REDOX REACTIONS

1. (6 points) Balance each of the following half-reactions in acid solution. (You may use H₂O and H⁺ as needed.)

   The conversion of U⁴⁺ to UO₂⁺ is _____________________________ (oxidation)(reduction).
   \[ \text{U}^4+ (aq) \rightarrow \text{UO}_2^+ (aq) \]

   The conversion of nitrate ion to nitrogen monoxide is an _____________________________ (oxidation)(reduction).
   \[ \text{NO}_3^- (aq) \rightarrow \text{NO}(g) \]

2. (8 points) The following reaction (done in acid solution) is one way to prepare elemental iodine in the laboratory.

   \[ \text{MnO}_2(s) + \text{I}^- (aq) \rightarrow \text{Mn}^{2+} (aq) + \text{I}_2(g) \]

   Give the balanced half-reaction involving manganese.

   *This half-reaction is (an oxidation)(a reduction)______________________________

   Give the balanced half-reaction involving iodine.

   *This half-reaction is (an oxidation)(a reduction)______________________________

   Write the net balanced equation for the reaction of MnO₂ and I⁻:
Thermodynamics

1. (4 points) Based on your experience and common sense, which of the following processes would you describe as product-favored and which are reactant-favored under standard conditions?

<table>
<thead>
<tr>
<th>Reaction</th>
<th>Product- or Reactant-Favored</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) Hg(ℓ) → Hg(s)</td>
<td>____________________________</td>
</tr>
<tr>
<td>(b) 2 HgO(s) → Hg(ℓ) + O₂(g)</td>
<td>____________________________</td>
</tr>
<tr>
<td>(c) C(s) + O₂(g) → CO₂(g)</td>
<td>____________________________</td>
</tr>
<tr>
<td>(d) NaCl(s) → NaCl(aq)</td>
<td>____________________________</td>
</tr>
</tbody>
</table>

2. (7 points) Indicate whether each statement below is true or false.

a) _____ The entropy increases in all product-favored reactions.

b) _____ Reactions with a negative free energy change (ΔG°_rxn < 0) are product-favored and occur with rapid transformation of reactants to products.

c) _____ Some product-favored processes are endothermic.

d) _____ Exothermic processes are always product-favored.

e) _____ The entropy of a substance increases on going from the liquid to the vapor state at any temperature.

f) _____ An exothermic reaction will always be product-favored.

g) _____ Reactions with a positive ΔH°_rxn and a negative ΔS°_rxn can never be product-favored.

3. (2 points) Which substance has the higher entropy in each of the following pairs?

a) Dry ice (solid CO₂) at -78 °C or CO₂(g) at 0 °C. __________________

b) Liquid water at 25 °C or liquid water at 50 °C. __________________
4. (7 points) Enthalpy and entropy changes are given for the thermite reaction (the reduction of iron(III) oxide with aluminum).

\[
\text{Fe}_2\text{O}_3(s) + 2 \text{ Al}(s) \rightarrow 2 \text{ Fe}(s) + \text{Al}_2\text{O}_3(s) \\
\Delta H^\circ = -851.5 \text{ kJ} \\
\Delta S^\circ = -363.12 \text{ J/K}
\]

The reaction is product-favored at 25 °C. Prove that this is the case and explain your reasoning.

Is the reaction \textit{enthalpy-} or \textit{entropy-driven?} _______________________________

5. (4 points) Sodium reacts violently with water.

\[
\text{Na}(s) + \text{H}_2\text{O}(l) \rightarrow \text{NaOH}(aq) + \frac{1}{2} \text{H}_2(g)
\]

The sign of the enthalpy change, \(\Delta H^\circ_{\text{rxn}}\), is predicted to be (+)(–) ___________________ and the sign of the entropy exchange, \(\Delta S^\circ_{\text{rxn}}\), is predicted to be (+)(–) ___________________.

6. (4 points) The free energy change, \(\Delta G^\circ\), is given for each reaction. Predict whether \(K_{\text{eq}}\) will be less than 1 (<1) or greater than 1 (>1).

