For NH_3 at atmospheric pressure, the value of $\Delta\nu_{\frac{1}{2}} \approx \frac{1}{2}\pi^2(\mu^2/h)N$ comes out to be 4.5×10^{10} sec.$^{-1}$ $=1.5$ cm^{-1}. Cornell,[7] in measurements made in this laboratory, finds an average half-width of 1.45 cm^{-1} in the 7920A band of NH_3, and of 0.81 in the 10,230A band. The agreement as to order of magnitude is gratifying in view of the present inaccuracies in both experiment and theory.

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[7] S. D. Cornell, Phys. Rev. this issue. We are indebted to Mr. Cornell for the use of his material before publication.

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Vapor Pressure of Caesium by the Positive Ion Method

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The positive ion currents from pure tungsten filaments in saturated caesium vapor at bulb temperatures from $-35°C$ to $+73°C$ were measured for filament temperatures from 1000° to 1800°K. The results were corrected for the cooling effect of the leads and for photoelectric emission from the caesium film on the platinum deposited on the bulb which was used as an ion collector. The vapor pressures in mm of Hg are given for solid Cs ($T<302°K$) by

$$\log_{10}p_S=10.5460-1.00\log_{10}T-4150/T$$

and for liquid Cs ($T>302°K$) by

$$\log_{10}p_L=11.0531-1.35\log_{10}T-4041/T.$$

The vapor pressures given by these equations are believed to be accurate to within one percent from 220° to 350°K, within 3 percent up to 600° and within about 8 percent at 1000°K.

In some early studies of the effects of caesium vapor on thermionic phenomena[1, 2] it was observed that with a negatively charged cylinder surrounding a hot filament, positive ion currents were obtained which are independent (over wide ranges) of filament temperature and of voltage, but increase rapidly as the caesium vapor pressure is raised. These results were interpreted as indicating that every caesium atom which strikes a filament (above about 1200°K) is converted into an ion. The ion current thus serves as a measure of the pressure.

The vapor pressure p of caesium, in baryes, was found to be accurately expressed (in a temperature range from 0 to 40°C) by the equation

$$\log_{10}p=10.65-3992/T. \quad (1)$$

The experimental data and the details of the method by which this equation was obtained have not been published.

These results have been criticized by Rowe[3] who compared them with measurements of Kröner[4] in the range from 250° to 350°C. Rowe found that Kröner's data could be expressed by

$$\log_{10}p_{mm}=7.165-3966/T, \quad (2)$$

while Eq. (1) expressed in the same units is

$$\log_{10}p_{mm}=7.525-3992/T. \quad (3)$$

The Langmuir-Kingdon (L-K) values of Eq. (3) are greater than those calculated from Kröner's data by a factor that varies from 1.85 at 27°C to 2.02 at 327°C. Rowe believed that the positive ion method is at fault, and that the discrepancy can be explained by assuming that the caesium ions that leave the filament have a double charge.

More recently Taylor and Langmuir[5] have measured the limitations of the caesium ion current by space charge in a cylindrical collector.

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* Dr. Taylor died January 22, 1937.

[1] I. Langmuir and K. H. Kingdon, Phys. Rev. **21**, 380 (1923) and Science **57**, 58 (1923).

[2] I. Langmuir and K. H. Kingdon, Proc. Roy Soc. **A107**, 61 (1925).

[3] H. Rowe, Phil. Mag. **3**, 544 (1927).

[4] A. Kröner, Ann. d. Physik (4) **40**, 438 (1913).

[5] J. B. Taylor and I. Langmuir, Phys. Rev. **44**, 423 (1933); see especially p. 442.

These measurements prove that the value of e/m for the ions is within 1.5 percent of that of singly charged ions. The high energy (23 volts) required to remove a second electron from a Cs atom would preclude the possibility of double ionization by thermal means.

de Boer and Dippel[6] have examined available data on caesium vapor pressure and conclude that Kröner's data, Eq. (2), give the best values and imply that the L-K values of Eq. (3) are too high by a factor of about 2, although they consider that the temperature coefficient of Eq. (3) is probably accurate. They call attention to the fact that the equations for solid and liquid caesium should be different.

de Boer in his book[7] proposes other possible explanations for the high pressures that L-K obtained. He suggests that the freeing of electrons from the ion collecting surface by ion bombardment and by photoelectric emission may have increased the current. Also he thinks that the caesium pressure in the tube may have been higher than that corresponding to the bulb temperature because of the heating of the cylinder by the radiation from the filament.

