Concordia
UNIVERSITY

COURSE	GENERAL CHEMISTRY II	NUMBER CHEM206	SECTION /4 01

EXAMINATION	Final Examination	DATE April 28, 2005	TIME 0900-1200	# OF PAGES

INSTRUCTOR	Dr. Cerrie ROGERS

MATERIALS ALLOWED:	[X] NO	[ ] YES (PLEASE SPECIFY)	periodic table and formula sheet provided
CALCULATORS ALLOWED:	[ ] NO	[X] YES	non-programmable calculators allowed

Chem 206 --- GENERAL CHEMISTRY II

MARKING SCHEME

LAST NAME: _____   FIRST NAME: _____

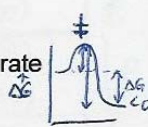STUDENT NUMBER: _____   SIGNATURE: _____

Instructions: PLEASE READ THIS PAGE WHILE WAITING TO START!

- *Make sure your exam has 13 pages, including this cover page & a periodic table.*
- *Write your student ID number on all pages.*
- *Write all answers legibly in the space provided (use the backs of pages for rough work).*
- *Non-programmable calculators are allowed; cell phones & electronic dictionaries are not.*
- *You may detach the periodic table and "potentially useful information" pages.*
- *SUGGESTION: Read ALL questions quickly BEFORE starting the exam.*

Mark breakdown: *approx. 15 min per page ⇨ 30 minutes extra to check your work.*

Page 2.	/ 13
Page 3.	/ 11
Page 4.	/ 9
Page 5.	/ 13
Page 6.	/ 8
Page 7.	/ 8
Page 8.	/ 11
Page 9.	/ 10
Page 10.	/ 10
Page 11.	/ 8

TOTAL: / 100   (MAXIMUM MARK = 101)

 # 1. (__/ **13 marks**) *one each* Circle the word(s) that correctly completes each of the following statements.

a) An object with a small heat capacity will feel warm to the touch after it absorbs a (LARGE / ⬭SMALL⬭) amount of heat.

b) A solution containing 0.500 M NaCl will freeze at a (⬭HIGHER⬭ / LOWER) temperature than a solution
$i=2$ ⟶ 1.00 M ions
containing 0.500 M $CaCl_2$. ⟹ 1.500 M ions $\Delta T_f = m \cdot K_f$ *depression* $\propto$ *ion conc*.
$i=3$

c) When a system is at equilibrium, the free energy of the system is at a (MAXIMUM / ⬭MINIMUM⬭).

d) When an ionic compound is observed to have a van't Hoff factor (i) less than we expect, we conclude that some ions remain (⬭PAIRED⬭ / UNPAIRED) when the substance dissolves.

e) If the equations for two reactions are added together, the equilibrium constants for the reactions must be (ADDED TO EACH OTHER / ⬭MULTIPLIED BY EACH OTHER⬭).

f) Based on the relative sizes of *smaller* nitrogen and *larger* phosphorus atoms, we would predict ammonia, NH_3, to be a (⬭STRONGER⬭ / WEAKER) base than phosphine, PH_3.

g) A solution of pH 12.0 would more likely contain (⬭0.01 M NaOH⬭ / 0.01 M NH_3).
⤷ pOH = 2.0 ∴ [OH⁻] = 10^{-2} M   *weak base*.

h) A reaction that is thermodynamically favourable in the forward direction will always have a larger rate constant in the (⬭FORWARD⬭ / REVERSE) direction.

i) To minimize indicator error during a titration, it is best to choose an indicator that changes colour at a pH very close to the (EQUILIBRIUM / ⬭EQUIVALENCE⬭) point of the titration.

j) When a chemical bond forms, energy is (⬭RELEASED⬭ / REQUIRED).

k) All Brønsted bases are also (LEWIS ACIDS / ⬭LEWIS BASES⬭).

l) A hydrogen bond can exist between a hydrogen atom bonded to nitrogen, oxygen or fluorine and any $\overset{\delta^+}{H}-\overset{\delta^-}{N}$ atom with a (⬭LONE PAIR⬭ / OPEN VALENCE).

m) Parts per million is a concentration unit based on the (⬭MASS⬭ / MOLES) of solute per million equivalent units of solvent.

