

Technical Comments

Comment on "Effects of Nonequilibrium Ablation Chemistry on Viking Radio Blackout"

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THE authors of this paper¹ conclude 1) that nonequilibrium chemical effects play a key role in determining radio blackout during descent of the Viking Lander into the Martian atmosphere, and 2) that for a boundary layer contaminated with ablation material containing sodium, a calculation allowing for effects of nonequilibrium chemistry results in electron densities two orders of magnitude lower than are calculated if local equilibrium is assumed. While the first conclusion is reasonable, the second is open to doubt because it is not based upon the best available data for the forward and backward rate coefficients k_f and k_b of the important reaction $\text{Na} + \text{M} \rightleftharpoons \text{Na}^+ + e^- + \text{M}$. The authors state that they found no literature values for k_f and k_b : both experimental²⁻⁹ and theoretical¹⁰⁻¹³ data, however, are available. For the 3000–8000 K temperature range of interest, these data may be represented, within a factor of 5, by $k_f = 8 \times 10^{24} T^{-2} \exp(-62400/T) \text{ ml mole}^{-1} \text{ sec}^{-1}$ and $k_b = 5.4 \times 10^{27} T^{-2} \text{ ml}^2 \text{ mole}^{-2} \text{ sec}^{-1}$, with no significant dependence on the nature of M. These values are some four orders of magnitude higher than those used by Evans, Schexnayder, and Grose, $k_f = 2.5 \times 10^{11} T^{0.5} \exp(-59670/T) \text{ ml mole}^{-1} \text{ sec}^{-1}$ and $k_b = 6 \times 10^{19} T^{-1} \text{ ml}^2 \text{ mole}^{-2} \text{ sec}^{-1}$. Although some uncertainties in k_f (stemming from lack of knowledge of the rates of population of excited electronic states of Na under nonequilibrium conditions^{4,10,12}) remain, it seems likely that use of the best available values for these rate coefficients in calculations otherwise identical to those carried out by Evans, Schexnayder, and Grose would result in significantly higher electron densities and earlier predicted onset of blackout.

References

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Received May 28, 1974.

Index categories: Reactive Flows; Thermochemistry and Chemical Kinetics.

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⁹ Ashton, A. F. and Hayhurst, A. N., "Kinetics of Collisional Ionization of Alkali Metal Atoms and Recombination of Electrons with Alkali Metal Ions in Flames," *Combustion and Flame*, Vol. 21, Aug. 1973, p. 69.

¹⁰ Fowler, G. N. and Preist, T. W., "Ionization Cross-Section in Flames," *Journal of Chemical Physics*, Vol. 56, Feb. 1972, pp. 1601–1605.

¹¹ Bates, D. R., Malaviya, V., and Young, N. A., "Electron-Ion Recombination in a Dense Molecular Gas," *Proceedings of the Royal Society of London, Ser. A*, Vol. 320, Jan. 5, 1971, pp. 437–458.

¹² Preist, T. W., "Interpretation of Collisional Ionization Rates in Flames," *Journal of the Chemical Society, Faraday Transactions I*, Vol. 68, April 1972, p. 661.

¹³ Dalidchik, F. I. and Sayasov, Y. S., "Recombination of Electrons and Ions in Triple Collisions in a Medium of Dipole Molecules," *Journal of Experimental and Theoretical Physics (USSR)*, Vol. 52, No. 6, 1967, p. 1592.

Reply by Authors to D. E. Jensen

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D. E. JENSEN has indeed found a misstatement in our paper.¹ As the result of an oversight, the sodium ionization rate, $\text{Na} + \text{M} \rightleftharpoons \text{Na}^+ + e^- + \text{M}$, was incorrectly included in a list of reaction rates for which no literature values are available. He cites eight experimental and four theoretical papers which give values for this rate. Since these papers are listed in his comment, we do not repeat the references here, but only add that most of them were a part of our files at the time the research on the Viking entry was done and that they figured in our estimate of the best value to use in the boundary-layer calculations.

The two exchange rates, $\text{Na}^+ + \text{NO} \rightleftharpoons \text{NO}^+ + \text{Na}$ and $\text{Na}^+ + \text{O}_2 \rightleftharpoons \text{O}_2^+ + \text{Na}$, were also inadvertently included in the list, but, in fact, Farragher² and Henderson³ have published experimentally measured values for them. There are no other errors of fact in the paper, so far as we know.

It is true that an earlier onset of blackout would be predicted by a four-order-of-magnitude increase in the sodium ionization rate. However, as was explained in a footnote, such a large value yields theoretical predictions of electron concentration in the RAM-C boundary layer which are out of accord with flight-measured values. The effect on RAM C-III predictions of varying the Na ionization rate (and some others, as well) is discussed in a paper⁴ just published. Because of the RAM-C results, we feel that the rates used for the Viking blackout predictions are appropriate.

References

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Received June 26, 1974.

Index categories: Reactive Flows; Thermochemistry and Chemical Kinetics.

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