<table>
<thead>
<tr>
<th>Reaction</th>
<th>(\Delta G^\circ_{\text{rxn}})</th>
<th>Predicted (K) (&lt;1 or &gt;1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\text{N}_2(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}(g))</td>
<td>+173 kJ</td>
<td>__________________________</td>
</tr>
<tr>
<td>(\text{N}_2(g) + 3 \text{H}_2(g) \rightleftharpoons 2 \text{NH}_3(g))</td>
<td>−32.9 kJ</td>
<td>__________________________</td>
</tr>
</tbody>
</table>

7. (3 points) Calculate the standard entropy change, \(\Delta S^\circ_{\text{rxn}}\), for the following reaction:

\[
\text{C}_2\text{H}_5\text{OH}(l) + 3 \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 3 \text{H}_2\text{O}(g)
\]

(a) 266.7 J/K
(b) 217.8 J/K
(c) 36.7 J/K
(d) −188.8 J/K
(e) none of the above
8. (4 points) Calculate the free energy change, $\Delta G^\circ_{\text{rxn}}$, for the reaction

$$\text{HgS(s) + O}_2(\text{g}) \rightarrow \text{Hg(} \ell \text{) + SO}_2(\text{g})$$

(a) $-249.6 \text{ kJ}$
(b) $+249.6 \text{ kJ}$
(c) $-300.2 \text{ kJ}$
(d) $-50.6 \text{ kJ}$
(e) $+300.2 \text{ kJ}$
(e) none of the above

The reaction is (product-favored) (reactant-favored) _____________________________

9. (6 points) Sulfur undergoes a phase transition between 80 ˚C and 100 ˚C.

$$\text{S}_8(\text{rhombic}) \rightarrow \text{S}_8(\text{monoclinic})$$

$\Delta H^\circ_{\text{rxn}} = 3.213 \text{ kJ/mol and } \Delta S^\circ_{\text{rxn}} = 8.7 \text{ J/K}$

$\Delta G^\circ$ for the phase transition at 25 ˚C is $+0.62 \text{ kJ}$. What is the value of $K_{\text{eq}}$ for the reaction at this temperature?

(a) 1.3
(b) 0.78
(c) 0.62
(d) 0.25
(e) none of the above

At about what temperature is the conversion of one form of sulfur to the other form predicted to be product-favored?

(a) 25 ˚C
(a) 80˚C
(b) 96.3 ˚C
(c) 100 ˚C
(d) 110 ˚C
(e) none of the above
CHEMICAL KINETICS

1. (8 points) A few drops of blue food dye were added to water followed by a solution of bleach. (Initially, the concentration of dye was about $3.4 \times 10^{-5}$ M, and the bleach (NaOCl) concentration was about 0.034 M.) The dye faded as it reacted with the bleach in a FIRST-ORDER REACTION. The color change was followed by a spectrophotometer, and the data are plotted here.

Write the rate law for this reaction, where “blue dye” is the reactant.

What is the average rate of reaction over the first 3 minutes? __________

(a) $-0.73 \times 10^{-2}$ mol/L•min
(b) $-0.34 \times 10^{-2}$ mol/L•min
(c) $-0.25 \times 10^{-2}$ mol/L•min
(d) $-0.20 \times 10^{-2}$ mol/L•min
(e) none of the above

What is the approximate half-life of the reaction? ________________ minutes

(a) 8.0 min
(b) 4.0 min
(c) 2.0 min
(d) 1.0 min
2. (10 points) Consider the reaction of NO and Cl₂: 2 NO(g) + Cl₂(g) → 2 NOCl(g)

The rate equation for this reaction is: Rate = \( k [NO]^2[Cl₂] \)

The order of the reaction with respect to [NO] is _________________. The overall reaction order is ________________.

Data for one experiment are as follows:

When [NO] = 0.250 mol/L and [Cl₂] = 0.250 mol/L, then Rate = 1.43 \times 10^{-6} \text{ mol/L} \cdot \text{s}

What is the value of the rate constant \( k \) for the reaction? _______________________.