13

Can discuss energy dispersal vs. matter dispersal in place of ΔG for complete marks

ID #: _marking scheme_

**# 2. (__/ 5 marks)** A scientist from the 19th century, Marcellin Berthoulet, stated that "all exothermic reactions are spontaneous". Is his statement correct? Explain. *[Evaluate the science, not the historical reference....]*

(NO) ✓

Spontaneous if $\Delta G < 0$ ✓ where $\Delta G = \Delta H - T\Delta S$ ✗ } *if all T-dep well explained but ΔG not specified ⇒ max 4*

Exothermic means $\Delta H < 0$ ✓ which is favourable but not sufficient to guarantee spontaneity. The entropic factor can outweigh the exothermicity if ΔS is negative ✓ and the temperature is sufficiently high ✓ that $|T\Delta S| > \Delta H$; in such cases, an exothermic reaction would not ✗ be spontaneous.

(5) worth 2

1 → any comments about entropically disfavoured rxns' spontaneity depending on relative magnitudes of ΔH & ΔS but without mentioning temp.

1.5 → if mention above plus T is important but not specifically

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 # 3. (__/ 15 marks) Sodium bicarbonate can decompose via the following reaction:

$$2\,NaHCO_3(s) \rightleftharpoons Na_2CO_3(s) + CO_2(g) + H_2O(g)$$

–1 if do backward Hess's law.
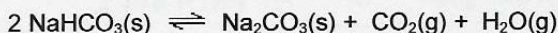
SUBSTANCE (at 298K)	ΔH°_f (kJ/mol)	S°_f (J/mol·K)
$NaHCO_3(s)$	2(-948)	2(102)
$Na_2CO_3(s)$	1(-1131)	1(136)
$CO_2(g)$	1(-394)	1(214)
$H_2O(g)$	1(-242)	1(189)

a) (3 marks) Calculate ΔH°_{rxn} and ΔS°_{rxn} for this reaction.

$$\Delta H^\circ_{rxn} = \sum n\Delta H^\circ_f\ products - \sum n\Delta H^\circ_f\ reactants$$

$$0.5 = [1(-1131)+1(-394)+1(-242)] - [2(-948)]\ kJ$$

$$= -1767 - (-1896)\ kJ$$

0.5 = $\boxed{+129\ kJ}$ for equation as written, at 298 K

1.5

-0.5 units, -0.5 SF

$$\Delta S^\circ_{rxn} = [1(136)+1(214)+1(189)] - [2(102)]\ J/K$$

$$= 539 - 204\ \ J/K$$

$\boxed{+335}\ J/K$ for equation as written, at 298 K

1.5

if scaled per 1 mole $NaHCO_3$, do not penalize (as long as clearly stated)

b) (3 marks) Calculate ΔG°_{rxn} for this reaction at 125°C (398K). *[Assume ΔH°_{rxn} and ΔS°_{rxn} do not change.]*

$$\Delta G^\circ_{rxn} = \Delta H^\circ_{rxn} - T\Delta S^\circ_{rxn}$$

$$= 129\ kJ - (398\ K)(0.335\ kJ/K)$$

$$= 129\ kJ - 133.3\ kJ$$

$$= -4.33\ kJ$$

$$\therefore \Delta G^\circ_{rxn} \doteq -4\ kJ$$

3

(6)

(1 SF)
(-0.5 SF more than 3)
(math error -0.5)

If forget to convert to kJ (-1)
⇒ $\Delta G = -133201\ kJ$!
$\doteq -133\,000\ kJ \cdots$

If scaled to 1 mol $NaHCO_3$
⇒ $\Delta G = -2.165\ kJ$
$= -2.17\ kJ\cdot mol$
full marks

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3. CONTINUED FROM PREVIOUS PAGE...

c) **(2 marks)** Calculate the value of the thermodynamic equilibrium constant K_p for this reaction at 125°C.
[Note: if you cannot do part (c), use a K_p value of 15.0 (which is not correct) to answer parts (d) and (e).]

2

$$\Delta G = -RT \ln K_{eq} \quad \text{where } K_{eq} = K_p \text{ when only gases involved}$$
$$\text{in the K expression} \quad \text{~not correct...}$$

✓ $K_p = e^{-\Delta G/RT}$ _units_ $\checkmark 0.25$ $R_{0.25}$ $T_{0.25}$

0.25 sign

$$= e^{-[(-4330 J)/(8.314 \ J\cdot mol^{-1} K^{-1})(398 K)]}$$

$$= e^{+1.308}$$

$$\therefore K_p = 3.70 \quad \checkmark \doteq 4 \quad (1 SF)$$

If scale to one mole NaHCO₃
$$K_p = \exp\left(-\frac{-2165 \ J/mol}{8.314 \ J/mol\cdot k \cdot 398K}\right)$$
$$= e^{+0.65}$$
$$= 1.92 \doteq 2$$

d) **(1 mark)** Is the reaction product-favoured or reactant-favoured at 125°C? How can you tell?

