Chemistry 2850 Spring 2007 Practice Final Examination

Time: 3 h   Questions: 11   Marks: 116
Aids permitted: graphing calculator, one 8.5×11-inch formula sheet
Write all answers in the booklets provided.

Useful data

$F = 96\,485.3383\,\text{C/mol}$

$h = 6.626\,068\,8 \times 10^{-34}\,\text{J/Hz}$

$k_B = 1.380\,650\,3 \times 10^{-23}\,\text{J/K}$

$R = 8.314\,472\,\text{J}\,\text{K}^{-1}\text{mol}^{-1}$

To convert degrees Celsius to Kelvin, add 273.15.

Species	$\Delta \bar{H}_f^\circ$ (kJ/mol)	$\Delta \bar{G}_f^\circ$ (kJ/mol)	$\bar{C}_P$ ($\text{J}\,\text{K}^{-1}\text{mol}^{-1}$)
$CH_{4(g)}$	-74.81	-50.72	35.31
$CO_{2(g)}$	-393.51	-394.37	37.1
$F^-_{(aq)}$	-335.35	-281.52	
$H_2O_{(l)}$	-285.830	-237.140	75.40

Reduction process	$\mathcal{E}^\circ$ (V)
$O_{2(g)} + 4H^+_{(aq)} + 4e^- \rightarrow 2H_2O_{(l)}$	$+1.229$

1. What does the word "reversible" mean in thermodynamics? [2 marks]

2. Suppose that someone told you that a second-order reaction has a half-life of 30 s at 25°C. Is this a meaningful statement? Explain briefly. [3 marks]

3. What information can we get about a reaction from studying the ionic-strength dependence of the rate constant? [3 marks]

4. What is the difference between specific acid catalysis and general acid catalysis? [2 marks]

5. Sketch the PV diagram of a Carnot engine. Label each curve on your diagram with the type of process it corresponds to (e.g. adiabatic or isothermal). Indicate what feature of your sketch corresponds to the total work done. [6 marks]

6. Compare the relaxation methods (as a group) to flash photolysis. How are these two groups of methods similar? How are they different? To what kinds of reactions can you apply one set of methods or the other? [10 marks]

7. Sketch a methane/oxygen fuel cell. What are the half-reactions? Where do these half-reactions occur? In what direction do electrons flow? What is the standard potential of this cell? (Some of these questions can be answered in your diagram.) [12 marks]

8. When scientific papers are submitted to scientific journals, they are sent for peer review, i.e. they are sent to experts in the field for an opinion regarding their correctness and novelty. I recently reviewed a paper in which the following passage appeared:[1]

    A part of the biochemical energy becomes heat:

 $$\Delta q = \eta \Delta U, \tag{1}$$

    where Δq is the change in heat, and η is the efficiency of the energy conversion between ΔU and Δq.

    What is wrong with this statement? [2 marks]

9. Arrhenius theory assumes that the preexponential factor and activation energy are both independent of temperature. However, more advanced theoretical approaches to kinetics typically predict that these quantities are temperature dependent. Calculate the rate constant for a first-order solution-phase reaction with $\Delta^{\ddagger}S^{\circ} = 80 \, \mathrm{J \, K^{-1} mol^{-1}}$ and $\Delta^{\ddagger}H^{\circ} = 100 \, \mathrm{kJ/mol}$ at 300, 350, 400, 450 and 500 K. Produce an Arrhenius plot using your rate constants. Is this graph straight? What activation energy and preexponential factor do you get from your graph? How do these values compare to those you would calculate directly from $\Delta^{\ddagger}S^{\circ}$ and $\Delta^{\ddagger}H^{\circ}$ at, say, 300 K? What do you conclude about the temperature dependence of the preexponential factor and activation energy predicted by transition-state theory? [22 marks]

10. The acid dissociation constant of hydrofluoric acid is 6.6×10^{-4} at 25°C.

    (a) Calculate the standard free energy of formation of aqueous HF. [8 marks]

    (b) Using Debye-Hückel theory, calculate the concentrations of the H^+ and F^- ions in a 0.10 mol/L aqueous solution of HF. Assume a unit activity coefficient for molecular HF. [12 marks]

    (c) Calculate the pH of the above solution. [3 marks]

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[1]I have changed the symbols to those used in this course.

11. (a) Consider the following reaction mechanism:

$$A + A \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} B$$
$$A + B \overset{k_2}{\rightarrow} 3P.$$
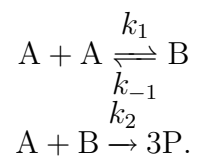
    i. What is the overall reaction stoichiometry? (Give your answer in terms of the smallest whole-number coefficients.) [2 marks]

    ii. Derive the rate law for this mechanism. [10 marks]

    iii. Under what conditions would you get a simple third-order rate law? What is the connection between the rate constants in the mechanism and the observed rate constant under these conditions? [4 marks]

(b) Derive an integrated rate law for a simple third-order reaction with stoichiometry $A \rightarrow P$ and rate $v = k[A]^3$. [6 marks]

(c) Suppose that we have obtained the following data:

t/min	5	10	30	60	90	120
$[A]/\text{mmol}\,L^{-1}$	1.08	0.89	0.72	0.56	0.47	0.43

Are these data consistent with third-order kinetics? If so, what is the rate constant? [9 marks]