THERMIONIC PHENOMENA CAUSED BY VAPORS OF RUBIDIUM AND POTASSIUM

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Abstract

Thermionic effects similar to those studied by Langmuir and Kingdon for caesium have been found for rubidium and potassium. Because of the difference in the electron affinity of tungsten (4.53 volts) and that of an atom of rubidium or potassium (4.16 and 4.32 volts respectively) positive ions are formed which at filament temperatures above 1000° are drawn to the cylindrical collector from the coaxial filament. Below this temperature the ions are adsorbed on the surface of the filament and decrease its work function raising the electron emission. The degree of *thermal ionization* at various filament temperatures is found to be within the experimental error of that determined from Saha's equation. At low temperatures the filament is partially covered by adsorbed ions and the *electron emission* increases exponentially with the reciprocal of the temperature. A transition region is reached as the average life of an atom on the surface becomes shorter and then the emission decreases logarithmically with the reciprocal of the temperature. The curves and values are given. The *positive ion emission* increases logarithmically with the reciprocal of the temperature until a certain fraction of the atoms striking the filament is ionized. Further increase in temperature causes every atom to be ionized. The coincidence of experimentally determined points with the theoretical space charge curve shows each ion to have the mass of a single atom in the range of pressures studied.

Vapor pressure of rubidium and potassium.—The vapor pressure of rubidium and potassium is calculated from the maximum ion current; for rubidium $\log p = 10.55 - 4132/T$ and for potassium $\log p = 11.83 - 4964/T$; here p is in bars.

THE thermionic effects caused by caesium vapor have previously been studied by Langmuir and Kingdon.[1,2,3] This work was undertaken in order to compare the similar effects caused by the vapors of the other alkali metals.

A tungsten filament heated above 1200°K in caesium vapor was found to convert every caesium atom striking it to a caesium ion. This is due to the fact that the electron affinity of tungsten (work function) is 4.53 volts while that of caesium (ionizing potential) is only 3.88 volts. It was shown that by decreasing the work function of the filament to 2.69 volts by allowing a monatomic layer of thorium

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

[2] K. H. Kingdon and I. Langmuir, Phys. Rev. **21**, 380 (1923).

[3] I. Langmuir and K. H. Kingdon, Proc. Roy. Soc. A **107**, 61 (1925).

atoms to accumulate on the surface,[4] the positive ion emission became negligible.[3] The positive ions formed at the pure tungsten surface must be drawn to it by an image force. Below 1200°K they evaporate so slowly that the surface becomes partially covered by adsorbed caesium ions. This however lowers the electron affinity of the surface and when about 20 percent is covered the electron affinity of the surface is less than that of the atoms of caesium and no more ions are formed. However this decrease in the electron affinity greatly increases the electron emission from the surface. At a pressure of caesium corresponding to 20°C they obtained 4×10^{-5} amps. per cm^2 at a filament temperature of 670°K. Since the ionizing potentials of rubidium and potassium are 4.16 volts and 4.32 volts respectively it was expected that vapors of these metals would produce similar effects.

Apparatus

The tubes contained a pure tungsten filament of diameter 0.0051 cms mounted coaxially with a nickel cylinder of diameter 1.905 cms. In some tubes this collector was 2.54 cms long and in others 5.08 cms. This cylinder was between two other cylinders of the same diameter and of length 7.62 cms, the distance between them being from .08 cms to .16 cms. At each end of the filament a 6 mil tungsten spring took up the expansion due to heating. The tubes were exhausted by means of a condensation pump while being baked out at 360°C for 3 hours. The collectors were freed from gas by being heated to redness by means of induced high frequency currents. The filaments were flashed at a high temperature while the tubes were on the pump.