As a matter of fact, Kingdon before 1924 was thoroughly familiar with all of these possible sources of error and took precautions to avoid them. The remarkable constancy of ion current as the filament temperature and the voltage on the collector are raised was described,[1] and these facts prove that the errors suspected by de Boer could not have been present in the experiments.

Recently van Liempt[8] has reviewed all the literature on this subject and proposes the following equation for the whole temperature range from 0°C to 700°C,

$$\log_{10} p_{mm} = 6.62 - 3701/T. \qquad (4)$$

Eucken[9] has developed general equations based on the second and third laws of thermodynamics for the vapor pressures of metals, taking into account the specific heats of the liquid and vapor phases in order to get the temperature coefficient of the latent heat. For caesium, using the data of Kröner,[4] Hackspill,[10] L and K[2], he obtains

$$\log_{10} p_{mm} = 11.38 - 1.45 \log_{10} T - 4075/T. \qquad (5)$$

A comparison of the vapor pressures of caesium at various temperatures from all these equations is given in Table I.

Eucken's equation is the only one that gives reasonably good agreement with the various experimental determinations over the whole range of temperature. It should be noted that while Rowe and de Boer believe that the true vapor pressure is only 50 percent of that given by L and K, Eucken from the same experimental data obtains a value only 3 percent lower than L and K. In view of the lack of agreement shown by the data in Table I more accurate vapor pressure determinations by the positive ion method are needed, over as wide a range of temperature as possible.

The Positive Ion Method[11]

With a given pressure of caesium and with a sufficiently strong accelerating field for ions to overcome space charge, there is a critical filament temperature, T_c, above which every caesium

TABLE I. *A comparison of vapor pressure data for caesium. Pressures in mm of Hg.*

t °C	T °K	L-K Eq. (3) 0–60°C	Kröner Eq. (2) 250–350°C	v. Liempt Eq. (4) 0–700°C	Eucken Eq. (5) 0–700°C	T–L Eq. (16) or (17)
26.9	300	1.654×10^{-6}	8.85×10^{-7}	1.92×10^{-6}	1.603×10^{-6}	1.721×10^{-6}
126.9	400	3.51×10^{-3}	1.78×10^{-3}	2.33×10^{-3}	2.63×10^{-3}	2.74×10^{-3}
226.9	500	0.348	0.1714	0.165	0.207	0.212
326.9	600	—	3.60	2.83	3.63	3.70
526.9	800	—	161.4	98.6	119.3	121.
726.9	1000	—	1581.	830.	902.	916.

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[6] J. H. de Boer and C. J. Dippel, Zeits. f. physik. Chemie **B21**, 273 (1933).

[7] J. H. de Boer, *Electron Emission and Adsorption Phenomena* (Cambridge University Press, 1935), p. 65.

[8] J. A. M. van Liempt, Receuil des trau chimiques d. Pay.-Bas. **55**, 157 (1936).

[9] A. Eucken, Metallwirtschaft **15**, 27, 63 (1936).

[10] L. Hackspill, Ann. chim. phys. [8] **28**, 611 (1913).

[11] Reference 5. See particularly Fig. 18, pp. 440, 445 and 447.

atom that strikes the filament escapes as an ion. Below T_c the ion emission is very small although it is sufficiently large to be measurable at temperatures as much as 100° below T_c.

Thermodynamic considerations place an upper limit to the fraction of the incident atoms that can be ionized, but with caesium vapor in contact with pure tungsten and with an accelerating field produced by more than -45 volts on the collector this theoretical limit is 0.9998 at 1200°K and 0.9977 at 1800°K.

