Surname :________________Given name :________________________________

Student number:________________________

Chemistry 1311F
Test 2 V1, November 19, 2015
80 minutes
You may remove the last 2 pages
Professor: Wendy Pell

1. a) (1 point) Determine the order of a reaction if the rate constant has units $M^{-5/2}\,s^{-1}$

3.5

$R = k(M^{-5/2}s^{-1})\,[\,]^x$

$x = 7.5$

b) (1 point) How would you adjust the ~~pressure~~ volume of a reaction vessel to favour production of ~~products~~ reactants in the following reaction: $2\,C(s) + O_2\,(g) \rightleftharpoons 2CO(g)$

- less moles
- INCREASE pressure, decrease volume

c) (1 point) Write the equilibrium constant, K, for
$Zn(s) + 2H^+\,(aq) \rightleftharpoons H_2(g) + Zn^{2+}\,(aq)$

$$K = \frac{[Zn^{2+}]\,P_{H_2}}{[H^+]^2}$$

d) (1 point) What is the conjugate base of ~~trimethyl amine, $(CH_3)_3N$~~ ? trichloroacetic acid

Cl_3COO^-

e) (1 point) Potassium ~~dihydrogen phosphate~~ sulphate, KH_2PO_4, is an acidic salt ~~What hydrolysis reaction occurs when dihydrogen phosphate anion, $H_2PO_4^-$ is added to water?~~

$SO_4^{2-}(aq) + H_2O \rightleftharpoons HSO_4^-(aq) + OH^-$ (SO_4^{2-})

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2. The following mechanism was proposed for the formation of hydroiodic acid, HI, from hydrogen and oxygen gases:

$I_2 \rightleftharpoons 2I$ (fast equilibrium, with rate constants k_1 and k_{-1})

$I + H_2 \rightleftharpoons H_2I$ (fast equilibrium, with rate constants k_2 and k_{-2})

$H_2I + I \rightarrow 2HI$

a) (4 points) Determine the overall rate law for this mechanism

RxN: $I_2 + H_2 \rightarrow 2HI$

RDS is 3rd step $R = k_3 [H_2I][I]$

H_2I & I are both intermediates, use fast equilibrium steps to get alternate expression for $[H_2I]$ and $[I]$

$k_1[I_2] = k_{-1}[I]^2$; $[I] = \left(\frac{k_1}{k_{-1}}[I_2]\right)^{1/2}$

$k_2[I][H_2] = k_{-2}[H_2I]$ $[H_2I] = \frac{k_2}{k_{-2}}[H_2][I] = \frac{k_2}{k_{-2}}[H_2]\left(\frac{k_1}{k_{-1}}[I_2]\right)^{1/2}$

$R = k_3 \frac{k_2}{k_{-2}}[H_2]\left(\frac{k_1}{k_{-1}}[I_2]\right)^{1/2} \times \left(\frac{k_1}{k_{-1}}[I_2]\right)^{1/2}$

$= \frac{k_3 k_2 k_1}{k_{-2} k_{-1}}[H_2][I_2] = k_T [H_2][I_2]$

1.4

b) (1 point) If $k_1 = 1.4\times10^{-3}\ s^{-1}$; $k_{-1} = 1.27\times 10^{-3}\ M^{-1}s^{-1}$; $k_2 = 1.13\times10^{-3}\ M^{-1}s^{-1}$; $k_{-2} = 1.48\times 10^{-3}\ s^{-1}$ and $k_3 = 15$ (15.0) $M^{-1}s^{-1}$ determine the overall rate constant for the reaction.

$k = \frac{k_3 k_2 k_1}{k_{-2} k_{-1}} = \frac{15.0\ M^{-1}s^{-1}(1.13\times10^{-3}\ M^{-1}s^{-1})(1.40\times10^{-3}\ s^{-1})}{(1.48\times10^{-3}\ s^{-1})(1.27\times10^{-3}\ M^{-1}s^{-1})}$

$= 12.6\ M^{-1}s^{-1}$

c) (1 points) How might you determine if your mechanism is correct?

1) do an experiment to see if RxN is 1st order in $[H_2]$ & first order in $[I_2]$

2) detect intermediate

3) add a 'sink' for intermediates and see if rxn stops.