The smaller plate currents were measured by means of a Leeds and Northrup testing galvanometer and the larger ones by means of a microammeter. A General Electric deflection potentiometer gave the filament current. With the tube as constructed the two outer cylinders act as guard cylinders and the temperature of the part of the filament in the center cylinder is not affected more than 0.1 percent at 750°K by cooling effect of the leads. The temperature scale used is that of Forsythe and Worthing.[5]

Thermal Ionization

In the paper[3] referred to, the modified form of Saha's equation was used to determine the degree of thermal ionization. The equilibrium constant is given by

$$K_n = n_e n_p / n_a$$

[4] I. Langmuir, Phys. Rev. **22**, 357 (1923).
[5] W. E. Forsythe and A. G. Worthing, Astrophys. J. **61**, 146 (1925).

where n_e, n_p and n_a are respectively the number of electrons, of positive ions and of atoms per unit volume. For any alkali metal

$$\log_{10} K_n = 15.365 + \frac{3}{2}\log_{10} T - \frac{11{,}600\ V}{2.303\ T}$$

where V is the ionizing potential and T the absolute temperature. This expression for K_n has the dimensions of number per unit volume. Experimentally we have to do with currents and may define

$$K_I = I_e I_p / I_a$$

Where I_e and I_p are respectively the electron and positive ion emission per unit area at any filament temperature and I_a is the current density corresponding to the ionization of every atom hitting the filament. Then

$$K_I = eK_n\sqrt{\frac{kT}{2\pi m_e}} = 2.481\times 10^{-14}\ K_n\ \sqrt{T} \quad \text{amp. per cm}^2$$

For rubidium

$$\log_{10} K_I = 1.7792 + 2\log_{10} T - 20{,}932/T$$

The equilibrium constants found experimentally at various filament temperatures were about one-half those calculated theoretically. That is with a filament temperature of 1302°K the equilibrium constant was found to correspond to a filament temperature of 1273°K. The logarithm of the emission was plotted against the square root of the voltage to correct for the Schottky[6] effect. At any filament temperature the slopes were found to be the same for both ions and electrons and about double that calculated from Schottky's formula. Thus it is seen that the results obtained for the equilibrium constant are probably within the experimental error furnishing further verification of Saha's assumptions.

Electron Emission

As in the case of caesium at low temperatures a tungsten filament in rubidium or potassium vapor becomes covered with a layer of adsorbed atoms. As the temperature of the filament is increased the electron emission increases logarithmically with the reciprocal of the temperature. However as the filament temperature is further increased the current reaches a maximum and then decreases as the temperature is raised due to the evaporation of the atoms at the higher temperatures.

[6] W. Schottky, Phys. Zeits. **15**, 872 (1914).

By flashing the filament in oxygen before introducing the alkali metal the filament becomes covered with a layer of oxygen atoms which is not evaporated off below 1600°K. This layer tends to hold the alkali metal on at higher temperatures and thus the emission at a given filament temperature is higher from an oxygen coated filament in the alkali metal vapor than from a pure tungsten filament.

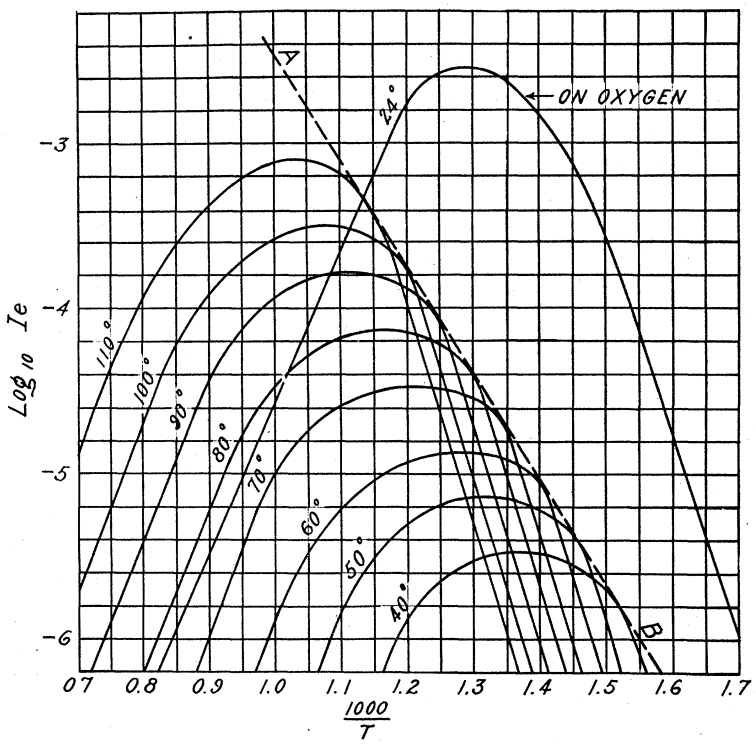

Fig. 1. Electron emission in amperes per cm² from a tungsten filament in rubidium vapor at various pressures. Temperature of bulb in °C on each curve.

