Table 2. Minimum energy (E) path for $F + H_2 \rightarrow FH + H$. Distances ($R$) are in Bohr radii (*19*); 338-configuration first-order wave functions were used.

R_{H-F}	R_{H-H}	E (kcal/mole)	System
∞	1.42	0.00	Reactants
6.0	1.42	0.00	
4.0	1.42	0.25	
3.6	1.43	0.44	
3.4	1.43	0.75	
3.2	1.44	1.27	
3.0	1.44	1.61	
2.90	1.45	1.66	Saddle point
2.8	1.48	1.59	
2.63	1.5	1.18	
2.36	1.6	− 2.15	
2.03	1.8	−12.30	
1.85	2.0	−20.70	
1.80	2.2	−25.30	
1.78	2.5	−29.15	
1.77	3.0	−32.91	
1.76	∞	−34.44	Products

the exothermicity into product translational energy. Qualitatively, a surface is termed attractive if the exothermicity is released as the A atom approaches the BC molecule. In the same way, the surface is repulsive if the energy is released as AB and C separate. Mixed energy release is said to occur if the AB and BC internuclear separations simultaneously change as the energy is released. More quantitatively, several procedures have been proposed (*17*) for categorizing surfaces as percent attractive, mixed, and repulsive. Muckerman (*15*) applied these classifications to four semiempirical London-Eyring-Polanyi-Sato (LEPS) (*18*) surfaces for FH_2. By Polanyi's rectilinear method, three of the four surfaces were found to be 0 percent attractive and 100 percent repulsive. Our ab initio surface is also 100 percent repulsive by the rectilinear method. We have also categorized the present surface by Polanyi's minimum path method and find 23 percent attractive, 22 percent mixed, and 55 percent repulsive. This minimum path characterization is far more flexible than the rectilinear, which (taken literally) might lead one to expect all the exothermicity to be converted to product translation. Further, the simple minimum path description of our surface is consistent with the experimental finding (*7*) that the $F + H_2 \rightarrow FH + H$ reaction yields a large amount of FH vibrational excitation (approximately 67 percent of the exothermicity).

A feature not apparent from the minimum energy path or the graphics is a small long-range attraction between FH and H. When diatomic FH is held at its experimentally determined equilibrium internuclear separation, 1.7328 Bohrs (*19*), this attraction is strongest at an H-H distance of 4.75 Bohr radii and amounts to 0.24 kcal/mole (or 120°K) in our CI calculations. This attraction is predicted to be 0.25 kcal/mole from the present SCF calculations, and it was 0.22 kcal/mole in our earlier work (*1*). Jaffe and Anderson (*20*) have carried out classical trajectory calculations for $F + H_2$ on a modified LEPS potential surface with an attraction of 4.8 kcal/mole between FH and H. Our calculations suggest that such a large attraction is not realistic. Finally, the present computations do not predict a long-range attraction between F and H_2.

For systems with more than three electrons, a priori potential energy surfaces approaching quantitative accuracy are now feasible. Our methods can be extended to the study of potential surfaces for several distinctly different types of $A + BC$ reactions, including $H + F_2$ (calculations now in progress), $Li + HF$, and $Li + F_2$.

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Chlorination at Power Plants: Impact on Phytoplankton Productivity

Abstract. *Studies of the effects of passage through a power plant on river phytoplankton have shown that chlorination depresses rates of photosynthesis and respiration to a much greater extent than does heating.*

The addition of chlorine in the form of hypochlorite or as gaseous chlorine is a procedure carried out several times daily in the routine operation of power-producing plants and sewage-processing plants. As a bacteriocide, chlorine acts as an antifouling agent in the costly hardware of cooling systems and as reducer of biological oxygen demand at the site of sewage release (thus moving the problem downstream). As the number of installations pouring chlorine into our waterways increases, the total chlorine load increases, and chlorine effects are exacerbated.

We can find nowhere in the literature a presentation of the direct relationship between chlorine concentration and productivity of phytoplankton, nearly all emphasis having been placed on heating and sudden thermal shock (*1*). The relationship has been referred to, however (*2*). Although anxious to avoid minimizing the many effects of heating river water we contend that the very specific effect of depression of plankton photosynthesis (PS) and respiration (R) in the vicinity of power plants in routine operation is for the most part due to the addition of chlorine.

We determined rates of PS and R by using the light-dark bottle incubation technique and determined changes in

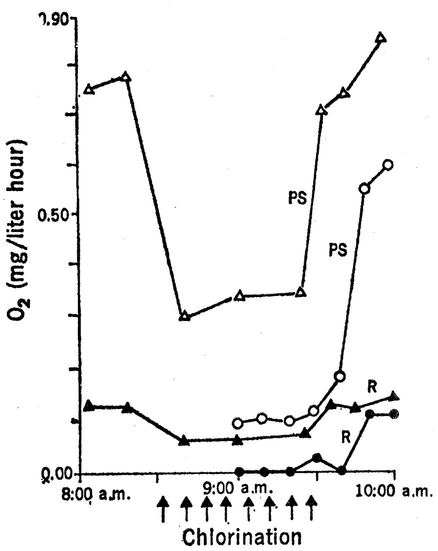

Fig. 1. Sequential rates of photosynthesis (PS, open symbols) and respiration (R, closed symbols) of samples collected from plant discharge before, during, and after chlorination on 2 September 1971 (circles) and 13 September 1971 (triangles).

the amounts of dissolved oxygen by Winkler titration. The data presented were obtained by incubating 300-ml samples of river water at a depth of 1 m for 2 to 4 hours near solar noon at ambient river temperature. Titration of 200-ml samples with 0.025N sodium thiosulfate gives concentrations of dissolved oxygen within 0.02 part per million (ppm) of the mean of ten samples at oxygen concentrations near 8 ppm. Relying on this precision, we usually made our analyses singly or with only one replicate.

