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Richard A. Ogg Jr.

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RICHARD A. OGG, JR.
Department of Chemistry, Stanford University, California
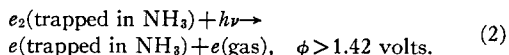March 14, 1946

THE previous studies[1] of *inner* photoelectric effect (i.e., of photo-conductivity) of metal-ammonia solutions have been extended to include the *external* photoelectric effect—i.e., the emission of electrons into the vapor phase. Extremely dilute (some 10^{-5} to 10^{-4} molar) sodium solutions were employed, in a special photo-cell maintained just above the freezing point of ammonia. The light source was a tungsten filament projection lamp, in conjunction with a carefully tested set of light filters. The quantum efficiency of photoelectric emission appeared to be similar in magnitude to that previously observed[2] for relatively concentrated solutions, but the spectral dependence proved entirely different. Whereas the long wave-length threshold[2] varies from some 7700A for a saturated solution to some 8500–8700A for a 4×10^{-2} molar solution, the highly dilute systems here studied displayed their *maximum* sensitivity in the near infra-red. Exact determination of the corresponding threshold requires more precise work with an infra-red monochromator, but with the filters employed it is estimated to be in the region around 15,000A. The extremely dilute solutions in question would thus appear to possess a work function of the order of one-half of that of the concentrated solutions.

The extraordinary difference in photoelectric behavior of extremely dilute and relatively concentrated sodium-ammonia solutions is best explained by the previously proposed[1,3] equilibrium between trapped electron pairs and trapped single electrons, and by the striking difference in absorption spectrum[3] between these two components. At the very great dilutions employed in the present studies, the proportion of trapped pairs is negligible, and the estimated photo-threshold at $\lambda \sim 15,000$A corresponds to the work function of the process

$$e(\text{trapped in NH}_3) + h\nu \rightarrow e(\text{gas}), \quad \phi \sim 0.8 \text{ volt.} \quad (1)$$
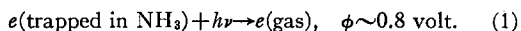
However, measurements of magnetic susceptibility[4,5] indicate that even the most dilute solution previously studied[2] is characterized by a great predominance of trapped electron pairs over trapped single electrons. Further, in the red and near infra-red regions, the absorption coefficient[3] of trapped pairs greatly exceeds that of trapped single electrons. Consequently, in such solutions the above process (1) is quantitatively negligible, and the observed photo-threshold at $\lambda < 8700$A corresponds to the work function of the process

$$e_2(\text{trapped in NH}_3) + h\nu \rightarrow$$
$$e(\text{trapped in NH}_3) + e(\text{gas}), \quad \phi > 1.42 \text{ volts.} \quad (2)$$

The possibility of precise experimental determination of the work function for process (1) is especially interesting as affording an *upper limit* to the "solvation energy" of single electrons in liquid ammonia solution. (The excess over the "true" energy results from application of the Franck-Condon principle to the non-adiabatic removal of the electron from the solvent cavity). This allows a strictly *experimental* approach to the long standing theoretical problem[6] of separation of *sums* of solvation energies of positive and negative ions into the respective contributions of the individual ionic species.

The difference in work functions between processes (2) and (1) provides an *upper limit* (for reasons similar to those outlined above) to the dissociation energy of the trapped electron pair into two electrons trapped in separate cavities. The *provisional* value obtained here seems not unreasonably greater than that roughly estimated from the temperature dependence of the magnetic susceptibilities,[4,5] and from current calorimetric studies which show dilute (some 10^{-2} to 10^{-1} molar) sodium-ammonia solutions to display a definitely *negative* heat of dilution—in contrast to the *positive*-effect expected for simple electrolytes, and experimentally observed with ammonia solutions of sodium bromide.[7]

[1] R. A. Ogg, Jr., J. Am. Chem. Soc. **68**, 155 (1946).
[2] J. Häsing, Ann. d. Physik [5] **37**, 509 (1940).
[3] R. A. Ogg, Jr., J. Chem. Phys. **14**, 115 (1946).
[4] E. Huster, Ann. d. Physik **33**, 477 (1938).
[5] S. Freed and N. Sugarman, J. Chem. Phys. **11**, 354 (1943).
[6] For literature references, see O. K. Rice, *Electronic Structure and Chemical Binding* (McGraw-Hill Book Company, Inc., New York, 1940).
[7] C. A. Kraus and F. C. Schmidt, J. Am. Chem. Soc. **56**, 2297 (1934).