Figs. 1 and 2 give the family of curves of the electron emission of filaments in the presence of rubidium and of potassium vapor. The ordinates are the common logarithms of I_e, the electron current in amp per cm², and the abscissas are the reciprocals of the absolute temperature of the filament multiplied by 1000. The temperature of the bulb which fixed the vapor pressure is given in degrees Centigrade on each curve. Before each reading the filament was flashed at a high temperature to drive off any impurities.

In the curves with the metal adsorbed on the pure tungsten surface we see that, as in the case of caesium, each curve consists of three

parts: (1) a low-temperature region where the logarithm of the emission is a straight line when plotted against the reciprocal of the temperature; (2) an intermediate region where the plot in Figs. 1 and 2 is curved; (3) a high temperature region where again the logarithm of the current is a linear function of the reciprocal of the temperature. The curves are very much alike and differ principally in being displaced parallel to their envelope A B. These displacements are proportional to the

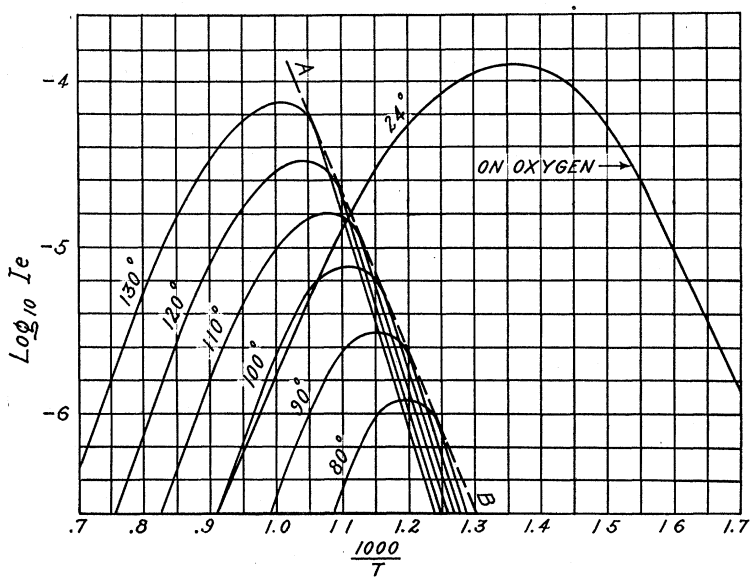

Fig. 2. Electron emission in amperes per cm² from a tungsten filament in potassium vapor at various pressures. Temperature of bulb in °C on each curve.

logarithms of the pressures of the vapor. Thus in regions (1) and (2) we may say that approximately

$$I_e = \alpha p^{\gamma} \epsilon^{-\beta/T}$$

From the curves in Figs. 1 and 2 we obtain the results shown in Table I for the constants α, β and γ.

I is in amp. per cm² and p in bars.

Positive Ion Emission

The positive ion emission at any vapor pressure increases exponentially with the reciprocal of the filament temperature until the emission is about 20 percent of the maximum when there is a definite discontinuity. Further increase in temperature causes every atom to be ionized. Thus, as in the case of caesium, there is the same evidence of

the existence of two surface phases on the filament, one in which only a fraction of the atoms is ionized and the other in which all of them are. There is a definite boundary between them and the rate at which