With cooperation and support by the Northern States Power Company of Minneapolis (*3*), we made a preliminary examination of productivity in the St. Croix River in the vicinity of the Allen S. King Plant. Unusual patterns of depression of phytoplankton PS and R seemed unrelated to either the ambient river temperature, the temperature of the condenser cooling water, the temperature in the cooling-water discharge canal, or the temperature at the site of incubation (whether at the elevated temperature in the discharge canal, or in the river at ambient temperature). We then questioned plant personnel about irregularities in plant operations and discovered that chlorine is added not at a continuous rate, but in concentrated doses lasting 1 hour, four times daily. We found good agreement between times of chlorine addition and the incidence of severe depression (greater than 50 percent of control) of PS and R.

The passage of river water through the King Plant takes no more than 11 minutes from uptake to return; this includes passage through the cooling towers, when they are being used. Some 10^6 liters of river water per minute are pumped through the steam condenser, this volume representing up to one-third or even one-half the total for the river during late summer. Also at this time the total daily chlorine addition is greatest, apparently deemed necessary for effective removal of attached bacteria. The King Plant adds chlorine not to the steam-condenser water, but to water in a subsidiary cooling system; this water passes throughout the plant boiler system. A chemist at the King Plant, D. Taylor, determined by the orthotolidine method that a sample we obtained within the plant during chlorine injection contained 2700 ± 100 parts of chlorine per billion parts of water. We have no chlorine determinations for the river water pumped through the plant at the point that it is returned to the river.

During August and September 1971, we made several studies to check the magnitude of the chlorine effect on PS and R. Throughout this period the river ambient temperature remained in the range of 23° to 25°C and the temperature of the condenser cooling water in the range of 32° to 36°C.

Compared to the control sample, which was taken upstream from the plant site, samples taken from the plant condenser discharge and from various points in the discharge canal during times when no chlorine was being injected showed depression in PS of 5 to 15 percent and stimulation of R up to 50 percent. Control PS and R rates were generally 0.6 to 0.9 part of oxygen per million per hour and 0.05 to 0.1 part of oxygen per million per hour, respectively. Similar comparisons made during the time of chlorine addition showed depression of PS between 50 and 90 percent, and often elimination of measurable R (Fig. 1).

To investigate the chlorine depression of PS and R, we incubated the plant sample containing chlorine [2700 parts per billion (ppb)] and six serial dilutions of it, 1 : 1 with river water, in the usual way at ambient river temperature. The chlorine concentrations ranged from 46 to 2700 ppb. We assume from previous experience that the activity of the plant sample before chlorine injection would be within 10 to 20 percent of that of the control.

As shown in Fig. 2, both PS and R

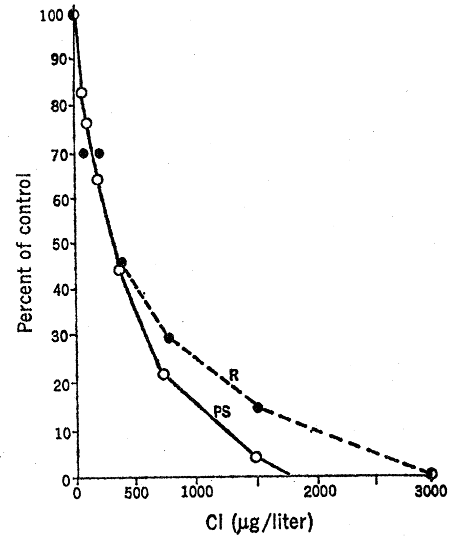

Fig. 2. Effect of chlorine addition on rates of photosynthesis (PS, open circles) and respiration (R, closed circles), expressed as percentage of control.

are depressed to 50 percent of control at a chlorine concentration of 320 μg/liter, and both are reduced to zero at or below the maximum chlorine concentration (2700 ppb). The chlorine concentrations in Fig. 2 were estimated from the dilutions of the highest concentration, but the dilution curve indicates the general trend. The chlorine concentrations in the diluted samples should be determined quantitatively, and the St. Croix River should be checked for other possible sources of chlorine addition.

Additional data not included here strongly suggest a relationship between the passing of chlorine-rich pumped water through the cooling towers of the power plant and 70 to 80 percent recovery of PS and R rates. The role of cooling towers in driving off chlorine and restoring the productive capacity of the river water, and whether this is in all cases a positive attribute, should be investigated.

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