Surname :________________Given name :________________________________

Student number:_________________________

Chemistry 1311D
Test 2 V1
November 19, 2013
80 minutes You may remove last 2 pages

Question	Maximum Marks	
1	2	
2	7	
3	8	
4	5	
5	6	
6	8	
7	6	
Total	42	

1. **(2 points)** The Claus process, which is used to remove sulfur found as sulfur dioxide in petroleum, is based on the reaction:

$$2H_2S(g) + SO_2(g) \rightleftharpoons 3S(s) + 2H_2O(g).$$

Assume temperature and volume are constant unless otherwise specified and considering each change separately; state the effect (increase, decrease, no change) that the change has on the original equilibrium values of the quantity specified in the second column.

Change	Quantity	Effect
Add S	Amount H_2O	No effect
Add H_2S	Amount SO_2	Reduce SO_2
Remove SO_2	Amount S	Decrease S
Add SO_2	Value of K	No effect

2. The following rate data were collected for the reaction:

$$2A(g) + 2B(b) + C(g) \rightarrow 3G(g) + 4F(g)$$

Initial concentration (mol L^{-1})

Experiment	$[A]_o$ moles L^{-1}	$[B]_o$ moles L^{-1}	$[C]_o$ moles L^{-1}	Initial rate (Moles of G) $L^{-1}s^{-1}$
1	10×10^{-3}	100×10^{-3}	700×10^{-3}	2.0×10^{-3}
2	20×10^{-3}	100×10^{-3}	300×10^{-3}	4.0×10^{-3}
3	20×10^{-3}	200×10^{-3}	200×10^{-3}	16×10^{-3}
4	10×10^{-3}	100×10^{-3}	400×10^{-3}	2.0×10^{-3}
5	4.62	0.177×10^{-3}	12.4×10^{-3}	?

a) **(4 points)** What is the order for each reactant and the order overall? (Show your work!)

Expts 1 & 4

$[A_o]$ unchanged $[B]_o$ unchange

$\frac{R_1}{R_4} = \frac{[C_o]_1^x}{[C_o]_2^x}$; $\frac{2\times10^{-3}}{2\times10^{-3}} = \left(\frac{700\times10^{-3}}{400\times10^{-3}}\right)^x$; $1 = \left(\frac{7}{4}\right)^x$ $x = 0$; 0th order in [C]

Expt 1 & 2

[C] – immaterial [B] constant

$\frac{R_1}{R_2} = \frac{[A_o]_1^x}{[A_o]_2^x}$; $\frac{2\times10^{-3}}{4\times10^{-3}} = \left(\frac{10\times10^{-3}}{20\times10^{-3}}\right)^x$; $\frac{1}{2} = \left(\frac{1}{2}\right)^x$ $x = 1$; 1st order in [A]

Expt 2 & 3

[A] unchanged [C] doesn't mater

$\frac{R_2}{R_3} = \frac{[B_o]_2^x}{[B_o]_3^x}$; $\frac{4\times10^{-3}}{16\times10^{-3}} = \left(\frac{100\times10^{-3}}{200\times10^{-3}}\right)^x$ $\frac{1}{4} = \left(\frac{1}{2}\right)^x$ $x = 2$; 2nd order in [B]

Overall 2+1 = 3rd order

b) **(1 point)** Write the rate law for the reaction.

$R = k[A][B]^2 = \frac{1}{3}\frac{\Delta G}{\Delta t}$

c) **(1 points)** Determine the reaction rate constant.

Expt 1 $\frac{1}{3}(2\times10^{-3}) = k[10\times10^{-3}][100\times10^{-3}]^2$

$6.667\times10^{-4} = k\ 1.0\times10^{-4}$

$k = 6.67$ mole^{-2} L^{-2} s^{-1} or. 20

d) **(1 points)** Predict the initial rate for experiment 5.

$R = k[A][B]^2$

$= 6.67[4.62][0.177\times10^{-3}]^2$

$= 9.65\times10^{-7}$ Moles/sL

or 2.89×10^{-6} $\frac{\text{Moles G}}{\text{L s}}$.

3. The gas phosphine, PH_3, decomposes by the reaction:

$$4PH_3(g) \rightarrow P_4(s) + 6H_2(g).$$

In an experiment, pure phosphine was placed in a rigid, sealed 1.00 L flask at 0.64 bar and 298 K. After equilibrium was attained, the total pressure in the flask was found to be 0.93 bar.

a) **(4 points)** Calculate equilibrium partial pressures of $H_2(g)$ and $PH_3(g)$.