The critical temperature increases with increasing caesium pressure. The data of Fig. 18 of the previous paper show breaks at the critical temperature T_c which can be expressed as a function of μ_a, the rate of arrival of Cs atoms (atoms·cm^{-2}·sec.$^{-1}$) at the filament, by

$$\log_{10} \mu_a = 27.791 - 14350/T_c. \qquad (6)$$

The temperatures calculated in this way, however, are those at which the filament goes over spontaneously to the emitting condition—it does not return to the nonemitting condition until a somewhat lower temperature is reached. Eq. (6) thus gives an upper limit to T_c.

To utilize this emission to measure μ_a we must know the area of the emitting part of the filament. The portions of the filament near the leads where the temperature is below T_c give no appreciable ion emission. This difficulty can be avoided by using a tube like that described in the previous paper[5] where the guard-ring principle was used to get the emission only from the central part of the filament. With such a tube it was found that an increase in voltage from 45 to 310 did not produce a change in ion emission as great as 0.05 percent. When the filament temperature was raised above 1400° the light from the filament liberated photoelectrons from the caesium film on the cylindrical conducting walls of the tube and increased the observed current.

An analysis of the data showed that these photoelectric currents i_e increased with the filament temperature according to the relation

$$\log_{10} (i_e) = A - 12270/T, \qquad (7)$$

where the constant A depended on the condition of the caesium film. After subtracting these photocurrents it was found that the ion emission was independent of temperature within the experimental error.

There is, however, a difficulty in using the tube of the previous experiments for accurate vapor pressure measurements. If the caesium vapor in such a tube is kept saturated, sufficient caesium deposits on the folds of glass which separate the three cylindrical sections to cause considerable conductivity between the sections and to decrease the accuracy of the measurements. Local heating coils on the glass folds were used in the experiments to prevent this conductivity, but these disturb the isothermal conditions desired in the vapor pressure measurements. Experiments with metallic cylinders (as early as 1923) had shown that at low pressures relatively large amounts of caesium are adsorbed on the cylinders and are very slowly given up as the cylinders become heated by radiation from the filaments. Under such conditions it is impossible to make sure of having equilibrium vapor pressure.

Our present knowledge of the heat conductivity of tungsten[12] and of the temperature distribution[13] along the filament near the leads has greatly decreased the need for guard rings to eliminate end effects. It was therefore decided to use a tube of very simple construction having a single hair-pin filament and a deposit of platinum on the inner surface of the bulb to serve as an ion-collecting electrode. The effective length of the emitting part of the filament was determined by calculating the distance from the leads to a point where the temperature is T_c. Visual observations were also made of the positions of the points where the filaments were just visibly incandescent (about 1050°K).

Description of Tube

The tube used in all the experiments recorded in this paper was made from a cylindrical glass bulb 5 cm in diameter and 15 cm long. Near its lower end a side tube 1 cm in diameter and 5 cm long was provided to contain the caesium. Through the walls of the tube two platinum wires were sealed to provide contact with the

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[12] I. Langmuir and J. B. Taylor, Phys. Rev. **50**, 68 (1936).

[13] I. Langmuir, S. MacLane and K. B. Blodgett, Phys. Rev. **35**, 478 (1930).

platinum deposit. A platinum hairpin filament was mounted in the tube and vaporized in high vacuum until the resistance between the two platinum wires fell to 20 ohms.

The platinum filament was then removed and a pure tungsten hairpin filament of 0.00513 cm diameter and 18.90 cm total length was mounted in the bulb. This filament was of wire from the same spool as that used in the previous experiments.[5] The leads were of such heavy tungsten (20 times the filament diameter) that they were not appreciably heated by conduction from the filament. The leads were about 10 cm long and extended up through narrow glass tubes which extended above the bulb so that when desired their upper ends could be kept above the level of the insulating oil in which the rest of the tube was completely immersed during the experiment.

