

The Vapor Pressure of Barium

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Citation: [The Journal of Chemical Physics](#) **3**, 627 (1935); doi: 10.1063/1.1749565

View online: <http://dx.doi.org/10.1063/1.1749565>

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mately equal intensities (and say that one member is really much stronger) by assuming that the transition probabilities are so high, that each line is completely absorbed in the light path in the conglomerate.

Because of this uncertainty, it has not been considered advisable at present to draw an energy level diagram.

CONCLUSIONS

The existence of levels at 21 cm^{-1} and 41 cm^{-1} above the basic one has been proven; the probable existence of higher levels is indicated. These levels must yet be regarded as of uncertain origin. The existence of a constant energy difference between "low temperature" lines is described.

OCTOBER, 1935

JOURNAL OF CHEMICAL PHYSICS

VOLUME 3

The Vapor Pressure of Barium

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(Received July 1, 1935)

The vapor pressure of barium has been determined for temperatures from 525 to 750°C by a method based on molecular effusion. The metal was obtained by decomposition of barium azide in vacuum. The evaporated deposits were determined by microtitration to about 10^{-8} mole. The values obtained for the pressure range from 5×10^{-5} to 2×10^{-2} mm. They are well represented by the equation: $\log p$ (in mm) $= 6.99 - 8980/T$. This corresponds to a latent heat of evaporation of 4.09×10^4 cal. mole.

INTRODUCTION

DATA on the vapor pressure of metals are very useful in work on thin metal films, since one of the simplest methods of obtaining such films is that of evaporation in vacuum. If a knowledge of the thickness of the deposit is required, it is mostly necessary to know the rate of evaporation from the source as a function of the temperature. For relatively volatile metals of low ionization potential such as the alkali metals, the ionization method of Langmuir and Kingdon¹ has been used down to very low values of pressure. Accurate measurements have been made for Hg, Cd, Zn and some others, including alkali metals, by using the Knudsen method² of molecular effusion. In these cases the temperatures are so low, that the metal can be placed in direct contact with the glass wall of the tube and its temperature controlled from the outside by a suitable furnace. Vapor pressure values for a number of the less volatile metals, have been computed by Langmuir³ and his collaborators⁴

from measurements of the rate of evaporation from filaments. To obtain the vapor pressure from such data, one must know the reflection coefficient r of the emitting surface for atoms of the vapor in equilibrium with the metal. This quantity has not, in general, been determined by direct experiments. In the work referred to, r was assumed to be negligible compared with unity. In the effusion method the uncertainty about r is eliminated, since here the rate of evaporation is measured from a hole in the wall of an enclosure containing the metal. The relation between such a source and a filament source is clearly similar to that between a "hohlraum" black body emitter and a plane surface of the same temperature in thermal radiation: the emissivity of the surface corresponds to the quantity $1 - r$, the accommodation coefficient, in the case of evaporation. Recently one of us has reported some new vapor pressure determinations for calcium, using a method based on molecular effusion.⁵ In continuation of this work, we have now measured vapor pressures for barium by the same method but with a new, improved apparatus.

¹ Langmuir and Kingdon, Proc. Roy. Soc. A107, 61 (1925).

² Knudsen, Ann. d. Physik 29, 179 (1909).

³ Langmuir, Phys. Rev. 2, 329 (1913).

⁴ Jones, Langmuir and Mackay, Phys. Rev. 30, 201 (1927).

⁵ Rudberg, Phys. Rev. 46, 763 (1934).

