

Rogers F05

COURSE	*	NUMB	ER -	SECTION
	GENERAL CHEMISTRY II		·CHEM 206	/2 51
EXAMINATION	Final Examination	DATE	December 19, 2005	1900-2200
INSTRUCTOR	Dr. Cerrie ROGERS			
MATERIALS AL	LOWED: X NO		YES (PLEASE SPECIFY)	
CALCULATORS	S ALLOWED: NO	×	YES programmable co	alculators must be reset

Chem 206 --- GENERAL CHEMISTRY II

	 Non-programmable calculators are allowed to remove the periodic 	
:	 Non-programmable calculators are allowed 	owed, cell priories & electronic dictionaries are not.
•		awad: call phonos & clastronic dictionaries are not
		provided (use the backs of pages for rough work).
•	 Write your student ID number on <u>all</u> page 	
		cluding this page, information sheet & periodic table.
I	Instructions: PLEASE READ THI	IS PAGE WHILE WAITING TO START.
	STUDENT NUMBER:	SIGNATURE:
	LAST NAME: Marking Oche	ml FIRST NAME:

Mark breakdown:	Page 2.	/ 17
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	TOTAL:	/ 100 (MAXIMUM MARK = 104)

1. (__/ 17 marks) TRUE OR FALSE? Circle T or F to describe each of these statements.

1 mark each:

- T /(F) According to the first law of thermodynamics, a system's internal energy cannot change.
- T /F When a system is at equilibrium, there is no reaction occurring in either direction at the molecular level.
- F If a mixture is cloudy, it is more correct to describe it as a colloidal dispersion than as a solution.
- T IF If three reactions occur in sequence, the equilibrium constant for the overall reaction will be the same as the smallest of the three equilibrium constants.
- (1) / F Oil and water are immiscible because the hydrogen bonds between water molecules are much stronger than the dipole—induced-dipole interactions between water and oil molecules.
- T /F A catalyst increases the rate constant for a reaction by increasing the pre-exponential (also known as the frequency factor, A) for the reaction.
- T IF Half-life is useful for understanding radioactive substances, because the half-life of any first-order process (such as radioactive decay) depends on the initial concentration of decaying substance.

2 marks each:

- The activation energy for the reaction $A \rightarrow B$ is the same as the activation energy for the reaction $B \rightarrow A$, regardless of the difference in thermodynamic stability of the two substances A and B.
- T /F If a compound with a pK_a of 9.0 is placed into a solution with a pH of 7.4, the majority of the compound's molecules will be present in their conjugate base form.
- For a proposed mechanism to be described as "consistent with experiment", the experimentally observed rate law for the reaction must be the same as the expected rate law for the first step in the proposed mechanism.
- T /F A reaction mixture whose reaction quotient is less than the value of the reaction's equilibrium constant will be faster in the direction that leads to reactants, until equilibrium is reached.

(A) where B is too small proceeds find

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2. (_/4 marks) People often describe the reaction of an acid with a base as "neutralization".) In what ways is this accurate, and in what situations might this description be misleading?

accurate... Tharsh properties of acid + base are

(1) acids have lawpH bases have kigh pH, + react to gield less extreme pH,

3 strong acid + strong base yields salt + water, where the salt is comprised of species that have essentially no acidic/basic properties -> solution is neutral in pH after ixn.

ie xconjugate base of strong acid & (conjugate acid of strong base are each extremely weak + do not deprotonate or protonate water significantly.

3. (__/ 12 marks) Consider these two carboxylic acids:

a) (4 marks) Based on the structures of the two acids, which do you expect to be stronger? Explain.

Only difference: IH replaced by CI, and Cl has larger X than H. Acids are stronger if the bond to the S+H being attacked by an incoming base is more polar w(not necessarily weaker!). or, weaker conjugatebox

The cl in acid@ has a larger electronegativity than carbon, so the Cl acts as an electron-withdrawing group (inductive effect). This means the cl "pulls" on the electron density in the Cl-C bond; and this effect carries through the molecule's bonds + makes the o pull more strongly on the O-H bond's electron pair, which makes the H look more electron-poor (Lewis acidic). This enhances the of the or lone fair wed made closely the or the H and makes it more lattractive to the

incoming base (Lewis base), compared to in acid (1) that lacks this electron-withdrawing Cl. For more stable conjugase correlates to strunger acid

