length. In view of the accuracy obtained there appears to be little doubt that the wave-length as indicated by refraction agrees with the grating value.

It was thought worth while to recalculate the wave-length from photographic results of Bearden and Stauss[1] using the newer data now available on the fundamental constants, the wave-lengths of the critical absorption edges of Si L and O K and the effective number of electrons in the K and L shells. Larsson's values appear to be too high, so no attempt was made to include them. Table II gives the various wave-lengths computed for a $\lambda^{2.75}$ absorption law.

Consistent errors in the photographic experiments may easily explain the failure of exact agreement with the grating results. On adding the percent deviation from the grating value one finds the values to agree to within 0.03 percent. Thus contrary to previous conclusions it now appears that the previous as well as the present experimental results substantiate the grating values of x-ray wave-lengths instead of the crystal wave-lengths.

TABLE II.

	Crystal	Grating	Refraction
	Bearden		
Cu $K\alpha_1\alpha_2$	1.5380	1.5416	1.5404
Cu $K\beta$	1.3888	1.3921	1.3916
Mo $K\alpha_1\alpha_2$	0.7089	0.7105	0.7098
Mo $K\beta$	.6307	.6322	.6324
	Stauss		
Mo $K\alpha_1$	.7075	.7091	.7096
Mo $K\beta$	.6307	.6322	.6333

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The Vapor Pressure of Calcium between 500 and 625°C

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The vapor pressure of solid calcium has been measured between 500 and 625°C, by the method of molecular effusion. The amount evaporated was determined by microtitration to better than 10^{-6} g. The results are well represented by the empirical equation: $\log p$ (in mm) $=8.15-9670/T$. The present values for the pressure are about ten times smaller than those previously reported by Pilling for the same temperatures. Since the specific heat of solid calcium is known as a function of T, the "vapor pressure constant," or "chemical constant," can be computed. The new pressure data lead to the correct value for this constant, but the old ones do not. For the heat of evaporation at $T=0$ the value 4.53×10^4 cal./mole is obtained.

INTRODUCTION

IN experiments on thin metal films the material is often deposited by evaporation in vacuum from a hot source of controlled temperature. The amount deposited in a given time can then be calculated from the geometry of the apparatus, if the vapor pressure of the metal is known for the temperature in question. Except for the alkali metals, mercury and a few others, vapor pressure data in the range usually involved in evaporation work are very meager. The following is a report on some new pressure determinations for calcium, which were undertaken in connection with electron scattering experiments with thin calcium films.

METHOD

Consider an enclosure of absolute temperature T, containing ideal gas particles of mass m at a pressure p. From kinetic theory it is known, that the number of particles escaping in unit time through a small opening δs in the wall into a solid angle element δo in a direction making an angle θ with the normal to δs, is given by:

$$dn/dt=p(2\pi mkT)^{-\frac{1}{2}}\delta s(\delta o/\pi)\cos\theta,$$

where k is Boltzmann's constant. Introducing instead the gas constant pro mole R, the molecular weight M and the number of moles N, one obtains:

$$p=(dN/dt)(2\pi MRT)^{\frac{1}{2}}\pi/\delta s\delta o\cos\theta. \qquad (1)$$

The condition that δs should be small means essentially, that the linear dimensions of the opening should be small compared to the mean free path in the gas, so that the process is one of molecular effusion. This was the case in the present experiments, in which dN/dt was measured as a function of T and p computed from (1), δs, θ and δo being known constants of the apparatus.

Apparatus

The essential parts of the apparatus are shown in Fig. 1. The calcium gun G, shown in detail to the right, is a small piece of molybdenum rod, 6 mm in diameter, with a 3 mm hole for a tungsten heating spiral. The calcium is contained in a cylindrical pit, 9.5 mm deep and 2.15 mm in diameter. A copper/constantan thermocouple of fine wire (B. & S. 40 and 38) is introduced through a third small hole near the bottom of the pit and held in position by a small nickel rivet. Opposite G is a long glass plate with a hole in it, acting as a diaphragm, D. A glass slider S, guided by two glass rods R and operated by a magnet from outside, can be moved over the diaphragm, so that a number of small microscope cover-glass plates C can be placed, one at a time, about 5 mm above the hole in D and exposed to the shower of calcium atoms from G. The tube is connected to a fast mercury diffusion pump over a liquid air trap.

