

Reactions of Metals in Nitric Acid: Writing Equations and Calculating Electromotive Force of Redox Reaction

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S Supporting Information

ABSTRACT: This letter to the editor comments on the paper, “Writing reactions of metals with nitric acid: A mnemonic device for introductory chemistry students”.

KEYWORDS: High School/Introductory Chemistry, Inorganic Chemistry, Mnemonics/Rote Learning, Acids/Bases, Metals, Oxidation/Reduction, Reactions

I read with interest the prepared communication by Mikhail Kurushkin published in this *Journal*.¹ In that communication,¹ only two of the factors affecting the composition of the reaction products were studied: namely, (i) the activity of metal and (ii) the concentration of acid. Kinetics of metal reaction in nitric acid, and maybe the possibility of formation of different reaction gaseous products (N_2O , N_2 , NO , NO_2 , NH_3 ,² and H_2 ,³) are also influenced by the shape of metal; for example, a piece of thin wire or powder. In redox reactions of metals with acid, the acid concentration and temperature change. It should be taken into account that the reaction rate is also determined by the difficulty of formation of the gas phase and the solubility of gas (N_2 , N_2O , NO , NO_2 , NH_3 are slightly soluble in water) in the acid solution. For motivated chemistry students, it is important not only to write reaction equations of metals with nitric acid of various concentration, but also to calculate their electromotive force (EMF), indicate the most “thermodynamically favorable”⁴ reaction, and use the value obtained to select the prevailing gaseous product.

In the communication,¹ cadmium has been selected as the starting point: all metals above Cd in a typical activity series ($E^\circ = -0.40\text{ V}$) are considered reactive; all metals below and including Cd are considered less reactive. In the present work, metals are divided into two groups on the basis of the value of their standard potential E° ^{5,6} in a typical activity series: reactive metals with $E^\circ > 0$ and less reactive ones, with $E^\circ < 0$. Nitric acid has also been divided into three groups: very dilute acid with concentration less 5%, dilute acid with concentration 5–20%, and concentrated acid of 60–70%.

Below, two mnemonic schemes (Figure 1) similar to Fleming’s left-hand rule and Fleming’s right-hand rule⁷ are proposed.

The mnemonic schemes have one (Figure 1A) or two (Figure 1B) inputs and five outputs for every finger; gaseous products are listed in a clockwise direction toward increasing nitrogen oxidation number. According to the literature^{8,9} data, N_2O is formed in the reactions of Fe and Al in dilute nitric acid; therefore, this gas is also shown in Figure 1A. When Mn and Mg react with 10–20% HNO_3 , the gaseous mixture (H_2 , N_2 , N_2O , NO), which contains approximately 80% of H_2 ,⁸ forms (see Supporting Information.)

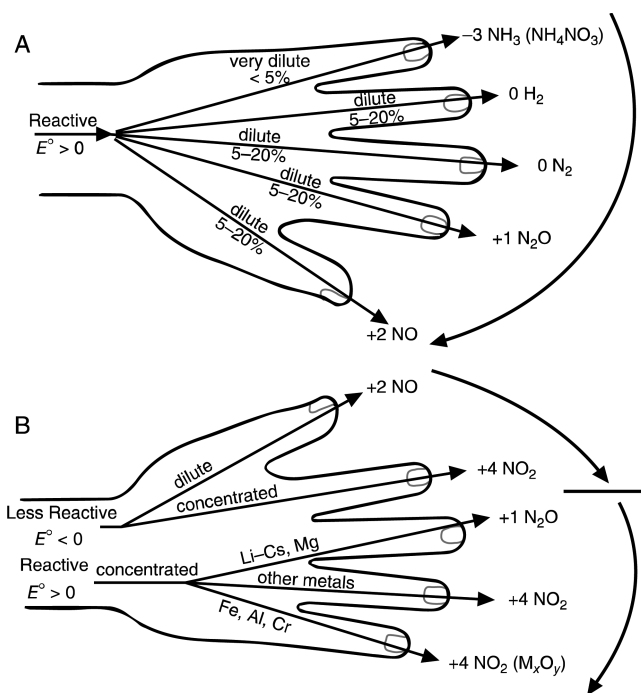
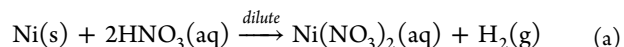
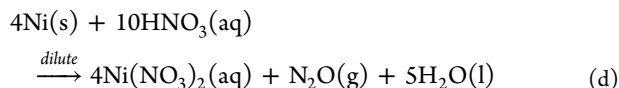
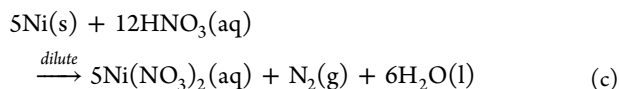
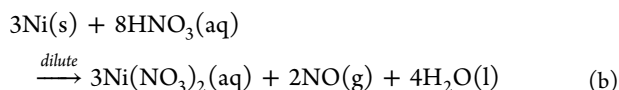