	$4PH_3 \longrightarrow$	P_4	$+ \; 6H_2$
i	0.64	—	—
c	$-4x$		$6x$
e	$0.64-4x$		$6x$

$$P_T(eq) = 0.93 \text{ bar} = 0.64-4x + 6x = 0.64+2x$$

$$= P_{PH_3} + P_{H_2}$$

$$0.29 = 2x$$

$$x = 0.145$$

$$P_{H_2} = 6(0.145) \text{ bar} = 0.87 \text{ bar}$$

$$P_{PH_3} = .64 - 4(0.145) = 0.06 \text{ bar}$$

b) **(2 points)** Calculate the mass (in grams) of phosphorous once equilibrium was reached.

$$n_{P_4} \cong n_{H_2} \times \frac{1P_4}{6H_2} = 3.51 \times 10^{-2} \text{ moles} \times \frac{1}{6} = 5.85 \times 10^{-3} \text{ moles}$$

$$n_{H_2} = \frac{PV}{RT} = \frac{0.87 \text{bar} (1L)}{0.08314\ (298)} = 3.51 \times 10^{-2} \text{ moles}$$

$$\text{mass } P_4 = M_{P_4} n_{P_4} = 4(30.97)(5.85 \times 10^{-3} \text{ moles}) = 0.725 g$$

c) **(2 points)** What is K_c for this reaction?

$$K_p = \frac{P_{H_2}^6}{P_{PH_3}^4} = \frac{(0.87)^6}{0.06^4} = 3.3459 \times 10^4$$

K_c:

$$K_p = K_c (RT)^{\Delta n}$$

$$K_c = \frac{K_p}{(RT)^{\Delta n}} = \frac{3.3459 \times 10^4}{(.08314 \times 298)^{6-4}} = 54.5$$

d) **(4 points)** Given $\Delta_f H^\circ$ data below for phosphorus species, determine K , the equilibrium constant, for this reaction at 450 K.

$$4PH_3(g) \rightarrow P_4(s) + 6H_2(g)$$

Substance	P_4 (s, white)	P(g)	P(s, red)	P_2(g)	P_4(g)	PH_3(g)
$\Delta_f H^\circ$ (kJ/mol)	0	314.6	-17.6	144	58.9	5

$$\Delta_{rxn} H^\circ = \Delta_f H^\circ_{P_4(s)} + 6\,\Delta_f H^\circ_{H_2(g)} - 4\,\Delta_f H^\circ_{PH_3(g)}$$

$$= 0 + 6(0) - 4(5) = -20\text{ kJ}$$

$$\ln \frac{K_1}{K_2} = \frac{\Delta_{rxn} H^\circ}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln \frac{K(450)}{33459} = \frac{-20\times10^3\text{ J}}{8.314}\left(\frac{1}{298} - \frac{1}{450}\right) = -2.726$$

$$K(450) = 2.2\times10^3$$

$$K_c = 3.57$$

e) **(1 point)** A catalyst is added to the reaction mixture. What is the role of a catalyst and how will this affect the equilibrium concentrations?

Catalyst changes mechanism & speeds up reaction. It does <u>not</u> impact equilibrium concentrations & is <u>NOT</u> consumed.

4. A solution contains 0.64 M of dimethylammonium chloride, $(CH_3)_2NH_2Cl$. Dimethyl amine, $(CH_3)_2N$, has a K_b of 1.3×10^{-3},

a) **(2 points)** What happens when the solid dimethylammonium chloride, $(CH_3)_2NH_2Cl$ salt is added to water? Write all relevant chemical reations (Hint: dissolution and hydrolysis).

$$\underset{\text{soluble salt}}{(CH_3)_2NH_2Cl(aq)} \longrightarrow \underset{\text{weak acid}}{(CH_3)_2NH_2^+(aq)} + Cl^-(aq)$$

$$\underset{\text{Acid}}{(CH_3)_2NH_2^+(aq)} + H_2O(l) \rightleftharpoons H_3O^+(aq) + \underset{\text{base.}}{(CH_3)_2NH(aq)}$$

b) **(4 points)** Determine the equilibrium concentration of ALL species and the pH in an aqueous solution of 0.64 M $(CH_3)_2NH_2Cl$.

$$(CH_3)_2NH_2^+(aq) + H_2O(l) \rightleftharpoons H_3O^+(aq) + (CH_3)_2NH(aq)$$

$(CH_3)_2NH_2^+$	H_3O^+	$(CH_3)_2NH$
0.64M	–	–
$-x$	x	x
$0.64-x$	x	x

$$Ka = \frac{[H_3O^+][(CH_3)_2NH]}{[(CH_3)_2NH_2^+]} = \frac{x^2}{0.64-x}$$

$$= \frac{kw}{Kb} = \frac{10^{-14}}{1.3\times10^{-3}} = 7.69\times10^{-12}$$

small Ka, ∴ x small compared to 0.64

$$7.69\times10^{-12} = \frac{x^2}{.64}$$

$$x = 2.22\times10^{-6}\ M = [H_3O^+] = [(CH_3)_2NH]$$

$$[(CH_3)_2NH_2^+] = 0.64$$

pH = 5.65

$[(CH_3)_2NH_2^+]$ 0.64 M

$[H_3O^+] = [(CH_3)_2NH] = 2.2\times10^{-6}$ M

$[OH^-] = 4.5\times10^{-9}$ M

Bonus: What is the significance of the intermediate and the transition state species in chemical kinetics? Intermediates are molecules formed during 1 step of chemical mechanism and consumed in a subsequent step.