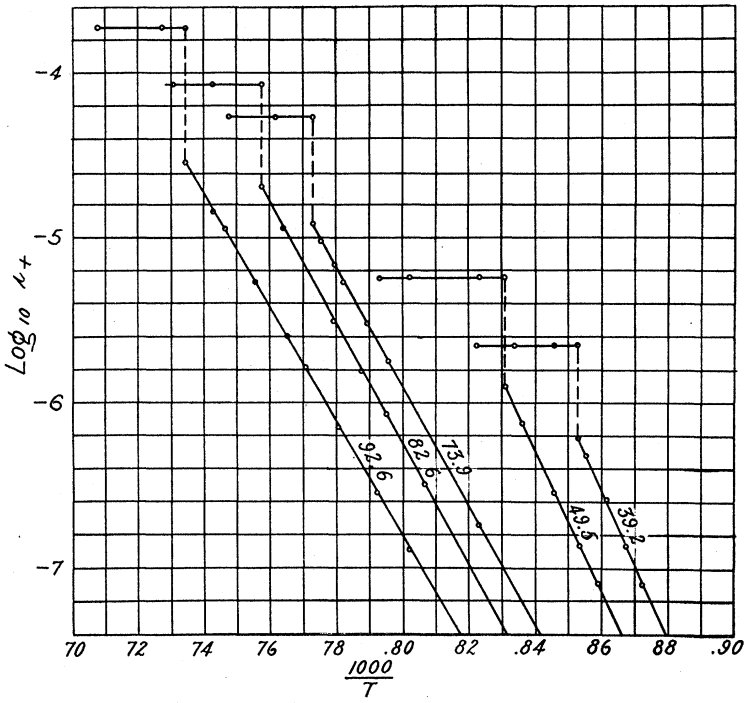

Fig. 3. Positive ion emission in amperes from a tungsten filament of area 0.0405 cm² in rubidium vapor at various pressures. Collector voltage = −200. Temperature of bulb in °C on each curve.

TABLE I

Values of the constants α,β,γ of Eq. (1).

Filament coating	α	β	γ
Rubidium on tungsten			
Region (1)	2.86×10^{12}	32,000	−1.12
Region (3)	2.08×10^{-12}	−24,000	+2.52
Rubidium on adsorbed oxygen			
Region (1)		28,000	
Region (3)		−23,000	
Potassium on tungsten			
Region (1)	5.9×10^{9}	30,800	−0.328
Region (3)	1.27×10^{-13}	−25,600	+2.66
Potassium on adsorbed oxygen			
Region (1)		19,700	
Region (3)		−23,000	

it moves along the filament can be easily measured by observing the microammeters in series with the three collectors. This velocity is found to depend upon the collector voltage and filament temperature. Langmuir and Kingdon[7] have obtained for caesium curves similar to those in Figs. 3 and 4.

If every atom is converted into a single ion a measure of the maximum positive ion current would be an accurate way of determining the vapor

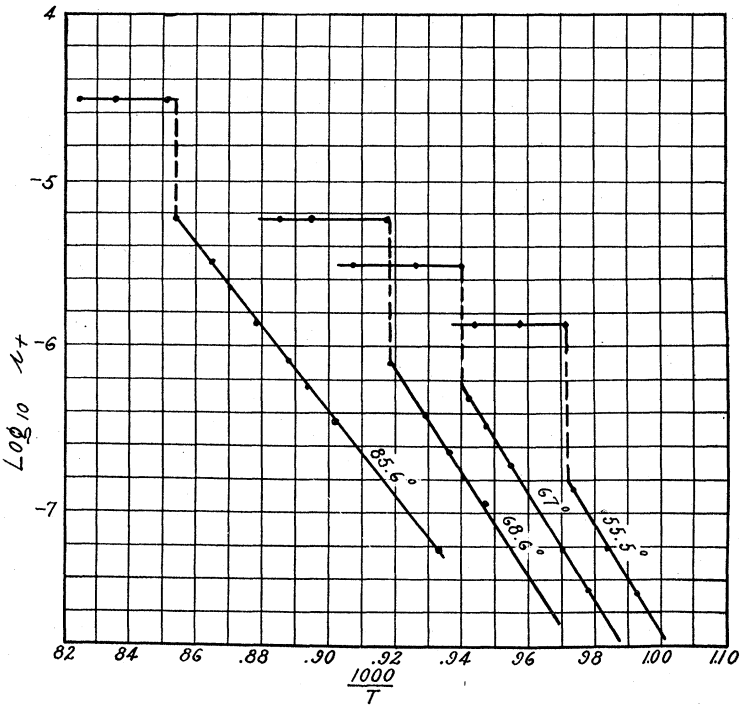

Fig. 4. Positive ion emission in amperes from a tungsten filament of area 0.081 cm² in potassium vapor at various pressures. Collector voltage = −200. Temperature of bulb in °C each on curve.

pressure. The currents limited by space charge with long coaxial cylinders is given by[8]

$$i = 14.68 \times 10^{-6} \sqrt{m_e/m_p}\ V^{3/2}/r\beta^2$$

here i is in amperes per cm length of filament, m_e and m_p the masses of an electron and positive ion respectively, V the potential of the collector below the filament in volts, r the radius of the collector and β^2 a

[7] Langmuir and Kingdon, unpublished work.

