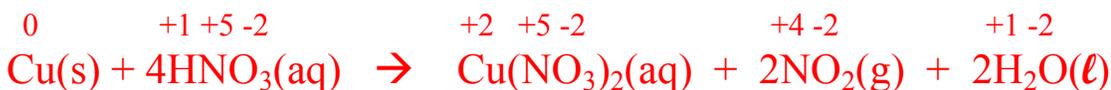


ANALYSIS OF THE REACTIONS:

Part A — Oxidation Reduction Reaction:



1. Copy the equation: $\text{Cu(s)} + 4\text{HNO}_3(\text{aq}) \rightarrow \text{Cu(NO}_3)_2(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$



- Assign oxidation numbers to each element.
- Use oxidation numbers to identify the species oxidized and reduced.

Cu oxid # was 0 and went up to +2 so copper was oxidized
– increased oxidation #

N in nitrate ion had an oxidation # +5 and in the NO_2
the oxidation # went down to +4
– so nitrogen was reduced – decreased oxidation #

- Write the half reaction to show the change in copper.



- Draw the electron configuration for copper atom.

Note: This is not the drawing.



However the stability of a full d subshell in level 3

explains this electron configuration rather than the above that follows the “rules”

- Assign quantum numbers to each of the valence electrons.

The electron in the 4s orbital 4 0 0 $\frac{1}{2}$

$n=4$ the principal quantum number designates the energy level

$l=0$ designates the s orbital

$m_l=0$ the only possible orientation of the s orbital (thus only one s orbital)

$m_s = \frac{1}{2}$ the up spin of the electron or $-\frac{1}{2}$ down spin

The electron in the 3d orbital 3 2 0 $\frac{1}{2}$

$n=3$ the principal quantum number designates the energy level

$l=2$ designates the d orbital

$m_l = -2$ or -1 or 0 or $+1$ or $+2$ five possible orientations of the d orbital
thus five different d orbitals

$m_s = \frac{1}{2}$ the up spin of the electron or $-\frac{1}{2}$ down spin

- Name and describe the bonding in solid copper metal.

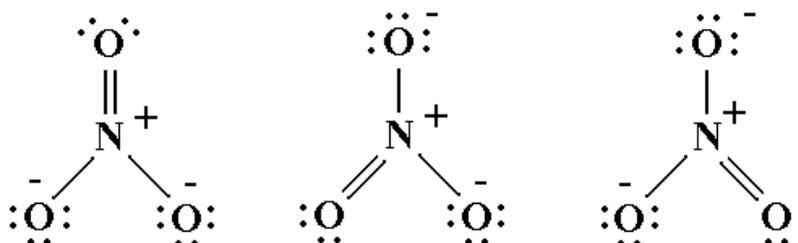
Metallic bonds hold the copper atoms in fixed positions. A sea of free moving electrons is shared between all the atoms. The solid metal conducts electricity as the electrons have a charge and are to move.

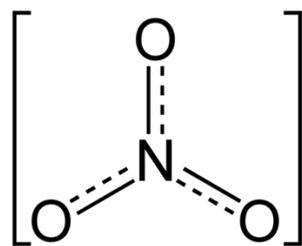
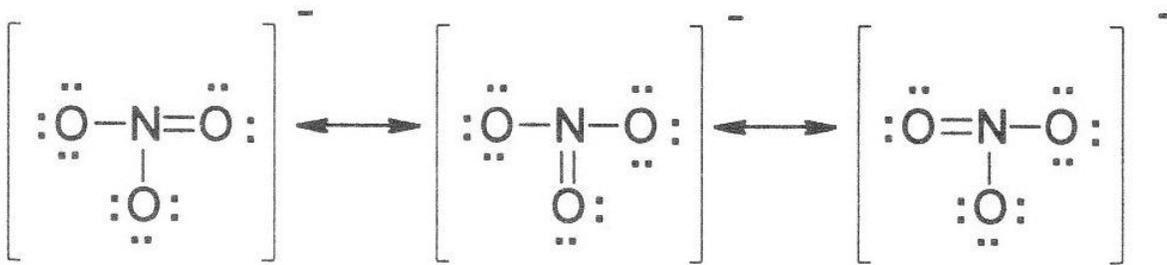
- Name and describe the attractions of copper (II) ions in solution.

Positive copper ions are attracted to negative ends of water molecules by ion-dipole attractions.

- Draw the Lewis structure for nitrate ions.

This shows three possible resonance structures and the formal charges on each atom.





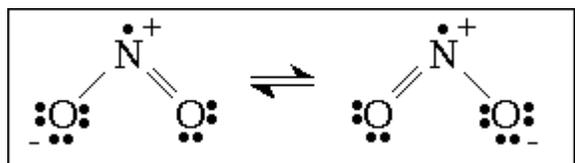
This shows the resonance hybrid. The dotted line shows the delocalized pi bonds spread over the four atoms. The pi bond is actually delocalized over the four atoms. This model is supported by the evidence that the three bond lengths are equivalent.

Determine the electron-pair geometry and orbital hybridization.

3 Bonding Pairs and 0 nonbonding pair (one pair of electrons in pi bond) so 3 e- pairs
3 electron pairs – need three hybrid orbitals sp^2

The three orbitals push each other as far apart as possible – trigonal planar at 120° electron pair geometry

- a. Draw the Lewis structure for nitrogen dioxide molecules. Determine the electron-pair geometry, molecular geometry and orbital hybridization. Caution: There are an odd number of electrons. The central atom nitrogen will not have a full octet.



2 Bonding Pairs and 1 nonbonding pair (well only one electron) so 3 electron pairs

3 electron pairs – need three hybrid orbitals sp^2

The three orbitals push each other as far apart as possible –

trigonal planar at 120° electron pair geometry

But there are only atoms at the bent locations – the molecular geometry.

