Chemistry 1A, Exam II
March 11, 2014
Professor R.J. Saykally

Name ____________________________
Student ID _______________________

1. (40) ____________
2. (30) ____________
3. (30) ____________
4. (20) ____________
5. (20) ____________
6. (20) ____________
7. (20) ____________
8. (20) ____________

TOTAL EXAM SCORE (200) ____________

Rules:
• Work all problems to 2 significant figures
• No lecture notes or books permitted
• No programmable or graphing calculators permitted
• Time: 90 minutes
• Show work in the provided boxes to receive any credit. Answers with no work shown will receive no credit
• Anything written outside of the provided boxes will not be graded
• Periodic Table, Tables of Physical Constants, Conversion Factors, and Useful Equations included
1. (10 Points each)
A) 100 mL of 0.25 M acetic acid (HAc) solution (aqueous) is prepared ($K_a = 1.9 \times 10^{-5}$). Calculate the pH.

B) 10 mL of 0.25 M NaOH (aqueous) solution is added to the acetic acid solution above. Calculate the new pH.
C) Write the charge balance equation for the solution made in part B.

D) What is the pH of the best buffer that can be made with acetic acid?
2. (10 Points Each)
A) Calculate the solubility (Mol L\(^{-1}\)) of PbI\(_2\) in pure water (K\(_{sp}\) = 1.4 x 10\(^{-8}\))

B) Calculate the solubility of PbI\(_2\) in 0.10 M NaI solution.
C) Calculate the pH (to 2 sig figs) of a solution made up by adding 20.0 mL of 2.0 x 10^{-3} M NaI solution to 100 mL of 4.00 x 10^{-7} M HCl.
3. (10 Points Each) Consider the carbonic acid system, H$_2$CO$_3$

$$K_{a1} = 4.3 \times 10^{-7}$$
$$K_{a2} = 4.8 \times 10^{-11}$$

A) Calculate the pH of a $3.0 \times 10^{-2}$ M solution of Na$_2$CO$_3$ in water (assume that is the initial concentration).
B) Calculate the pH of a $3.0 \times 10^{-2}$ M aqueous solution of baking soda (NaHCO$_3$) (assume that is the *initial* concentration).
C) Calculate the pH of a $3.0 \times 10^{-2}$ M aqueous solution of $\text{H}_2\text{CO}_3$ (assume that is the *initial* concentration).
4. (10 Points Each)
A) Mercury (II) is eliminated from the body by a first-order process and has a half-life in the body of 6 days. What would be the concentration (mg/L) of mercury (II) in the urine of a teenager after 30 days if therapeutic measures were not taken, assuming an initial mercury concentration of 1.54 mg L\(^{-1}\).

B) The rate constant for the above reaction is found to triple with a 10° temperature rise from 25 °C. Calculate the activation energy for the reaction.
5. **(10 Points Each)** The following mechanism has been proposed for the *gas phase* reaction between HBr and NO$_2$:

(1) \[ \text{HBr} + \text{NO}_2 \rightarrow \text{HOBr} + \text{NO} \quad \text{(slow)} \]

(2) \[ \text{HBr} + \text{HOBr} \rightarrow \text{H}_2\text{O} + \text{Br}_2 \quad \text{(fast)} \]

A) Apply the principle of detailed balance to the mechanism to obtain the equilibrium constant in terms of the individual rate constants.

B) Given the above, write the rate law for the rate determining step and indicate its molecularity.
6. **(10 Points Each)** In class, we studied the reaction of elemental iron with oxygen to form rust (Fe₂O₃).

A) If this reaction is *first-order* in oxygen, and the half-life is $3.0 \times 10^{-2}$ seconds, calculate the rate of this reaction (mol L⁻¹ s⁻¹) in air (21% oxygen by volume, assume STP).

B) Calculate the new rate if the above reaction is carried out in liquid oxygen (assume density of 0.5 g/cm³).
Consider this initial-rate data at a certain temperature for the reaction described by

$$2 \text{ICl}_\text{(g)} + \text{H}_2\text{(g)} \rightarrow \text{I}_2\text{(g)} + \text{2HCl}_\text{(g)}$$

<table>
<thead>
<tr>
<th>Trial</th>
<th>[ICl]₀ (M)</th>
<th>[H₂]₀ (M)</th>
<th>Initial rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.5</td>
<td>1.5</td>
<td>$3.7 \times 10^{-7}$</td>
</tr>
<tr>
<td>2</td>
<td>3.0</td>
<td>1.5</td>
<td>$7.4 \times 10^{-7}$</td>
</tr>
<tr>
<td>3</td>
<td>3.0</td>
<td>4.5</td>
<td>$2.2 \times 10^{-6}$</td>
</tr>
</tbody>
</table>

A) Determine the rate law for this reaction
B) Determine the rate constant for this reaction.
8. **(10 Points Each)** The mechanism for the reaction described by the equation

\[ A(g) \rightarrow B(g) \]

is suggested to be

(1) \[ A(g) + M(g) \rightleftharpoons A^*(g) + M(g) \]

(2) \[ A^*(g) \rightarrow B(g) \]

where M(g) is any gas molecule and * denotes an excited molecule.