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3. The reaction

$H_2SeO_3(aq) + 6I^-(aq) + 4H^+(aq) \rightarrow Se(s) + 2I_3^-(aq) + 3H_2O(l)$ was studied at 0°C and the following initial rate data were obtained:

	$[H_2SeO_3]_0$ (mol/L)	$[H^+]$ (mol/L)	$[I^-]$ (mol/L)	Initial Rate (mol / L s)
①	1.0×10^{-4}	2.0×10^{-2}	2.0×10^{-2}	1.67×10^{-7}
②	2.0×10^{-4}	2.0×10^{-2}	2.0×10^{-2}	3.33×10^{-7}
③	1.0×10^{-4}	1.0×10^{-2}	2.0×10^{-2}	0.42×10^{-7}
④	1.0×10^{-4}	2.0×10^{-2}	4.0×10^{-2}	13.3×10^{-7}

a) (5 points) What is the rate law for this reaction? $R = k[H_2SeO_3]^x[H^+]^y[I^-]^z$

$$\frac{R_1}{R_2} = \frac{1.67}{3.33} = \frac{[H_2SeO_3]_1^x}{[H_2SeO_3]_2^x} = \left(\frac{1.0}{2.0}\right)^x ; \quad 0.502 = (0.5)^x \quad x = 1$$

$$\frac{R_1}{R_3} = \frac{1.67}{0.42} = \frac{[H^+]_1^y}{[H^+]_2^y} = \left(\frac{2.0}{1.0}\right)^y ; \quad 3.98 = (2)^y \quad y = 2$$

$$\frac{R_1}{R_4} = \frac{1.67}{13.3} = \frac{[I^-]_1^z}{[I^-]_2^z} = \left(\frac{2.0}{4.0}\right)^z$$

$$0.125 = (0.5)^z$$
$$\log(.125) = z\log(.5)$$
$$-0.90 = z(-0.30) \quad z = 3$$

$$R = k[H_2SeO_3][H^+]^2[I^-]^3$$

b) (2 points) Determine the rate constant for this reaction (include units).

Using rate law above and experimental data.

$$1.67 \times 10^{-7} = k[1.0 \times 10^{-4}][2.0 \times 10^{-2}]^2[2.0 \times 10^{-2}]^3$$

$$k = 5.25 \times 10^5 \ M^{-5} s^{-1}$$

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4. A reaction vessel, at 77 °C, is filled with dinitrogen tetroxide, N_2O_4. Equilibrium is established

$$N_2O_4\,(g) \rightleftharpoons 2NO_2\,(g)$$

and the resulting concentrations of N_2O_4 and NO_2 are 9.6×10^{-3} M and 3.9×10^{-2} M, respectively.

a) (2 points) Determine the equilibrium constant for this reaction.

$$K_c = \frac{[NO_2]^2}{[N_2O_4]} = \frac{(3.9\times10^{-2})^2}{(9.6\times10^{-3})} = 0.158$$

$$K_p = K_c(RT)^{\Delta n} = 0.158(0.08314 \times 350)^{2-1}$$

$$= 4.61$$

b) (3 points) What is the equilibrium constant at 25 °C? if the rxn is endothermic with $\Delta_{RXN}H = 56.5$ kJ

$$\ln\frac{k_1}{k_2} = \frac{Ea}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{Ea}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

$$\ln\left(\frac{K_2}{4.61}\right) = \frac{56.5\times10^3}{8.314}\left(\frac{1}{350} - \frac{1}{298}\right)$$

$$\frac{K_2}{4.61} = 0.0337$$

$$K_2 = 0.157$$

c)(5points) The volume of the reaction vessel (in part a) doubles, and temperature is decreased to 25 °C. If the reaction is endothermic, with $\Delta_{RXN}H$ = 56.5 kJ, determine the total pressure once equilibrium is re-established. FONT

$K(298) = 0.157$

$P_{N_2O_4} = \left(\frac{n}{V}\right)(RT) = \left(\frac{9.6\times10^{-3}}{2}\right)(0.08314 \times 298) = 0.119$ bar

$P_{NO_2} = \left(\frac{3.9\times10^{-2}}{2}\right)(0.08314 \times 298) = 0.483$ bar

