

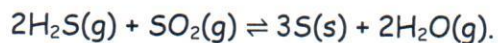
Surname : _____ Given name : _____

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	

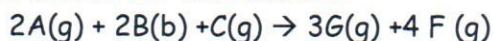
1. (2 points) The Claus process, which is used to remove sulfur found as sulfur dioxide in petroleum, is based on the reaction:



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:



Experiment	Initial concentration (mol L ⁻¹)			Initial rate (Moles of G) L ⁻¹ s ⁻¹
	[A] ₀ moles L ⁻¹	[B] ₀ moles L ⁻¹	[C] ₀ moles L ⁻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]₀ unchanged [B]₀ unchanged
 $\frac{R_1}{R_4} = \frac{[C]_1^x}{[C]_4^x}; \frac{2 \times 10^{-3}}{2 \times 10^{-3}} = \left(\frac{700 \times 10^{-3}}{400 \times 10^{-3}}\right)^x; 1 = \left(\frac{7}{4}\right)^x; x = 0; \text{0th order in } [C]$

Expt 1 & 2
 [C] - immaterial [B] constant
 $\frac{R_1}{R_2} = \frac{[A]_1^x}{[A]_2^x}; \frac{2 \times 10^{-3}}{4 \times 10^{-3}} = \left(\frac{10 \times 10^{-3}}{20 \times 10^{-3}}\right)^x; \frac{1}{2} = \left(\frac{1}{2}\right)^x; x = 1; \text{1st order in } [A]$

Expt 2 & 3
 [A] unchanged [C] doesn't matter
 $\frac{R_2}{R_3} = \frac{[B]_2^x}{[B]_3^x}; \frac{4 \times 10^{-3}}{16 \times 10^{-3}} = \left(\frac{100 \times 10^{-3}}{200 \times 10^{-3}}\right)^x; \frac{1}{4} = \left(\frac{1}{2}\right)^x; x = 2; \text{2nd order in } [B]$
 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 $\frac{1}{3}(2 \times 10^{-3}) = k [10 \times 10^{-3}] [100 \times 10^{-3}]^2$
 $6.6667 \times 10^{-4} = k 1.0 \times 10^{-4}$
 $k = 6.67 \text{ mole}^{-2} \text{ L}^{-2} \text{ s}^{-1}$ or 20

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

$$R = k [A] [B]^2 = 6.67 [4.62] [0.177 \times 10^{-3}]^2 = 9.65 \times 10^{-7} \text{ Moles/s L}$$

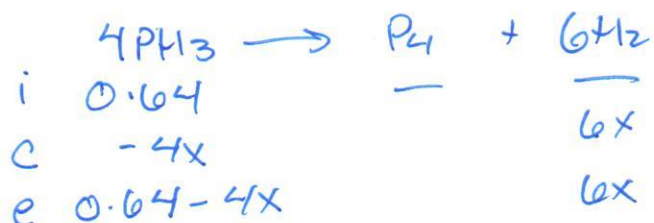
or $2.89 \times 10^{-4} \frac{\text{Moles G}}{\text{L s}}$

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



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 $\text{H}_2(\text{g})$ and $\text{PH}_3(\text{g})$.



$$\begin{aligned}
 P_T(\text{eg}) = 0.93 \text{ bar} &= 0.64 - 4x + 6x = 0.64 + 2x \\
 &= P_{\text{PH}_3} + P_{\text{H}_2} \\
 0.29 &= 2x \\
 x &= 0.145
 \end{aligned}$$

$$P_{\text{H}_2} = 6(0.145) \text{ bar} = 0.87 \text{ bar}$$

$$P_{\text{PH}_3} = 0.64 - 4(0.145) = 0.06 \text{ bar}$$

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

$$n_{\text{P}_4} = n_{\text{H}_2} \times \frac{1 P_4}{6 \text{H}_2} = 3.51 \times 10^{-2} \text{ moles} \times \frac{1}{6} = 5.85 \times 10^{-3} \text{ moles}$$

$$n_{\text{H}_2} = \frac{PV}{RT} = \frac{0.87 \text{ bar} (1 \text{ L})}{0.08314 (298)} = 3.51 \times 10^{-2} \text{ moles}$$

$$\text{mass P}_4 = M_{\text{P}_4} n_{\text{P}_4} = 4(30.97)(5.85 \times 10^{-3} \text{ moles}) = 0.725 \text{ g}$$

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

$$K_P = \frac{P_{\text{H}_2}^6}{P_{\text{PH}_3}^4} = \frac{(0.87)^6}{(0.06)^4} = 3.3459 \times 10^4$$

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

$$K_c = \frac{K_P}{(RT)^{\Delta n}} = \frac{3.3459 \times 10^4}{(0.08314 \times 298)^{6-4}} = 54.5$$

