# Chemistry 2000 Spring 2006 Final Examination

**Name:**_____ **Student number:**_____

**Time:** 3 hours

**Aids allowed:** Calculator

**Instructions:** Answer all questions in the spaces provided. You can use the backs of pages for scratch work or for extra answer space. If you do need to continue an answer on the back of a page, make sure that the continuation is clearly labeled.

Graphs should be drawn accurately on the graph paper attached to the back of this exam paper. Make sure that your graphs are clearly labeled with the question number.

| Question | 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 | 9 |
|---|---|---|---|---|---|---|---|---|---|
| Marks | /5 | /9 | /3 | /5 | /4 | /4 | /9 | /10 | /7 |
| Question | 10 | 11 | 12 | 13 | Total | | | | |
| Marks | /19 | /11 | /8 | /14 | /108 | | | | |

**Formulas and data**

| Order | Integrated rate law |
|---|---|
| 1 | $\ln x = \ln x_0 - kt$ |
| 2 | $\frac{1}{x} = \frac{1}{x_0} + kt$ |

$c^\circ = 1\,\text{mol/L}$ $\quad \ln k = \ln A - \frac{\bar{E}_a}{RT}$

$P^\circ = 1\,\text{bar}$ $\quad \Delta\bar{G} = \Delta\bar{G}^\circ + RT\ln Q$

$R = 8.314472\,\text{J K}^{-1}\text{mol}^{-1}$ $\quad \Delta\bar{G}^\circ = -RT\ln K$

To convert degrees Celsius to Kelvin, add 273.15.

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

| **Autoionization constant of water** | | | | |
|---|---|---|---|---|
| $T$ (°C) | 10 | 20 | 25 | 30 |
| $K_w$ | $0.29\times10^{-14}$ | $0.68\times10^{-14}$ | $1.01\times10^{-14}$ | $1.47\times10^{-14}$ |

| Species | $\Delta\bar{H}_f^\circ$ (kJ/mol) | $\Delta\bar{G}_f^\circ$ (kJ/mol) |
|---|---|---|
| $C_6H_{12}O_{6(s)}$ (α-D-glucose) | −1274.4 | −910.23 |
| $C_6H_{12}O_{6(aq)}$ (α-D-glucose) | −1263.06 | −914.25 |
| $Cl^-_{(aq)}$ | −167.080 | −131.218 |
| $F^-_{(aq)}$ | −335.35 | −281.52 |
| $FeCl_{2(s)}$ | −341.83 | −302.35 |
| $FeCl_{3(s)}$ | −399.41 | −333.91 |
| $Pb^{2+}_{(aq)}$ | 0.92 | −24.24 |

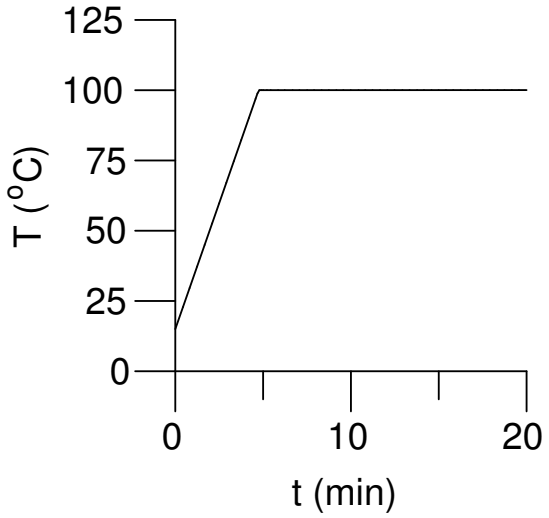
1. An initially *p*H-neutral solution of cysteine ($C_3H_7NO_2S$) reacts with solid HgO to form cystine ($C_6H_{12}N_2O_4S_2$) and metallic mercury. Balance the reaction. [5 marks]

2. 25 g of solid α-D-glucose (molar mass 180.156 g/mol) is dissolved in 100 mL of water, both initially at room temperature. Does the temperature increase or decrease, and by how much? Take the density of water to be 1 g/mL. [9 marks]

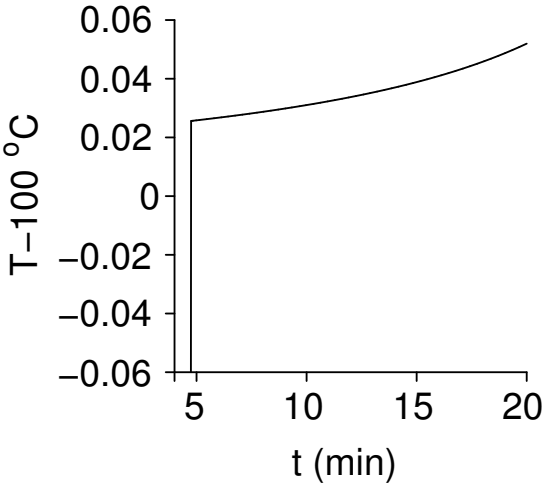
3. Selenocysteine is an unusual amino acid which occurs in some proteins. The R group of this amino acid is $-CH_2-SeH$. Draw the structure of the zwitterionic form of this amino acid. [3 marks]

4. Small peptides often have broader *p*H operating ranges than larger proteins. Suppose that a peptide has just two important acidic amino acids and that both must be protonated in order for the peptide to carry out its biological function. How would you expect the activity of this peptide to vary with *p*H? [5 marks]

5. The following graph shows the temperature vs time for an aqueous salt solution which is being heated at constant rate at sea level:




As we have been taught to expect, the temperature rises to the boiling point, and then levels off. However, if we look at a closeup of this curve, we see that the temperature in fact keeps rising:




What causes this slow rise in the temperature? [4 marks]