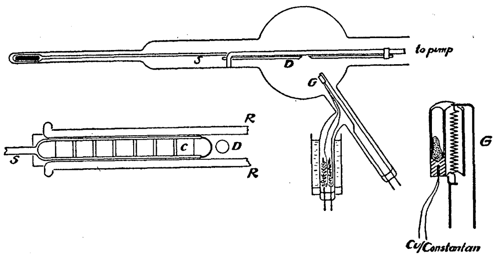

FIG. 1. Diagram of apparatus.

Experimental Procedure

The apparatus was baked at 400°C after assembly; the pressure of residual gas in the tube during the experiments was of the order of 1×10^{-7} mm or less. The experiments consisted in exposing each one of a series of cover-glass plates to the calcium beam for a measured time, during which the temperature of the gun was kept sensibly constant. The tube was then cut open and the amount deposited on each plate determined. Calcium turnings from Merck were used. The gun was first heated for a considerable time at various temperatures up to above 700°C, so that in all about 50 percent of the metal had distilled off before any measurements were taken. This should have removed any possible impurities of higher volatility, such as alkali metals. As a matter of fact, electron scattering experiments with films from different fractions obtained in the course of this distillation showed that they were all essentially calcium deposits.

The temperature of the gun could be kept constant to about 0.3°C without much difficulty. A second thermocouple, made from the same wire as the one in the tube, was calibrated with the freezing points of Al, Zn, Pb and Sn as standards. This thermocouple was protected by a sealed quartz tube containing H_2 at a pressure of about 5 mm; the tube had been drawn into a thin-walled capillary at the hot junction end. The calibration equation so obtained was then used to derive the temperature of the calcium gun from the measured e.m.f.

The calcium deposits on the plates appeared with very sharp edges, and there was no deposit on the upper side of D (due to reflected atoms). The color was a deep blue in transparent light, and almost like that of silver in reflected light. Most of the deposits, $10^{-6}-10^{-5}$ g/cm^2, were rather transparent; in the air of the room they deteriorated in a few minutes and became almost invisible. The deposit on a plate exposed to air is presumably a mixture of Ca, CaO, $Ca(OH)_2$ and $CaCO_3$, depending on the length of exposure, the final state being $CaCO_3$. In view of this, it would have been difficult to determine the amount deposited on a plate by weighing. Instead, the following method was adopted. The plate was placed in 2 cc of 0.004-n HCl, which was then heated to boiling. In this way Ca-metal, CaO, $Ca(OH)_2$ and $CaCO_3$ were all dissolved, neutralizing an amount of acid equivalent to the amount of Ca. This was determined after cooling by titrating the excess acid in the solution with 0.008-n KOH. All glassware used, including the cover glass plates, had been aged by boiling in HCl, in order to reduce the error due to alkali dissolved from the glass. As a further precaution, blank tests were made with plates introduced in the tube together with the others and treated exactly in the same way as these, except that they were never exposed to the beam. No effect was found.

Results

The results are contained in Tables I and II. The actual normality factor of the KOH was 0.00830. The hole in D, of radius 0.50 cm, had its center at a distance of 4.04 cm from the opening of the gun, on the normal to the end surface of the gun. The plane of the hole was inclined 34° to this normal. Hence $\delta o = 1.31_2 \times 10^{-2}\pi$, $\cos\theta = 1$ and $\delta s = 3.63 \times 10^{-2}$ cm^2, so that p (in mm) $= 2.28_2 \times 10^5 T^{\frac{1}{2}} dN/dt$. Double weight was assigned to No. 1 in taking the mean value for 501°C in Table II. Fig. 2 shows a plot of $\log p$ *vs.* $1/T$. The points fall fairly close to the straight line $\log p = 8.15 - 9670/T$.