The caesium used in the experiments had been fractionally distilled in vacuum in several stages. About 1.5 cc of it was sealed into a thin-walled spherical bulb and this was placed in a side tube (attached to the appendix) in which there was also a heavy-walled sealed glass tube containing a piece of iron. The entire tube (except the side arm containing the Cs capsule, which was held at a somewhat lower temperature to avoid attack of the glass by the Cs) was then baked one hour at 410°, one hour at 350° and one hour at 300°C. The filament was aged at 2400°K and flashed at 2800°K. The Cs capsule was then broken by dropping upon it the glass-encased iron weight which had been lifted magnetically. About half of the Cs was then slowly distilled into the appendix and the side tube containing the capsule was sealed off; very little gas was evolved (only enough to raise the pressure about 0.001 mm). The filament was run at 2500°K for 15 minutes in presence of the Cs vapor and then the tube was sealed off from the pump. The melting point of the Cs in the appendix was measured and found to be 28.6°C, indicating freedom from other alkali metals since traces of these greatly lower the melting point.

Experiments to Determine the Vapor Pressure

The tube was completely immersed in oil in a large Dewar flask, holding about 6 liters, which was constantly stirred. The platinum deposit was used to collect the ions emitted by the filament. The current was measured by a galvanometer giving 2.32×10^{-11} amperes per mm deflection. The bath temperatures were not thermostatically controlled since it was found that the drift of temperature was imperceptible during the course of measurements at any given temperature. The temperatures were read to the nearest 0.1° by a calibrated thermometer. As a precaution against any changes in T_c which might conceivably result from contamination of the filament surface by oxygen sputtered from oxide on the walls by ion bombardment, the filament was momentarily flashed at 2600°K before each set of readings at a given bath temperature. No detectable changes in ion current resulted from this flashing.

Tables II and III give typical data. The reasonably satisfactory agreement between D(calc.) $(246+i_e)$ and D(corr.) shows that the increase

Table II. *Data taken with tube at* $-34.5°C$. T_M, *temperature at center of filament calculated from* $A/d^{\frac{3}{2}}$ *given in the Jones-Langmuir tables.** D, *galvonometer deflection (proportional to ion current).* ΔL, *distance (cm) to point on filament at temperature* T_c *(Eq. (8)) where emission begins.* $L=L_0-2\Delta L$; *effective filament length.* $D(corr.)=DL_0/L$, *calculated current if leads did not cool filament (should be independent of* T_M, *except for photoelectric emission).* i_e, *photoelectric emission calculated from Eq. (7).* $D(calc.)=246+i_e$. $T_c=788°K$; $V=-120$ *volts;* $A=10.277$; $D_0=246$; $I_p=1.874\times10^{-8}$ *amp. cm*$^{-2}$; $L_0=18.9$ *cm.*

T_M	D	ΔL cm	L_0/L	D(corr.)	i_e	D(calc.)
1100	215	1.27	1.155	248	0.13	246
1200	224	0.92	1.108	248	1.1	247
1300	234	0.68	1.078	252	6.9	253
1400	262	0.45	1.050	275	33	279
1500	364	0.41	1.046	381	125	371
1600	630	0.33	1.037	653	405	651
1700	1310	0.27	1.030	1350	1140	1386
1800	2950	0.22	1.024	3020	2880	3126

* H. A. Jones and I. Langmuir, Gen. Elec. Rev. **30**, 310, 354, 408 (1927).

Table III. *Data taken with tube at* $+39.9°C$. $T_c=1081°K$; $V=-80$ *volts;* $D_0=2.14\times10^6$; $I_p=1.630\times10^{-4}$ *amp. cm*$^{-2}$.

T_M	$10^{-4}D$	ΔL cm	L_0/L	$10^{-4}D$ (corr.)
1100	130	2.99	1.46	190
1200	177	1.62	1.206	214
1300	188	1.11	1.134	213
1400	197	0.82	1.095	216
1500	200	0.63	1.071	214
1600	205	0.50	1.055	216
1700	208	0.40	1.044	217
1800	211	0.33	1.036	218

of D(corr.) with T_m is accounted for by the photoemission. The data of Table II thus give $D_0 = 246$ as the true ion current from the whole length of uncooled filament. Converting this to amperes and dividing by 0.3046, the total surface area of the filament, gives I_p, the positive ion current density.

In Table III at a higher bulb temperature the currents are more than 10,000 times greater and thus the photoelectric currents are negligible. It is seen that D(corr.) is satisfactorily constant, the marked variation of D with T_M being entirely accounted for by the cooling effect of the leads. The low value of D(corr.) at 1100 would be brought to normal by only a few degrees' change in T_c (which is only 19° less than T_M). The data confirm the accuracy of the choice of T_c.

