

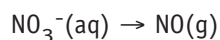
REDOX REACTIONS

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

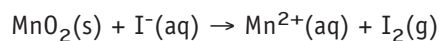
The conversion of U⁴⁺ to UO₂⁺ is _____ (*oxidation*)(*reduction*).



The conversion of nitrate ion to nitrogen monoxide is an _____ (*oxidation*)(*reduction*).



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



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?

<u>Reaction</u>	<u>Product- or Reactant-Favored</u>
(a) $\text{Hg}(\ell) \rightarrow \text{Hg}(\text{s})$	_____
(b) $2 \text{HgO}(\text{s}) \rightarrow \text{Hg}(\ell) + \text{O}_2(\text{g})$	_____
(c) $\text{C}(\text{s}) + \text{O}_2(\text{g}) \rightarrow \text{CO}_2(\text{g})$	_____
(d) $\text{NaCl}(\text{s}) \rightarrow \text{NaCl}(\text{aq})$	_____

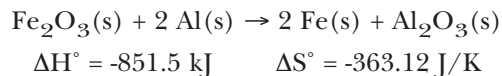
2. (7 points) Indicate whether each statement below is *true* or *false*.

- a) _____ The entropy increases in all product-favored reactions.
- b) _____ Reactions with a negative free energy change ($\Delta G^\circ_{\text{rxn}} < 0$) 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 $\Delta H^\circ_{\text{rxn}}$ and a negative $\Delta S^\circ_{\text{rxn}}$ can never be product-favored.

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

- a) Dry ice (solid CO_2) at -78°C or $\text{CO}_2(\text{g})$ 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).



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

Is the reaction *enthalpy-* or *entropy-driven*? _____

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

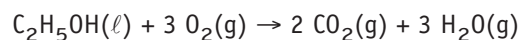


The sign of the enthalpy change, $\Delta H^\circ_{\text{rxn}}$, is predicted to be (+) (-) _____ and the sign of the entropy exchange, $\Delta S^\circ_{\text{rxn}}$, is predicted to be (+) (-) _____.

6. (4 points) The free energy change, ΔG° , is given for each reaction. Predict whether K_{eq} will be less than 1 (<1) or greater than 1 (>1).

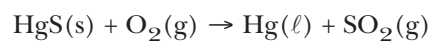
Reaction	$\Delta G^\circ_{\text{rxn}}$	Predicted K (<1 or >1)
$\text{N}_2(\text{g}) + \text{O}_2(\text{g}) \rightleftharpoons 2 \text{NO}(\text{g})$	+173 kJ	_____
$\text{N}_2(\text{g}) + 3 \text{H}_2(\text{g}) \rightleftharpoons 2 \text{NH}_3(\text{g})$	-32.9 kJ	_____

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



- (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

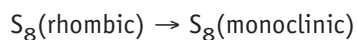
8. (4 points) Calculate the free energy change, $\Delta G^\circ_{\text{rxn}}$, for the reaction



- (a) -249.6 kJ
- (b) +249.6 kJ
- (c) -300.2 kJ
- (d) -50.6 kJ
- (e) +300.2 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.



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

ΔG° for the phase transition at 25 °C is +0.62 kJ. What is the value of K_{eq} for the reaction at this temperature?

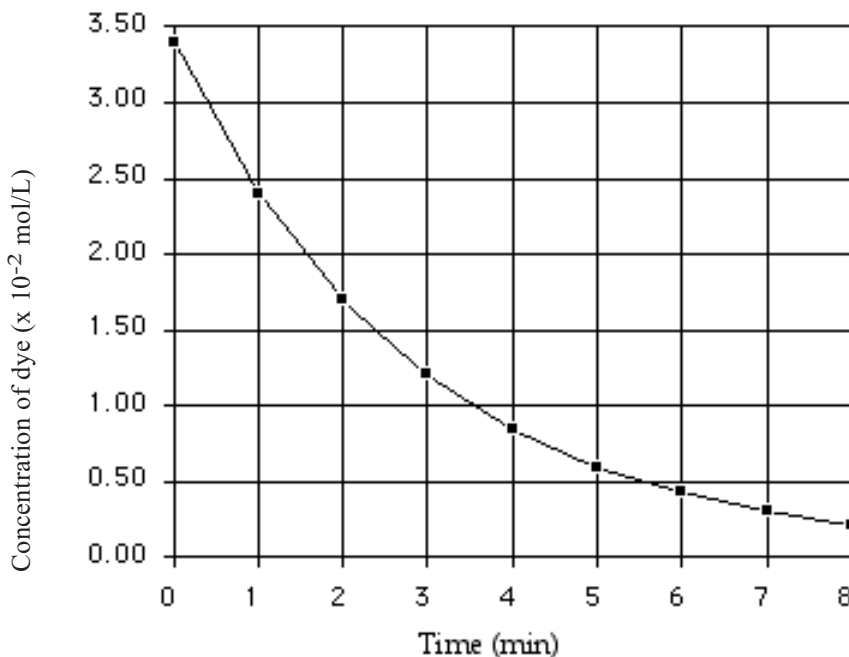
- (a) 1.3
- (b) 0.78
- (c) 0.62
- (d) 0.25
- (e) none of the above