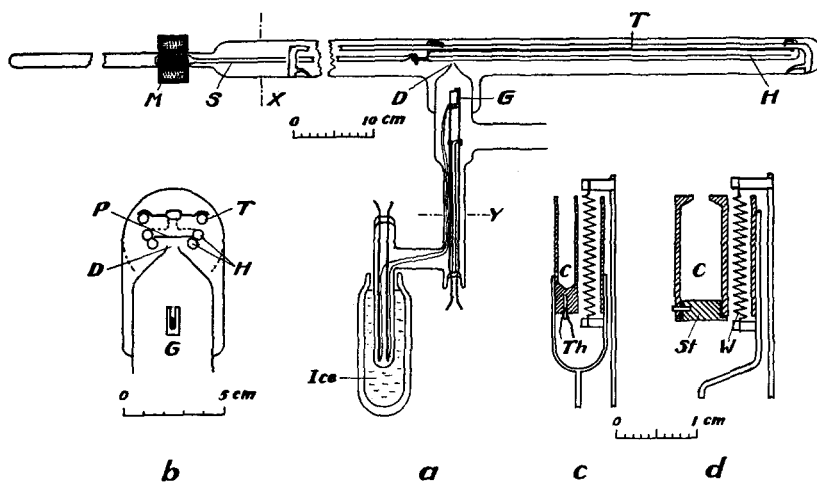


FIG. 1.

APPARATUS

Fig. 1 is a diagram of the essential parts of the apparatus. It consists of a big T-tube, shown from the side in *a*; *b* is an enlarged section through the central part of the T. The metal evaporates from a hole in the top of the heated gun *G*, and a well-defined beam of atoms, limited by the diaphragm *D*, enters the horizontal part of the tube. This part has a long plateholder *H*, made of glass rod, which can be loaded with some twenty microscope cover glass plates *P*. The plateholder rests on two glass tracks *T*, sealed to the main tube; by means of the slider *S*, operated from the outside by the magnetic coil *M*, the plateholder can be moved along the tracks and any one of the plates exposed to the beam emerging from *D*. The tube can be cut open at *X* and *Y* for removal of the plates and reloading of the gun.

Two different constructions have been used for the barium gun. Vertical sections of these are shown in *c* and *d*. In each case the gun is made of a piece of molybdenum rod (shaded in the figure), heated by radiation from a tungsten spiral *W*. The barium is contained in *C*. The thermocouple *Th* of chromel/platinum wire, 6 and 5 mils, respectively, is shown with the smaller gun, which is practically identical with the one previously used in the work on calcium.

In the larger gun the thermocouple was introduced in a similar fashion, but from the side. This gun has a larger container with a stopper *St* at the bottom to facilitate loading.

EXPERIMENTAL PROCEDURE

It was impractical to load the gun directly with metallic barium, because of the rapidity with which the metal reacted with the air. Instead the gun was filled with barium azide BaN_6 , which was subsequently decomposed by heating in vacuum into barium and nitrogen. The azide was made by passing gaseous HN_3 , obtained from sodium azide and sulfuric acid, through a suspension of barium hydroxide in water under reduced pressure, as recommended by Hoth and Pyl.⁶ The crystallized product was washed with alcohol on the filter and kept in a vacuum desiccator.

After the tube had been assembled and a vacuum of the order of 10^{-6} mm obtained, the temperature of the gun was raised very slowly, while the ionization gauge was closely watched for a rise in pressure. As soon as the decomposition started, the heating current was lowered or turned off. The speed of the reaction could be followed from the gauge indications and con-

⁶ Hoth and Pyl, *Zeits. f. angew. Chem.* **42**, 888 (1929).

trolled by varying the heating current. In order to get a good yield of barium it was found necessary to control the reaction rate rather carefully, since a sudden local rise in pressure at the bottom of the container *C* would easily blow the fluffy powder of azide out of the gun. The danger of this is greatest at the start of the reaction. The time required for the decomposition of an azide charge was usually of the order of 1 to 2 hours. At the end of this time the temperature was gradually raised to values above 500°C. The entire tube was then baked at 400°C after which the pressure was of the order of 10^{-7} mm. The gun was now heated and some barium allowed to distil. This should have removed any small amounts of more volatile impurities that might have been present. For this first evaporation it was usually found necessary to bring the temperature up to the melting point of barium, before the metal would start to evaporate. Once this had been done, however, barium could be distilled at any time and at any temperature, without further melting. It thus appears as if the powdered metal resulting from the decomposition of the azide were covered with some impervious skin, which is removed by melting the metal. It was found that the capacity of the small gun was not large enough to allow all the plates *P* to be utilized with a single charge of the gun. The larger gun was designed to provide a greater capacity. However, tests showed that there was a considerable loss of barium with this gun, due to leakage at the stopper when the metal was melted, so that the number of exposures obtained from a single charge was about the same as with the smaller gun.