Similar arguments: conj. base of @ is more stable than O's due to inductive stabilization by Ew-cerpulling o's lone pair closery More stable lone pair viess basic

4

choice 1.0

explain

effect

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SF for (b) only (-035

ID#: marking schen D HA + H20 =

3. continued... units #025

b) (4 marks) Using the thermodynamic data in the table, calculate ΔG°_{nm} for the reaction of each of these acids with water at 25°C. Would these reactions become more or less product-favoured at higher temperatures? Why? calo Alloxn, Asrxn - lose 1

Thermodynamic data for the reaction of the acids with water, in aqueous solution at 25°C		
Acid	ΔH° _{rxn} (kJ/mol)	ΔS° _{rxn} (J/mol-K)
СН₃СООН	-0.57	-92.6
CICH₂COOH	-4.70	-70.8

05 AGrxn = AHorxn - TASixn mismatched units -0.5

For CH3 COOH:

ΔG° xn = -0.57 KJ - (298K) (-0.0926 KJ) = 27.02 KJ/mol reactantfavoured

1 For CH₂Cl CooH: W - (298 K) (-0.0708 KJ) = 16, 40 KJ/mol

slightly less reactant favoured.

Each reaction is entropically unfavourable (DS*xxx < 0), which means that at higher temperatures, the TDS term will become a larger positive number. Thus, as Tt, DGoxn will become more positively and the reactions will be even less productfavoured.

also accept le Châtelier's principle explanation but need to specify affect to get fell marks.

c) (4 marks) Using the thermodynamic data provided, calculate the acid dissociation constant, K_a, for each of the acids at 25°C. Which acid is stronger according to these K_a's? Explain briefly.

 $| For CH_{3}COOH : | K = e^{-(27.02 \text{ KJ/mol}) \cdot (1000 \text{ J/kJ})/((8.314 \text{ J/mol} \cdot \text{k})(298 \text{ k}))} = e^{-(10.91 \text{ J/mol}) \cdot (1000 \text{ J/kJ})/((8.314 \text{ J/mol} \cdot \text{k})(298 \text{ k}))} = e^{-(16.40 \text{ KJ/mol})(1900 \text{ J/kJ})/((8.314 \text{ J/mol} \cdot \text{k})(298))} = e^{-6.619} = 1.335 \times 10^{3}$ $| K = e^{-(16.40 \text{ KJ/mol})(1900 \text{ J/kJ})/((8.314 \text{ J/mol} \cdot \text{k})(298))} = e^{-6.619} = 1.335 \times 10^{3}$

These equilibrium constants are Ka's because they are derived from (0.5) the reaction of each acid with water: HA + H20 = A- + H30+

is more product favorured than that of CH3 COOH (although neither rxn is actually product favoured, and both acids are therefore "weak). Thus, CectzcooH is a stronger acid than CH3COOH.

4. (__/ 9 marks) A forensic chemist is given a white solid that is suspected of being pure cocaine ($C_{17}H_{21}NO_4$, molar mass 303.35 g/mol). She dissolves 1.22 \pm 0.01 g of the solid in 15.60 \pm 0.01 g of benzene, and finds that the freezing point is lowered by 1.32 \pm 0.04 °C. [The K_f of benzene is 5.12 °C·kg/mol.]

a) (5 marks) Use the experimental data to calculate the molar mass of the white solid.

b) (4 marks) Assuming that the <u>percent uncertainty</u> in the calculated molar mass is the same as the percent uncertainty in the temperature change, calculate the uncertainty in the molar mass. Could the chemist accurately state that the substance is cocaine? For example, is the uncertainty small enough to distinguish cocaine from codeine (C₁₈H₂₁NO₃, molar mass 299.36 g/mol)?

1.0 % uncertainty in $\Delta T = \frac{0.04 \, ^{\circ}\text{C}}{1.32 \, ^{\circ}\text{C}} \times 100\% = 3.03\% \text{ uncertainty (2SF.)}$

Thus: uncertainty in MM = 0.0303 × 303.3 = 9.2 4 /mol=uncertainty

Thus: (experimental MM = 303.3 ± 9.2 g/mol @R 303 ± 9. g/mol
(better)

The MM of codeine is 299.36 g/mol, which lies within the range of 294 - 312 g/mol determined via experiment for the white solid.

0.5 [Therefore: No, the chemist cannot be certain that the white solid is cocaine.