The transition state determines the magnitude of the activation energy — it is a particular molecular configuration that is required before reactants become products

5. a) **(3 points)** The K_a of formic acid, HCOOH, is 1.8×10^{-4}; determine the ratio of concentrations of the formate anion, $[HCOO^-]$ to formic acid, $[HCOOH]$ in a 1 L buffer solution which has a pH of 3.65.

pH = 3.65

$$pKa = -\log(1.8\times10^{-4}) = 3.74$$

$$pH = pKa + \log\frac{[HCOO^-]}{[HCOOH]}$$

$$3.65 = 3.74 + \log\frac{[HCOO^-]}{[HCOOH]}$$

$$-0.09 = \log\frac{[HCOO^-]}{[HCOOH]}$$

$$\frac{[HCOO^-]}{[HCOOH]} = 0.813$$

b) **(1 point)** 1.65 g of solid $Ca(OH)_2$ are added to the buffer solution, what happens to the pH (increase, decrease or stay the same)? Justify you answer.

pH will increase, you added a base, ∴ concentration of H_3O^+ will go down.

c) **(2 point)** Which buffer species reacts with $Ca(OH)_2$? Write the net ionic equation for this reaction. OH^- will react with the acid HCOOH

$$OH^-(aq) + HCOOH(aq) \longrightarrow H_2O(l) + HCOO^-(aq)$$

f) **(2 points)** What is $[HCOO^-]/[HCOOH]$ after addition of 1.65 g $Ca(OH)_2$ if the pH of 1L of the buffer solution changed by 0.05 units?

pH went from 3.65 to 3.70

$$pH = pKa + \log\frac{[HCOO^-]}{[HCOOH]}$$

$$3.70 = 3.74 + \log\frac{[HCOO^-]}{[HCOOH]}$$

$$-0.04 = \log\frac{[HCOO^-]}{[HCOOH]}$$

$$\frac{[HCOO^-]}{[HCOOH]} = 0.913$$

g) **(4 points) (Continued from previous page)** What were the original concentrations of HCOOH and $HCOO^-$ in the buffer (given a 0.05 unit change in pH after the addition of $Ca(OH)_2$)?

$$\frac{[B]_i}{[A]_i} = 0.813 = \frac{n_{Bi}}{n_{Ai}} \qquad n_{Bi} = 0.813\, n_{Ai}$$

$$\frac{[B]_F}{[A]_F} = 0.913 = \frac{n_{BF}}{n_{AF}} \qquad \begin{array}{l} n_{BF} = n_{Bi} + n_{OH^-} \text{ added} \\ n_{AF} = n_{Ai} - n_{OH^-} \text{ added} \end{array}$$

$$n_{OH^-} = n_{Ca(OH)_2} \times \frac{2OH^-}{1Ca(OH)_2} = \frac{\text{mass } Ca(OH)_2}{\mathcal{M}_{Ca(OH)_2}} \times \frac{2OH^-}{1\,Ca(OH)_2} = \frac{1.65g}{74.08g/mol} \times \frac{2}{1} = 0.0445$$

$$0.913 = \frac{n_{Bi} + 0.0445}{n_{Ai} - 0.0445} = \frac{0.813n_{Ai} + 0.0445}{n_{Ai} - 0.0445}$$

$$0.913n_{Ai} - 0.0406 = 0.813n_{Ai} + 0.0445$$

$$0.1\, n_{Ai} = 0.0851$$

$$n_{Ai} = 0.851 \text{ moles} \longrightarrow 0.85M \text{ in } HCOOH$$

$$n_{Bi} = (0.813)(0.851) = 0.692 \text{ moles} \longrightarrow 0.69M \text{ in } HCOO^-$$

6. **(2 points)** Complete the following acid/base reactions (paying particular attention to the arrow used and states of products) and, where appropriate, **identify acid/base conjugate pairs**:

a) $\underset{A}{(CH_3)_3NH^+ (aq)} + \underset{B}{H_2O (l)} \rightleftharpoons \underset{B}{(CH_3)_3N (aq)} + \underset{A}{H_3O^+ (aq)}$

b) $ClO_4^-(aq) + H_2O (l) \cancel{\longrightarrow}$ No rxn

c) $\underset{B}{HCOO^-(aq)} + \underset{A}{H_2O (l)} \rightleftharpoons \underset{A}{HCOOH (aq)} + \underset{B}{OH^- (aq)}$

d) $\underset{A}{HNO_2(aq)} + \underset{B}{NH_3 (aq)} \longrightarrow \underset{B}{NO_2^- (aq)} + \underset{A}{NH_4^+ (aq)}$