A) Assuming that \([A^*]\) is governed by steady-state conditions, derive the rate law for the production of \(B(g)\) in terms of \([A], [M]\), and the appropriate \(k (k_1, k_{-1}, k_2)\) values and enter it in the space below.
B) What is the rate law in the low pressure limit?
Quantum:

\[ E = h\nu \]
\[ \lambda \nu = c \]
\[ \lambda_{\text{de Broglie}} = h / p = h / mv \]
\[ E_{\text{kin}} (e^-) = hv - \Phi = hv - hv_0 \]
\[ E_n = \frac{Z^2}{n^2} R_n \]
\[ \Delta x \Delta p \sim h \]
\[ p = mv \]

Particle in a box (1-D Quantum):
\[ E_n = \frac{n^2 \hbar^2}{8mL^2}; n = 1, 2, 3... \]

Vibrational:
\[ E_v = (v + \frac{1}{2}) \hbar \omega / 2\pi; \omega = (k/m)^{1/2} \]

Rotational:
\[ E_n = n(n + 1) \hbar \omega; B = \hbar / 8\pi^2 I; I = 2mr^2 \]
\[ m = m_A m_B / (m_A + m_B) \]

Ideal Gas:
\[ PV = nRT \]
\[ E_{\text{kin}} = \frac{3}{2} RT \]
\[ \nu_{\text{rms}} = \sqrt{\frac{3RT}{M}} \]

Constants:
\[ N_0 = 6.02214 \times 10^{23} \text{ mol}^{-1} \]
\[ R_w = 2.179874 \times 10^{18} \text{ J} \]
\[ R_a = 3.28984 \times 10^{15} \text{ Hz} \]
\[ k = 1.38066 \times 10^{-23} \text{ J K}^{-1} \]
\[ h = 6.62608 \times 10^{-34} \text{ J s} \]
\[ m_e = 9.101939 \times 10^{-31} \text{ kg} \]
\[ c = 2.99792 \times 10^8 \text{ m s}^{-1} \]
\[ T (K) = T (\text{C}) + 273.15 \]
\[ F = 96,485 \text{ C/mol} \]
\[ 1 \text{ V} = 1 \text{ J/C} \]

Gas Constant:
\[ R = 8.31451 \text{ J K}^{-1} \text{ mol}^{-1} \]
\[ R = 8.20578 \times 10^{-2} \text{ L atm K}^{-1} \text{ mol}^{-1} \]
\[ 1 \text{ nm} = 10^{-9} \text{ m} \]
\[ 1 \text{ kJ} = 1000 \text{ J} \]
\[ 1 \text{ atm} = 760 \text{ mm Hg} = 760 \text{ torr} \approx 1 \text{ bar} \]
\[ 1 \text{ L atm} \approx 100 \text{ J} \]

Thermodynamics:
\[ \Delta G^o = \Delta H^o - T\Delta S^o \]
\[ \Delta H^o = \sum \Delta H^o \text{(products)} - \sum \Delta H^o \text{(reactants)} \]
\[ \Delta S^o = \sum S^o \text{(products)} - \sum S^o \text{(reactants)} \]
\[ \Delta G^o = \sum \Delta G^o \text{(products)} - \sum \Delta G^o \text{(reactants)} \]
\[ S = k_B \ln W \]
\[ \Delta S = q_{\text{rev}} / T \]
\[ \Delta E = q + w \]
\[ w = - P_{\text{ext}} \Delta V \]
for aA + bB ⇌ cC + dD
\[ Q = \frac{[C]^c [D]^d}{[A]^a [B]^b} \]
At equilibrium, Q = K
\[ \Delta G = \Delta G^o + RT \ln Q \]
\[ G = G^o + RT \ln(a); a = \text{activity} = \gamma P / P^o \text{ or } \gamma(A) / [A]^o \]
\[ \Delta G^o = - RT \ln K \]
\[ \Delta G^o = - nF \Delta C^o \]
\[ \Delta C = \Delta C^o - (RT/nF) \ln Q \]
\[ \ln K = - \frac{\Delta H^o}{R} \frac{1}{T} + \frac{\Delta S^o}{R} \]
\[ \Delta T = i k_B \lambda m \]
\[ \Pi = i mRT \]
\[ P_{\text{total}} = P_A + P_B = X_A P_A^o + X_B P_B^o \]

Acid Base:
\[ \text{pH} = - \log[H_3O^+] \]
\[ \text{pX} = - \log X \]
\[ \text{pH} = pK_a + \log \frac{[A^-]}{[HA]} \]

Kinetics:
\[ [A]_t = [A]_0 e^{-kt} \]
\[ \ln[A]_t = \ln[A]_0 - kt \]
\[ t_{1/2} = \ln 2 / k \]
\[ 1/[A]_t = 1/[A]_0 + kt \]
\[ k = A e^{(-E_a/RT)} \]
\[ \ln(k_1 / k_2) = E_a / R (1 / T_2 - 1 / T_1) \]
\[ t_{1/2} = 1/[A]_0 k \]
\[ t_{1/2} = [A]_0 / k t \]