1

$$\underbrace{K > 1 \quad (\text{and } \Delta G < 0)}_{\text{either } \checkmark} \quad \therefore \text{ the reaction is product-favoured.}$$

$$\therefore K_p = P_{CO_2} \cdot P_{H_2O}$$

e) **(6 marks)** If solid $NaHCO_3$ and solid Na_2CO_3 are placed into a sealed container that initially contains 0.500 atm of $CO_2(g)$ and 0.100 atm of $H_2O(g)$, what will be the total pressure in the container when the system reaches equilibrium at 125°C?

6

$$2 NaHCO_3 {(S)} \rightleftharpoons Na_2CO_3{(S)} + CO_2{(g)} + H_2O{(g)}$$
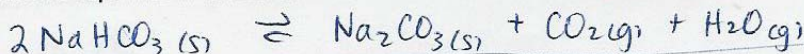
initial	present		present	0.500 atm	0.100 atm
Δ	(−2x)		(+x)	✓ + x	✓ + x
eqm	(−2x)		(+x)	0.500 + x	0.100 + x

} this 1 mark is lost if use wrong rxn or backwards

$$K_p = P_{CO_2} \cdot P_{H_2O} \checkmark \text{ because } Na_2CO_3 \text{ & } NaHCO_3 \text{ are solids}$$
$$\therefore \text{ do not contribute to pressure}$$

math error −0.5

$$3.700 = (0.500+x)(0.100+x)$$
$$3.700 = 0.0500 + 0.500x + 0.100x + x^2$$
$$\boxed{0 = x^2 + 0.600x - 3.65} \checkmark$$

✓ algebra

$$x = \frac{-0.600 \pm \sqrt{0.600^2 - 4(-3.65)}}{2}$$
$$= \frac{-0.600 \pm \sqrt{14.96}}{2}$$
$$= (-0.600 \pm 3.87) \div 2$$
$$= 1.635, \quad \cancel{-2.235} \checkmark$$
$$\therefore x = 1.64 \text{ atm} \checkmark$$

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$$\text{So, } P_{CO_2} = 0.500 + 1.64 \\ = 2.14 \text{ atm} \Big\} \checkmark$$

$$P_{H_2O} = 0.100 + 1.64 \\ = 1.74 \text{ atm} \Big\}$$

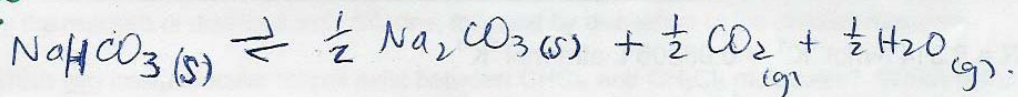$$\therefore P_{TOTAL} = P_{CO_2} + P_{H_2O} \checkmark$$
$$\boxed{P_{TOT} = 3.88 \text{ atm}} \checkmark$$
$$\boxed{P_{TOT} \doteq 4 \text{ atm}}$$

#3e) If use $K_p = 1.92$ (scaled to 1 mole $NaHCO_3$)

Full marks :

$$NaHCO_{3\,(S)} \rightleftharpoons \tfrac{1}{2} Na_2CO_{3\,(S)} + \tfrac{1}{2} CO_{2\,(g)} + \tfrac{1}{2} H_2O_{(g)}.$$

$$K_p = \sqrt{P_{CO_2}} \sqrt{P_{H_2O}}$$

$$0.500+x \qquad 0.100+x$$

$$\therefore K_p^2 = P_{CO_2} \cdot P_{H_2O}$$

$$3.69 = P_{CO_2} \cdot P_{H_2O}$$

∴ same result as if used other K_p & other eqn
(as it should be!)

Lose 1 mark :

$$2\,NaHCO_{3\,(S)} \rightleftharpoons Na_2CO_{3\,(S)} + CO_{2\,(g)} + H_2O_{(g)}$$
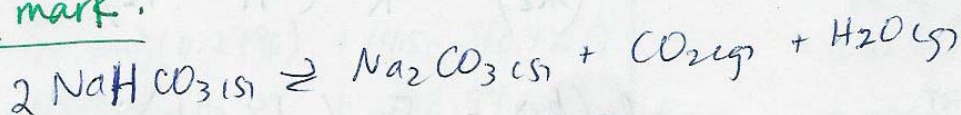
✗ $$K_p = P_{CO_2} \cdot P_{H_2O} = 1.92.$$

