This was presumably due to the effect of positive ions emitted by the filament acting on the space charge sheath surrounding the filament.

These measurements are being extended by one of us using thoriated and oxide as well as tungsten filaments.

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E. A. Johnson[3]

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June 18, 1934.

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Reflection Coefficient of Electrons[1]

In an attempt to interpret their experimental results upon the degree of ionization of potassium atoms on a hot tungsten filament the authors have suggested[2] that the results could be explained by assuming that the ratio $(1-r_+)/(1-r_a)$,—where r_+ and r_a are the reflection coefficients of positive ions and atoms, respectively,—is about 2. They were not aware at that time that Taylor and Langmuir[3] had proved definitely that the reflection coefficient of caesium atoms from tungsten is equal to zero to within less than one percent. Since it seems very likely that the reflection coefficient of potassium atoms is also zero, it becomes necessary to seek a different interpretation for one of the experimental observations in the note; namely the absence of an intercept in the plot, log ν_+/ν_a *versus* $1/T$. The purpose of the present note is to set forth a new interpretation.

The equilibrium constant[4] for the thermal ionization of potassium vapor is given by

$$K=\bar{\nu}_+\bar{\nu}_\epsilon/\bar{\nu}_a=(\omega_+\omega_\epsilon/\omega_a)(2\pi m_\epsilon kT/h^2)^{\frac{3}{2}}\exp\left[-I_\epsilon/kT\right], \qquad (1)$$

where $\bar{\nu}_+$, $\bar{\nu}_a$ and $\bar{\nu}_\epsilon$ are, respectively, the number of ions, atoms and electrons per cm³ in an equilibrium mixture. If we replace the number per cm³ of each kind of particle by its rate of evaporation, we have

$$\frac{\nu_+\nu_\epsilon}{\nu_a}=\frac{(1-r_+)(1-r_\epsilon)}{(1-r_a)}\frac{\omega_+\omega_\epsilon}{\omega_a}\frac{2\pi m_\epsilon k^2}{h^3}T^2\exp\left[-\frac{I_\epsilon}{kT}\right]. \qquad (2)$$

Upon multiplying by the charge ϵ of the electron, putting r_a equal to zero, and introducing numerical values for the statistical weights of the particles, we obtain

$$\nu_+ i/\nu_a=(1-r_+)(1-r_\epsilon)(2\pi m_\epsilon k^2\epsilon/h^3)T^2\exp\left[-I_\epsilon/kT\right], \qquad (3)$$

in which i is the saturation electron current per cm² at zero field. The emission of electrons from tungsten may be represented by the empirical equation

$$i=A'T^2\exp\left[-\phi_0\epsilon/kT\right]. \qquad (4)$$

Substituting for i in (3) and replacing $2\pi m_\epsilon k^2\epsilon/h^3$ by A, we have

$$\nu_+/\nu_a=(1-r_+)(1-r_\epsilon)(A/A')\exp\left[-(I-\phi_0)\epsilon/kT\right]. \qquad (5)$$

If log ν_+/ν_a is plotted against $1/T$ the intercept is equal to log $(1-r_+)(1-r_\epsilon)A/A'$. Since A/A' may be obtained from thermionic data, the product $(1-r_+)(1-r_\epsilon)$ may be calculated from the experimental value of the intercept. Both r_+ and r_ϵ must lie between zero and unity; consequently maximum limits can be set to their values. On the basis of the very small intercept, log $(1-r_+)(1-r_\epsilon)A/A'$, which we have obtained in recent experiments it appears that the maximum value of r_+ (or r_ϵ) is of the order 0.1.

Becker and Brattain[5] in a recent paper in the *Physical Review* discuss in considerable detail the question of thermionic emission of electrons from metals. They conclude that it is unlikely that r_ϵ should ever exceed 0.1. The measurement of the degree of ionization of potassium vapor on a tungsten wire appears to furnish experimental evidence in favor of their conclusion.

If in Eq. (1) we express $\bar{\nu}_\epsilon$ by

$$\bar{\nu}_\epsilon=\omega_\epsilon(2\pi m_\epsilon kT/h^3)^{\frac{3}{2}}\exp\left[-\phi\epsilon/kT\right], \qquad (6)$$

where $\phi\epsilon$ is the work function at the temperature T, we obtain

$$\bar{\nu}_+/\bar{\nu}_a=(\omega_+/\omega_a)\exp\left[-(I-\phi)\epsilon/kT\right] \qquad (7)$$

and

$$\frac{\nu_+}{\nu_a}=\frac{(1-r_+)}{(1-r_a)}\frac{\omega_+}{\omega_a}\exp\left[-\frac{(I-\phi)\epsilon}{kT}\right]. \qquad (8)$$

If we consider the reflection coefficients to be very small or zero, then it is evident that there is a factor which cancels the ratio of statistical weights, ω_+/ω_a in Eq. (8). Such a factor probably is the temperature coefficient α of the work function (discussed by Becker and Brattain[5]). We may write with them

$$\phi=\phi_0+\alpha T, \qquad (9)$$

where

$$\exp\left[-\alpha\epsilon/k\right]=\omega_+/\omega_a=\tfrac{1}{2}. \qquad (10)$$

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Urbana, Illinois,
June 19, 1934.

