1998 Free Response Questions

- All simplifying assumptions are justified within 5%.
- One point deduction for a significant figure or math error, applied only once per problem.
- No credit earned for numerical answer without justification.

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1) Solve the following problem related to the solubility equilibria of some metal hydroxides in aqueous solution.

a) The solubility of $Cu(OH)_2$ is 1.72×10^{-6} gram per 100. milliliters of solution at 25 °C.

(i) Write the balanced chemical equation for the dissociation of $Cu(OH)_2(s)$ in aqueous solution.

(ii) Calculate the solubility (in moles per liter) of $Cu(OH)_2$ at 25 °C.

(iii) Calculate the value of the solubility-product constant, K_{sp}, for $Cu(OH)_2$ at 25 °C.

b) The value of the solubility-product constant, K_{sp}, for $Zn(OH)_2$ is 7.7×10^{-17} at 25°C.

(i) Calculate the solubility (in moles per liter) of $Zn(OH)_2$ at 25°C in a solution with a pH of 9.35.

(ii) At 25°C, 50.0 milliliters of 0.100-molar $Zn(NO_3)_2$ is mixed with 50.0 milliliters of 0.300-molar NaOH. Calculate the molar concentration of $Zn^{2+}(aq)$ in the resulting solution once equilibrium has been established. Assume that volumes are additive.

2) An unknown compound contains only the three elements C,H, and O. A pure sample of the compound is analyzed and found to be 65.60 percent C and 9.44 percent H by mass.

(a) Determine the empirical formula of the compound.

(b) A solution of 1.570 grams of the compound in 16.08 grams of camphor is observed to freeze at a temperature 15.2 Celsius degrees below the normal freezing point of pure camphor. Determine the molar mass and apparent molecular formula of the compound. (The molal freezing-point depression constant, K_f, for camphor is 40.0 kg-K-mol^{-1}.)

(c) When 1.570 grams of the compound is vaporized at 300 °C and 1.00 atmosphere, the gas occupies a volume of 577 milliliters. What is the molar mass of the compound based on this result?

(d) Briefly describe what occurs in solution that accounts for the difference between the results obtained in parts (b) and (c).

3) $C_6H_5OH(s) + 7\ O_2(g) \rightarrow 6\ CO_2(g) + 3H_2O(l)$

When a 2.000-gram sample of pure phenol, $C_6H_5OH(s)$, is completely burned according to the equation above, 64.98 kilojoules of heat is released. Use the information in the table below to answer the questions that follow.

Substance	Standard Heat of Formation, $\Delta H°_f$, at 25°C (kJ/mol)	Absolute Entropy, S°, at 25°C (J/mol-K)
C(graphite)	0.00	5.69
$CO_2(g)$	-395.5	213.6
$H_2(g)$	0.00	130.6
$H_2O(l)$	-285.85	69.91
$O_2(g)$	0.00	205.0
$C_6H_5OH(s)$	?	144.0

(a) Calculate the molar heat of combustion of phenol in kilojoules per mole at 25°C.

(b) Calculate the standard heat of formation, $\Delta H°_f$, of phenol in kilojoules per mole at 25°C.

(c) Calculate the value of the standard free-energy change, $\Delta G°$ for the combustion of phenol at 25°C.

(d) If the volume of the combustion container is 10.0 liters, calculate the final pressure in the container when the temperature is changed to 110°C. (Assume no oxygen remains unreacted and that all products are gaseous.)

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(a) Solutions of tin(II) chloride and iron(III) chloride are mixed.

(b) Solutions of cobalt(II) nitrate and sodium hydroxide are mixed.

(c) Ethene gas is burned air.

(d) Equal volumes of equimolar solutions of phosphoric acid and potassium hydroxide are mixed.

(e) Solid calcium sulfite is heated in a vacuum.

(f) Excess hydrochloric acid is added to a solution of diamminesilver(I) nitrate.

(g) Solid sodium oxide is added to distilled water.

(h) A strip of zinc is added to a solution of 6.0-molar hydrobromic acid.

5) An approximately 0.1-molar solution of NaOH is to be standardized by titration. Assume that the following materials are available.

