Chem. 6C Midterm 2
Version A
November 13, 2007

Name_____

Student Number _____

TA Name_____

Section Time_____

All work must be shown on the exam for partial credit. Points will be taken off for incorrect or no units. Non graphing calculators and two hand-written 3" × 5" note cards are permitted.

Problem 1 (of 10 possible)	
Problem 2 (of 15 possible)	
Problem 3 (of 16 possible)	
Problem 4 (of 20 possible)	
Problem 5 (of 10 possible)	
Problem 6 (of 16 possible)	
Problem 7 (of 26 possible)	
Problem 8 (of 22 possible)	
Problem 9 (of 15 possible)	
Midterm Total (of 150 possible)	

NO PARTIAL CREDIT FOR QUESTION 1 WILL BE GIVEN

1) *(5 pts)* Write the shorthand notation for $Cu^{2+}(aq) + H_2(g) \rightarrow 2H^+(aq) + Cu^+(aq)$.

$$Pt(s)|H_2(g)|H^+(aq)||Cu^{2+}(aq),Cu^+(aq)|Pt(s)$$

(2 pts) In the equation $Cu^{2+}(aq) + H_2(g) \rightarrow 2H^+(aq) + Cu^+(aq)$ which species is oxidized?

` $H_2(g)$

(3pts) Which species is the strongest reducing agent?

$Hg_2^{2+}(aq) + 2e^- \rightarrow 2Hg(l)$	$E^o = 0.79$ V
$In^{2+}(aq) + e^- \rightarrow In^+(aq)$	$E^o = -0.40$ V
$Al^{3+}(aq) + 3e^- \rightarrow Al(s)$	$E^o = -1.66$ V

$Al(s)$
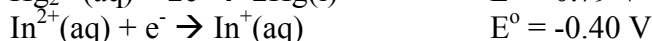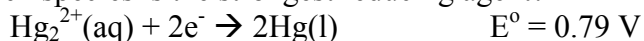
2) *(15 pts)* The reaction $2NO(g) + H_2(g) \rightarrow N_2O(g) + H_2O$ has been proposed to happen via the following mechanism

$NO(g) + NO(g) \leftrightarrows N_2O_2(g)$ (rate constants k_1 and k_1')
$N_2O_2(g) + H_2(g) \rightarrow N_2O(g) + H_2O(l)$ (rate constant k_2)

However nothing is known about the size of the rate constants. Derive an expression for the rate of formation of N_2O.

Rate of formation of $N_2O = k_2[N_2O_2][H_2]$
N_2O_2 is an intermediate therefore it needs to be eliminated from the rate expression by using the steady state approximation
Rate of formation of $N_2O_2 = k_1[NO]^2$
Rate of consumption of $N_2O_2 = k_1'[N_2O_2]$
Rate of consumption of $N_2O_2 = k_2[N_2O_2][H_2]$
Net rate of formation of $N_2O_2 = k_1[NO]^2 - k_1'[N_2O_2] - k_2[N_2O_2][H_2]$
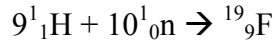The steady state approximation states that the net rate of formation of an intermediate must equal 0
$0 = k_1[NO]^2 - k_1'[N_2O_2] - k_2[N_2O_2][H_2]$
$[N_2O_2] = k_1[NO]^2(k_1' + k_2[H_2])^{-1}$
Rate of formation of $N_2O = k_2 k_1[H_2][NO]^2(k_1' + k_2[H_2])^{-1}$

3) *(10 pts)* What is the binding energy per nucleon of $^{19}_9F$ in J? The atomic mass of $^{19}_9F$ is 18.9984 u.

$9\,^1_1H + 10\,^1_0n \rightarrow\ ^{19}_9F$
Change mass of neutron into atomic mass units
1.67495×10^{-27} kg (1 u / 1.6605×10^{-27} kg) = 1.0087 u
$\Delta m = m(^{19}_9F) - (9{\cdot}m(^1_1H) + 10{\cdot}m(^1_0n))$
$= 18.99894 - (9{\cdot}1.0078\ u + 10{\cdot}1.0087\ u)$
$= -0.15826\ u$
-0.15826 u (1.6605×10^{-27} kg / 1 u) = -2.6279×10^{-28} kg
$E_{bind} = |\Delta m|{\cdot}c^2 = |-2.6279\times10^{-28}\ kg\,|{\cdot}(3\times10^8\ m{\cdot}s^{-1})^2$
$= 2.36512\times10^{-11}$ J
E_{bind} per nucleon = 2.36512×10^{-11} J / 19 nucleons = 1.24×10^{-12} J·nucleon^{-1}

