column 3, the vapor pressure of the metal; column 4, the calculated latent heat of evaporation of the liquid; while column 5 gives the calculated latent heat of evaporation of the solid at the absolute zero. These are both expressed in cal. (gm atom)$^{-1}$. Equation 2b which assumes the third law of thermodynamics was used to calculate the values λ_L and λ_0. The references to the original papers are given in column 6.

Except for the value given by Greenwood for the boiling point of iron, the values of λ_0 in Table IX for nickel and iron are seen to be in fair agreement with those in Table V.

There is, however, a large discrepancy between the values of λ_0 calculated for copper and silver in Table IX and those given in Table VI.

However, if we plot $\log_{10}p_{\text{obs}}+(B/C-0.5)\log_{10}T+DT/C$ against $1/T$ for the data on copper and silver in Table IX, we find that straight lines having the slopes that we have already used (i.e., 17330 and 15010 for copper and silver respectively) fit the data as well as any other straight line that could be drawn. Thus the discrepancy between these data of Table IX and those of Tables VII and VIII represents a parallel displacement of the semi-log plot against $1/T$. An error of the temperature obtained by optical pyrometers, such as would be caused by a wrong value for the emissivity, would produce this kind of parallel displacement.

TABLE IX

Values of the vapor pressure and latent heat of evaporation of various metals.

Metal	T^0K	P(baryes)	λ_L	λ_0	Ref.	Metal	T^0K	P(baryes)	λ_L	λ_0	Ref.
Nickel	2789	5.1×10^4	86000	90340	25	Copper	2138	2.0×10^4	73000	75750	34
	2777	4.8×10^4	86100	90440	26		2328	1.4×10^5	70500	73250	34
	2895	7.4×10^4	86700	91040	26		2348	1.4×10^5	71000	73750	34
	2613*	4.0×10^4	82700	87043	26		2643	1.0×10^6	68700	71450	34
Iron	2925	4.0×10^4	94300	96975	27	Silver	1933	1.4×10^5	57600	60230	35
	2723*	4.0×10^4	88900	91575	27		2053	3.5×10^5	57000	59630	35
	2723	1.0×10^3	71400	74075	28		2228	1.0×10^6	56800	59430	35
Copper	810	6.7×10^{-4}		58200	29		1933	1.4×10^5	57650	60280	36
	2373	1.0×10^6	60300	63050	30		1953	1.6×10^5	56800	59430	36
	2253	1.3×10^5	68000	70750	31		2031	2.7×10^5	57600	59230	36
	2453	3.4×10^5	68800	71550	31		2083	4.0×10^5	57300	59930	36
	2583	1.0×10^6	66700	69450	31		2213	9.9×10^5	56400	59030	36
	2148	2.7×10^4	71900	74650	32		1000	1.5×10^{-1}		60600	37
	2378	1.7×10^5	70600	73350	33		1453	1.9×10^2	63100	65730	38
	2443	2.8×10^5	69700	72450	33		1589	1.1×10^3	63200	65830	38
	2488	4.0×10^5	69000	71750	33		1708	5.2×10^3	62400	65030	38
	2518	5.4×10^5	68300	71050	33		2373†	1.0×10^6	60100	62730	38
	2573	1.0×10^6	66600	69350	33						

* Estimated by the authors for the pure metals as they believe the first results are in error due to a small amount of carbon being present.

† Estimated by von Wartenburg.

We have recently performed several experiments in which nickel, copper and silver were caused to evaporate rapidly when heated by an atomic hydrogen flame[38] from a 60 ampere arc between tungsten electrodes. A known weight of nickel was melted in a magnesia cupel and heated rapidly to 2869°K by holding the atomic hydrogen flame on a portion of the melted surface. The temperatures were measured by an optical pyrometer with a red screen ($\lambda = 0.665\mu$). After a measured interval of time, the sample was

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cooled quickly and the rate of loss in weight per unit area determined. The emissivity of liquid nickel was assumed to be $E_\lambda = 0.36$ for $\lambda = 0.665\mu$.

The rate of evaporation of nickel heated to 2869°K in hydrogen was found to be 0.0188 as great as the rate of evaporation in vacuum as given in Table VIII. This *evaporation factor* is of the same order of magnitude as has been found for the evaporation of tungsten filaments in gas filled lamps, as compared with evaporation of similar filaments in vacuum.[39] A filament 0.0254 cm diameter in nitrogen at about atmospheric pressure evaporated 0.023 as fast as in vacuum. An equation given by Fonda indicates that this evaporation factor would approach 0.0018 for wires or rods of very large diameter. The higher diffusion coefficient in hydrogen and the effect of the blast of hydrogen seem adequate to explain the fact that our evaporation factor is ten times as great.

Copper and silver were evaporated in a similar manner, and, using the values $E_\lambda = 0.11$ and 0.07 for liquid copper and silver respectively with the evaporation factor 0.0188 obtained from the experiments on nickel, we obtained rates of evaporation of these metals which agreed well with the rates calculated from the measurements obtained on the evaporation of filaments and rods. The accuracy of our temperature data is supported by the work of Rosenhain and Ewen who used thermocouples for temperature measurements.

The data from the rather crude experiments using the atomic hydrogen flame are summarized in Table X. Column 1 gives the metal; column 2, the calculated boiling point of the metal; column 3, the maximum surface temperature which we succeeded in obtaining; column 4, the energy loss by radiation in watts per cm; column 5, the energy loss by evaporation in the same units; while column 6 gives the ratio of the energy loss by evaporation to the total energy loss.

TABLE X

Values of the energy losses by radiation and evaporation from nickel, copper and silver surfaces.

1 Metal	2 B. P. °K.	3 Max. Temp. °K	4 W (rad.)	5 W (evap.)	6 $\frac{W\text{ (evap.)}}{W\text{ (total)}}$
Nickel	3650	2869	140	60	0.30
Copper	3110	2838	37	300	0.865
Silver	2740	2665	20	328	0.943

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GENERAL ELECTRIC COMPANY.
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