Discussion

The only other pressure data for calcium in this temperature range are those published by Pilling.[1] He determined the loss of weight per unit time and unit surface, W, of a piece of the metal placed in an evacuated Pyrex tube of the desired temperature. Experiments with Zn and Cd, for which the vapor pressures were known from other work, showed that the expression: $(W/p)(T/M)^{\frac{1}{2}}$ was a constant, which had the same value for both metals. Assuming the same relation to hold for calcium, he was able to calculate p from the measured value of W for this metal. The data so obtained are included in Fig. 2, together with the line: $\log p = 9.73 - 10{,}170/T$, which represents the vapor pressure of calcium in this region according to Pilling. It will be seen, that the values for p obtained in the present work are smaller than those of Pilling by a factor of about 10.

In calibrating the thermocouple in the present work two freezing curves were taken for each standard point; the two curves repeated within about 0.1°C. It is believed that the temperatures in Table II are correct to 1°C. The error in the volumetric determination of the calcium deposits may be estimated from the difference between the two values obtained for 501°C. The resulting inaccuracy in p is probably about 10 percent. In calculating the vapor pressure from the amount of calcium on the plate it is assumed, that the number of calcium atoms deposited is equal to the number striking the plate. If there were an appreciable reflection coefficient R, the

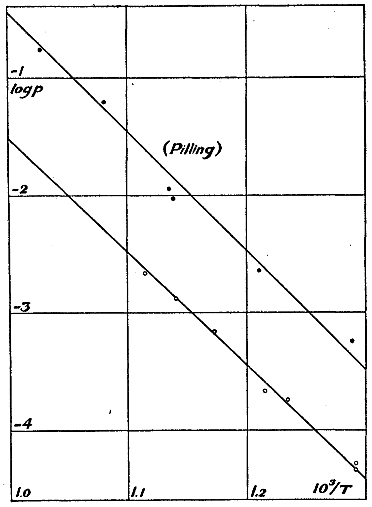

FIG. 2. Variation of vapor pressure of calcium with the temperature.

TABLE I. *Calculation of the rate of deposition of calcium.*

No.	°C	Seconds	cc KOH	Mole KOH/sec.	Mole Ca/sec. $=dN/dt$
7	624.2	1500	0.113	6.27×10^{-10}	3.13×10^{-10}
6	603.1	1200	0.058	4.02×10^{-10}	2.01×10^{-10}
9	579.0	3600	0.090	2.08×10^{-10}	1.04×10^{-10}
5	550.3	5400	0.042	6.45×10^{-11}	3.23×10^{-11}
8	536.5	14,520	0.097	5.55×10^{-11}	2.77×10^{-11}
1	500.8	43,200	0.074	1.42×10^{-11}	7.11×10^{-12}
3	500.8	21,600	0.042	1.61×10^{-11}	8.07×10^{-12}

TABLE II. *Calculation of the vapor pressure of calcium as a function of temperature.*

No.	°C	T	p (mm)	$\log p$	$1/T \times 10^3$
7	624	897	2.14×10^{-3}	$0.330 - 3$	1.115
6	603	876	1.31×10^{-3}	$0.117 - 3$	1.141
9	579	852	6.91×10^{-4}	$0.840 - 4$	1.173
5	550	823	2.11×10^{-4}	$0.325 - 4$	1.215
8	536	810	1.80×10^{-4}	$0.255 - 4$	1.235
1	501	774	4.53×10^{-5}	$0.656 - 5$	1.292
3	501	774	5.13×10^{-5}	$0.710 - 5$	1.292
Mean	501	774	4.72×10^{-5}	$0.674 - 5$	1.292

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[1] Pilling, Phys. Rev. **18**, 362 (1921).

