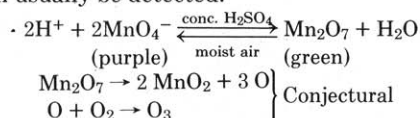# letters

Hazard in "Permanganate Volcano" Demonstration

To the Editor:

On November 23, 1979, in Roger Adams Laboratory at the University of Illinois, a serious explosion occurred while a teaching assistant was practicing a lecture demonstration illustrating the basicity of MnO_4^- and the instability of Mn_2O_7, sometimes referred to as the "permanganate volcano."

The demonstration involves soaking $KMnO_4$ crystals on the bottom of an Erlenmeyer flask with concentrated sulfuric acid. Volatile, green Mn_2O_7 forms, which reacts with moisture in the air to give a purple fog of $HMnO_4$. Usually addition of a few drops of water was necessary to cause a rapid volcano-like decomposition of Mn_2O_7 to MnO_2 and oxygen. An odor of ozone can usually be detected.

$$\cdot\, 2H^+ + 2MnO_4^- \underset{\text{moist air}}{\overset{\text{conc. } H_2SO_4}{\rightleftharpoons}} Mn_2O_7 + H_2O$$
$$\text{(purple)} \qquad\qquad \text{(green)}$$
$$\left.\begin{array}{l} Mn_2O_7 \rightarrow 2\,MnO_2 + 3\,O \\ O + O_2 \rightarrow O_3 \end{array}\right\} \text{Conjectural}$$

The explosion occurred during a second trial in which enough sulfuric acid was added to completely cover the $KMnO_4$. The mixture turned brown immediately obscuring the green color of Mn_2O_7. The assistant walked to a chalkboard about 20 ft away to practice his discussion of the reactions when the mixture detonated. The shock wave shattered two panels of green chalkboard four feet away. A graduated cylinder next to the reaction flask remained standing, but the upper one-third was missing. No trace of the reaction flask was found. Manganese stains were visible 40 ft from the explosion center. The teacher, 20 ft from the explosion center, was not injured.

We conjecture that the excess sulfuric acid contained the explosive material, allowing more reaction to occur before it blew up. (Containment of $H_2 + O_2$ mixtures in soap bubbles or balloons greatly enhances the explosions.) However, we will not seek "safe" conditions for doing this dramatic demonstration. Mn_2O_7 is too touchy to allow its formation under any circumstances. **This demonstration should be abandoned by any who currently use it.** A cursory search of the literature reveals reports of three previous accidents (*1, 2*) involving Mn_2O_7, and only a few scientific studies of its formation and properties (*3–6*).

Accidents have occurred as follows. A few drops of dark green liquid Mn_2O_7 in a separatory funnel was being examined by being held to the light. It detonated, badly cutting the neck of the observer. Glass fragments made clean holes through two walls of a buret and broke nearby window glass (*1*). The reaction of Mn_2O_7 with stopcock grease was blamed for the explosion. A second explosion involved hot concentrated H_2SO_4 from a cracked retort leaking into an open dish of $KMnO_4$ crystals. "Purple rain" was observed in both cases.

A third accident occurred when concentrated sulfuric acid was mixed with $KMnO_4$ crystals in a flask with moist walls. The heat of hydration of sulfuric acid was sufficient to cause detonation of Mn_2O_7 formed (*2*).

All the scientific studies found emphasize the danger of explosions when producing or handling Mn_2O_7. It first appears in a doctoral thesis in 1861. Walker (*4*) had reported explosions when $KMnO_4$ is treated with "oil of vitriol," in 1853. Thorpe and Hambly (*5*), in 1888, describe properties of Mn_2O_7, $HMnO_4$, and MnO_3. O. Glemser and H. Schröder (*6*) provide the most thorough study, in which they emphasize the need for care in handling Mn_2O_7. They determined its detonation temperature as 55°C, describe explosions as one-fourth as powerful as TNT. ($\Delta H = -177.4$ kcal/mole) Dissociation

pressure $= 10^{50}$ torr. It is more sensitive to shock than fulminate of mercury ($Hg(CNO)_2$) but less so than nitroglycerin.

T. S. Briggs (*7*) recommends solutions of Mn_2O_7 in CCl_4 or CCl_3F for organic oxidations. However, such solutions last only one day and evolve MnO_3Cl, phosgene ($COCl_2$), oxygen and MnO_2.

G. W. Watt's study of the reaction of Mn_2O_7 with S_8 was beset by frequent explosions (*8*).

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In Appreciation

To the Editor:

As I read the January issue I was deeply moved by the generosity, kindness and sentiments of the authors, and by the thoughtfulness, creativity and care of the editors and production staff. The warmth of the words of so many old friends, the flood of memories they brought, and the realization that all of you worked so hard to prepare this priceless expression of regard turned my thoughts to a poem someone taught me when I was a child:

> From quiet homes and first beginnings
> Out to the uncovered ends
> There's nothing worth the wear of doing
> But the laughter and the love of friends.

> *Author Unknown*

Thank you Joe, Debbie, Derek and all who contributed to this touching and inspiring tribute.

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On the Validity of Bond Free Energies

To the Editor:

Amador has recently published [*J. CHEM. EDUC.,* **56,** 453 (1979)] a table of "bond free energies," which he proposes to use in calculating $\Delta G°$ of reaction in the same way that bond energies or enthalpies are used to calculate $\Delta H°$ of reaction for gaseous species.

The absence heretofore of such tables, which he finds "amazing," is of course due to the inability of such a table to handle the $T\Delta S°$ term in $\Delta G° = \Delta H° - T\Delta S°$. Amador's table was derived in an unspecified way from published free energies of formation of an appropriate set of (mostly) organic compounds. Presumably to get a best fit of the data, the bond free energies were chosen either implicitly or explicitly to minimize the variation in $\Delta G°$ of reaction due to this entropy term. For each of ten reactions Amador calculates the free energy change, $\Delta G°_{calc}$, from his bond free energies, and compares the result with $\Delta G°_{accpt}$, the accepted value from the literature. The agreement between $\Delta G°_{calc}$ and $\Delta G°_{accpt}$ is surprisingly good. However, the effect of the $T\Delta S°$ term