When an exposure was to be made, the gun was first heated until the steady temperature required had been attained. The plateholder was then moved so as to expose the desired plate to the beam. After a measured length of time, during which the temperature was kept sensibly constant, the plate was removed from the beam in the same manner.

The temperature of the gun could be kept constant to about 0.3°C. The chromel/platinum thermocouple was calibrated before assembly, with the freezing points of Cu, Al and Zn as standards. During the calibration the thermocouple was protected by a sealed quartz tube,

containing hydrogen at a pressure of about 5 cm; the tube had been drawn into a thin-walled capillary at the hot junction end.

The barium deposits on the plates appeared with very sharp defining edges, except for the one at 750°C, which showed a slightly diffuse edge. No deposits could be detected on neighboring parts of the tube not directly exposed to the beam. This indicates that there was no appreciable reflection of atoms from the plates. In transparent light the deposits showed a deep black color, in contrast to the films of calcium which are blue. At a thickness of some 50 atom layers the barium deposits became visible. Through a completed exposure, which in general had about 1000 layers, the lighted filament of the gun could still be seen. When air was admitted to the tube, the deposits turned white almost instantaneously. To determine the amount of barium on a plate the method already used with calcium was adopted. The plate was placed in 2 cc of 0.001*N* HCl, which was then heated to boiling. In this way all the barium, whether present as metal, BaO, Ba(OH)₂ or BaCO₃, was dissolved, and an equivalent amount of HCl neutralized. This was determined after cooling by titrating the excess acid in the solution with 0.002*N* NaOH. The plates as well as all other glassware had been aged by boiling in HCl before use, in order to avoid errors due to alkali dissolved from the glass. As a further precaution several unexposed plates were taken from the plateholder and treated in the same way as the others, each time that deposits were analyzed. The mean value obtained from these blanks was actually used to find the number of Ba-equivalents in any particular sample for which the excess acid had been determined.

RESULTS

The quantity measured in these experiments is dN/dt , the number of moles emitted per second from the opening δs in the gun, at temperature *T*, into a solid angle $\delta\omega$ (defined by the size and position of *D* with respect to *G*) in a direction making an angle θ with the normal to δs . From this the pressure *p* of the vapor in *G* can be computed:

TABLE I.

No.	°C	Sec.	cc NaOH	NORMALITY	MOLE Ba ($\times 10^3$)	MOLE Ba/sec. $= dN/dt$
2.08	525	45000	0.071	0.00182	0.65	1.43×10^{-12}
1.06	550	37800	0.175	0.00190	1.66	4.40×10^{-12}
3.10	550	28800	0.179	0.00172	1.54	5.34×10^{-12}
2.10	575	18000	0.119	0.00182	1.08	6.01×10^{-12}
1.02	600	9000	0.161	0.00190	1.53	1.70×10^{-11}
3.16	610	5400	0.184	0.00172	1.58	2.93×10^{-11}
2.14	625	7200	0.191	0.00182	1.74	2.43×10^{-11}
4.13	650	3600	0.108	0.00187	1.01	2.81×10^{-11}
3.13	650	4500	0.250	0.00172	2.85	4.78×10^{-11}
1.15	650	2760	0.145	0.00190	1.38	5.00×10^{-11}
2.15	675	1500	0.120	0.00182	1.09	7.27×10^{-11}
4.14	700	900	0.129	0.00187	1.21	1.34×10^{-10}
4.16	700	900	0.149	0.00187	1.39	1.55×10^{-10}
2.18	725	480	0.112	0.00182	1.02	2.12×10^{-10}
1.19	750	240	0.138	0.00190	1.31	5.47×10^{-10}

TABLE II.