(6 pts) Calculate the energy change when one $^{235}_{92}U$ nucleus undergoes the fission reaction
$^{235}_{92}U + {}^1_0n \rightarrow\ ^{142}_{56}Ba + {}^{92}_{36}Kr + 2\,^1_0n.$
The masses needed are $^{235}_{92}U$, 235.04 u; $^{142}_{56}Ba$, 141.92 u; $^{92}_{36}Kr$, 91.92; and ^1_0n, 1.0087 u.
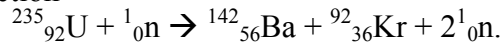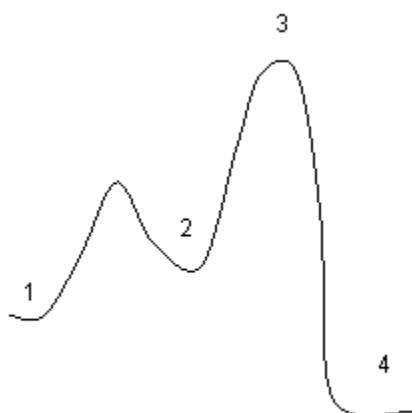
$\Delta m = m(^{142}_{56}Ba) + m(^{92}_{36}Kr) + 2{\cdot}m(^1_0n) - m(^{235}_{92}U) - m(^1_0n)$
$= 141.92\ u + 91.92\ u + 2(1.0087\ u) - 235.04\ u - 1.0087\ u\ = -\,0.1913\ u$
-0.1913 u (1.6605×10^{-27} kg / 1 u) = -3.1765×10^{-28} kg
$E = |m|{\cdot}c^2 = 3.1765\times10^{-28}$ kg$(3\times10^8\ m{\cdot}s^{-1})^2 = -2.86\times10^{-11}$ J

4) Use the following reaction diagram to answer the following questions

(3 pts) Which number represents a reaction intermediate?

      2

*(3 pts)* Which number represents a transition state or an activated complex?

      3

(3 pts) Is this reaction endothermic or exothermic?

      Exothermic

(5 pts) If an overall reaction has a $\Delta G_{rxn} = 45$ kJ·mol^{-1} and an activation barrier of 75 kJ·mol^{-1} what is the activation barrier of the reverse reaction?

      30 kJ·mol^{-1}

(6 pts) Draw a reaction diagram for a system without a catalyst and with a catalyst. Make sure to label the diagram (original pathway, catalyzed path way, activation energies, coordinates, reactants and products).
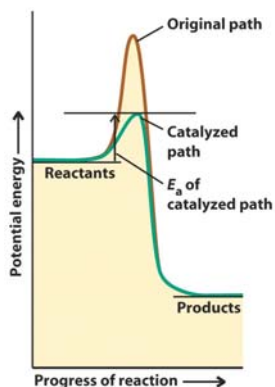
5) *(10 pts)* The decomposition of hydrogen iodide ($2HI(g) \rightarrow H_2(g) + I_2(g)$) has a rate constant of 9.51×10^{-9} $L \cdot mol^{-1} \cdot s^{-1}$ at 500 K and 1.10×10^{-5} $L \cdot mol^{-1} \cdot s^{-1}$ at 600 K. Find E_a?

$\ln(k) = \ln(A) - E_a \cdot R^{-1} \cdot T^{-1}$

Eq_1: $\ln(9.51 \times 10^{-9} \ L \cdot mol^{-1} \cdot s^{-1}) = \ln(A) - E_a \cdot (8.3145 \ J \cdot mol^{-1} \cdot K^{-1})^{-1} \cdot (500 \ K^{-1})$

$-18.47 = \ln(A) - 2.41 \times 10^{-4} \ mol \cdot J^{-1} \cdot E_a$

Eq_2: $\ln(1.10 \times 10^{-5} \ L \cdot mol^{-1} \cdot s^{-1}) = \ln(A) - E_a \cdot (8.3145 \ J \cdot mol^{-1} \cdot K^{-1})^{-1} \cdot (600 \ K^{-1})$

$-11.42 = \ln(A) - 2.00 \times 10^{-4} \ mol \cdot J^{-1} \cdot E_a$

$Eq_1 - Eq_2 = -18.47 + 11.42$

$= \ln(A) - 2.41 \times 10^{-4} \ mol \cdot J^{-1} \cdot E_a - \ln(A) + 2.00 \times 10^{-4} \ mol \cdot J^{-1} \cdot E_a$

$-7.05 = -4.10 \times 10^{-5} \ mol \cdot J^{-1} \cdot E_a$

$E_a = 1.72 \times 10^5 \ J \cdot mol^{-1}$

6) *(10 pts)* A living tree contains $^{14}_{6}C$ ($t_{1/2} = 5600$ y) and has a specific activity of 750 counts per hour. A wooden artifact of the same size recovered from an archeological site gives a count of 90 counts per hour. What is the age of the artifact?

$k = \ln2 \ / \ t_{1/2} = \ln2 \ / \ 5600 = 1.24 \times 10^{-4} \ y^{-1}$

$[A]_t = [A]_o e^{-k \cdot t}$

$90 = 750 e^{-(1.23 \times 10\text{-}4 \ y\text{-}1 \cdot t)}$

$t = 17089$ y

(6 pts) Explain why carbon dating works?