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 3.4×10^{-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) -0.73×10^{-2} mol/L•min
- (b) -0.34×10^{-2} mol/L•min
- (c) -0.25×10^{-2} mol/L•min
- (d) -0.20×10^{-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: $2 \text{NO(g)} + \text{Cl}_2\text{(g)} \longrightarrow 2 \text{NOCl(g)}$

The rate equation for this reaction is: Rate = $k [\text{NO}]^2 [\text{Cl}_2]$

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 = 1.43×10^{-6} mol/L•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) 1.43×10^{-6} mol/L•s
- (b) 4.29×10^{-6} mol/L•s
- (c) 8.58×10^{-6} mol/L•s
- (d) 12.9×10^{-6} mol/L•s
- (e) none of the above

3. (5 points) The following statements relate to the reaction $\text{H}_2\text{(g)} + \text{I}_2\text{(g)} \rightarrow 2\text{HI(g)}$ for which the rate law is “Rate = $k[\text{H}_2][\text{I}_2]$.” Decide whether each of the following statements is *true* or *false*.

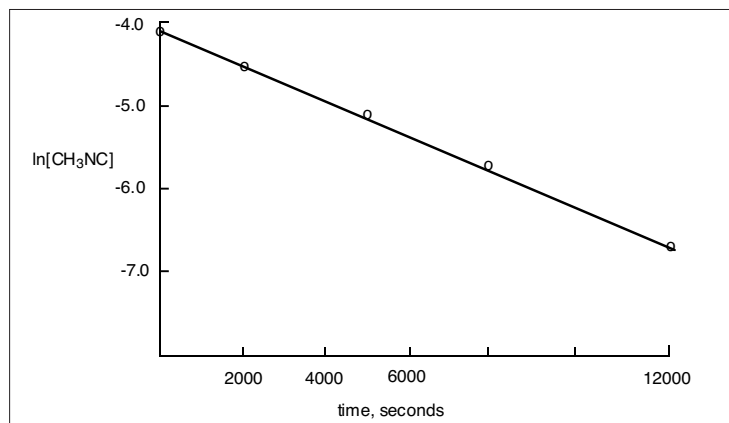
- (a) _____ The reaction must occur in a single step.
- (b) _____ This is a second order reaction overall.
- (c) _____ Raising the temperature will cause the value of k to decrease.
- (d) _____ Raising the temperature lowers the activation energy for this reaction.
- (e) _____ If the concentrations of 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.

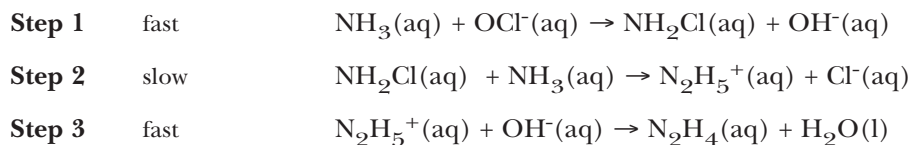
5. (3 points) Radioactive iodine is used in brain scans. Iodine-131 isotope has a half-life of 8.04 days. If you inject 5.6 mg of ^{131}I into a patient, approximately how much remains after 40 days?
- 5.6 mg
 - 2.8 mg
 - 1.4 mg
 - 0.70 mg
 - 0.35 mg
 - 0.175 mg

6. (5 points) The isomerization reaction
- $$\text{CH}_3\text{NC}(\text{g}) \rightarrow \text{CH}_3\text{CN}(\text{g})$$
- occurs slowly when CH_3NC 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 CH_3NC after 6,000 s?
- 0.017 M
 - 0.0067 M
 - 0.0041 M
 - 0.0025 M
 - none of the above

7. (4 points) The industrially important reducing agent hydrazine, N_2H_4 , is produced from NH_3 and OCl^- in basic, aqueous solution. A proposed mechanism is



- (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.*)