What is the rate of the reaction when [NO] = 0.750 mol/L and [Cl₂] = 0.250 mol/L? 
(a) 1.43 \times 10^{-6} \text{ mol/L} \cdot \text{s}
(b) 4.29 \times 10^{-6} \text{ mol/L} \cdot \text{s}
(c) 8.58 \times 10^{-6} \text{ mol/L} \cdot \text{s}
(d) 12.9 \times 10^{-6} \text{ mol/L} \cdot \text{s}
(e) none of the above

3. (5 points) The following statements relate to the reaction H₂(g) + I₂(g) → 2HI(g) for which the rate law is “Rate = k[H₂][I₂].” Decide whether each of the following statements is true or false.

(a) __________ The reaction must occur in a single step.
(b) __________ This is a second order reaction overall.
(c) __________ Raising the temperature will cause the value of \( k \) to decrease.
(d) __________ Raising the temperature lowers the activation energy for this reaction.
(e) __________ If the concentrations of both reactants are doubled the rate will double.

4. (4 points) Decide whether each of the following statements is true or false.

(a) __________ Reactions are faster at a higher temperature because activation energies are lower.
(b) __________ Rates increase with increasing concentration of reactants because there are more collisions between reactant molecules.
(c) __________ At higher temperature a larger fraction of molecules have enough energy to get over the activation energy barrier.
(d) __________ Catalyzed and uncatalyzed reactions have identical mechanisms.
5. (3 points) Radioactive iodine is used in brain scans. Iodine-131 isotope has a half-life of 8.04 days. If you inject 5.6 mg of $^{131}$I into a patient, approximately how much remains after 40 days?

(a) 5.6 mg  
(b) 2.8 mg  
(c) 1.4 mg  
(d) 0.70 mg  
(e) 0.35 mg  
(f) 0.175 mg

6. (5 points) The isomerization reaction

$\text{CH}_3\text{NC}(g) \rightarrow \text{CH}_3\text{CN}(g)$

occurs slowly when $\text{CH}_3\text{NC}$ is heated. To study the rate of this reaction at 488 K, data on $[\text{CH}_3\text{NC}]$ were collected at various times. Analysis led to the graph pictured here.

(a) What is the rate law for this reaction?

(b) What is the approximate concentration of $\text{CH}_3\text{NC}$ after 6,000 s?

i 0.017 M  
ii 0.0067 M  
iii 0.0041 M  
iv 0.0025 M  
v none of the above

7. (4 points) The industrially important reducing agent hydrazine, $\text{N}_2\text{H}_4$, is produced from $\text{NH}_3$ and $\text{OCl}^-$ in basic, aqueous solution. A proposed mechanism is

**Step 1** fast $\text{NH}_3(aq) + \text{OCl}^-(aq) \rightarrow \text{NH}_2\text{Cl}(aq) + \text{OH}^-(aq)$

**Step 2** slow $\text{NH}_2\text{Cl}(aq) + \text{NH}_3(aq) \rightarrow \text{N}_2\text{H}_5^+(aq) + \text{Cl}^-(aq)$

**Step 3** fast $\text{N}_2\text{H}_5^+(aq) + \text{OH}^-(aq) \rightarrow \text{N}_2\text{H}_4(aq) + \text{H}_2\text{O}(l)$

(a) Which step of the three is rate determining? ________________________

(b) What is the rate equation for the rate determining elementary step?

(c) What is the overall stoichiometric equation?
8. (6 points) Nitrogen oxides, NO\(_x\) (a mixture of NO and NO\(_2\) is collectively designated as NO\(_x\)), play an essential role in the production of pollutants found in photochemical smog. The NO\(_x\) in the atmosphere is slowly broken down to N\(_2\) and O\(_2\) in a first-order reaction. The average half-life of NO\(_x\) in the smokestack emissions in a large city during daylight is 3.9 h. Starting with 1.50 mg in an experiment, what quantity of NO\(_x\) remains after 12.0 h? (Show detailed calculations.)