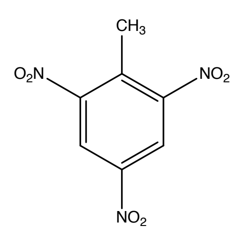
Chemistry 2740 Spring 2018 Final Examination

Time: 3 hours
Marks: 103
Aids allowed: calculator, 8.5×11-inch formula sheet
Useful data is given on page 5.
Instructions: You can answer the questions in any order, but make sure that you clearly label each of your answers with the question number in your exam booklet(s).
Briefly note any procedures you carried out on your calculator (e.g. solving equations, linear regression, etc.). You need not give me a key-by-key account of what you did, but do keep in mind that I need to have something to mark, especially if your final answer is incorrect.
If you use a graph to answer a question, make sure to provide a reasonable sketch of the graph, including properly labeled axes. This is important even if you only use regression data from the graph.

1. Most of the diamonds used in cutting tools are synthetic diamonds, made by applying a large pressure and high temperature to graphite. A typical apparatus uses a pressure of 5 GPa and a temperature of 1500 °C. To make diamonds, 0.2 to 0.3 g of graphite (enough to make a 1–1.5 carat diamond) is rapidly brought up to the operating temperature and pressure and held under these conditions for several hours, during which time the graphite is completely converted to diamond. How much work is done in converting 0.25 g of graphite to diamond? Assume that the density of graphite under the operating conditions is $2.4 \times 10^3\,\mathrm{kg\,m^{-3}}$, and that the density of diamond is $3.5 \times 10^3\,\mathrm{kg\,m^{-3}}$. [6 marks]

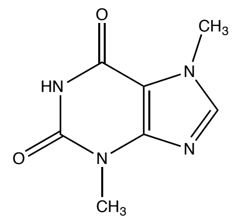
2. When a nitrogen-containing compound like trinitrotoluene (TNT, $C_7H_5N_3O_6$) is burned in a bomb calorimeter, the nitrogen is liberated as N_2.



The enthalpy of combustion of TNT was measured by bomb calorimetry and found to be $-3419\,\mathrm{kJ\,mol^{-1}}$.[1] Calculate the standard enthalpy of formation of TNT. [4 marks]

[1] P. E. Rouse, Jr., *J. Chem. Eng. Data* **21**, 16 (1976).

3. Theobromine is a compound found in chocolate. It has a similar structure as caffeine, and has somewhat similar physiological effects.



The solubility of theobromine in water at 288.07 K is $1.71 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$, and the solubility at 328.15 K is $7.98 \times 10^{-3}\,\mathrm{mol\,L^{-1}}$.[2]

(a) Calculate the enthalpy of solution, i.e. the enthalpy change when theobromine dissolves in water. [6 marks]

(b) Calculate the standard free energy of solution at 25 °C. [6 marks]

(c) Calculate the standard entropy of solution. [2 marks]

4. A lead-acid battery has the following cell diagram:

$$\mathrm{Pb_{(s)}, PbSO_{4(s)} | H_2SO_{4(aq)} | PbO_{2(s)}, PbSO_{4(s)}}$$

The anode is made of a lead grid into which lead(II) sulfate is deposited during the reaction. The cathode is similarly made of a lead grid that has been coated with lead(IV) oxide. The lead oxide in the cathode is replaced by lead(II) sulfate during the reaction. The lead grid at the cathode is a material compatible with the other battery components, and only serves to carry electrons.

The unbalanced half-reactions are the following:

$$\mathrm{Pb_{(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)}}$$
$$\mathrm{PbO_{2(s)} + HSO^-_{4(aq)} \rightarrow PbSO_{4(s)}}$$

(a) Balance the reaction that occurs in a lead-acid battery. [5 marks]

(b) Sketch a single cell of a lead-acid battery, labeling all of the major components [electrodes, solution(s), etc.]. Your diagram should include an external circuit, and show in which directions electrons will travel through this circuit. Note that the cell diagram does not show a salt bridge. Explain why a salt bridge is not required here. [4 marks]

(c) The concentration of sulfuric acid in a typical lead-acid battery is $5.0\,\mathrm{mol\,L^{-1}}$. The mean ionic activity coefficient of H_2SO_4 (i.e. of an $H^+ + HSO_4^-$ pair) at this concentration at 25 °C is 0.2603, and the activity of water is 0.601 66.[3] Calculate the emf of a lead-acid cell operating under these conditions. [9 marks]

[2] J. Zhong et al., *J. Chem. Eng. Data* **62**, 2570 (2017).

[3] Both values obtained by interpolation from the tables of B. R. Staples, *J. Phys. Chem. Ref. Data* **10**, 779 (1981).