$$(0.500+x)(0.100+x) = 1.92$$

$$0.0500 + 0.600x + x^2 = 1.92$$

$$x^2 + 0.600x - 1.87 \quad = 0$$

$$x = \frac{-0.600 \pm \sqrt{0.600^2 - 4(1)(-1.87)}}{2}$$

$$= \frac{-0.600 \pm \sqrt{0.36 + 7.48}}{2}$$

$$= \left(-0.600 \pm \sqrt{7.84}\right) \div 2$$

$$= (-0.600 \pm 2.8) \div 2$$

$$x = 1.1 , \cancel{-1.7}$$

∴ $P_{CO_2} = 0.500 + 1.1 = 1.600$ atm

$P_{H_2O} = 0.100 + 1.1 = 1.200$ atm

$P_{TOTAL} = 2.800$ atm
$\doteq 2.80$ atm

$MM = 84.93 \, g/mol$ ID #: _marking scheme_

$\uparrow MM = 119.37 \, g/mol$

 # 4. (__/ 13 marks) Dichloromethane (CH_2Cl_2) and chloroform ($CHCl_3$) are industrially important solvents. They are prepared by the reaction of methane with chlorine, followed by distillation of the product mixture.

2

a) **(2 marks)** Which <u>two</u> intermolecular forces exist between $CHCl_3$ and CH_2Cl_2 molecules? Which is the stronger of these two forces?
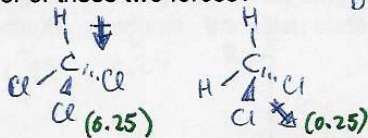
Both are somewhat polar (0.25)   0.75 (STRONGER)

$\therefore$ ① dipole-dipole interactions ← STRONGER

② London-dispersion forces 0.75   0.5

(structures drawn) (0.25)   (0.25)   NOT HYDROGEN BONDING.

b) **(6 marks)** At 25°C, the vapour pressure of pure $CHCl_3$ is 205 mm Hg, and the vapour pressure of pure CH_2Cl_2 is 415 mm Hg. What is the predicted vapour pressure (in mm Hg) at 25°C above a mixture of 15.0 g of $CHCl_3$ and 27.5 g of CH_2Cl_2?   [*Assume the mixture behaves as an ideal solution*]

6

$$\boxed{P_{TOT} = P_{CHCl_3} + P_{CH_2Cl_2}} \quad \checkmark \quad \boxed{P_{solv} = X_{solv} \, P^\circ_{solv}} \checkmark \quad \rightarrow \text{(Raoult's law)}$$

SOLUTION COMPOSITION:

$$= P^\circ_{CHCl_3} \cdot X_{CHCl_3} + P^\circ_{CH_2Cl_2} \cdot X_{CH_2Cl_2}$$

$$= (205 \, mm \, Hg) X_{CHCl_3} + (415 \, mm \, Hg) X_{CH_2Cl_2}$$

$$= (205 \, mmHg)\left(\frac{0.1257 \, mol}{0.4495 \, mol}\right) + (415 \, mm)\left(\frac{0.3238}{0.4495}\right)$$

$$= (205 \, mm)(0.2796) + (415 \, mm)(0.7204)$$

$$P_{TOT} = \underset{0.0754 \, atm}{57.32 \, mm \, Hg} \checkmark + \underset{0.393 \, atm}{298.97 \, mm \, Hg} \checkmark$$

$$\boxed{\therefore P_{TOT} = 356.29 \doteq 356 \, mm \, Hg} \checkmark \approx 0.468 \, atm$$

$\# \, n_{CHCl_3} = \dfrac{15.0 \, g}{119.37 \, g \cdot mol^{-1}}$
$= 0.1257 \, mol \checkmark$

$\# \, n_{CH_2Cl_2} = \dfrac{27.5 \, g}{84.93 \, g \, mol^{-1}}$
$= 0.3238 \, mol \checkmark$

$\# \, n_{TOTAL} = 0.4495 \, mol \checkmark$

If treated system as if only ONE was volatile: max <u>4</u>.

c) **(5 marks)** Using <u>kinetics arguments</u> (*i.e.*, discussion of rates...), explain how a volatile liquid comes to equilibrium with its vapour when it is placed into an <u>evacuated, sealed container</u>.

