5. CONCLUSION

The results of the present investigation demonstrate that any redox system, consisting of colored dye and another redox couple, is capable of exhibiting the photogalvanic effect when exposed to visible light. Whether the system will be useful for radiant energy conversion depends principally on the photoinduced potential which is developed.

The riboflavin-diethanolamine and riboflavin-triethanolamine photogalvanic systems have been found to give maximum photopotentials of ca. 520 mV and 430 mV, respectively-much higher than that produced by the famous and extensively studied thionine-iron system. The photopotentials which are related to the position of the photostationary state with respect to equilibrium in the dark, are found to be dependent on the concentrations of riboflavin and diethanolamine/triethanolamine, solution pH and temperature. Introduction of oxygen or some water-soluble organic solvent also affect the cell potential.

Riboflavin has a reduction potential of -0.186 V at pH 7. The standard redox potentials for diethanolamine and triethanolamine are unknown buts are believed to be much higher than that for riboflavin since neither diethanolamine nor triethanolamine reacts with riboflavin in the dark. Similar reaction schemes have been proposed

for the two systems. Under illumination riboflavin is photoreduced by diethanolamine (or triethanolamine). Reduced riboflavin in the vicinity of the illuminated electrode is capable of transferring its electrons to the electrode and, in the process, is reoxidized. Meanwhile, electron flow in the external circuit results in accumulation of electrons in the dark electrode and a cathodic current flowing in the external circuit from the dark electrode to the illuminated electrode. Now, riboflavin in the dark compartment undergoes reduction by extracting electrons from the dark electrode. Finally, oxidized diethanolamine (or oxidized triethanolamine) diffusing from the illuminated compartment to the dark compartment, accepts electrons from reduced riboflavin, diffuses back to the illuminated half-cell and completes the cycle. When each system is in its photostationary state there is a net electron flow in the external circuit from the illuminated electrode to the dark electrode and a net cathodic current in the opposite direction.

Evidence obtained from further studies so far provides sufficient support to the proposed reaction scheme. Normally, the photopotential behavior of a photogalvanic system is such that after the first illumination cycle, the dark potential is never recovered. This is also the case with the present systems. The inability to recover the original dark

potential is believed to be related to the irreversibility of some reaction steps. When oxygen is admitted into either of the two systems, this irreversibility is apparently removed and the dark potential is again obtained.

The effect of oxygen is also seen when the photocurrent behavior is examined and can be interpreted in terms of the oxidizing action of oxygen. Thus, introduction of oxygen reduces the concentration of RbH_2 in the illuminated half-cell and reduces the negative component of the photocurrent, while the same process in the dark half-cell increases the positive component of the photocurrent.

The general effect of temperature elevation is to slightly decrease the photopotential and to increase both components of the photocurrent considerably. The photopotential decrease is expected from the Nernst equation and is associated with a small shift in photo-stationary state toward the dark equilibrium state. Increased mobility of the active species, on the other hand, is believed to be largely responsible for the increases in i_+ and i_-. As far as the performance of the cell is concerned, however, the photovoltage and photocurrent delivered by each cell are the values at the photostationary state (PC_{eq}). Both cells should therefore be operated at ambient temperature or with only the dark compartment at elevated temperatures.

Varying the diffusion length between the two electrodes has virtually no effect on the photocurrent and aids in the elucidation of the reaction scheme. The constancy of i_+ and i_- under such conditions implies that the main electrode-active species do not have to diffuse from one electrode to the other-thus, the conclusion that Rb and RbH$_2$ are the main electrode-active species.