Figure 1. Suggested mnemonic schemes indicate the reduction product in nitric acid. (A) Left-hand schemes for reactive metals in dilute nitric acid; (B) right-hand scheme for less reactive metals in dilute and concentrated nitric acid, and for reactive metals in concentrated nitric acid.

To determine the most “thermodynamically favorable”⁴ reaction, it is necessary to calculate the EMF E° of all possible reactions. Therefore, equations of the possible redox reactions are written, as shown in the example for Ni metal:





Afterward, values of the standard potential^{5,6} are written:

$$\begin{aligned} E^\circ(\text{Ni}^{2+}/\text{Ni}) &= -0.25 \text{ V}; \quad E^\circ(2\text{H}^+/\text{H}_2) = 0.00 \text{ V}; \\ E^\circ(\text{NO}_3^-/\text{NO}) &= +0.96 \text{ V}; \quad E^\circ(\text{NO}_3^-/\text{N}_2) = +1.25 \text{ V}; \\ E^\circ(\text{NO}_3^-/\text{N}_2\text{O}) &= +1.12 \text{ V} \end{aligned}$$

Calculation of EMF for the reactions follows:

$$\begin{aligned} E_1^0 &= E^\circ_{\text{oxid. agent}} - E^\circ_{\text{reduc. agent}} = E^\circ(2\text{H}^+/\text{H}_2) \\ &- E^\circ(\text{Ni}^{2+}/\text{Ni}) = 0.00 \text{ V} - (-0.25 \text{ V}) = +0.25 \text{ V} \end{aligned} \quad (1)$$

$$\begin{aligned} E_2^0 &= E^\circ(\text{NO}_3^-/\text{NO}) - E^\circ(\text{Ni}^{2+}/\text{Ni}) \\ &= +0.96 \text{ V} - (-0.25 \text{ V}) = +1.21 \text{ V} \end{aligned} \quad (2)$$

$$\begin{aligned} E_3^0 &= E^\circ(\text{NO}_3^-/\text{N}_2) - E^\circ(\text{Ni}^{2+}/\text{Ni}) = +1.25 \text{ V} \\ &- (-0.25 \text{ V}) = +1.50 \text{ V} \end{aligned} \quad (3)$$

$$\begin{aligned} E_4^0 &= E^\circ(\text{NO}_3^-/\text{N}_2\text{O}) - E^\circ(\text{Ni}^{2+}/\text{Ni}) \\ &= +1.12 \text{ V} - (-0.25 \text{ V}) = +1.37 \text{ V} \end{aligned} \quad (4)$$

Values of EMF for the reactions lead to the conclusion: Under standard conditions (STP), all reactions take place. The comparison of EMF values shows that $E_3^0 > E_4^0 > E_2^0 > E_1^0$ ($1.50 \text{ V} > 1.37 \text{ V} > 1.21 \text{ V} > 0.25 \text{ V}$). Because Ni is a moderately reactive metal, situated between H_2 and Mn in the metal activity series, reaction d can be eliminated. As the relation between EMF and free-energy change is expressed by¹⁰

$$\Delta G^0 = -n \cdot F \cdot E^0$$

formation of NO, but not H_2 or N_2O , is “thermodynamically favorable” in dilute nitric acid.

The suggested mnemonic schemes have already been used for one year and successfully work for the reactions between metals and nitric acid. Requiring calculation of EMF has already been used for five years, which allows students to indicate the most “thermodynamically favorable” reaction and to select the prevailing gaseous product. The same requirements apply to reactions of metals with hydrochloric and sulfuric acids.

■ ASSOCIATED CONTENT

§ Supporting Information

The Supporting Information is available on the ACS Publications website at DOI: 10.1021/acs.jchemed.5b00328.

Examples of the equations of the possible redox reactions for the metals in nitric acid discussed in this article; calculation of electromotive force EMF for the reactions; indication of the most “thermodynamically favorable”

reaction, and selection of the prevailing gaseous product (PDF DOCX)

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Notes

The authors declare no competing financial interest.

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