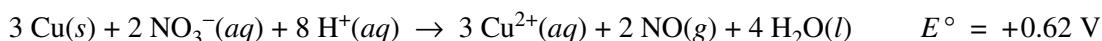


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Question 3

Answer the following questions related to chemical reactions involving nitrogen monoxide, NO(g).

The reaction between solid copper and nitric acid to form copper(II) ion, nitrogen monoxide gas, and water is represented by the following equation.



- (a) Using the information above and in the table below, calculate the standard reduction potential, E° , for the reduction of NO_3^- in acidic solution.

Half-Reaction	Standard Reduction Potential, E°
$\text{Cu}^{2+}(aq) + 2 e^- \rightarrow \text{Cu}(s)$	+0.34 V
$\text{NO}_3^-(aq) + 4 \text{H}^+(aq) + 3 e^- \rightarrow \text{NO}(g) + 2 \text{H}_2\text{O}(l)$?

$E_{\text{rxn}}^\circ = E_{\text{NO}_3^-}^\circ - E_{\text{Cu}^{2+}}^\circ = E_{\text{NO}_3^-}^\circ - 0.34 \text{ V} = 0.62 \text{ V}$ $\Rightarrow E_{\text{NO}_3^-}^\circ = 0.62 \text{ V} + 0.34 \text{ V} = 0.96 \text{ V}$	<p>One point is earned for the correct calculation of the standard reduction potential.</p>
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- (b) Calculate the value of the standard free energy change, ΔG° , for the overall reaction between solid copper and nitric acid.

$\Delta G^\circ = -n \mathcal{F} E^\circ = -(6)(96,500 \text{ C mol}^{-1})(0.62 \text{ V})$ $= -360,000 \text{ J mol}^{-1} = -360 \text{ kJ mol}^{-1}$	<p>One point is earned for the correct value of n, the number of moles of electrons.</p> <p>One point is earned for calculating the correct value of ΔG°, with correct sign and consistent units.</p>
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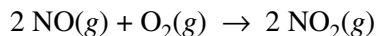
- (c) Predict whether the value of the standard entropy change, ΔS° , for the overall reaction is greater than 0, less than 0, or equal to 0. Justify your prediction.

<p>$\Delta S^\circ > 0$. Even though there is a loss of 7 moles of ions in solution, the value of ΔS° for the overall reaction will be greater than zero because two moles of NO gas will be produced (there are no gaseous reactants).</p>	<p>One point is earned for the correct answer with a justification that is based on the gaseous state of one of the products.</p>
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Question 3 (continued)

Nitrogen monoxide gas, a product of the reaction above, can react with oxygen to produce nitrogen dioxide gas, as represented below.



A rate study of the reaction yielded the data recorded in the table below.

Experiment	Initial Concentration of NO (mol L ⁻¹)	Initial Concentration of O ₂ (mol L ⁻¹)	Initial Rate of Formation of NO ₂ (mol L ⁻¹ s ⁻¹)
1	0.0200	0.0300	8.52×10^{-2}
2	0.0200	0.0900	2.56×10^{-1}
3	0.0600	0.0300	7.67×10^{-1}

(d) Determine the order of the reaction with respect to each of the following reactants. Give details of your reasoning, clearly explaining or showing how you arrived at your answers.

(i) NO

Comparing experiments 1 and 3, the tripling of the initial concentration of NO while the initial concentration of oxygen remained constant at 0.0300 mol L ⁻¹ resulted in a nine-fold increase in the initial rate of formation of NO ₂ . Since $9 = 3^2$, the reaction is second order with respect to NO.	One point is earned for the correct answer with justification.
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(ii) O₂

Comparing experiments 1 and 2, the tripling of the initial concentration of O ₂ while the initial concentration of NO remained constant at 0.0200 mol L ⁻¹ resulted in a tripling in the initial rate of formation of NO ₂ . Since $3 = 3^1$, the reaction is first order with respect to O ₂ .	One point is earned for the correct answer with justification.
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(e) Write the expression for the rate law for the reaction as determined from the experimental data.

