Chemistry 2000 Spring 2001 Section B
Final Examination

Time: 3 hours

Aids allowed: Calculator. In particular, periodic tables and other written or printed materials are excluded.

Additional data is given at the end of this paper.

Write all your answers in the booklets provided. Your answers need not be entered into the booklets in order, provided all answers are labeled clearly with the question number. Answer all questions in section 1. In other sections, you have some choice. Do not answer more than the required number of questions. Extra answers will not be marked.

1 Answer all questions in this section.

Total value of questions in this section: 70 marks

1. The following data have been obtained for the reaction

$$2H_{2(g)} + 2NO_{(g)} \rightarrow 2H_2O_{(g)} + N_{2(g)}$$

at 700°C:

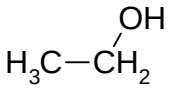
$[H_2]$ (mol/L)	[NO] (mol/L)	rate $(\text{mol}\,\text{L}^{-1}\text{s}^{-1})$
0.0050	0.025	1.2×10^{-6}
0.010	0.025	2.4×10^{-6}
0.010	0.0125	0.60×10^{-6}

Determine the rate law and rate constant. [7 marks]

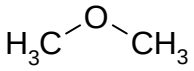
2. Calculate the pH of a $6.3 \times 10^{-4}\,\text{mol/L}$ solution of potassium hydroxide in water at 25°C. [4 marks]

3. Calculate the pH of a $6.3 \times 10^{-4}\,\text{mol/L}$ aqueous sodium sulfite (Na_2SO_3) solution at 25°C. The K_b of the sulfite ion is 1.6×10^{-7}. [8 marks]

4. Which of the following two compounds



ethanol



dimethyl ether

would you expect to have the higher vapor pressure? Explain briefly. [3 marks]

5. Pure solid NH_4HSe is placed in a 2.0 L container at 24.8°C. The container is evacuated. The pressure then rises due to the reaction

$$NH_4HSe_{(s)} \rightleftharpoons NH_{3(g)} + H_2Se_{(g)}.$$

The equilibrium constant for this reaction is 8.46×10^{-5}. What is the total pressure at equilibrium? [6 marks]

6. The reaction $2H_{2(g)} + S_{2(g)} \rightleftharpoons 2H_2S_{(g)}$ is in equilibrium at 700°C when $P_{H_2} = 16.6\,\text{atm}$, $P_{S_2} = 8.98 \times 10^{-5}\,\text{atm}$, and $P_{H_2S} = 57.9\,\text{atm}$. What is the equilibrium constant for this reaction? [3 marks]

7. 2.5 g of solid sodium acetate (CH_3COONa) is dissolved in 100 mL of a 0.4 mol/L aqueous HCl solution at 25°C. What is the pH of the resulting solution? The K_a of acetic acid is 1.8×10^{-5}. [10 marks]

8. Calculate the solubility of zinc hydroxide ($Zn(OH)_2$) in a pH 8 buffer at 25°C. For this compound, $K_{sp} = 1.8 \times 10^{-14}$. [7 marks]

9. A 50 g piece of metal is heated to a temperature of 120°C, then immersed in 800 g of water initially at 21.3°C in a sealed and well-insulated container. The equilibrium temperature is 23.0°C. What is the specific heat capacity of the metal? [4 marks]

10. (a) Calculate the enthalpy change for the neutralization of aqueous acetic acid by hydroxide. [3 marks]

    (b) Given that $\Delta\bar{H}^\circ = -55.815\,\text{kJ/mol}$ for the reaction

$$H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)},$$

calculate the enthalpy change for the dissociation of acetic acid into its ions. [4 marks]

11. Calculate the solubility product of lead (II) chloride at 25°C. [5 marks]

12. Insects are cold-blooded, meaning that they don't regulate their internal temperatures. Since all processes in living organisms rely on chemical reactions, many of their behaviors display temperature sensitivity. Tree crickets chirp at a rate of about 200 chirps per minute at 27°C. This rate falls to about 40 chirps per minute at 5°C. Assuming that the difference is mainly due to a reduction in a rate constant, determine the activation energy for the underlying chemical process. [6 marks]

2 Answer *one* question in this section

Total value of questions in this section: 10 marks

1. An aqueous sodium bromide solution has a vapor pressure of 27.8 torr at 30°C. The vapor pressure of pure water at this temperature is 31.8 torr. What is the *molality* of the solution? [10 marks]