Clean, dry 50 mL buret	Analytical balance
250 mL Erlenmeyer flask	Phenolphthalein indicator solution
Wash bottle filled with distilled water	Potassium hydrogen phthalate, KHP, a pure solid monoprotic acid (to be used as the primary standard)

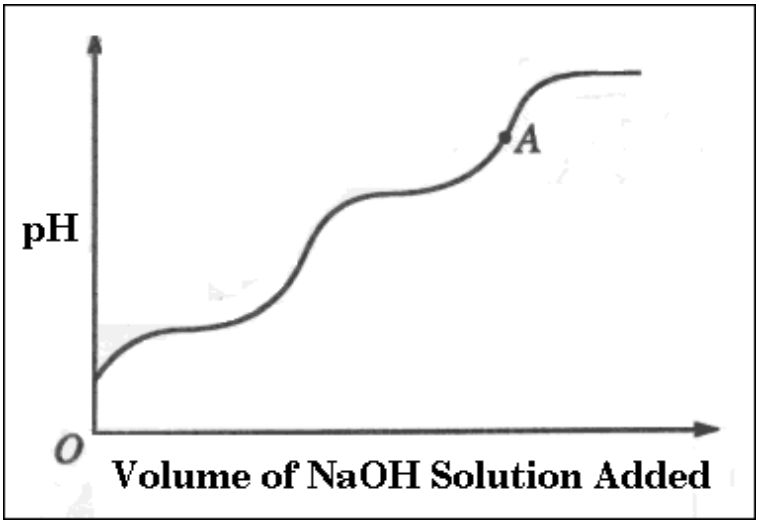
(a) Briefly describe the steps you would take, using materials listed above, to standardize the NaOH solution.

(b) Describe (i.e., set up) the calculations necessary to determine the concentration of the NaOH solution.

(c) After the NaOH solutions has been standardized, it is used to titrate a weak monoprotic acid, HX. The equivalence point is reached when 25.0 mL of NaOH solution has been added. In the space provided at the right, sketch the titration curve, showing the pH changes that occur as the volume of NaOH solution added increases from 0 to 35.0 mL. Clearly label the equivalence point on the curve.

(d) Describe how the value of the acid-dissociation constant, K_a, for the weak acid HX could be determined from the titration curve in part (c).

(e) The graph below shows the results obtained by titrating a different weak acid, H_2Y, with the standardized NaOH solution. Identify the negative ion that is present in the highest concentration at the point in the titration represented by the letter A on the curve.



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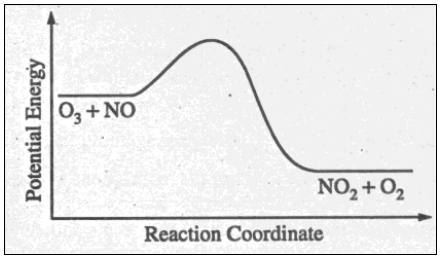
6) Answer the following questions regarding the kinetics of chemical reactions.

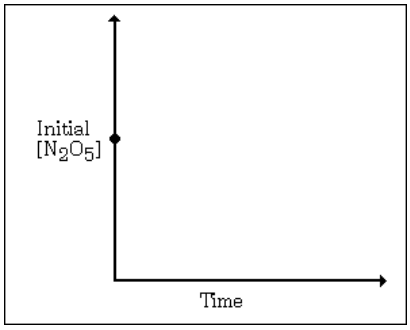
(a) The diagram below at right shows the energy pathway for the reaction $O_3 + NO \rightarrow NO_2 + O_2$.

Clearly label the following directly on the diagram.
(i) The activation energy (E_a) for the forward reaction
(ii) The enthalpy change (ΔH) for the reaction