values for p in Table II would be too low by a factor $(1-R)$. Several tests have been made, however, which indicate that the reflection coefficient is inappreciable in this apparatus. In connection with the electron scattering experiments a target was placed in the calcium beam with the back to the gun, so that the front face was exposed only to atoms reflected from the walls of the evaporation chamber. No trace of a calcium film could be found on this face after exposures 20 times longer than those that would produce a detectable film, when the front side was facing the gun. In the present experiments the fact that the deposits exhibit a sharp edge also indicates that reflection is small. The best evidence for this is however the total absence of a deposit around the hole on the upper face of the diaphragm D. Assuming that the angular distribution of reflected atoms follows Lambert's law, the density of the deposit at a point in the upper face of D is given by

$$\sigma=(R\sigma_0/\pi)\int h^2 ds/r^4, \tag{2}$$

where h is the height of C above D and r the distance of the point in question from the element ds; the integral is to be extended over the entire area of the deposit on C of density σ_0. Higher reflections than the second have been neglected. The integral in (2) has been evaluated graphically for the case of a point, located on the normal to C and D through a point on the edge of the almost circular deposit on C. For this case $\sigma=0.3R\sigma_0$. The density at this point of D after the entire set of plates has been exposed should therefore be at least $10\times 0.3R\sigma_0$, while a density of $(1/4)\sigma_0$ would have been detected, if present. Equating the two, one obtains as an upper limit for the reflection coefficient $R=1/12$. This should probably be regarded as a rather conservative estimate.

There were some difficulties in measuring the relative position of the diaphragm and the gun accurately in this apparatus. It is possible that the value used for δo is off by 10 to 15 percent for this reason. This would give a systematic error in the values for p of the same magnitude. Assuming such an error in δo and a reflection coefficient 1/12, the pressure values in Table II could possibly be 20–25 percent too low.

The weak point in Pilling's work is the assumption that $(W/p)(T/M)^{\frac{1}{2}}$ has the same value for Ca, as for Zn and Cd. This quantity depends in a complicated way on the reflection coefficients of glass and metal at the test temperature T. As a result, the rate of evaporation per unit surface of the metal under these circumstances is only a few tenths of 1 percent of the molecular effusion rate for the same temperature and pressure according to Pilling.

Comparison with Theory

It is interesting to try to fit the experimental data to the well-known vapor pressure equation of thermodynamics. For monatomic vapors this equation may be written in the form

$$\ln p=-\Lambda_0/RT+(5/2)\ln T-(1/R)f(T)+i \tag{3}$$

or

$$\begin{aligned}\log p \text{ (in mm)}=-0.4343\Lambda_0/RT&+(5/2)\log T\\ &-(0.4343/R)f(T)+0.4343i-3.1249\end{aligned} \tag{4}$$

with

$$f(T)=\int_0^T\frac{dT'}{T'^2}\int_0^{T'}C_s dT''+\sum\nolimits_\nu\Lambda_\nu\left(\frac{1}{T_\nu}-\frac{1}{T}\right). \tag{5}$$

Here Λ_0 is the heat of evaporation at $T=0$, C_s the specific heat of the solid at constant pressure and Λ_ν the heat of transition at the transition point T_ν; the summation is to be extended over all transitions for which $T_\nu<T$. Λ_0, C_s and Λ_ν are all referred to one mole of the substance; i is the "vapor pressure constant" or "chemical constant." From statistical mechanics, the value of this constant in the case of Ca should be given by:

$$i=\ln\left[(2\pi m)^{3/2}k^{5/2}/h^3\right]. \tag{6}$$

Extensive measurements of C_s for calcium in the range 10–200°K have been published by Clusius and Vaughen;[2] they find that the specific heat can be represented by $C_s=4.41\times10^{-5}T^3$ for $T<19$. Eastman, Williams and Young[3] have

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[2] Clusius and Vaughen, J. Am. Chem. Soc. **52**, 4686 (1930).

[3] Eastman, Williams and Young, J. Am. Chem. Soc. **46**, 1178 (1924).

measured C_s for 293–878°K. They find a transition point $Ca_\alpha \rightleftarrows Ca_\beta$ at $T_1 = 673$ with a heat of transition $\Lambda_1 = 100 \pm 25$ cal./mole. The existence of this transition point was confirmed by Ebert, Hartmann and Peisker[4], who showed by x-ray analysis that Ca_α had a face-centered cubic, and Ca_β an hexagonal structure.[5] From these data the function $f(T)$ has been computed by numerical integration. The values of $0.4343f(T)/R$ are given in Table III.

