

(g, gas) although ammonia also begins to decompose appreciably above 675°K.

Any reaction sequence which sums only to the decomposition of water must involve highly endothermic reactions driven at high temperatures by large increases in entropy. Reaction 4 is such a reaction, although I am not able to comment on the practicality of the overall reaction sequence.

LESTER R. MORSS

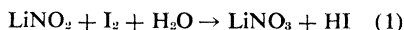
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#### References

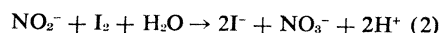
1. W. E. Winsche, K. C. Hoffman, F. J. Salzano, *Science* **180**, 1325 (1973).
2. B. M. Abraham and F. Schreiner, *ibid.*, p. 959.
3. J. W. Mellor, *Mellor's Comprehensive Treatise on Inorganic and Theoretical Chemistry* (Wiley, New York, 1967), vol. 8, suppl. 2, p. 362.
4. G. G. Durrant, R. O. Griffith, A. McKeown, *Trans. Faraday Soc.* **32**, 999 (1936); E. Abel, *Monatsh. Chem.* **81**, 7 (1950).

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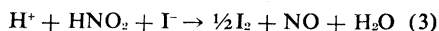
We welcome this opportunity to clarify the question raised by Morss, which has also been raised by others. The key to the cycle we proposed is the reaction



which is also the one being questioned. This reaction can just as well be written

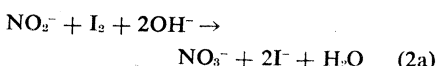


Since it is well known that  $\text{NO}_2^-$  oxidizes  $\text{I}^-$  to iodine in acid solution, and further since the solution becomes acid as reaction 1 progresses and there is a surfeit of  $\text{NO}_2^-$  present, the obvious conclusion seems to be that only the parasitic reaction 3 will occur



for which the standard Gibbs free energy  $\Delta G^0 = -42.46$  kJoule. That conclusion is, however, a little hasty. The first question to ask is, What is the pH value for which  $\Delta G$  of reaction 1 will be zero?

The solution of  $\text{LiNO}_2$  will initially be alkaline because the dissociation constant of  $\text{HNO}_2$  is small,  $4 \times 10^{-4}$ . Reaction 2 can be rewritten



for which  $\Delta G^0 = -104.22$  kJoule. Assuming that the activities ( $a$ ) of  $\text{I}^-$  and  $\text{NO}_3^-$  are equal and that the activity of  $\text{NO}_2^-$  remains close to unity, we obtain after appropriate substitutions

$$\text{pH} = 4.8656 + 3/2 \log a_{\text{I}^-} \quad (4)$$

For unit activity of  $\text{I}^-$ , reaction 2a will have  $\Delta G = 0$  at a pH of 4.9. We have thus established thermodynamically that reactions 1, 2, and 2a will go as written, which is one of the points at issue. Further, Berthoud and Berger (1) reported that in a solution of  $\text{NO}_2^-$  buffered to the acid side (pH 6.5) iodine was completely transformed to iodide.

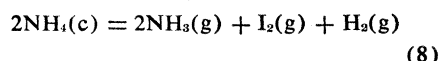
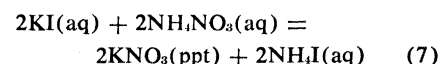
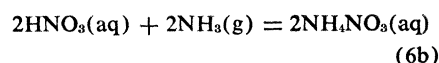
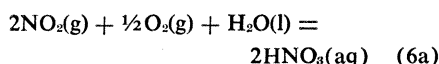
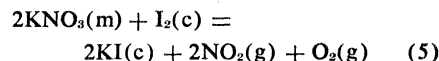
The second question is whether there are reasonable conditions which will make  $\Delta G = 0$  for the parasitic reaction 3. If it is assumed that the activities of  $\text{I}_2$ ,  $\text{H}_2\text{O}$ , and  $\text{I}^-$  are unity and that a small amount of NO will be generated to develop a pressure of 1 atm then  $\Delta G$  for reaction 3 will be zero at pH 5.4. Then reaction 1 is thermodynamically possible and conditions can be found which suppress reaction 3. Furthermore, the matter of relative rates also enters the picture, about which we can say nothing.

We have not succeeded in maintaining conditions that will make reaction 1 practical, although we have extracted HI by distillation. We have found that

## Keweenaw Volcanic Sequence

Baksi and Watkins (1) state that there are only four plateau basalt accumulations that exceed  $2 \times 10^5$  km<sup>3</sup> in volume, and do not list one that might even be the largest one of all—the Keweenaw volcanic sequence of the Lake Superior region. Although their source, Holmes (2), gives only  $1.2 \times 10^5$  km<sup>3</sup> for the Keweenaw, one of the more active workers in the field, White (3), estimates a volume in excess of  $4 \times 10^5$  km<sup>3</sup> for the Keweenaw in the Lake Superior area alone, a volume second only to that cited by Holmes for the Deccan of India ( $7 \times 10^5$  km<sup>3</sup>). This was probably a conservative estimate; inasmuch as the Keweenaw volcanic sequence probably extends from Lake Superior as far as Kansas along the midcontinental

the reactions we suggested in our report (2) will not go under conditions that will make a practical cycle. Our work has, however, produced the following modified sequence, which is much more promising



where m means molten; c, crystalline; g, gas; l, liquid; aq, aqueous; and ppt, precipitate. The potassium salts were used in this sequence because the solubility characteristic of  $\text{KNO}_3$  permits the efficient conversion of  $\text{NH}_4\text{NO}_3$  into iodide (reaction 7).

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gravity high and perhaps into the lower peninsula of Michigan in the other direction, its volume may even exceed that of the Deccan.

This does not affect the data or conclusions of Baksi and Watkins, but we who toil with the Keweenaw hate to see our favorite sequence of rocks downgraded.

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