2. (a) The normal boiling and freezing points of sulfur dioxide are -10°C and -72.7°C, respectively. The triple point is -75.5°C and 1.65×10^{-3} atm. Draw a rough sketch of the phase diagram of sulfur dioxide, labeling all regions and special points. [8 marks]

   (b) Which is more dense, solid or liquid sulfur dioxide? [2 marks]

3 Answer *one* question in this section.

Total value of questions in this section: 20 marks

1. Suppose that we want to make iron (III) chloride from iron (III) oxide by reacting the latter with chlorine gas:

$$\mathrm{Fe_2O_{3(s)}} + 3\mathrm{Cl_{2(g)}} \rightarrow 2\mathrm{FeCl_{3(s)}} + \frac{3}{2}\mathrm{O_{2(g)}}.$$

   (a) Calculate the equilibrium constant for this reaction at 25°C. [4 marks]

   (b) Is the reaction spontaneous at 25°C if the partial pressures of oxygen and chlorine are, respectively, 0.02 atm and 0.9 atm? [4 marks]

   (c) If the reaction *isn't* spontaneous under the conditions given above, suggest a set of conditions which would make it spontaneous. If the reaction *is* spontaneous, calculate the maximum pressure of oxygen such that the reaction remains spontaneous at fixed chlorine pressure. [4 marks]

   (d) Calculate the equilibrium constant at 150°C. Is the reaction spontaneous at this temperature under the conditions of question 1b? [8 marks]

2. (a) For the reaction

$$\mathrm{SCO_{(g)}} + \mathrm{H_2O_{(g)}} \rightarrow \mathrm{CO_{2(g)}} + \mathrm{H_2S_{(g)}},$$

   $\Delta\bar{H}^\circ = -33\,\mathrm{kJ/mol}$. SCO's structure is analogous to that of CO_2:

S=C=O

   Estimate the S=C bond enthalpy. [6 marks]

   (b) The absolute entropies of the reactants and products are given in the following table:

Substance	$CO_{2(g)}$	$H_2O_{(g)}$	$H_2S_{(g)}$	$SCO_{(g)}$
$\bar{S}^\circ$ ($\mathrm{JK^{-1}mol^{-1}}$)	213.785	188.835	205.81	231.57

   Calculate the standard entropy change for the reaction. [2 marks]

   (c) Calculate the standard free energy change at 25°C. [2 marks]

   (d) Calculate the equilibrium constant at 25°C. [2 marks]

   (e) Calculate the equilibrium constant at 100°C. [4 marks]

   (f) Would the reaction be spontaneous at 100°C if $P_{\mathrm{H_2O}} = 0.04$, $P_{\mathrm{CO_2}} = 0.03$, $P_{\mathrm{H_2S}} = 0.2$ and $P_{\mathrm{SCO}} = 0.05\,\mathrm{atm}$? [4 marks]

Useful data and equations

$k = k_\infty e^{-\bar{E}_a/(RT)}$

$\Delta\bar{G}^\circ = \Delta\bar{H}^\circ - T\Delta\bar{S}^\circ$

$\Delta\bar{G} = \Delta\bar{G}^\circ + RT\ln Q$

$\Delta\bar{G}^\circ = -RT\ln K$

At 25°C, $K_w = 10^{-14}$.

To convert degrees Celsius to Kelvin, add 273.15.

$R = 8.314\,510\,\mathrm{J\,K^{-1}mol^{-1}}$

The specific heat capacity of water is $4.184\,\mathrm{J\,K^{-1}g^{-1}}$.

Molar masses

Element	M (g/mol)
C	12.011
H	1.0079
Na	22.9898
O	15.9994

Bond enthalpies

Bond	$\Delta\bar{H}_b$ (kJ/mol)
C=O	803
H-O	464
H-S	339

Standard thermodynamic properties at 25°C

Species	$\Delta\bar{H}_f^\circ$ (kJ/mol)	$\Delta\bar{G}_f^\circ$ (kJ/mol)
$CH_3COO^-_{(aq)}$	−485.60	−376.89
$CH_3COOH_{(aq)}$	−485.26	−404.09
$Cl^-_{(aq)}$	−167.080	−131.218
$FeCl_{3(s)}$	−399	−334
$Fe_2O_{3(s)}$	−824	−742
$H_2O_{(l)}$	−285.830	−237.129
$OH^-_{(aq)}$	−230.015	−157.22
$Pb^{2+}_{(aq)}$	0.92	−24.24
$PbCl_{2(s)}$	−359.41	−314.10