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



Substance	$\text{P}_4(\text{s, white})$	$\text{P}(\text{g})$	$\text{P}(\text{s, red})$	$\text{P}_2(\text{g})$	$\text{P}_4(\text{g})$	$\text{PH}_3(\text{g})$
$\Delta_f H^\circ$ (kJ/mol)	0	314.6	-17.6	144	58.9	5

$$\begin{aligned} \Delta_{\text{rxn}} H^\circ &= \Delta_f H^\circ_{\text{P}_4(\text{s})} + 6 \Delta_f H^\circ_{\text{H}_2(\text{g})} - 4 \Delta_f H^\circ_{\text{PH}_3(\text{g})} \\ &= 0 + 6(0) - 4(5) = -20 \text{ kJ} \end{aligned}$$

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

$$\ln \frac{K(450)}{3459} = \frac{-20 \times 10^3 \text{ J}}{8.314} \left(\frac{1}{298} - \frac{1}{450} \right) = -2.726$$

$$K(450) = 2.2 \times 10^3$$

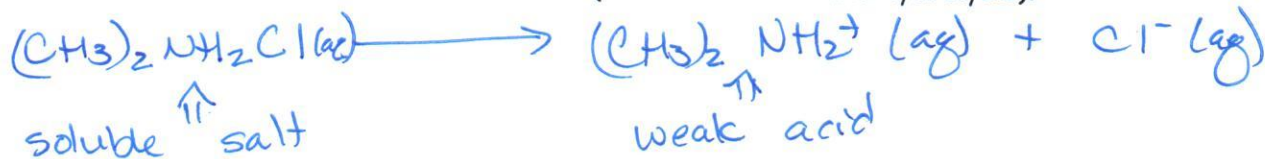
$$K_c = 3.57$$

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?

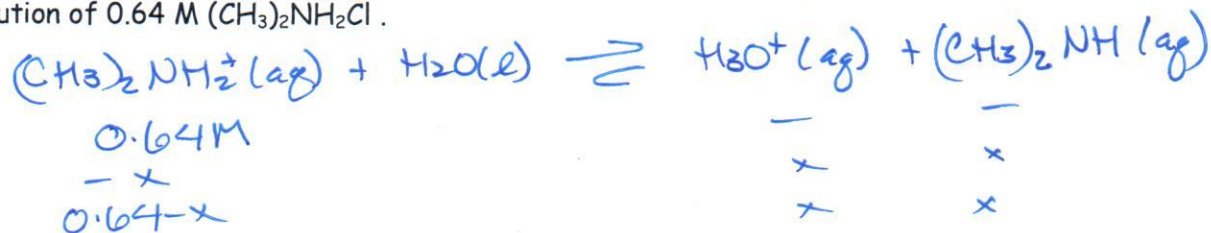
Catalyst changes mechanism & speeds up reaction. It does not impact equilibrium concentrations & is NOT consumed.

4. A solution contains 0.64 M of dimethylammonium chloride, $(\text{CH}_3)_2\text{NH}_2\text{Cl}$. Dimethyl amine, $(\text{CH}_3)_2\text{N}$, has a K_b of 1.3×10^{-3} ,

a) (2 points) What happens when the solid dimethylammonium chloride, $(\text{CH}_3)_2\text{NH}_2\text{Cl}$ salt is added to water? Write all relevant chemical reactions (Hint: dissolution and hydrolysis).



b) (4 points) Determine the equilibrium concentration of ALL species and the pH in an aqueous solution of 0.64 M $(\text{CH}_3)_2\text{NH}_2\text{Cl}$.



$$K_a = \frac{[\text{H}_3\text{O}^+][(\text{CH}_3)_2\text{NH}]}{[(\text{CH}_3)_2\text{NH}_2^+]} = \frac{x^2}{0.64 - x}$$

$$= \frac{K_w}{K_b} = \frac{10^{-14}}{1.3 \times 10^{-3}} = 7.69 \times 10^{-12} \quad \text{small } K_a, \therefore x \text{ small compared to } 0.64$$

$$7.69 \times 10^{-12} = \frac{x^2}{0.64}$$

$$x = 2.22 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+] = [(\text{CH}_3)_2\text{NH}]$$

$$[(\text{CH}_3)_2\text{NH}_2^+] = 0.64$$

$$\text{pH} = 5.65$$

$$[(\text{CH}_3)_2\text{NH}_2^+] = 0.64 \text{ M}$$

$$[\text{H}_3\text{O}^+] = [(\text{CH}_3)_2\text{NH}] = 2.2 \times 10^{-6} \text{ M}$$

$$[\text{OH}^-] = 4.5 \times 10^{-9} \text{ M}$$

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, $[\text{HCOO}^-]$ to formic acid, $[\text{HCOOH}]$ in a 1 L buffer solution which has a pH of 3.65.

$$\text{pH} = 3.65$$

$$\text{p}K_a = -\log(1.8 \times 10^{-4}) = 3.74$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$$

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

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

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

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

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

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



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

pH went from 3.65 to 3.70

$$\text{pH} = \text{p}K_a + \log \frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$$

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

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

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