Calculation of T_c

It has been pointed out that T_c given by Eq. (6) is an upper limit. A method of calculating the value of T_c at which the boundary between the emitting and nonemitting phases is stationary has been outlined in a previous paper.[14] Fig. 1 illustrates the calculations of T_c by this method. The ordinates represent $\nu_a + \nu_p$ as a function of θ. Here ν_a was calculated from columns 2 and 3 of Table I of reference 5, while ν_p is 7 times the value of ν_p given by columns 4 and 5 of this table. The factor 7 takes into account the effect of the field in increasing the ion emission as was shown on p. 445 of reference 5. Unpublished experiments[15] on the rate of movement of the boundary between the emitting and the nonemitting surface phases have furnished the experimental justification of the procedure we are now using to calculate T_c.

The two curves in Fig. 1 are calculated for $T = 800°$ and $T = 1111°$. The horizontal lines AA' and BB' are so drawn that the areas enclosed between this line and the upper and lower portions of the curve are equal. That is $\int(\nu_a + \nu_p - \mu_a)d\theta = 0$, when the integration extends between the two outer intersections of the horizontal line with the curve (points A, A' or B and B'). From the location of these lines we find

$$\text{at } T_c = 800 \quad \mu_a = 1.9 \times 10^{11},$$
$$\text{at } T_c = 1111 \quad \mu_a = 2.1 \times 10^{15}.$$

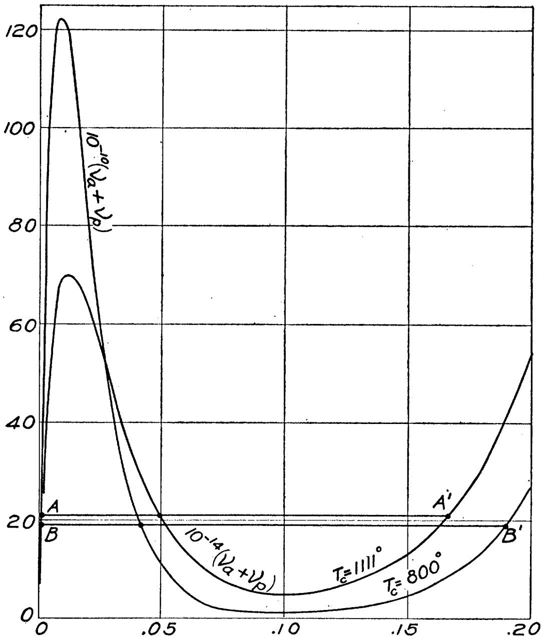

FIG. 1. Plot of $\nu_a + \nu_p$ as a function of θ, at two temperatures T_c to determine the value of μ_a at which the boundary between the emitting and nonemitting phases is stationary.

Plotting log μ_a against $1/T$ as in Fig. 18 of reference 5 we find

$$\log_{10} \mu_a = 25.66 - 11500/T_c \qquad (8)$$

for the relation between μ_a and the temperature T_c, which gives a stationary phase boundary. The values of μ_a vary with bulb temperature and can be calculated from p, the vapor pressure of Cs in Table IV by Eq. (10). The last column of Table IV contains values of T_c calculated in this way.

Calculation of ΔL

The value of $x - x_0$ was first calculated from the data of Table II of reference 13, taking the lead temperature to be 300°K. Then the heat flow Q into the lead was obtained by Eq. (37)[13]; this was used to calculate the correction Δx given by Eq. (75) which allows for the higher values of heat conductivity λ which were found for temperatures below 1500°K. The actual correc-

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[14] I. Langmuir, J. Chem. Phys. **1**, 1 (1933). See especially p. 7, also see reference 5, p. 441.

[15] I. Langmuir and J. B. Taylor, Phys. Rev. **40**, 463 (1932).