TABLE III. *Calculation of the term 0.4343f(T)/R appearing in Eq. (4).*

No.	T	$(5/2) \log T$	$\log p$	$\frac{0.4343f(T)}{R}$	$\log p + \frac{0.4343f(T)}{R} - (5/2) \log T$	$\frac{1}{T} \times 10^3$
7	897	7.382	0.330–3	2.491	0.439–8	1.115
6	876	7.356	0.117–3	2.458	0.219–8	1.141
9	852	7.326	0.840–4	2.419	0.933–9	1.173
5	823	7.289	0.325–4	2.372	0.408–9	1.215
8	810	7.278	0.255–4	2.350	0.327–9	1.235
1	774	7.222	0.656–5	2.287	0.721–10	1.292
3	774	7.222	0.710–5	2.287	0.775–10	1.292
mean	774	7.222	0.674–5	2.287	0.739–10	1.292

If $\log p + 0.4343f(T)/R - (5/2) \log T$ is plotted as a function of $1/T$, a straight line should result. Fig. 3 shows such a plot. Computation gives for the best straight line to represent the data of Table III the equation:

$$\log p + 0.4343f(T)/R - (5/2) \log T = -9\,950/T + 3.56_6. \quad (7)$$

If Pilling's data are treated in the same way, the following equation is obtained:

$$\log p + 0.4343f(T)/R - (5/2) \log T = -10\,580/T + 5.26_1. \quad (8)$$

This line and the points calculated from Pilling's data are also shown in Fig. 3.

From the constants of these equations the heat of evaporation and the vapor pressure constant can be calculated. The values so obtained are given in Table IV together with the theoretical value of i according to (6).

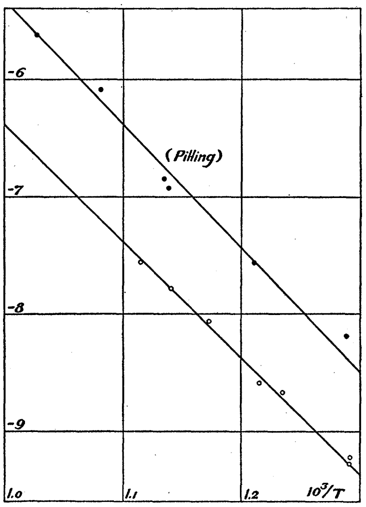

FIG. 3. Plot of $\log p + 0.4343f(T)/R - 5 \log T/2$ against $1/T$.

TABLE IV. *Heat of evaporation and vapor pressure constant of calcium.*

	Pilling	Present work	Theory
Heat of evaporation, Λ_0	4.84×10^4 cal./mole	4.53×10^4 cal./mole	—
Vapor pressure constant, i	19.3	15.4	15.71

The close agreement with the theoretical value of i may be regarded as a check on the correctness of the vapor pressure data obtained in the present work. It should be mentioned, however, that the boiling point measurements for liquid calcium by Hartmann and Schneider[6] at pressures from 10 to 200 mm appear to be about equally difficult to reconcile with Pilling's results and with my own. It is not possible at present to calculate the vapor pressure constant from these data, since the heat of fusion and the specific heat of liquid calcium are unknown.

CONCLUSION

By using calcium guns of suitable aperture, it would be possible to extend the vapor pressure curve obtained with the present method towards higher pressures, as well as towards lower ones. It is intended to do this, presently. It is also planned to measure the vapor pressures of strontium and barium by the same method.

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[4] Ebert, Hartmann and Peisker, Zeits. f. anorg. u. allg. Chem. **213**, 126 (1933).

[5] These authors give $T_1 = 723$ as the transition point; Cf., Rinck, C. R. **192**, 421 (1931).

[6] Hartmann and Schneider, Zeits. f. anorg. u. allg. Chem. **180**, 275 (1929).