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[1] Since the present note was written a Letter to the Editor has appeared (A. L. Reimann, Phys. Rev. **45**, 898 (1934)) discussing one of the points emphasized herein.

[2] Copley and Phipps, Phys. Rev. **45**, 344 (1934).

[3] Taylor and Langmuir, Phys. Rev. **44**, 423 (1933).

[4] Fowler, *Statistical Mechanics*, p. 281, Cambridge Press, (1929).

[5] Becker and Brattain, Phys. Rev. **45**, 694 (1934).

Hopfield's Rydberg Series and the Ionization Potential and Heat of Dissociation of N_2*

Recent work has made it very probable that the heat of dissociation of N_2, long in dispute, is close to 7.4 volts.[1, 2, 3] Herzberg and Sponer[2] give 7.34±0.02 volts.[4] This value is based on a careful consideration of emission bands and predissociation phenomena studied by Kaplan, Vegard, Coster and Brons, Van der Ziel, and others.

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* *Added in proof:* Cf. also, H. Beutler, Naturwiss. **20**, 759 (1932).

[1] Cf. J. Kaplan, Phys. Rev. **45**, 898 (1934).

[2] G. Herzberg and H. Sponer, Zeits. f. physik. Chemie **B26**, 1(?), 1934. The writer is indebted to Dr. Herzberg for the opportunity to see this article in proof.

[3a] W. W. Lozier, Phys. Rev. **44**, 575 (1933).

[3b] Lozier, Phys. Rev. **45**, 840 (1934).

[4] A possible difficulty with a value 7.4 volts for $D(N_2)$ is that it requires D of the A' state of N_2^+ to be about 3.1

From electron impact data, Lozier[3] gets 8.62±0.02 volts for an energy of dissociation of N_2^+; as he has pointed out, the products of dissociation at this energy can hardly be unexcited ($^4S+^3P$). If the N^+ is assumed excited to ^1D(1.89 volts), one obtains 6.73 volts for the heat of dissociation $D(N_2^+)$ into unexcited atom and ion; but dissociation into $^1D+^4S$ seems unlikely.[5] If the N is assumed excited to ^2D(2.37 volts), $D(N_2^+)$ comes out 6.25 volts. Other possibilities are too improbable.[3] The value 6.25 volts combined with the ionization potential 15.65 ±0.02 volts for N_2 determined by Tate, Smith and Vaughan,[6] gives 7.42 volts for $D(N_2)$, in good agreement with the above spectroscopic value.[4]

It seems desirable to call attention at this time to a Rydberg series of N_2 absorption bands reported some time ago by Hopfield.[7] Hopfield's data closely fit the Rydberg formula $\nu=151{,}240-R/(m-0.092)^2$, with $m=3, 4, 5, 6, 7, \cdots$. The limit ($\nu=151{,}240=18.67$ volts) must be identified, as Hopfield pointed out, with the ionization of N_2 to form an excited state of N_2^+. There can now be practically no doubt that this state is the well-known A', $^2\Sigma^+_u$ state of N_2^+, which is 3.156 volts above the $^2\Sigma^+_g$, probably normal, state of N_2^+. (The $^2\Pi_u$ state of N_2^+ is probably only a little above the $^2\Sigma^+_g$, but its exact location is uncertain, and there is a bare possibility that it might be the normal state.)

If $^2\Sigma_g^+$ is the normal state of N_2^+, then the minimum ionization potential of N_2 must be $18.67-3.156=15.51$ volts. This value is in good enough agreement with the value 15.65 of Tate, Smith and Vaughan so that we may safely accept the above interpretation. The fact that it is a little *lower* than that of Tate, Smith and Vaughan, tends to eliminate the possibility that $^2\Pi_u$ can be below $^2\Sigma_g^+$, since the Tate-Smith-Vaughan value must belong to the minimum potential, whether the latter be $^2\Sigma_g^+$ or $^2\Pi_u$. That the Hopfield potential 18.67 volts really belongs to $A'\,^2\Sigma_u^+$, not to some other neighboring spectroscopically not yet known state, is quite sure on theoretical grounds, since the electron configuration theory gives no possibility of such an additional state.