No.	°C	T	$10^{-6} \times A$	ρ (mm)	$\log p$	$10^3 \times 1/T$
2.08	525	798	1.323	5.34×10^{-3}	0.728-5	1.253
1.06	550	823	1.035	1.31×10^{-4}	0.117-4	1.215
3.10	550	823	0.991	1.52×10^{-4}	0.182-4	1.215
2.10	575	848	1.323	2.32×10^{-4}	0.366-4	1.176
1.02	600	873	1.035	5.22×10^{-4}	0.718-4	1.145
3.16	610	883	0.991	8.65×10^{-4}	0.937-4	1.131
2.14	625	898	1.323	9.65×10^{-4}	0.985-4	1.111
4.13	650	923	1.653	1.22×10^{-3}	0.088-3	1.084
3.13	650	923	0.991	1.44×10^{-3}	0.158-3	1.084
1.15	650	923	1.035	1.57×10^{-3}	0.196-3	1.084
2.15	675	948	1.323	2.97×10^{-3}	0.473-3	1.059
4.14	700	973	1.437	6.01×10^{-3}	0.779-3	1.028
4.16	700	973	1.437	6.94×10^{-3}	0.841-3	1.028
2.18	725	998	1.323	8.86×10^{-3}	0.947-3	1.002
1.19	750	1023	1.035	1.81×10^{-2}	0.258-2	0.978

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

or p (in mm) $= AT^{1/2} dN/dt$,
where

$$A = 7.501 \times 10^{-4} (2\pi MR)^{1/2} \pi / \delta s \delta \theta \cos \theta.$$

Here M is the molecular weight for the vapor and R the gas constant pro mole. This equation holds provided the dimensions of the hole in the gun are small compared to the mean free path in the vapor, so that the process is one of molecular effusion.

The results of the analysis are given in Table I; the pressures calculated from these data are listed in Table II. Four different sets of exposures were taken. Of these the last one was obtained with the larger gun. In each case the first figure in the plate number stands for the particular set to which the plate belongs; the remaining two give the position of the plate on the holder. The different sets have somewhat different A -

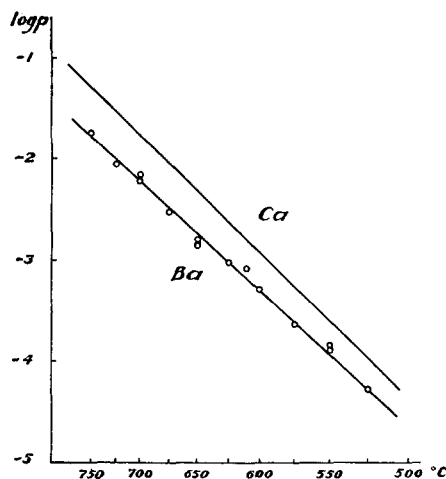


FIG. 2.

values as listed in Table II, mainly because the vertical distance between G and D , which enters in $\delta \theta$, varied. This distance was determined with a cathetometer; the values found were 2.77, 2.75, 2.71 and 3.17 cm for the four sets. The opening D had a diameter of 0.421 cm. The angles, which were only estimated, were usually negligible, never exceeding 8° . The diameter of the circular hole δs was 0.207 cm for the small gun, and 0.202 cm for the large one. In the second set the area of the hole was reduced 25 percent by a speck of oxide, resulting from an accident when the barium azide was decomposed. The high A value for No. 4.13 is due to a lateral shift of the plateholder, which reduced the effective solid angle for this exposure.