TABLE IV. *Data for calculation of vapor pressure. Probable error in* $\log_{10} p = \pm 0.0043 = \pm 1.0$ *percent in* p. *Probable error in* t_B *(calc.) is* $\pm 0.10°$.

t_B	T	Accelerating Voltage	Lowest T_M Used	I_p amp. cm^{-2}	$\log_{10} p_{\text{bar}}$ +10	Diff. obs. minus calc. $\times 10^4$	Δt	T_c
−34.5°C	238.6	120	1100	1.874×10^{-8}	3.8973	− 29	−0.04°	788°K
−30.0	243.1	80	1000	3.85×10^{-8}	4.2146	+ 6	+ .01	805
−20.0	253.1	80	1000	1.736×10^{-7}	4.8772	+ 62	+ .10	844
0	273.1	5–80	1000	2.88×10^{-6}	6.0313	− 75	− .14	921
+ 3.6	276.7	160	1100	3.816×10^{-6}	6.2384	+ 76	+ .15	936
17.9	291.0	160	1200	1.904×10^{-5}	6.9475	+ 16	+ .03	992
19.8	292.9	80	1100	2.315×10^{-5}	7.0341	− 15	− .03	1000
25.4	298.5	40–160	1500	4.234×10^{-5}	7.3001	+ 68	+ .15	1025
30.2	303.3	30–125	1100	6.66×10^{-5}	7.5005	− 31	− .07	1042
38.2	311.3	45–160	1300	1.382×10^{-4}	7.8231	− 81	− .20	1072
39.9	313.0	80	1100	1.630×10^{-4}	7.8960	− 25	− .06	1081
46.2	319.3	300	1300	2.856×10^{-4}	8.1439	+ 23	+ .06	1106
67.8	340.9	320	1300	1.637×10^{-3}	8.9162	+111	+ .32	1193
72.7	345.8	320	1400	2.247×10^{-3}	9.0568	− 90	− .27	1208

tion used ranged from 75 to 95 percent of the value of Δx given by Eq. (75) since a study of possible transition curves between λ determined in reference 12 with that used in reference 13 showed that only for temperature T_c as high as 1500° should the full value of Δx be used. This is the most uncertain part of the determination of ΔL, but the possible error introduced into the calculation of L_0/L is not serious,[16] being of the order of 1 percent at $T_M = 1100$ and 0.5 percent at 1300°.

CALCULATION OF VAPOR PRESSURE

Data like those in Tables II and III were obtained at a series of other temperatures and the values of I_p, the ion current density, are recorded in column 5 of Table IV. In some of the experiments several negative voltages were used on the collector as shown in column 3. In every case within the ranges given there was no measurable change in current. At the higher bulb temperatures such as 46°C it became necessary to employ higher voltages to overcome the space charge of the ion current.

An attempt was made to use a bulb temperature of 88°C, but the current was limited by space charge even at 350 volts. Higher voltages seem undesirable because of possible gas evolution by ion bombardment.

In all cases except the measurement at 25.4°, T_M was varied from the value given in column 4 up to 1800°K. At 0°C the photocurrent was perceptible only above 1400°; at 30.2°C it was not observable even at 1800°. However, the observations above 1600° did not seem to be as accurate as those between 1400 and 1600°.

Dividing the I_p by 1.592×10^{-19}, the electron charge in coulombs, gives μ_a the number of atoms per sq. cm which strike the filament. This is related to the pressure p, in baryes, by the equation

$$p = (2\pi m K T)^{\frac{1}{2}} \mu, \tag{9}$$

from which we obtain for Cs ($M = 132.8$)

$$\log_{10} p = \log \mu_a + 0.5 \log_{10} T - 18.3621, \tag{10}$$

where T is now the bulb temperature.

The values of $\log_{10} p$ calculated in this way from I_p are given in column 6.

EQUATION FOR VAPOR PRESSURE

The data above the horizontal line in Table IV are for solid caesium, while the lower part contains data for liquid caesium. The latent heat of fusion must be taken into account in comparing these results. It should be noted that in the range covered by the experiments the pressure increases by a factor of about 140,000, which is about 43 per cent of the whole logarithmic range

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[16] It was planned in these experiments to determine T_c by actual observation of the temperature T_M at which the emission suddenly increased and then after the filament was transferred to another bulb with clear walls to use an optical pyrometer to determine the points near the leads where the temperature is T_c with a series of values of T_M. In this way L_0/L could be determined with high accuracy. Dr. Taylor's untimely death interrupted these experiments and necessitates the more troublesome and less accurate calculations of L_0/L.

up to atmospheric pressure. Over any such wide range, especially if we are to extrapolate to higher temperatures, it is necessary to consider the temperature variation of the latent heat of vaporization, by taking into account the specific heats of the vapor and liquid.