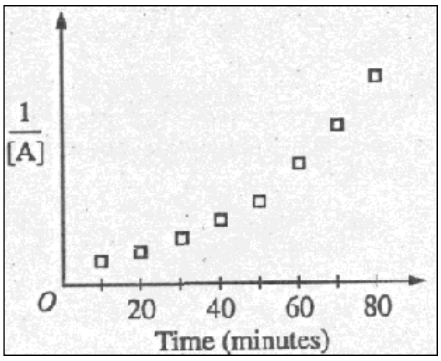


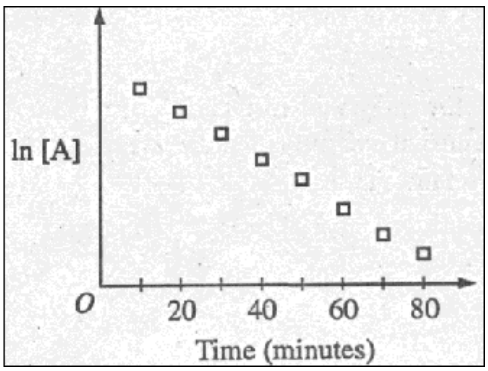
(b) The reaction $2\ N_2O_5 \rightarrow 4\ NO_2 + O_2$ is first order with respect to N_2O_5.

(i) Using the axes at right, complete the graph that represents the change in $[N_2O_5]$ over time as the reaction proceeds.
(ii) Describe how the graph in (i) could be used to find the reaction rate at a given time, t.
(iii) Considering the rate law and the graph in (i), describe how the value of the rate constant, k, could be determined.
(iv) If more N_2O_5 were added to the reaction mixture at constant temperature, what would be the effect on the rate constant, k? Explain.



(c) Data for the chemical reaction $2A \rightarrow B + C$ were collected by measuring the concentration of A at 10-minute intervals for 80 minutes. The following graphs were generated from analysis of data.





Use the information in the graphs above to answer the following.

(i) Write the rate-law expression for the reaction. Justify your answer.
(ii) Describe how to determine the value of the rate constant for the reaction.

7) $C(s) + H_2O(g) \leftrightarrows CO(g) + H_2(g)\ \ \Delta H° = +131\ kJ$

A rigid container holds a mixture of graphite pellets (C(s)), $H_2O(g)$, CO(g), and $H_2(g)$ at equilibrium. State whether the number of moles of CO(g) in the container will increase, decrease, or remain the same after each of the following disturbances is applied to the original mixture. For each case, assume that all other variables remain constant except for the given disturbance. Explain each answer with a short statement.

(a) Additional $H_2(g)$ is added to the equilibrium mixture at constant volume.
(b) The temperature of the equilibrium mixture is increased at constant volume.
(c) The volume of the container is decreased at constant temperature.
(d) The graphite pellets are pulverized.

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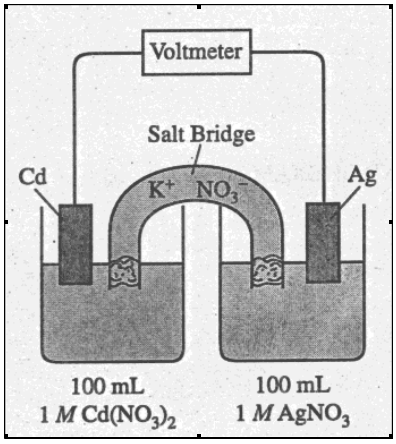

Answer the following questions regarding the electrochemical cell shown above.

(a) Write the balanced net-ionic equation for the spontaneous reaction that occurs as the cell operates, and determine the cell voltage.

(b) In which direction do anions flow in the salt bridge as the cell operates? Justify your answer.

(c) If 10.0 mL of 3.0-molar $AgNO_3$ solution is added to the half-cell on the right, what will happen to the cell voltage? Explain.

(d) If 1.0 grams of solid NaCl is added to each half-cell, what will happen to the cell voltage? Explain.

(e) If 20.0 mL of distilled water is added to both half-cells, the cell voltage decreases. Explain.

9) Answer each of the following using appropriate chemical principles.

(a) Why does it take longer to cook an egg in boiling water at high altitude than it does at sea level?

(b) When NH_3 gas is bubbled into an aqueous solution of $CuCl_2$, a precipitate forms initially. On further bubbling, the precipitate disappears. Explain these two observations.

(c) Dimethyl ether, $H_3C\text{-}O\text{-}CH_3$, is not very soluble in water. Draw a structural isomer of dimethyl ether that is much more soluble in water and explain the basis of its increased water solubility.

(d) Identify a chemical species that is

(i) capable of oxidizing $Cl^-(aq)$ under standard conditions

(ii) capable of reducing $Cl_2(aq)$ under standard conditions. In each case, justify your choice.