5. (_/ 12 marks) Chlorine dioxide (ClO₂) is a gas used as a disinfectant in municipal water-treatment plants. It dissolves in basic solution to produce the strong oxidizing agents ClO₃ and ClO₂.

 $2CIO_2(g) + 2OH^-(aq) \rightarrow CIO_3^-(aq) + CIO_2^-(aq) + H_2O(I)$

a) (5 marks) Using the kinetic data given in the table, determine the rate law for this reaction and the average value of its rate constant at 298 K.

Kin	etic data fo	r reaction	at 298 K
Run #	[CIO ₂] ₀ (mol/L)	[OH ⁻] ₀ (mol/L)	Initial rate (mol/L·s)
1	0.060	0.030	0.0248
2	0.020-3	0.030	0.00827;+3
3	0.020	0.090 x3	0.0247=x3

The rxn is first order wit each reactant:

[rate = k [ClO2]'[OH-]' (Cos if omit k)

run (1): $k = \frac{\text{rate}}{(\text{clo}_2]_0 [\text{OH}^-]_0} = \frac{0.0248 \text{ moV L·S}}{(0.060 \text{ mol/L})(0.030 \text{ mol/L})} = 13.8 (\text{mol/L})^{-1} \text{s}^{-1} \text{ K}$

Same for run @ 3 vr average = (13.8 + 13.8 + 13.7) - 3 W = 13.8 M-15-1

b) (2 marks) Does the balanced chemical equation correctly represent the mechanism of this reaction? Did you need to analyze kinetic data to make this conclusion? Why or why not?

Not the equation cannot represent the mechanism, because it suggests that the reaction would be quatermolecular. Four species colliding simultaneously is highly improbabled we can deduce this without a Ldoing any experiments - just common sense.

c) (2 marks) What can you deduce about the nature of the rate-limiting step of this reaction?

The experimental rate law is second order overally which suggests 2 that the rate-limiting step involves one molecule of cloz and ene molecule of our in a single-collision reaction (elementary d) (3 marks) If this reaction was performed at 298 K using an initial CIO₂ concentration of 0.015 M in a

solution with pH 11.75, what would be the initial reaction rate?

- rate = k [Clo2]. [OH-]. If pH=11.75, pOH=14-11.75 = 2.25 W = (13.8 M-15-1)(0.015 M)(5.62×10-3 M) (10H-]= 10-2.25 = 5.62×10-3 M) U rate = 1.7 × 10-3 M s-1 W > pH=-log[H30] 0.25

6. (__/ 10 marks) Imagine you are sitting in a hot sauna. The stove (heater) in the sauna has a layer of rocks on top of it, so that you can pour water onto them to create steam, which makes the sauna feel hotter.

a) (5 marks) Imagine you poured 225 mL of 45°C water onto the hot rocks, and it all evaporated to form steam. How much heat needed to be absorbed from the hot rocks? $[\Delta H^{\circ}_{vap}]$ of $H_2O(I)$ at $100^{\circ}C = 40.68$ kJ/mol; other data on information sheet.]

First: heat the from 45° -> 100°C V 2 steps... Second: Veraporate at 100°C -> steam (endothermic)

q = m C OT V (endothermic)

q = DH vap x # nv fdon't notice units

2.25 = (225 mL x 1.00 g) (4.184 J) (55°C)

1.75 = (40.68 kJ) (225g v m) (18,02 g mol-1) Veraporating 507.9 KJ (only 3 SF)
(: no decimal places) Quarming = 51.8 KI (only 2 SF...) (: no decimal places)

Total heat required = qwarming + qevaporating V = 51.8 + 507.9 KJ = 559.6 -: 9 = 560. KJ V (no decimal places) absorbed from rocks.

b) (5 marks) If 2.5% of the steam from part (a) condensed onto 1.25 m² of your skin (about half your body's surface area), by how many degrees would the temperature of your skin rise? Find DT. Assume that:

the heat was transferred quantitatively into the outer 1.0 mm of skin.

the density and heat capacity of skin are the same as water, since human cells are ~90% water.