Fortunately excellent calorimetric data are available from the work of Rengade.[17] He gives for the specific heats (at constant pressure)

$$\left.\begin{array}{l}\text{Solid Cs}\\ C_S=6.92+0.0036\,t\text{ cal. (g atom)}^{-1}\text{ deg.}^{-1},\\ \text{Liquid Cs}\\ C_L=8.00-0.0045\,t\text{ cal. (g atom)}^{-1}\text{ deg.}^{-1},\end{array}\right\} \quad (11)$$

where t is the temperature centigrade.

The vapor pressure curve can be put in the form

$$\log_{10} p=A+(2.5-C/R)\log_{10} T-B/T, \quad (12)$$

where the gas constant $R=1.986$.

The temperature coefficient of C_L was measured only between 28° and 100°C. It is certain that C_L at higher temperatures cannot fall below the Dulong and Petit value of a solid, 6.3, and thus the temperature coefficient of C_L at higher temperatures must decrease. We may therefore neglect the temperature coefficient of C_S and C_L if we use average values for the range of most interest. We chose for the coefficient $(2.5-C/R)$ the value -1.00 for solid and -1.35 for liquid Cs which correspond to $C_S=6.95$ (at $+6°$) and $C_L=7.65$ (at 78°C). The figures in parenthesis are the temperatures at which, by Eq. (11), C_S and C_L have the values chosen. These values should permit a wide extrapolation of the vapor pressure data.

Rengade gives 500.6 as the latent heat of fusion of Cs. For the alkali metals the values of L/T_F, where T_F is the temperature of fusion, are very nearly the same: -7.1 for Na; 7.1 for K; 7.0 for Rb and 6.95 for Cs. This is strong evidence that Rengade's value of L is accurate. The value of B for solid and liquid caesium should differ by $L/4.573$, so that we have

$$B_S=B_L+109. \quad (13)$$

The values of A_S, A_L, B_S and B_L for Eq. (12) have been chosen by the method of least squares to fit the data of Table IV, to satisfy exactly Eq. (13), and to give $p_S=p_L$ at $T=302$°K (the melting point).

The final equations which best represent the data are:

For solid caesium ($T<302°$), p in baryes

$$\log_{10} p_S=13.6710-1.00\log_{10} T-4150/T. \quad (14)$$

For liquid caesium ($T>302°$), p in baryes

$$\log_{10} p_L=14.1781-1.35\log_{10} T-4041/T. \quad (15)$$

To express the pressures in mm of Hg the equations are

$$\log_{10} p_S=10.5460-1.00\log_{10} T-4150/T, \quad (16)$$

$$\log_{10} p_L=11.0531-1.35\log_{10} T-4041/T. \quad (17)$$

Column 7 of Table IV gives the difference between $\log_{10} p$ in column 6 and the values of $\log_{10} p$ calculated by Eqs. (14) or (15), multiplied by 10^4. The "probable error" of the data for a single temperature is thus 1 percent in pressure.

Column 8 gives the amount by which t_B would have to be raised to give the observed pressure by Eqs. (14) or (15). The errors in pressure thus correspond to a "probable error" in temperature of 0.10°.

The change in slope of the $\log_{10} p/vs.\ 1/T$ plot at the melting point is very apparent if the data in column 6 are plotted accurately. This may be better illustrated by applying Eq. (15), for liquid Cs, to calculate the pressure at $-34.5°$. We obtain a value of $\log_{10} p_L$ of 4.0320, whereas Eq. (14) gives $\log_{10} p_S=3.9002$. Thus p_L is 36 percent higher than p_S—a difference 36 times greater than the probable error.

The vapor pressures determined by this positive ion method are thus much more accurate than those obtained by other methods. They should also be particularly free from systematic errors. No attempt was made in these experiments to obtain greater accuracy than shown by these results. We believe that the method is capable of high precision if the cooling effects of the leads are properly determined by temperature measurements. Filaments of smaller diameter and greater length would also reduce the errors.