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

function of the ratio of the diameters of the collector and filament. In this case $\beta^2 = 1.04$.

In Figs. 5 and 6 are plotted the theoretical ion currents limited by space charge assuming the mass of a positive ion to be that of a single atom. The points were experimentally determined and corrected for

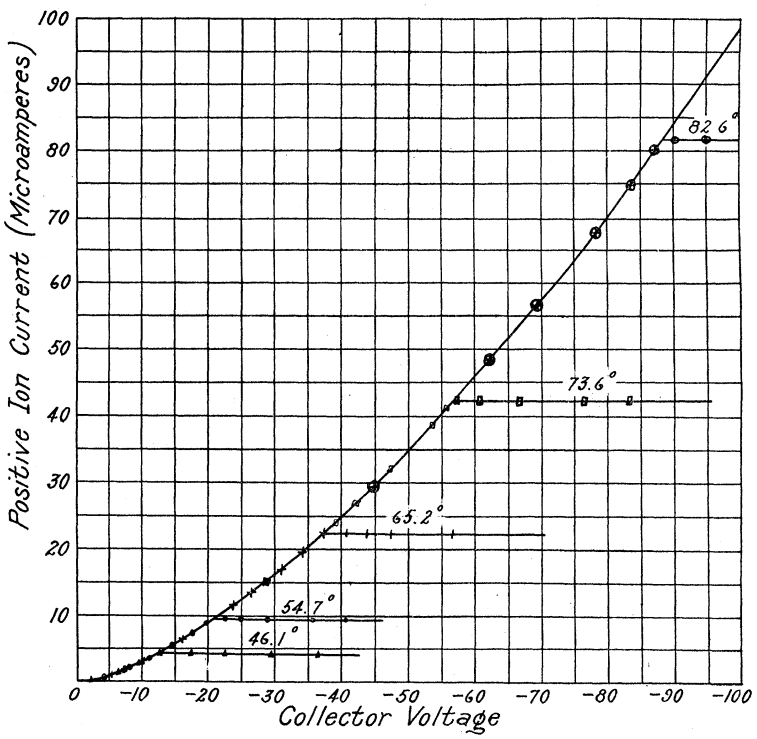

Fig. 5. Rubidium positive ion current limited by space charge at various vapor pressures. Full line is theoretical curve $I_+ = 0.0985\ V^{3/2}$. Temperature of bulb in °C on each curve.

contact potential. They check very accurately with the theoretical curve, showing that in the range of pressures studied the mass of the positive carrier is that of a single atom.[9]

Vapor Pressure

From the kinetic theory we know that the maximum positive ion current i_+ is $ep/\sqrt{2\pi mkT}$ abamperes per cm^2 where e is the charge on

[9] Since this work was done H. E. Ives in Jour. Frank. Inst. **201**, 62 (1926) claims this is not true at vapor pressures below those corresponding to a temperature of 60°C for caesium, rubidium and potassium.

an electron, p the pressure in bars, m the mass of an atom, k the Boltzmann constant and T the absolute temperature.
For rubidium