Find mass of skin + use mc DT = q to find DT, where q is heat released by condensing Volume of skin warmed up = 1.25 m2 x (1.00 mm w) = 1.25 × 10-3 m3

Treating skin as if it were like water: convert m3 to mL to relate to mass $V = 1.25 \times 10^{-3} \text{ m}^3 \times \left(\frac{100 \text{ cm}}{\text{1 m V}}\right)^3 = 1.25 \times 10^{-3} \text{ m}^3 \times \frac{10^6 \text{ cm}^3 \text{ V}}{1.3}$ 2.5

and by definition, for H20, 1cm³ = 1mL (given)

w = 1250 mL × 1g m = 1250 g of H20"

Iml

Iml

2.5

9 = mCDT = 0T = 9 = 507900 J × 0.025 = 2.43°C = 2.4°C

(1250g)(4.184 J/g°C) (2sf)

Mete: 9 skin = 9 cendensing = 9 evaporating ier heat comes from condensation process releasing energy

(common sense for crazy answer ±0.28)

#6b) more detailed unit conversion:

Cleaner conversion from skin volume to cm³:

$$V = \left[1.25 \text{ m}^2 \times \frac{100 \text{ cm}}{1 \text{ m}} \right] \times \left[1.00 \text{ mm} \times \frac{1 \text{ cm}}{10 \text{ mm}} \right]$$

area of skin thickness

$$= \left[1.25 \text{ m}^2 \times \frac{100^2 \text{ cm}^2}{1 \text{ m}^2} \right] \times \left[0.100 \text{ cm} \right]$$

$$= \left(1.25 \times 10000 \text{ cm}^2 \right) \times 0.100 \text{ cm}$$

$$= \left[1.2500 \text{ cm}^2 \times 0.100 \text{ cm} \right]$$

$$= \left[1.2500 \text{ cm}^3 \times 0.100 \text{ cm} \right]$$

#7b) Alternate approach to finding pH of buffer solution after reaction with acid:

Using full equilibrium treatment:

$$H2A + H2O = HA^{-} + H3O^{+} \text{ (set of set of se$$

8. (__/ 13 marks) At high temperatures, a dynamic equilibrium exists between carbon monoxide, carbon dioxide and solid carbon:

 $C(s) + CO_2(g) \rightleftharpoons 2CO(g)$ $\Delta H^{\circ} = -172.5 \text{ kJ}$

At 850°C, the equilibrium constant K_c is 0.153.

a) (3 marks) What is the value of K_p ? okifdon't show work here $K = (0.1)^2$ Kp = (Pco) w but P=(n)RT

where here Drigases = 2-1=1

= (0.153) (0.08206 Ladm) (850+173 K

-. Kp = 14.1 W b) (6 marks) If solid carbon plus 1.50 atm of CO₂ are placed in a 1.00 L container, what would be the pressures of CO₂ and CO when equilibrium has been established at 850°C?

cannot use approximation : Kp > initial Put

(14.1) (1.50-x)=4x2 0=4x2+14.1x-21.15 V 1.5 calculations

13

 $\chi = -\frac{14.1 \pm \sqrt{(14.1)^2 - 4(4)(-21.15)}}{2(4)}$

=(-14,1 ± \(537.21 \) +8

Din Pco2 = 1 = 1.13 atm√ (other is negative) Pco2 = 1.50 - 1.13 = 0.37 atm√ PCD = 2(1.13) = 2.26 atm

= (-0.153 + J0.06325')+8

Some (0,01628-12) MIN +2 x XX where [coz] = P/RT = 0.01628 M

\$ Kc = 0.153 = [CO] = (2x) W

(0.153)(0.01628-x)=4x2

cannot use approximation x

VO = 4x2 +0.153x -0.002490

x = -0.153 ± \0.1532-4(4)(-0.002490)

Pco = 2(0.01231)x RT

c) (2 marks) How will the equilibrium pressure of CO change if the temperature is decreased? Why? The reaction is exothermical in the forward direction : wheat can be treated like a product. If thermal energy is decreased by decreasing temperature, the equilibrium will shift righter :. the co pressure (product) will INCREASE

d) (2 marks) How will the equilibrium pressure of CO change if some argon is added? Why?

Argon is an inert gasythat is not involved in the reaction. Adding Ar does not affect the partial pressures (concentrations) of the reactants/products so the reaction is unaffected x The PCO will not change

Full marks if specify that Ardres not react with coxporce! I supported!

9. (__/7 marks) Sodium fluoride is added to many municipal water supplies to reduce tooth decay.

Would a 0.00423 M solution of NaF feel much different than pure water? That is, would it have a neutral pH?