$\text{rate} = k [\text{NO}]^2 [\text{O}_2]$	One point is earned for the correct expression for the rate law.
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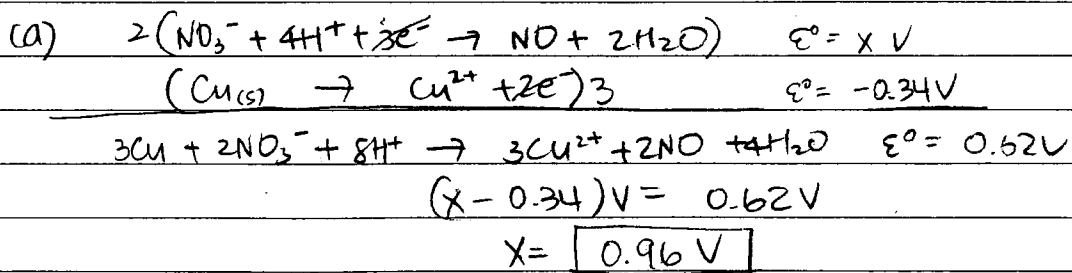
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Question 3 (continued)

- (f) Determine the value of the rate constant for the reaction, clearly indicating the units.

<p>Because the coefficient for NO₂ in the balanced equation is 2, the rate of the reaction is defined as $\frac{1}{2}$ the rate of the appearance of NO₂.</p> <p>From part (e) above, $k = \frac{\text{reaction rate}}{[\text{NO}]^2[\text{O}_2]}$</p> $= \frac{\left(\frac{1}{2}\right)(\text{rate of formation of NO}_2)}{[\text{NO}]^2[\text{O}_2]}$ <p>Substituting data from experiment 1,</p> $k = \frac{\left(\frac{1}{2}\right)(8.52 \times 10^{-2} \text{ mol L}^{-1} \text{ s}^{-1})}{(0.0200 \text{ mol L}^{-1})^2(0.0300 \text{ mol L}^{-1})}$ $= 3.55 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$	<p style="text-align: center;">One point is earned for calculating the correct value of the rate constant.</p> <p style="text-align: center;">One point is earned for including the correct units.</p>
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Note: a rate constant value of $7.10 \times 10^3 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ earns the point if the rate of reaction is assumed to be the same as the rate of formation of NO₂.



$$\begin{aligned}
 \text{(b)} \quad \Delta G^\circ &= -nF^\circ \cdot \mathcal{E}^\circ \\
 &= -6 \text{ mol e}^- \cdot \frac{96500 \text{ C}}{1 \text{ mol e}^-} \cdot 0.62 \frac{\text{J}}{\text{C}} \cdot \frac{\text{kJ}}{10^3 \text{ J}} = \boxed{-360 \text{ kJ}}
 \end{aligned}$$

(c) ΔS° is greater than 0 because the reaction becomes more disordered on product side since gas and liquid, which are more "disorganized" than solid and aqueous, are produced

$$\begin{aligned}
 \text{(d)} \quad \text{(i)} \quad \frac{\text{Rate}_3}{\text{Rate}_1} &= \frac{k[\text{NO}]^x[\text{O}_2]^y}{k[\text{NO}]^x[\text{O}_2]^y} = \frac{7.67 \times 10^{-1} \text{ M/s}}{8.52 \times 10^{-2} \text{ M/s}} = \frac{k[0.0600]^x [0.0300]^y}{k[0.0200]^x [0.0300]^y} \\
 \boxed{\text{Rate} = k[\text{NO}]^2} & \qquad 9.00 = 3^x \qquad x = 2 \\
 \text{NO is second order} &
 \end{aligned}$$

$$\begin{aligned}
 \text{(ii)} \quad \frac{\text{Rate}_2}{\text{Rate}_1} &= \frac{k[\text{NO}]^x[\text{O}_2]^y}{k[\text{NO}]^x[\text{O}_2]^y} = \frac{2.56 \times 10^{-1} \text{ M/s}}{8.52 \times 10^{-2} \text{ M/s}} = \frac{k[0.0200]^x [0.0900]^y}{k[0.0200]^x [0.0300]^y} \\
 \boxed{\text{Rate} = k[\text{O}_2]^1} & \qquad 3.00 = 3^y \qquad y = 1 \\
 \text{O}_2 \text{ is first order:} &
 \end{aligned}$$

$$\text{(e)} \quad \boxed{\text{Rate} = k[\text{NO}]^2[\text{O}_2]^1}$$

$$\begin{aligned}
 \text{(f)} \quad & 8.52 \times 10^{-2} \text{ M/s} = k(0.0200 \text{ M})^2(0.0300 \text{ M})^1 \\
 & \boxed{k = 7.10 \times 10^3 \frac{1}{\text{M}^2 \cdot \text{s}}}
 \end{aligned}$$

(a) $E_{cell}^{\circ} = E_{reduction} - E_{oxidation}$

$+0.62 = (x) - (0.34)$

$E^{\circ} = +0.96 V$

(b) $\Delta G = -nFE^{\circ}$

$\Delta G = (96,500 \frac{C}{mole})(+0.62)(-6e)$

$\Delta G = -358980 J$

(c) The ΔS for the overall reaction is less than zero because ΔG is $-$.