5. The solubility product of silver(I) bromate ($AgBrO_3$) at 25 °C is 5.38×10^{-5}. Using Debye-Hückel theory, calculate the solubility of silver(I) bromate in water. The relative permittivity of water at this temperature is 78.37. [11 marks]

6. Methyl tertiary butyl ether (MTBE) has been used as a fuel additive for improving engine performance. Although it does not appear to have any health effects at low doses, when it escapes from underground fuel tanks, it gives water an unpleasant taste even at very low concentrations, making the contaminated ground water undrinkable. MTBE is removed from groundwater by a number of processes. The following data were obtained from groundwater samples at one site in Connecticut following a state-wide ban on the use of MTBE in gasoline:[4]

t/months	3.9	10.7	14.1	18.1	21.4	24.0	29.0	29.8	33.8
[MTBE]/ppb	172	38	60	56	38	54	28	24	23

t is the time since the Connecticut ban went into effect.

(a) The authors of this study claim that MTBE dissipates from the environment with first-order kinetics. Do you agree with this claim? [6 marks]

Note: Environmental data show a lot more variability than data from laboratory experiments, so take that into account in deciding whether you agree with their claim or not.

(b) Regardless of your conclusion above, estimate the half-life of MTBE at this site based on a first-order model. [4 marks]

(c) MTBE might be detectable by humans in drinking water down to concentrations of 15 ppb.[5] For this site, assuming that the first-order model is correct, how many months after the ban would it take before the MTBE concentration fell to levels undetectable by humans? [4 marks]

7. Ogura studied the decomposition of hydrogen peroxide by the enzyme catalase.[6] He obtained the following data at pH 7.0 and 30 °C with an enzyme concentration of 1.2×10^{-7} mol L^{-1}.

$[H_2O_2]$/mol L^{-1}	0.31	0.64	1.16	1.85	2.82	3.75	4.89
v/mol L^{-1}s^{-1}	1.18	1.88	2.55	2.98	3.36	3.58	3.76

Determine the turnover number (the rate constant associated with product formation in the Michaelis-Menten mechanism) and Michaelis constant of this enzyme. [9 marks]

[4] M. J. Metcalf et al., *J. Contam. Hydrol.* **187**, 47 (2016).

[5] A. J. Stocking et al., *J. Am. Water Works Assoc.* **93**(3), 95 (2001).

[6] Y. Ogura, *Arch. Biochem. Biophys.* **57**, 288 (1955). Only a subset of Ogura's data is included in this question to reduce the work involved.

8. Bromomethane is used extensively as a fumigant to kill a variety of pests. It is both a greenhouse gas and an ozone depleting chemical. Larin and coworkers have studied the gas-phase reaction $Cl^\bullet + CH_3Br \longrightarrow CH_2Br^\bullet + HCl$.[7] The rate constant for this reaction varies with temperature as follows:

T/K	294	306	315	328	337	350	360
$k/10^5\,\mathrm{m^3mol^{-1}s^{-1}}$	2.70	3.01	3.35	3.72	4.14	4.61	5.14

Calculate the enthalpy and entropy of activation for this reaction. What does the entropy of activation tell you about the transition state of this reaction? [11 marks]

9. The reaction of NO with hydrogen in the gas phase produces nitrogen and water. The mechanism is thought to be the following:

$$2\,NO_{(g)} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} N_2O_{2(g)}$$

$$H_{2(g)} + N_2O_{2(g)} \xrightarrow{k_2} N_2O_{(g)} + H_2O_{(g)}$$

$$H_{2(g)} + N_2O_{(g)} \xrightarrow{k_3} N_{2(g)} + H_2O_{(g)}$$

   (a) Determine the overall reaction. [2 marks]

   (b) The NO/N_2O_2 equilibrium is fast. Derive a rate law for this mechanism. What are the predicted orders of reaction with respect to NO and H_2? [14 marks]

[7] I. K. Larin et al., *Kinet. Catal.* **59**, 11 (2018).

Useful data

Constants and conversion factors

$0\,\mathrm{K} = -273.15\,^\circ\mathrm{C}$
$F = 96\,485.342\,\mathrm{C\,mol^{-1}}$
$h = 6.626\,0688 \times 10^{-34}\,\mathrm{J\,Hz^{-1}}$
$k_B = 1.380\,6503 \times 10^{-23}\,\mathrm{J\,K^{-1}}$
$R = 8.314\,472\,\mathrm{J\,K^{-1}mol^{-1}}$
$\varepsilon_0 = 8.854\,187\,817 \times 10^{-12}\,\mathrm{C^2J^{-1}m^{-1}}$

$$\left.\begin{array}{l} \ln\gamma_i = -Az_i^2(\varepsilon T)^{-3/2}\sqrt{I_c} \\ \ln\gamma_\pm = -A|z_+z_-|(\varepsilon T)^{-3/2}\sqrt{I_c} \end{array}\right\} \text{with } A = 1.107 \times 10^{-10}$$

Standard thermodynamic data at 298.15 K

Species	$\frac{\Delta_f H^\circ}{\mathrm{kJ\,mol^{-1}}}$	$\frac{\Delta_f G^\circ}{\mathrm{kJ\,mol^{-1}}}$
$CO_{2(g)}$	−393.51	−394.37
$H_2O_{(l)}$	−285.830	−237.140
$HSO^-_{4(aq)}$	−885.75	−752.87
$PbO_{2(s)}$	−276.6	−219.0
$PbSO_{4(s)}$	−918.39	−811.24