It is possible to extend the measurements of vapor pressure by the positive ion method to very

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[17] Rengade, Comptes rendus **156**, 1897 (1913). See *International Critical Tables*, Vol. 2, 458 and Vol. 5, p. 93.

TABLE V. *Coefficients A and B in Eq. (18) which give the vapor pressure of Cs in mm within 0.5 percent for specified temperature ranges.*

T_N	Range °K	A	B
263°K	224- 302	7.6920	4036
355	302- 408	7.0223	3833
479	408- 551	6.8460	3760
647	551- 745	6.6706	3662
873	745-1000	6.4942	3529

much lower temperatures by using the accumulation method described in the previous paper.[5] For example, if the filament is flashed to clean it and is then allowed to remain in a lower pressure of caesium for a time sufficient to give 10^{10} ions per cm^2, these ions will give a ballistic kick on an electrometer (or vacuum tube) if the filament is again flashed. The difficulties due to photoelectric effect are also largely eliminated by this method. An accumulation time of ten hours and a sensitiveness of 10^{10} ions would correspond to a pressure of about 10^{-12} baryes or a temperature of about −70°C. With a good electrometer it is possible to detect ballistic kicks of 100 electrons which would be obtained in 10 hours by accumulation at a pressure of 10^{-20} baryes or an average of one atom per cubic meter. Of course, special means would then have to be adopted to avoid photoelectric effects. Dr. Kingdon in this laboratory detected the presence of caesium by galvanometer kicks at temperatures of about −70° but made no accurate measurements.

The pressures in mm of Hg by Eqs. (16) and (17) are given in the last column of Table I for comparison with the older data. The agreement with Eucken's equation from 500 to 1000°K is excellent. The greatest error is at low temperatures, Eucken's value being about 7 percent low at 300°.

The L-K equation between 250° and 330°K is the best single equation of this type that can represent the data. At 262° and at 314° the agreement is perfect. The greatest deviation between 250° and 330° is 4 percent at the melting point (302°K).

In calculating vapor pressures it is far more convenient to use an equation of the form

$$\log_{10} p = A - B/T \qquad (18)$$

than to use equations like (14) to (17) with a term containing log T. In the neighborhood of a selected temperature T_N it is always possible[18] to represent vapor pressure over a fairly wide range by Eq. (18) by proper choice of A and B.

The values of A and B to be used in specified ranges to get p_S or p_L within 0.5 percent are given in Table V.

Examination of Table I shows that the large discrepancies which troubled Rowe, de Boer, Dippel and v. Liempt are not real, but are due to their attempt to extrapolate over too wide a range of temperature by Eq. (18). Thus Kröner's data, as expressed by Eq. (2), agree exactly ($p = 5.20$ mm) with our Eq. (17), or Table V, at 342°C, which is within the range 250 to 350°C covered by his experiments. At 250°C Kröner's data give 0.382 as compared to our 0.454 mm (or 16 percent too low). Hackspill's data are evidently not very accurate for they cannot be represented by Eq. (18). His measurement at the highest temperature (397°C), however, agrees exactly with our value of 15.9 mm at this temperature. His data at temperatures from 272° to 350°C are from 8 to 15 percent high, while a measurement at 244°C is 35 percent low.

We have thus experimental justification for using Eq. (17) up to the temperatures of about 700°K. The accuracy of the measurements of p indicated by the data of Table IV and the wide range of pressure covered by these data give reason for believing that no large error can arise even in extrapolating to 1000°K. Thus, if there is a 1 percent progressive error in p between −34.5°C and +72.7°C, this would entail an error of only 2.4 percent at 1000°. If we consider that the specific heat of liquid Cs above 600° begins to deviate from the value 7.65, which we have assumed and has an uncertainty of 0.5 unit at 1000°, the error in p at 1000° would be only 5 percent. It is therefore probable that Eq. (17) gives p correctly within 8 percent even at 1000°K.

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[18] I. Langmuir, J. Am. Chem. Soc. **54**, 2798 (1932).