NO:
(d) (i) $\frac{8.52 \times 10^{-2}}{7.67 \times 10^{-1}} = .02^x$

$.33^x = .111$

$x = 2$

NO's order of reaction is 2, because when its concentration changed (+ O₂'s concentration didn't) from experiment 1 to 3, the rates changed also to mathematically (see above) result in a 2nd order reaction.

(ii) $\frac{.03^x = 8.52 \times 10^{-2}}{.09^x = 2.56 \times 10^{-1}}$

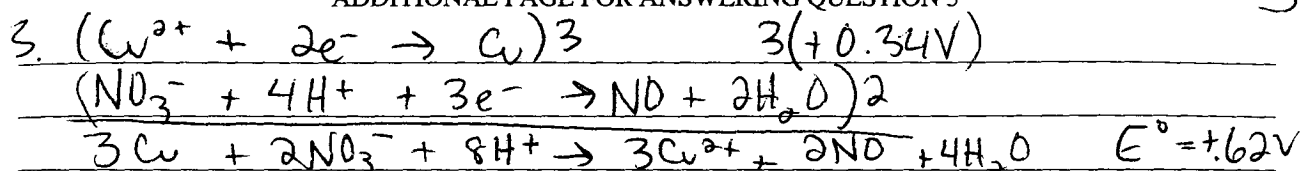
$.33^x = .33$

$x = 1$ } O₂'s order of reaction is 1, because when its concentration changed from experiment 1 to 2 (+ NO's concentration didn't), the rates changed to mathematically result in a 1st order reaction.

(c) rate = $k [NO]^2 [O_2]$

(f) $8.52 \times 10^{-2} \frac{mol}{Ls} = (k) (.02 \frac{mol}{L})^2 (.03 \frac{mol}{L})$

$k = 142 \frac{L}{mol^2 s^2}$



a)

$$0.62\text{V} - 3(0.34\text{V}) = \frac{-0.4\text{V}}{2} = -0.2\text{V}$$

b) $\Delta G^\circ = -nFE^\circ$

$$= -6F(.62\text{V})$$

$$\Delta G^\circ = -358.9 \text{ kJ/mol}$$

$$= -360 \text{ kJ/mol}$$

c) $\Delta S^\circ > 0$ because the spontaneity is increasing
(exothermic)

d) i) 2nd order

ii) 1st order

$$\frac{R}{[\text{NO}]^2[\text{O}_2]} = k \quad \text{for all 3 exp.}$$

e) rate = $k[\text{NO}]^2[\text{O}_2]$

f) $\frac{8.52 \times 10^{-2} \text{ mol/L}\cdot\text{s}}{(.02 \text{ mol/L})^2(.03 \text{ mol/L})} = 7100 \text{ s}^{-1}$

AP[®] CHEMISTRY
2008 SCORING COMMENTARY

Question 3

Overview

This question tested a diverse set of student skills. Parts (a) and (b) were intended to assess the ability of students to understand the relationship among standard reduction potentials of half-reactions and the cell potential, and the relationship between the cell potential and the change in Gibbs free energy of the reaction. Part (c) assessed students' ability to relate the change in entropy of the reaction to the phases of reactants and products given in the balanced equation. Parts (d), (e), and (f) required students to answer questions related to the kinetics of a different reaction; calculate reaction orders from experimental data; write a rate law that was consistent with the orders; and determine a rate constant. Those parts of the question were intended to assess the students' understanding of kinetics and the meaning of reaction orders, and their ability to write and interpret a rate law.

Sample: 3A
Score: 9

This response earned all 9 points: 1 for part (a), 2 for part (b), 1 for part (c), 1 for part (d)(i), 1 for part (d)(ii), 1 for part (e), and 2 for part (f).

Sample: 3B
Score: 6

The point was not earned in part (c) because ΔS° is greater, not less, than 0. No points were earned in part (f); although correct values are substituted into the rate law from part (e), both the value and the units in the final answer are incorrect.

Sample: 3C
Score: 4

The point was not earned in part (a) because the value calculated for E° is incorrect. Both points were earned in part (b). In part (c) the response correctly indicates that the value of ΔS° is greater than 0, but the point was not earned because the justification is insufficient. No points were earned in parts (d)(i) or (d)(ii) because the response does not show or explain how the orders of the reaction with respect to each reactant are determined. However, the point was earned in part (e) for providing a rate law consistent with the orders given in parts (d)(i) and (d)(ii). In part (f) 1 point was earned for calculating the value of the rate constant, but the second point was not earned because the units are incorrect.