$$i_+ = .457\ p/\sqrt{T} \text{ amperes per cm}^2$$

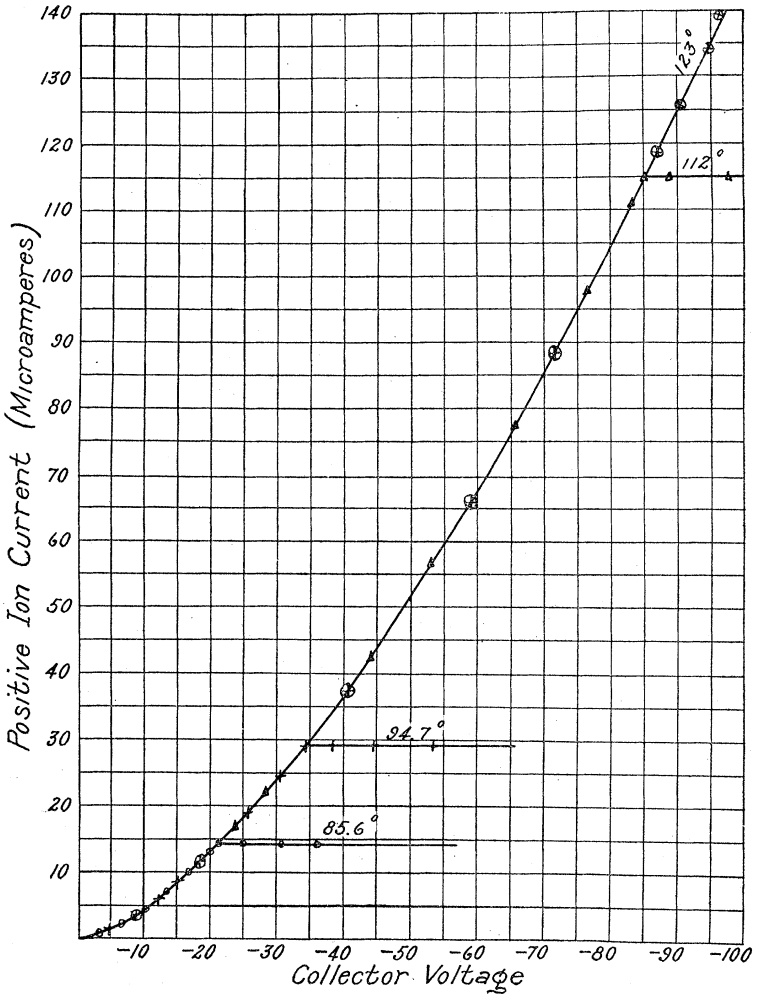

Fig. 6. Potassium positive ion current limited by space charge at various vapor pressures. Full line is theoretical curve $I_+ = 0.1452\ V^{3/2}$. Temperature of bulb in °C on each curve.

and for potassium

$$i_+ = .657\ p/\sqrt{T} \text{ amperes per cm}^2$$

Fig. 7 presents the vapor pressures of caesium, rubidium and potassium found by this method. The curve for caesium is taken from the results of Langmuir and Kingdon.[3]

For rubidium

$$\log_{10} p = 10.55 - 4132/T$$

For potassium

$$\log_{10} p = 11.83 - 4964/T$$

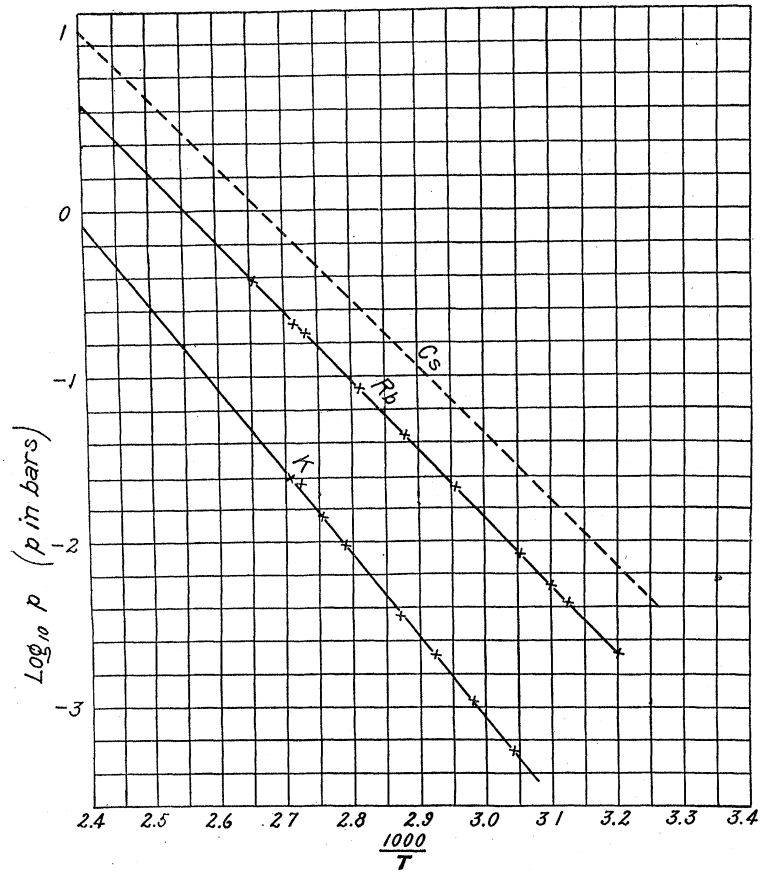

Fig. 7. Vapor pressures of Cs, Rb, and K at various temperatures as determined by the positive ion method.

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