On the Relative Rate of Energy Transfer from the Excited Argon Atom

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A reduction in the spark-breakdown potential[1] and the starting potential for the glow discharge in neon by small traces of argon[2] has long been recognized; it is often called the Penning effect. A similar effect of a contaminant gas in reducing W-values upon the ionization of rare gases under irradiation has been interpreted as resulting from energy transfer from the excited species of the latter, leading to the subsequent ionization of the former.[3] The effect has been employed in a sensitive detector for gas chromatography. Recently, Collinson et al. studied the effect in the argon butane system from the viewpoint of radiation chemistry in an electric field,[4] in which it was necessary for them to evaluate the relative rate constant for energy transfer, $k_8/(k_{2a}+k_{2b})$, as in their terminology;

$$Ar^*+B \rightarrow Ar+B^++e^- \quad (2a)$$

$$Ar^*+B \rightarrow Ar+(\text{uncharged species}) \quad (2b)$$

$$Ar^*+Ar\ (\text{or wall}) \rightarrow Ar+Ar\ (\text{or wall}) \quad (8)$$

They estimated the value from the known relative rate,[3] 4000, for the ionization of argon in trace amounts by metastable neon atoms to the de-excitation of the latter by ground-state neon atoms, together with the correction for the difference in cross-sectional areas for the various species. Thus, $k_8/(k_{2a}+k_{2b}) = (1/4000) \times (\sigma_{Ar}^2/\sigma_{Ne}\cdot\sigma_B)$, which, when suitable figures are supplied, yields 6000 as the value.

The objective of the present note is to show that the rate can be obtained also from their own data on ion current measurements.

In their system primary electrons produced by the action of radiation are accelerated to an energy capable of exciting argon to metastable states;

$$e^- \rightarrow e_{en}^- \quad (5)$$

$$e_{en}^-+Ar \rightarrow Ar^*+e^- \quad (6)$$

Let a "primary" electron - accelerated in the field between each collision - produce α metastable atoms per cm. of its path in field direction. Of the α metastable atoms,[5] a fraction proportional to $k_{2a}[B]/\{(k_{2a}+k_{2b})[B]+k_8[A]\}$ enters into Reaction 2a. Thus the increase in the number of electrons along the length, dx, is $N_x\cdot\alpha\cdot dx\cdot k_{2a}[B]/\{(k_{2a}+k_{2b})[B]+k_8[A]\}$ per N_x electrons. By intergrating from $x=0$ to $x=d$;

$$N/N_0=i/i_0=\exp(\alpha\cdot d\cdot k_{2a}[B]/\{(k_{2a}+k_{2b})[B]+k_8[A]\})$$

where N_0 is the number of electrons per sec., and i_0, the current produced initially by irradiation. This is essentially the equation for Townsend discharge,[6] as Collinson et al. noted, although they used a different (but equivalent) expression. If the equation applies to the present case, the plot of $1/\ln(i/i_0)$ vs. [A]/[B] should give straight lines, whose slope-to-intercept ratio should then yield the desired relative rate. The data of i/i_0 read from their Fig. 3, at least the initial portion of the curves where [B] is sufficiently small,[7] are shown to lie on straight lines in Fig. 1. The relative rate

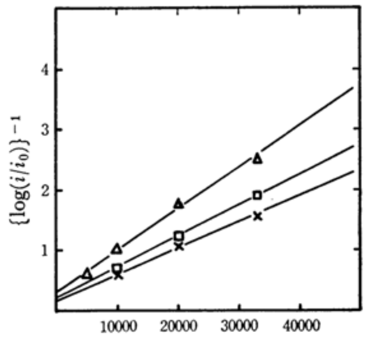

Fig. 1. Plot of $\{\log(i/i_0)\}^{-1}$ vs. [A]/[B]
Field strength; △, 3900 V./cm., □, 4800 V./cm., ×, 5700 V./cm.
(Read from Fig. 3 of Ref. 4.)

thus obtained is approximately 4500, this is in agreement with Collinson's estimation for any one of straight lines, and so seems to indicate the validity of the treatment. The value is of the same order as that of 2270 obtained recently by Lipsky when

1) F. M. Penning, *Naturwissenschaften*, **15**, 818 (1927).
2) F. M. Penning and C. C. J. Addink, *Physica*, **1**, 1007 (1934).
3) W. P. Jesse and J. Sadauski, *Phys. Rev.*, **100**, 1755 (1955).
4) E. Collinson, J. F. Todd and F. Wilkinson, *Discussions Faraday Soc.*, **36**, 83 (1963).
5) This statement only applies to the case where [B] is sufficiently low compared with [A]. At higher [B], e^- collides with B suppressing electron-multiplication sequence.
6) A. von Engel, "Ionized Gases," 2nd Ed., Chapter 7, Oxford University Press, London (1965).
7) See Ref. 5.

no electron multiplication occurs.[8] The agreement can be said to be fair if a large difference in the experimental conditions and the lack of exact data are taken into consideration. The larger value estimated in this paper may be due to the drastic change in conditions where electron multiplication predominates, and/or to the larger ion current measured by Collinson et al., which, as is pointed out by Lipsky, might be caused by the higher drift velocity of electrons in the presence of polyatomic contaminant than in that of pure argon. Corrections for the latter effect are expected to alter the value to bring it closer to Lipsky's value.

A similar study is now in progress with the Ar-NH_3 system, partly in connection with the sensitized production of hydrazine; the results will be published elsewhere.

8) M. M. Shahin and S. R. Lipsky, *J. Chem. Phys.*, **41**, 2021 (1964).