- b. List the electronegativity of both nitrogen and oxygen. Use the electronegativity to identify the bond. Describe the bond.

The electronegativity of nitrogen is 3.0 and oxygen is 3.5. So oxygen is more electronegative than nitrogen but not much more. With a difference of only 0.5, this is barely polar or on the boundary line for nonpolar. Since it is barely polar, the oxygen end is partially negative and the partially positive. These dipole lead to weak dipole dipole attractions between the molecules.

- c. Describe the attraction between nitrogen dioxide molecules. Explain why nitrogen dioxide is a gas at room temperature. Include the bonding between the atoms and attractions between molecules in your explanation.

Since it is barely polar, the oxygen end is partially negative and the partially positive. The electron pair spends a bit more time with the oxygen than the nitrogen since the oxygen is more electronegative – this separation of charge results in a dipole moment. These dipole lead to weak dipole dipole attractions between the molecules.

- d. Use attraction to explain why the nitrate ion is in solution, while nitrogen dioxide is a gas.

The minimal charge separation leads to very weak attractions between nitrogen dioxide molecules. These barely polar molecules are not very attracted to the water molecules nor to each other. So the nitrogen dioxide molecules are widely spaced a room temperature.

The nitrate ions with an extra electron in the group have a net negative charge and are attracted to the water molecules by strong ion-dipole attractions. The ions remain in solution.

4. Copy the net ionic equation. $\text{Cu(s)} + 4\text{H}^+(\text{aq}) + 2\text{NO}_3^-(\text{aq}) \rightarrow \text{Cu}^{2+}(\text{aq}) + 2\text{NO}_2(\text{g}) + 2\text{H}_2\text{O}(\ell)$
a. Use this equation to explain what happens to the hydrogen ions in solution.



Hydrogen ions react with the oxygen from the nitrate ions. The nitrate ions lose oxygen to hydrogen ions. The hydrogen ions end up in water molecules. The nitrogen atoms in the nitrate ions are reduced so they gained electrons.

b. Based upon the changes in this reaction, what do you expect to happen to the pH? Explain.

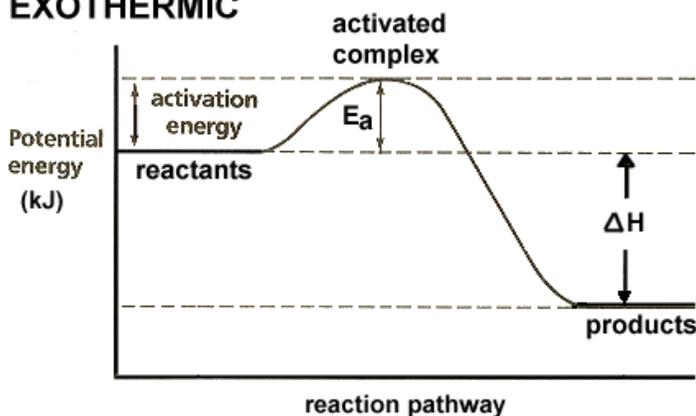
Since the hydrogen ions are reacting the concentration of hydrogen ions is decreasing and the pH is increasing. pH is the negative log hydrogen ion concentration – thus pH is inversely related the hydrogen ion concentration.

5. This reaction generates a great deal of heat.

a. Identify this reaction as either endothermic or exothermic. Justify your selection using the terms energy transfer, system and surroundings.

Energy was transferred from the system to the surroundings. The temperature of the surroundings increased- energy must have been transferred out of the system to surroundings to increase the temperature or average kinetic energy. The reaction is exothermic.

EXOTHERMIC



b. Draw the energy graph for the reaction.

c. Is this reaction favored based upon enthalpy? Justify your selection using the terms stability and relative energy of the products and reactants and the sign of the change in enthalpy.

The reaction is favored based upon enthalpy since the net enthalpy decreased so the products are more stable. Change tends towards to stability.

d. Calculate the change in enthalpy, entropy and free energy at room temperature.

ΔH_f° standard heats of formation are the energy changes associated with forming one more of the substance from its elements in their standard states. The zero is defined as element in standard state – an arbitrary zero from which relative comparisons can be made.



$$\begin{aligned} & \Sigma \Delta H_f^\circ \text{ products} - \Sigma \Delta H_f^\circ \text{ reactants} \\ & [2(-285.83 \text{ kJ}) + 2(33.18 \text{ kJ}) + 1(64.77 \text{ kJ})] - [0 + 2(-205.0) + 4(0)] = -30.53 \text{ kJ/mol} \end{aligned}$$

S° is defined by the second law of thermodynamics. The zero entropy is defined as a perfectly ordered crystal at 0K.

$$\begin{aligned} & \Sigma S^\circ \text{ products} - \Sigma S^\circ \text{ reactants} \\ & [2(69.91 \text{ J/K}) + 2(240.06 \text{ J/K}) + 1(-99.6 \text{ J/K})] - [33.15 \text{ J/K} + 2(146.4 \text{ J/K}) + 4(0)] = 194.38 \text{ J/K} \end{aligned}$$

Gibbs free energy takes into the change in enthalpy as well as change in entropy to determine whether or not the reaction is spontaneous. A negative change in enthalpy is favored while a positive change in entropy is favored. Thus a negative ΔG indicates a spontaneous process. You can see this by considering the equation below. If a reaction is favored based upon both enthalpy and entropy clearly the reaction will be spontaneous. Thus a neg – pos (pos) would yield a negative. So negative ΔG must be spontaneous.

$$\Delta G = \Delta H - T\Delta S = -30.53 \text{ kJ} - 295\text{K} (0.19438 \text{ kJ/K}) = -87.87 \text{ kJ}$$