Carbon-14 enters living things through photosynthesis and digestion of $^{14}CO_2$ and leaves organism's through respiration and excretions. But the ratio of Carbon-12 to Carbon-14 remains constant in living things. When an organism dies it can no longer exchange carbon with its surroundings. The Carbon-14 will slowly decay into Carbon-12 over time. The ratio of Carbon-14 to Carbon-12 can be used to estimate the time since the organism died

7) The reaction $CHCl_3(g) + Cl_2(g) \rightarrow CCl_4(g) + HCl(g)$, has been proposed to occur by the following mechanism

Elementary Reactions

(1) $Cl_2 \leftrightarrows Cl + Cl$ Rapid equilibrium, rate constants k_1 and k_1'

(2) $CHCl_3 + Cl \rightarrow HCl + CCl_3$ Slow, rate constant k_2

(3) $CCl_3 + Cl \rightarrow CCl_4$ Very Rapid, rate constant k_3

(3 pts) What is the molecularity of each of the elementary reactions?

1	unimolecular
2	bimolecular
3	bimolecular

(5 pts) What assumption is made in the steady state approximation?

The steady state approximation assumes that the concentration of intermediates is constant.

(5 pts) When can the pre-equilibrium condition be used?

The pre-equilibrium condition can be used when intermediates are formed in a rapid equilibrium reaction prior to a slow step in the mechanism.

(8 pts) What is the rate law for this reaction?

Rate $= k_2[CHCl_3][Cl]$

Pre equilibrium condition

$k_1[Cl_2] = k_1'[Cl]^2$ therefore $[Cl] = k_1^{\frac{1}{2}} \cdot k_1'^{-\frac{1}{2}}[Cl_2]^{\frac{1}{2}}$

Rate $= k_2 \cdot k_1^{\frac{1}{2}} \cdot k_1'^{-\frac{1}{2}}[Cl_2]^{\frac{1}{2}}[CHCl_3]$

(5 pts) If the rate law was experimentally found to be $k[Cl_2]^{\frac{1}{2}}[CHCl_3]$ then is the given mechanism definitely the mechanism? Explain.

The experimentally found rate law and the rate law derived from the mechanism are the same. Therefore it is possible that the given mechanism is correct. However you can never guarantee that the mechanism is correct because other mechanism can give the same rate law.

8) *(3 pts)* Nuclides with too many neutrons to be in the band of stability are most likely to decay by what mode?

Beta Particle Emission

(3 pts) The nuclide $^{208}_{81}Tl$ is the daughter nuclide resulting from the α-decay of what parent nuclide?

$^{212}_{83}Bi$
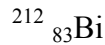
(4 pts) Which type of particle α, β, or γ can penetrate into a surface the farthest and which will do the most damage?

γ particles can penetrate the surface the farthest but α particles do the most damage

(3 pts) Electron capture transforms $^{40}_{19}K$ into what nuclide?

$^{40}_{18}Ar$

(3 pts) What is the daughter nuclide that is produced when $^{243}_{95}Am$ undergoes γ emission?

$^{243}_{95}Am$
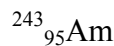
(6 pts) Calculate the frequency and wavelength of the γ radiation emitted as a result of a rearrangement of nucleons in a single daughter nucleus through which 2.2×10^{-14} J of energy is released?

$E = h\cdot v$
$2.2\times10^{-14}\,J = (6.626\times10^{-34}\,J\cdot s)v$
$v = 3.32\times10^{19}\,Hz$
$\lambda = c\cdot v^{-1}$
$\lambda = (3.0\times10^{8}\,m\cdot s^{-1})(3.32\times10^{19}\,Hz)^{-1}$
$\lambda = 9.04\times10^{-12}\,m$

9) *(15 pts)* A small portion of a cancer patient's brain is exposed for 27.0 min to 475 Bq of ^{60}Co for treatment of a tumor. If the brain mass exposed is 1.488 g and each β particle emitted has an energy of 5.05×10^{-14} J, what is the dose in rads?

t = 27.0 m = (27.0 m)(60 s / 1 m) = 1620 s
Bq is 1 disintegrations per second
Therefore
475 Bq = (# of disintegrations) / (1620 s)
# of disintegrations = 769500
Each disintegration gives off 5.05×10^{-14} J of energy
Therefore the total energy given off is =
# of disintegrations × energy each disintegration gives off
= 769500(5.05×10^{-14} J) = 3.895×10^{-8} J
This radiation is dispersed over a 1.488 g = .001488 kg sample
Therefore the energy / kg = 3.895×10^{-8} J / .001488 kg = 2.617×10^{-5} J·kg^{-1}
1 rad = 10^{-2} J·kg^{-1} change units to rads
2.617×10^{-5} J·kg^{-1} (1 rad / 10^{-2} J·kg^{-1}) = 2.62×10^{-3} rad