The occurrence of a Rydberg series of single bands is most reasonably interpreted on the supposition that each band is a (0,0) band, other possible bands being very much weaker. According to the Franck-Condon principle, this would mean that r_0 is nearly the same for the various excited N_2 electron states (upper levels of the Hopfield bands), and for the N_2^+ state to which the limit of the series corresponds, as for the normal state of N_2. This is in agreement with the conclusion that the limit of the series is $^2\Sigma_u^+$ of N_2^+, since the latter has $r_e=1.07$A, while the normal state of N_2 has $r_e=1.09$A. That the entire set of N_2 electron states converging to $^2\Sigma_u^+$ of N_2^+ have about the same r_e as $^2\Sigma_u^+$ of N_2^+ is to be expected, since all these states are nothing but N_2^+ ($^2\Sigma_u^+$) plus an electron in an excited orbit much larger than the N_2^+ core and so unable to affect appreciably the strength of the N−N bond. Similar relations are known in the Rydberg series of H_2 and He_2.

For a definite determination of the nature of the excited electron orbits in the Rydberg series states, we must await further data; the selection rules, however, require them to be of $_g$ type. For $m=3$, the types σ_g4s and σ_g3d are perhaps the most probable; σ_g3s and σ_g3p would have larger quantum defects than the observed defect 0.092 (this, however, becomes 1.092 if σ_g4s is correct; in that case one more member of the Rydberg series must exist at longer wave-lengths, in a region difficult to analyze because of the presence of many bands, according to a private communication from Dr. Hopfield). The large molecular orbitals σ_g4s, σ_g3d, etc., should not differ much from atomic orbitals $4s$, $3d\sigma$, etc., as we can see by approximately constructing them by adding two $4s$ or two $3d\sigma$ orbitals, one for each N atom, and noting that the distance between the two N nuclei is small compared with the dimensions of the $4s$ or $3d\sigma$ orbital. Similar atom-like molecular orbitals are known in the high excited states of He_2 and H_2, and should occur quite generally. Types such as Π_g3p and Π_g3d, although at first sight plausible, would probably give unstable states of N_2, as one sees after noting that their approximate construction requires *subtraction* of $3p\Pi$ or $3d\Pi$ atomic orbitals of two nearly coincident atoms, then normalizing.

The foregoing interpretation of Hopfield's Rydberg series makes it very probable that the correct value of the ionization potential of N_2 lies within the limits 15.51–15.52 volts. Combining this with Lozier's value of 6.25 volts for $D(N_2^+)$, we get $15.51+(6.25\pm0.02)-14.48=7.28\pm0.02$ volts for $D(N_2)$, in close agreement with the value 7.34 ±0.02 given by Herzberg and Sponer. Or conversely, from the H.S. value 7.34 for $D(N_2)$ one gets $14.48+7.34-15.51=6.31$ volts for $D(N_2^+)$; and $6.31-3.156=3.15$ volts for D of the A', $^2\Sigma_u^+$ state[4] of N_2^+. As rounded values for $D(N_2)$ and $D(N_2^+)$ we may then probably now accept with considerable confidence 7.3 volts and 6.3 volts.

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volts,[3b] whereas Birge estimates it to be 3.67±0.1 volts by a not very long extrapolation from the A' vibrational levels measured by Herzberg. Herzberg and Sponer,[2] however, accept without discussion the lowered value of D for the A' state; their value of $D(N_2)$ gives 3.17 volts for the A' state, if 15.65 volts[6] is used for the ionization potential of N_2.

[5] That the products of dissociation are $^4S+^1D$, as Lozier at first assumed (reference 3a) seems improbable, since this would require that the N_2^+ which is excited by electron impact and then at once dissociates in Lozier's work is some *quartet* state of N_2^+. It seems unlikely that such a state would be predominantly produced by electron impact from N_2 (state $^1\Sigma$), especially since this would necessarily involve simultaneous removal of one N_2 electron and removal of another.

[6] J. T. Tate, P. T. Smith and A. L. Vaughan, Phys. Rev. **43**, 1054A (1933).

[7] J. J. Hopfield, Phys. Rev. **36**, 789A (1930). Hopfield also reported an emission Rydberg series, appearing on the same photograph as the absorption series, and converging to the same limit. In conversation, however, Dr. Hopfield states that the reality of the emission series is doubtful. The absorption series, however, consists of a beautifully clear set of narrow bands, according to a reproduction which Dr. Hopfield has very kindly shown the writer. Dr. Hopfield informs me that there seems now to be no possibility that the bands belong to anything but N_2, although he first attributed them to He_2 (Phys. Rev. **35**, 1133 (1930)). Dr. Hopfield tells me that he intends to publish a more complete account of the bands shortly.

Using $D(O_2)$ and thermochemical data,[3a] we then have 5.25 volts as the best value for $D(NO)$.

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June 27, 1934.