N_2O_4	$\rightleftharpoons$	$2NO_2$
0.119		0.483
x		-2x
0.119 + x		0.483 - 2x

$$K = 0.157 = \frac{(0.483 - 2x)^2}{(0.119 + x)}$$

$$0.01868 + 0.157x = 0.2334 - 1.932x + 4x^2$$

$$4x^2 - 2.089x + 0.2147 = 0$$

$$x = \frac{2.089 \pm \sqrt{(2.089)^2 - 4(4)(.2147)}}{8}$$

$$= \frac{2.089 \pm 0.929}{8}$$

$= 0.377$ or 0.145 only real answer

$$P_T = (0.119 + x) + (0.483 - 2x)$$

$$= 0.119 + 0.483 - 0.145$$

$$= 0.457$$

$$= 0.46 \text{ bar}$$

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6. Lactic acid, $CH_3CH(OH)COOH$, is a weak organic acid. Salts of this acid are called lactates and calcium lactate, $Ca(CH_3CH(OH)COO)_2$, can be used as a source of calcium. For simplicity represent calcium lactate as $Ca(Lac)_2$.

a) (1 point) The alkaline salt $Ca(Lac)_2$ dissociates completely to form Ca^{2+} and $[Lac]^-$ in aqueous solution. Complete the hydrolysis reaction for the lactate anion in aqueous solution:

$[Lac]^-(aq) + H_2O\ (l) \rightleftharpoons$ [Lac]H (aq) + OH^- (aq)

or HLac (aq) + OH^- (aq)

b) (1 point) The pH of a solution of 0.26 M $Ca(Lac)_2$ is found to be 8.4, determine the $[OH^-]$ of the solution.

pH = 8.4

pOH = 14 − 8.4 = 5.6

$[OH^-] = 10^{-5.6} = 2.51 \times 10^{-6}$ M

c) (4 points) determine K_a for lactic acid.

$[Lac]^- + H_2O \rightleftharpoons OH^- + HLac$

2(.26) — 2.51×10^{-6} 2.51×10^{-6}

$$Kb = \frac{(2.51\times10^{-6})^2}{2(.26)} = \frac{[OH^-][HLac]}{[Lac]^-}$$

$= 1.21\times10^{-11}$

$Ka = Kw/Kb = 10^{-14}/1.21\times10^{-11} = 8.25\times10^{-4}$

$= 8.3\times10^{-4}$

Question	
1	/5
2	/6
3	/7
4	/10
5	/8
6	/6
Total	/42

BONUS: What is a chemist's favourite thing to do with a pumpkin?

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a) (1 point) Balance the chemical reaction:

$$CH_3OH\ (g) \rightleftharpoons CO\ (g) + 2\ H_2(g)$$

b) (1 point) Write the expression for the equilibrium constant

$$K = \frac{P_{H_2}^2 P_{CO}}{P_{CH_3OH}}$$

c) (4 points) A 4.72 g sample of methanol is placed in an empty 1.00 L flask and heated to 250 °C. After the system has reached equilibrium, a tiny hole is drilled in the side of the flask allowing gaseous compounds to effuse out of the flask. Measurements of the effusing gas show that it contains 33.0 times as much $H_2(g)$ as $CH_3OH(g)$. Determine the equilibrium constant, K, for this reaction.

CH_3OH $M = 32$ g/mol 4.72g/32 = 0.1475 moles.

T = 250°C = 523K

$P = \frac{n}{V}RT = .1475(523)(.08314) = 6.41$ bar

$CH_3OH \rightleftharpoons CO + 2H_2$

6.41

−x +x 2x

6.41−x x 2x

0.365 6.04 12.08

$2x = 33(6.41 - x)$

211.53 − 33x

35x = 211.53

x = 6.04

$$K = \frac{(6.04)(12.08)^2}{.365} = 2.4 \times 10^3$$

d) (2 points) What the mole fraction and partial pressure of the methanol in the vessel at equilibrium?

$P_T = 12.08 + 6.04 + .37 = 18.49$

$P_{CH_3OH} = 0.37$

$$X_{CH_3OH} = \frac{P_{CH_3OH}}{P_T} = 0.02$$

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