LETTERS TO THE EDITOR

Prompt publication of brief reports of important discoveries in physics may be secured by addressing them to this department. Closing dates for this department are, for the first issue of the month, the twentieth of the preceding month; for the second issue, the fifth of the month. The Board of Editors does not hold itself responsible for the opinions expressed by the correspondents.

The Surface Ionization of Potassium on Tungsten

According to a recent communication by Copley and Phipps,[1] the efficiency of ionization of potassium by hot tungsten is considerably greater than corresponds to the modified Saha equation, when the constants in it are given their usually accepted values. This equation is

$$\frac{\nu_+}{\nu_a}=\frac{1-r_+}{1-r_a}\cdot\frac{\omega_+}{\omega_a}\exp\left[\frac{(\phi-I)\epsilon}{kT}\right],$$

where ν_+/ν_a is the ratio of the rates of evaporation of ions and atoms, r_+ and r_a are the reflection coefficients, ω_+ and ω_a the statistical weights, $\epsilon\phi$ the work function of the tungsten, and I the ionization potential of potassium. The value of $(1-r_+)/(1-r_a)$ is usually assumed to be 1, ω_+/ω_a is $\frac{1}{2}$, and I is 4.32 volts. The work function of tungsten was taken by Copley and Phipps to be 4.52 e.v. With these values of the constants they obtained theoretical values of ν_+/ν_a only about half as great as those found experimentally.

It was pointed out by Copley and Phipps that it would be possible to reconcile their results with the requirements of the theory by assuming $(1-r_+)/(1-r_a)$ to have a value of about 2, instead of 1, so that it would cancel out the weight factor ω_+/ω_a. There is, however, an alternative way in which an apparently too high ν_+/ν_a could be accounted for, namely, by assuming for ϕ *in the operating range of temperatures* values substantially higher than that corresponding to the slope of a Richardson line for tungsten. As the writer has pointed out elsewhere,[2] the decrease in the concentration of free internal electrons associated with thermal expansion must tend to make ϕ increase with temperature, and it may easily be shown that the order of the rate of increase due to this cause is the same as would account for the measured value of the constant A, assuming the transmission of electrons through the emitting surface to be practically perfect.

The experimental range covered by Copley and Phipps extends, in round figures, from 1600° to 2500°K. Let us see what values of ν_+/ν_a might be expected at both these extreme temperatures and also at some intermediate temperature, say 2000°K. The electron emissions obtained from well-aged tungsten at 1600°, 2000° and 2500°K per *apparent* cm^2 of surface are 9.27×10^{-7}, 1.00×10^{-3} and 2.98×10^{-1} amp., respectively. According to Tonks,[3] the "roughness factor" for tungsten etched by heat treatment must be *at least* 1.225. We shall probably not be far wrong if we take a round 1.3 for this quantity. This would make the emissions per true cm^2 at the three temperatures 7.13×10^{-7}, 7.69×10^{-4} and 2.29×10^{-1} amp., respectively. From these data it is a simple matter to calculate the corresponding values of ϕ on the assumption that the true A has the theoretical value for perfect transmission, namely, 120 amp. cm^{-2} degree^{-2}. The values obtained in this way are 4.65, 4.68 and 4.72 volts, respectively. If these are now substituted in the modified Saha equation, $(1-r_+)/(1-r_a)$ being assumed equal to 1, values for ν_+/ν_a equal to 5.48, 4.06 and 3.20, respectively, are obtained. The corresponding ionization efficiencies are 84.6, 80.2 and 76.2 percent, respectively. These are represented by the crosses in Fig. 1. It will be seen that they agree with the experimental results, which are represented by the circles, within what appear to be the limits of experimental uncertainty.

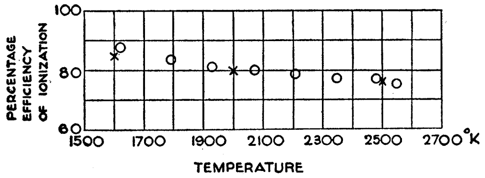

FIG. 1.

A. L. REIMANN

Research Laboratories of the
General Electric Company, Ltd.,
Wembley, England,
May 10, 1934.

---

[1] M. J. Copley and T. E. Phipps, Phys. Rev. **45**, 344 (1934).

[2] Letter to be published shortly in Nature.

[3] L. Tonks, Phys. Rev. **38**, 1031 (1931).

New Band System in Nitrogen—an Addition and Correction

Soon after writing a paper for this journal under the above title I received a letter from Professor G. Herzberg of Darmstadt in which he gave another formula for the bands, and consequently a new interpretation for the initial electronic state. The formula given by Herzberg is

$$\nu=49774.4+(1446.46v'-13.93v'^2)-(2345.16v''-14.445v''^2)$$

and the initial state is therefore the metastable $A\ {}^3\Sigma$ state.

I argued against this interpretation in my paper, but a little consideration showed me that the initial electronic level is the $A\ {}^3\Sigma$ level. I hesitated to make the major correction on the proof that this change would require, and it is for that reason that I present the alternative arguments here. Furthermore, it will be of interest to compare the arguments given here with that presented in my paper.