Properties of Evaporated Films of Aluminum over Chromium

Following the proposal by the author[1] that large astronomical mirrors be coated with metallic films by the evaporation process, considerable work has been done toward the development of the most suitable films for this use.[2, 3, 4] In coating the Crossley 36 inch reflector of the Lick Observatory,[4] aluminum was considered to be the best coating for astronomical purposes, for although its hardness is not great, it has excellent tenacity, untarnishability and reflectivity.

A film has been developed in this laboratory which greatly excels pure aluminum in the first of the above properties, and is comparable to it in the remaining three. The glass is first prepared by careful chemical cleaning, and is then bombarded with ions[5] in the vacuum chamber. A thin film of pure chromium is first evaporated upon the glass, and this is immediately covered by an aluminum film sufficient to make the two films opaque. A method of dissolving chromium placed directly upon glass has been found, and hence such films can be removed, if desired, without injury to the glass surface.

When first deposited this chromium-aluminum film can be scratched fairly easily, but it is hardened instantly by washing in water, alcohol, or even by condensed breath-moisture. The resulting hardness is astonishing; rubbing with a blunt steel instrument, or even with steel-wool affects the film only slightly. A test for resistance to abrasion was made by rubbing a small area of the film 500 times with cheesecloth and with wadded cotton as hard as the hand could rub. A slight increase in scattered light was noticed, but no appreciable decrease in reflectivity could be observed. It was also found that pure aluminum films are considerably harder after washing with water, but even after the water treatment, they are not as hard as the unwashed chromium-aluminum films. A hardened pure aluminum film which had satisfactorily withstood the "adhesive-tape test"[4] was completely removed from the glass after 50 hard rubs with cheesecloth or with wadded cotton. A chromium-aluminum sample was coated with a layer of kerosene soot onto which was dropped sand and grit, and the mirror was then cleaned with alcohol and water. This was repeated twenty times, with the result that only the faintest surface scratches could be detected. The same test with a hardened pure aluminum film showed a comparable scratching of the surface at the end of four times. These tests were performed upon Corning borosilicate glass.

The tenacity of the chromium-aluminum film is such that nothing has yet been found that will strip it from the glass, although several kinds of tape and glue have been tried.

The aluminum layer can be removed with KOH without removing the underlying chromium. Immersion for a few hours in a concentrated salt solution will likewise remove and dissolve the aluminum. Two samples have been immersed in water and in ethyl alcohol for 10 days without any deterioration of the film. This means that in laboratory use repeated cleaning with alcohol and water can be safely undertaken. Fumes of burning sulphur, of H_2S and of H_2O_2 have no apparent effect upon the films.

The reflectivity of both washed and unwashed films of chromium-aluminum has been measured from λ6000 to λ2900, and although it varies slightly among samples, it is as good as that reported by Williams and Sabine[3] for pure aluminum; *viz.*, 90 percent at λ6000 to 80 percent at λ3000, and very slightly less than that reported by Pettit.[6] The aluminum layer is sufficiently thick to act as the sole reflector, and hence might be expected to reflect as well as pure aluminum.

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Department of Physics,
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June 29, 1934.

[1] Williams, Phys. Rev. **41**, 255 (1932).
[2] Edwards, Phys. Rev. **43**, 205 (1933).
[3] Williams and Sabine, Astrophys. J. **77**, 316 (1933).
[4] Strong, Pub. Ast. Soc. Pac. **46**, 18 (1934).
[5] This well-known "clean-up" process for metals has been successfully employed by Strong in cleaning glass.
[6] Pettit, Pub. Ast. Soc. Pac. **46**, 27 (1934).

A Partial Interpretation of the Raman and Infrared Spectra of Benzene

By using the formulas for the normal frequencies of vibration recently published[1] I have been able to assign the Raman-active and infrared-active fundamentals of benzene to definite modes of vibration of the regular plane hexagon model for this molecule. In addition I have found what seems to be a clear-cut case of quantum-mechanical resonance between a fundamental and a combination level.

The selection of the lines to be ascribed to fundamentals has been discussed by others and the choice which I have made was in part based on these previous investigations. There should be seven Raman-active fundamentals and four infrared-active fundamentals, with the nine remaining fundamentals completely inactive. There are four bands in the fundamental region of the infrared which nearly all observers have estimated to be considerably stronger than the other bands. I have chosen these, which lie near 660, 1040, 1480 and 3080 cm^{-1}, as fundamentals. The ten strongest lines in the Raman spectrum, as observed by nearly all investigators, are at 605, 849, 991, 1178, 1584, 1605, 2947, 3047, 3060 and 3184 cm^{-1}. The lines at 991 and 3060 cm^{-1} have been previously ascribed to the symmetrical expansions of the molecule (ν_1 and ν_2 of Fig. 3, reference 1). The other nine active fundamental frequencies are functions of only three force constants besides those determined from ν_1 and ν_2. I therefore tried varying these three force constants until the calculated frequencies

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[1] E. Bright Wilson, Jr., Phys. Rev. **45**, 706 (1934).