DISCUSSION

From the magnitude of the pressures listed in Table II it is evident that the condition that the mean free path be large compared with the dimensions of the hole is fulfilled over this range, except perhaps for the highest point. The mean free path in the vapor at 750°C is about 0.6 cm. The fact that the edge of the deposit was slightly diffuse in this exposure may thus be an indication of collisions between atoms in the beam. It could, however, also be due to a very small amount of reflection of atoms from D at this temperature.

In Fig. 2 the values of $\log p$ from Table II have been plotted in the usual manner against an abscissa proportional to $1/T$. The straight line drawn was computed from the same data, assuming a linear relationship. Its equation is: $\log p = 6.99 - 8980/T$. The points obtained fit this line fairly well; the mean deviation from the line corresponds to an error of about 10 percent in the value of p . In computing this equation the values at 750 and 725°C, which will be seen to fit the line quite well, were also included. Actually these temperatures are above the melting point of barium, 710°C.⁷ Hence these points correspond to the vapor pressure over liquid barium and should therefore, strictly speaking, fall on a different line, intersecting the one for the solid at the melting point. Evidently the heat of fusion is so small compared to the heat of evaporation, that the change of slope is far beyond detection with the limited accuracy of these measurements.

⁷ Rinck, *Comptes rendus* **193**, 1328 (1931).

We have also included in Fig. 2 a line representing the vapor pressure of calcium obtained in the previous work by one of us.⁵ It will be seen that the calcium pressures are 2 to 3 times higher than those of barium for the same temperature in this range. From the slope of the barium curve the latent heat of evaporation is 4.09×10^4 cal./mole, a value somewhat smaller than that for calcium, *viz.*, 4.31×10^4 cal./mole. As in the case of calcium the vapor pressures for barium of from 12.5 to 26.5 mm in a small range near 1100°C, obtained by Hartmann and Schneider,⁸ using the boiling point method, are higher than one would expect from these low pressure measurements by the method of molecular effusion. Unfortunately there are no reliable data for the specific heat of barium. It is therefore not possible to compute the heat of evaporation at $T=0$ and the vapor pressure constant from these measurements at present.

⁸ Hartmann and Schneider, *Zeits. f. anorg. u. allg. Chem.* **180**, 275 (1929).

OCTOBER, 1935

JOURNAL OF CHEMICAL PHYSICS

VOLUME 3

The Thermal Equilibrium Between Ethylene Iodide, Ethylene and Iodine

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(Received July 26, 1935)

The thermal equilibrium between ethylene iodide, ethylene and iodine in the vapor state has been studied in the temperature range 50 to 125°C. The method devised involved measurements of the iodine vapor pressure by a photometric device utilizing photronic cells in a null-point arrangement. Iodine and ethylene iodide were both present as unsaturated vapors. The measurements gave results

which were found to agree with the extrapolation of Mooney and Ludlam's data for lower temperatures, but to disagree with the same authors' higher temperature determinations. The heat of dissociation of ethylene iodide is 13.4 ± 0.5 kcal. The position of equilibrium is given by: $\log K = -13,400/4.58T + 8.17$, where the equilibrium constant is expressed in atmospheres as units.

STUDY of this equilibrium has already been described in the literature. Mooney and Ludlam¹ investigated the gaseous equilibrium in the presence of solid iodine and ethylene iodide at temperatures from 10 to 65°C. The plot of the logarithm of the equilibrium constant against inverse temperature gave a curve which they chose to interpret as two straight lines. One, with a slope corresponding to a heat of reaction

¹ Mooney and Ludlam, *Proc. Roy. Soc. Edin.* **49**, 160 (1929).

of 13.4 kcal., was drawn in the temperature range 10 to 45°; the other, with 22.3 kcal. as the heat of reaction, represented the points from 45 to 65°. This second value they considered the more reliable of the two.

Polissar² studied the equilibrium in solution with carbon tetrachloride as the solvent. Between 122 and 152°C he obtained 11.3 kcal. as the heat of reaction. He interpreted the mechanism of the reaction with the aid of chains

² Polissar, *J. Am. Chem. Soc.* **52**, 956 (1930).