If we use Herzberg's formula and extrapolate the vibrational levels of the upper state by the method of Birge and Sponer we obtain a value of 10.4 volts for the total energy. If we use my formula, the value is 9.3 volts. In either case the values obtained by extrapolation are too high if our experience with this method is a good criterion. If we assume that the initial level is the $A\ {}^3\Sigma$ level, then Sponer's value of 8.18 volts for this level must be lowered to 6.14 volts and, as I pointed out in a paper in this journal,[1] the heat of dissociation of 9.4 volts which was obtained in that paper has to be lowered by the same amount, thus making the heat of dissociation 7.4 volts. Since $A\ {}^3\Sigma$ dissociates into a ${}^4S$ and a ${}^4D$ atom, its total energy should be 9.8 volts. This is less than the calculated value of 10.4 volts, but that is what one would expect. If we assume that $D(N_2)$ is 7.9 volts then the total energy should be 10.3 volts, and this agrees entirely too well with the 10.4 volt value obtained by extrapolation.

If we assume that the initial level is a new triplet level which dissociates into two ${}^4S$ atoms, then its total vibrational energy should be either 1.2 or 1.7 volts depending on the choice of 7.4 or 7.9 volts for $D(N_2)$. The extrapolation yields 3.1 volts for this energy, and it is seen that this is more than twice as large as 1.2 and about 80 percent larger than the 1.8 volt value. In either case, the error seems to be unusually large even for the extrapolation method. It seems therefore that the initial level is the $A\ {}^3\Sigma$ level.

Another argument leads to the same conclusion. This new band system in gaseous N_2 corresponds to the ϵ-system observed by Vegard in the luminescence of solid N_2.[2] In this system many more bands have been observed than in the gaseous system, and it was possible to calculate the average separations between the vibrational levels of the upper state. Nine pairs of bands originating on $v'=5$ and 6 gave an average difference of 1293 cm^{-1} for these two vibrational levels. The average of the observed differences as taken from the first-positive band system for which the $A\ {}^3\Sigma$ level is the lower level is 1292 cm^{-1}. The difference obtained from the formula given in my paper is 1229 cm^{-1}. A similar argument for the difference between $v'=4$ and 5 gives an average of 1323 cm^{-1} from 11 pairs of bands of the ϵ-system, and an average of 1323 cm^{-1} for this difference from the observed first-positive bands, and a calculated value of 1271 cm^{-1} from my formula. It must be concluded therefore that the initial level is the $A\ {}^3\Sigma$ level and that the heat of dissociation of nitrogen is 7.4 volts. A discussion of the connection between this new value and the electron impact measurements of Lozier and of Tate, Smith and Vaughan has been given in a letter in these columns by Dr. Lozier.

JOSEPH KAPLAN

University of California, at Los Angeles,
May 18, 1934.

---

[1] Kaplan, Phys. Rev. **42**, 100 (1932).

[2] Vegard, Zeits. f. Physik **75**, 44 (1932).

The Absorption Spectrum of Diatomic Arsenic

A new system of some eighty absorption bands has been discovered in the spectrum of arsenic between 2200A, and 2750A, which can be definitely assigned to the diatomic molecule. This includes the five faint fluorescence bands observed by Rosen[1] and tentatively ascribed to As_2. The whole system bears a striking resemblance to that of P_2, investigated by Herzberg,[2] where $\Delta G''$ is about 750 cm^{-1} and $\Delta G'$ 470 cm^{-1}. A preliminary analysis gives for arsenic ΔG values that are about 420 cm^{-1} for the lower and 270 cm^{-1} for the upper state. The vibrational levels of both states converge very slowly.

The emission spectrum of phosphorus is attributed by Herzberg to a ${}^1\Sigma_g{}^+ \leftarrow {}^1\Sigma_u{}^+$ transition, in which the upper potential curve is crossed by another, possessing a flat minimum and a lower heat of dissociation, which is either a ${}^3\Sigma_u{}^+$ or a ${}^3\Pi_u$ state. This causes predissociation in the upper and perturbation of the lower vibrational levels of the ${}^1\Sigma_u{}^+$ state. The plot of the $\Delta G'$ values of our arsenic bands shows a discontinuity at $v'=4$, which appears to represent perturbation similar to that observed by Herzberg.

G. E. GIBSON
A. MACFARLANE[3]

Department of Chemistry,
University of California,
Berkeley, California,
May 18, 1934.

---

[1] Rosen, Zeits. f. Physik **43**, 69 (1927).

[2] Herzberg, Nature **126**, 239 (1930); Ann. d. Physik (5), **15**, 677 (1932).

[3] Commonwealth Fellow.

Note on the Thermal History of the Earth

In a previous paper[1] the problem of the cooling of the earth has been treated under the simplifying assumption that the surface of the earth is either permanently at 0° or that it radiates into a medium at 0°.

The object of the present note is to amplify the treatment of the previous paper by taking into account the heat received from the sun.

If λ designates the average value of the solar constant, defined as the amount of heat received from the sun at the surface of the earth per unit area per unit time during normal incidence, then the total average rate of heat from

---

[1] Lowan, *On the Cooling of a Radioactive Sphere*, Phys. Rev. **44**, 769 (1933). This paper will be referred to as A.N.L.