6. What is the *p*H of a 1.3 mol/L solution of sodium hydroxide in water at **20**°C? [4 marks]

7. Dimethylphenols are gaseous pollutants generated during combustion of fuels such as gasoline and wood. The Henry's law constant for 2,5-dimethylphenol in water varies with temperature as follows:[1]

| $T$ (K) | 283 | 293 |
|---|---|---|
| $K_H$ ($\mathrm{mol\,L^{-1}atm^{-1}}$) | 3981 | 1270 |

   (a) Based on these data, is the process of dissolving 2,5-dimethylphenol in water endo- or exothermic? Explain briefly how you came to your conclusion. [5 marks]

   (b) If the maximum allowable concentration of 2,5-dimethylphenol in water is 2000 $\mu$g/L, what is the maximum partial pressure of this pollutant at 20°C? The molar mass of 2,5-dimethylphenol is 122.16 g/mol. [4 marks]

[1] P. Diévart et al., *Phys. Chem. Chem. Phys.* **8**, 1714 (2006).

8. Formamide decomposes to ammonia and carbon monoxide at high temperatures:

$$\mathrm{HCONH_{2(g)} \rightleftharpoons NH_{3(g)} + CO_{(g)}}$$

At 400 K, the equilibrium constant for this reaction is 157. If we put 3.5 bar of formamide into a sealed flask at 400 K, what are the equilibrium pressures of all the gases? [10 marks]

9. The decomposition of hydrogen peroxide into water and oxygen catalyzed by iodide ions occurs by the following mechanism:

$$H_2O_{2(aq)} + I^-_{(aq)} \xrightarrow{k_1} H_2O_{(l)} + OI^-_{(aq)} \quad \text{(slow)}$$

$$H_2O_{2(aq)} + OI^-_{(aq)} \xrightarrow{k_2} H_2O_{(l)} + O_{2(g)} + I^-_{(aq)} \quad \text{(fast)}$$

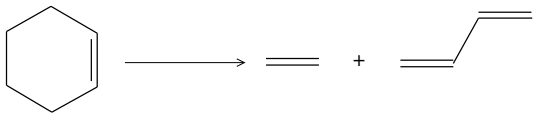
(a) What is the overall reaction? [2 marks]

(b) Identify an intermediate in this mechanism. [1 mark]

(c) What rate of reaction would you predict from this mechanism? [2 marks]

(d) What do you predict would happen to the rate if we doubled the concentration of $H_2O_2$, holding all other factors constant between two experiments? [2 marks]

10. At high temperatures in the gas phase, cyclohexene breaks down in a first-order process into ethene and 1,3-butadiene:



The rate constant has been measured at several temperatures:

| $T$ (K) | 1200 | 1300 | 1400 | 1500 | 1600 | 1700 |
|---|---|---|---|---|---|---|
| $k$ ($s^{-1}$) | $3.9 \times 10^3$ | $3.26 \times 10^4$ | $2.01 \times 10^5$ | $9.71 \times 10^5$ | $3.86 \times 10^6$ | $1.3 \times 10^7$ |

(a) Calculate the activation energy and preexponential factor of this reaction. [16 marks]

(b) If we carried out this experiment at 1200 K, how long would it take for the reaction to be 99% complete? [3 marks]

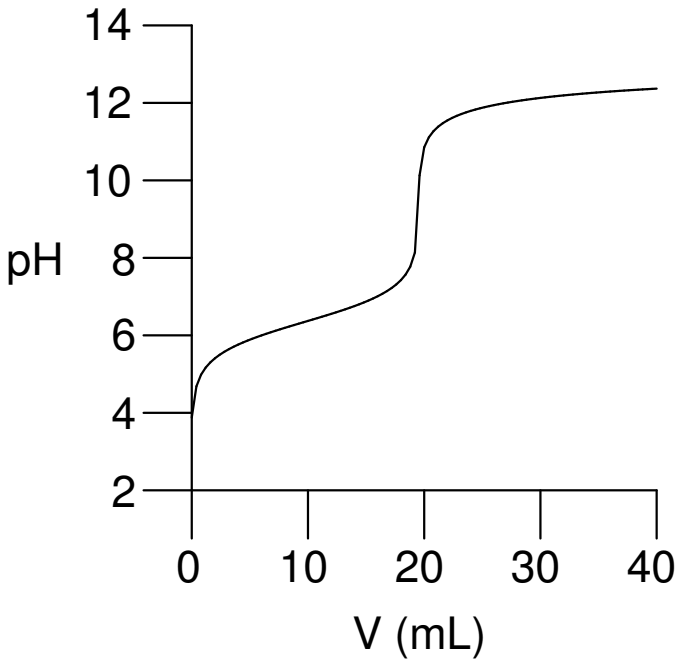
11. The solubility of lead (II) fluorochloride (PbFCl, molar mass 136.086 g/mol) in water at 25°C is 0.37 g/L.

    (a) Write down a balanced chemical reaction for the dissolution process. [1 mark]
    Hint: What would you write down for $PbF_2$ or for $PbCl_2$?

    (b) Calculate the solubility product of this compound. [4 marks]

    (c) Calculate the standard free energy of formation of solid PbFCl. [6 marks]

12. 0.1501 g of an unknown acid is dissolved in some water and titrated with 0.1025 mol/L NaOH solution. The following titration curve was obtained:




(a) Calculate the molar mass of the unknown acid. [6 marks]

(b) Determine the $pK_a$ of the unknown acid. [2 marks]

13. There are two common iron chlorides, namely $FeCl_2$ and $FeCl_3$. Suppose that we put a piece of solid iron into a sealed container with 0.6 bar of chlorine gas at 25°C. Use a thermodynamic argument to determine which of the iron chlorides, if any, you would expect to produce under these conditions. [14 marks]

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