# Reaction of Sodium Amalgam with Water

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THE solvated electron is now a well-established entity in the radiation chemistry of aqueous solutions.[1] We have examined the effects of substrates on the hydrogen yields in the reaction of sodium amalgam with dilute acid solutions to see whether it might be a significant intermediate in this reaction. Typical results for cupric perchlorate–perchloric acid solutions are shown in the Figure.
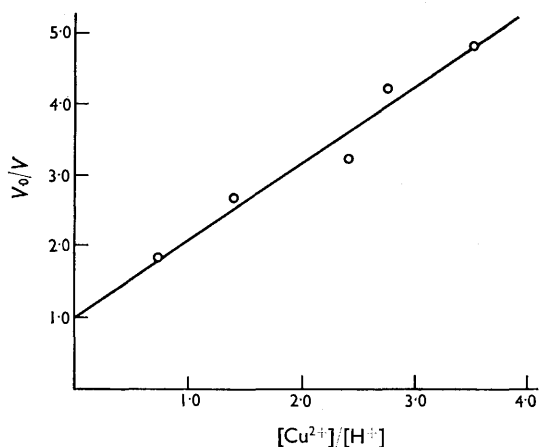
FIGURE

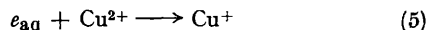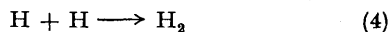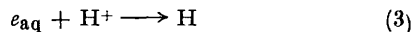*Hydrogen yields from cupric perchlorate–perchloric acid solutions*
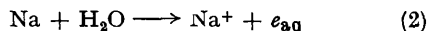
Ordinate: V_0/V
Abscissa: $[Cu^{2+}]/[H^+]$

As may be seen, the results conform to the equation

$$\frac{V_o}{V} = 1 + A \frac{[Cu^{2+}]}{[H^+]} \qquad (1)$$

where V and V_o are the volumes of hydrogen at N.T.P. evolved per gram of sodium in the presence

and absence respectively of cupric ion. This equation is consistent with the reaction scheme:

$$Na + H_2O \longrightarrow Na^+ + e_{aq} \qquad (2)$$

$$e_{aq} + H^+ \longrightarrow H \qquad (3)$$

$$H + H \longrightarrow H_2 \qquad (4)$$

$$e_{aq} + Cu^{2+} \longrightarrow Cu^+ \qquad (5)$$

if $A = k_5/k_3$. This scheme assumes that hydrogen is produced from the recombination of hydrogen atoms only and not of solvated electrons. The relative rate constants for recombination and scavenging[2,3] are $k_{e+e}/k_{e+Cu^{2+}} \simeq 0.3$ whereas $k_{H+H}/k_{H+Cu^{2+}} \simeq 190$ indicating that cupric ions would more readily suppress the recombination of solvated electrons.

Rate-constant ratios corresponding to k_5/k_3 have been measured for a variety of substrates and from the results presented in the Table, it will be seen that there is good agreement between the experimentally observed values and rate ratios calculated from known rate constants for the corresponding reactions of the solvated electron.

TABLE

Comparison of observed and calculated rate constant ratios

Substrate	Observed rate ratio	Calculated rate ratio	Reference
$Co(NH_3)_6^{3+}$	9.3	4.4	4
Cu^{2+}	1.2	1.4	5
Zn^{2+}	1.0	0.73	4
$Fe(CN)_6^{3-}$	0.56	0.13, 0.76	5, 6
Co^{2+}	0.45	0.59	4

It is interesting that the rate-constant ratio for the reaction of hydrogen atoms with ferricyanide and cupric ions[7] is 63 compared with the observed ratio of 0.47 from this work. This confirms that the solvated electron rather than the hydrogen atom is the scavengeable intermediate.

[1] E. J. Hart, J. K. Thomas, and S. Gordon, *Radiation Res. Suppl.*, 1964, **4**, 74.
[2] H. A. Schwarz, *Radiation Res. Suppl.*, 1964, **4**, 89.
[3] J. P. Sweet and J. K. Thomas, *J. Phys. Chem.*, 1964, **68**, 1363.
[4] J. H. Baxendale, E. M. Fielden, C. Capellous, J. M. Francis, J. V. Davies, M. Ebert, C. W. Gilbert, J. P. Keene, E. J. Land, A. J. Swallow, and J. M. Nosworthy, *Nature*, 1964, **201**, 468.
[5] S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani and J. K. Thomas, *J. Amer. Chem. Soc.*, 1963, **85**, 1375.
[6] J. Jortner, M. Ottolenghi, J. Rabani, and G. Stein, *J. Chem. Phys.*, 1962, **37**, 2488.
[7] J. Rabani, *J. Phys. Chem.*, 1962, **66**, 361.

The solvated electron has been identified in the reaction of sodium with ice[8] and it has been claimed that its spectrum may be observed in the reaction of sodium with water.[9] The results presented here show that it is an important kinetic intermediate in the reaction of sodium amalgam with water.

[8] J. E. Bennett, B. Mile, and A. Thomas, *Nature*, 1964, **201**, 919.
[9] J. Jortner and G. Stein, *Nature*, 1955, **175**, 893.