	To support your answer, show a full calculation of the pH of this solution. [The K _a of HF is 6.8×10 ⁻⁴ at 25°C.]
Ar.	Na F (s) dissolves to yield Nat and F in a 1:1 ratio (x)
此	chem. does not affect is a weak base, conjugate of weak acid, HF)
0,5	chem. Solution pH is optional weak acid, HF)
U,U	
IT	F + H20 = HF + OH W Where K6 = KW = 1 × 10 - 14
	F + H20 = HF + OH W Where Kb = Kw = 1 x10 14 W initial 0.00423M W 0 107 = OM Ka HF 6.8x10-4
1.5	F + H20 \rightleftharpoons HF + OH \checkmark Where $K_0 = \frac{K_W}{K_0 \text{ HF}} = \frac{1 \times 10^{-1} \text{ M}}{6.8 \times 10^{-4}}$ initial 0.00423 M \checkmark 0 $10^{-7} \approx 0 \text{ M}$ $+ \times$ $+ \times$ $+ \times$ $= 1.47 \times 10^{-11} \text{ M}$ egm $(0.00423 - \times) \text{ M} \checkmark \times \times$
(E	(0.00423-x) M × x x
	ezm (
	- wath!
10	Kb = 1.47 × 10" = [HF][OH] X
PST.	
	[147 ×10" = x2 W Because Ky < [F], by over 7
2	0.00423 - x orders of magnitude, it is a con the
	egm denominator.
1.5	10100 2
	$\chi = \sqrt{(1.47 \times 10^{-1})(0.00423)} = 56.22 \times 10^{-14}$
	7 J(I. 17 10 17
	x = 2.49 x 10-7 M V
	= [OH-]egm.
-	pH= 14-poHx = 14-(-log(2.49*x10-7 m))
1.5	$= 14 - (-\log(2.49 \times 10^{-8}))$
PH	
	. 11 5 7 42 × (2SF) = D(This solution would have a nearly
	pH = 7.40 v (25F) = teal of and would likely feel
	Comment and a star
0.	comment like regular water assessing like regular water ie: not sour or bitter lasting
	Q worth (e' not sound true to
_	This solution would have a nearly neutral pH and would likely feel comment like regular water assessing a worth like regular water ie: not sour or bitter lasting or slipping like base
-	7

Sorting

10. (_/ 10 marks) A saturated solution of an unidentified ionic salt with the formula MX2 exhibits an osmotic pressure of 74.4 mm Hg at 25°C. a) (3 marks) What is the total concentration of dissolved ions in this solution?

V = nRT where essentic pressure results from total solute particles N = T = $(74.4 \text{ mm Hg}) \times (\frac{1 \text{ atm u}}{760 \text{ mm Hg}}) = 0.09789 \text{ atm}$ in atm (0.08206 Leatim)(25 + 273 K)in atm $(N) = 4.00 \times 10^{-3} \text{ MeV}$ (3 Sf... extra digits: $4.003 \times 10^{-3} \text{ MeV}$)

total (one.)

b) (1 mark) Write a chemical equation that summarizes the processes occurring in this saturated solution.

M2 (ag) + 2 X (ag) eions in 12 lancessarily charges not necessarily stoich 0,5 MX2 (5) Langes att (ionic solid) includes 4 20? as shown but must balance (ions)

c) (6 marks) Assuming that MX2 is fully dissociated (i.e., no ion-pairing) in this saturated solution, what is wan't Hoff factor i = maximum the value of its K_{sp} ?

(x)=D i= 3 for MX2 can use[] directly XX Ksp = [M2+][X-]2

1) Use total ion concentration of saturated solution to determine individual for concentrations

Total (ion) = 4,003 x 10-3 M = [M2+] + [X-] VX and, ions formed in a 1 m2+: 2x ratio, sout x-] = 2[m2+]

Thuy: 4.003x10-3 M = (M2+) + 2 [M2+] ~ 4.003 x 10-3 M = 3 [M2+7 [M2+] = 1,334 x10-3 M V

So [X-] = 2[m2+] = 2.669×10-3 MV

2 Sub in to calculate value of Ksp:

Ksp = [1,334×10-3 M][2.669×10-3 M]²

Ksp = 9,50×10-9 V Sub in whatever 17's they got...

madarity...

Just for happy HOLIDAYS