5

Initially: liquid $\therefore$ rate$_{evaporation}$ = k_{evap}[liquid] = large $\checkmark$

Zero vapour $\therefore$ rate$_{condensation}$ = k_{cond}(vapour) = 0 $\checkmark$

As liquid evaporates: sealed container $\checkmark$ vapour accumulates $\checkmark$ & begins to recondense when it collides with liquid's surface $\checkmark$

$\therefore$ rate of condensation $\uparrow$ while rate of evap'n $\downarrow$ somewhat $\checkmark$ $\checkmark$

Eventually: rates become equal for evaporation + condensation $\checkmark$ system reaches equilibrium (dynamic!) a constant pressure of vapour will then exist of liquid $\checkmark$
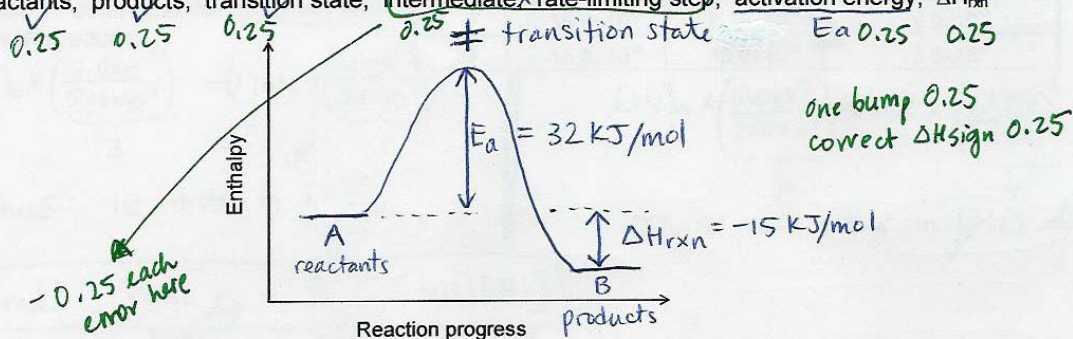
13

If rates of "rxn" presented, not evap/condensation: max 3

 # 5. (__/ 8 marks) A certain chemical reaction A → 2 B follows a <u>one-step</u> mechanism and has an activation energy of <u>32 kJ/mol</u>. The enthalpy change for the reaction is <u>-15 kJ per mole</u> of A reacted.

a) **(2 marks)** Draw an energy *vs.* reaction progress diagram that describes this reaction. Clearly label your diagram with any of the following labels (that apply) to this reaction:
    reactants, products, transition state, intermediate✗ rate-limiting step✗ activation energy, ΔH_{rxn} ✓

0.25   0.25   0.125   0.25 ‡ transition state   Ea 0.25   0.25

‡ transition state

$E_a = 32 \, KJ/mol$

one bump 0.25
correct ΔH sign 0.25

A
reactants

$\Delta H_{rxn} = -15 \, KJ/mol$

B
products

Enthalpy

Reaction progress

– 0.25 each error here

b) **(6 marks)** If you wanted to slow down this reaction by a factor of 1000 compared to its rate at room temperature (25°C), to what temperature should you cool the reaction mixture?   *[Assume the initial concentrations of reactants are the same at both temperatures and that the mechanism does not change.]*

<u>Given:</u> Rate at T_1 (25°C) = 1000 × Rate at T_2 (unknown)

$k_{T_1} [A]_o$ = 1000 $k_{T_2} [A]_o$

Since $[A]_o$ is same at both T and mechanism is same (Ea unchanged)

then $k_{T_1} = 1000 \, k_{T_2}$ ✓

<u>Use Arrhenius' equation:</u> $k = A e^{-Ea/RT}$ or $\boxed{\ln k = \ln A - Ea/RT}$ ✗

$\ln k_{T_1} = \ln A - \dfrac{Ea}{RT_1}$ and $\ln k_{T_2} = \ln A - \dfrac{Ea}{RT_2}$

Subtract these 2 equations:

$\ln k_{T_1} - \ln k_{T_2} = \ln A - \ln A - \dfrac{Ea}{RT_1} + \dfrac{Ea}{RT_2}$

silly math error –0.5
Ignore $\frac{Ea}{R}$ ∴ constant – 1.5

form error –1 | sign error: –0.5 → $\boxed{\ln\left(\dfrac{k_{T_1}}{k_{T_2}}\right) = -\dfrac{Ea}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)}$ ✓

but recall $k_{T_1} = 1000 \, k_{T_2}$
$Ea = 32000 \, J/mol$
$T_1 = 298 \, K$

$\ln\left(\dfrac{1000 \, k_{T_2}}{k_{T_2}}\right) = -\dfrac{Ea}{R}\left(\dfrac{1}{T_1} - \dfrac{1}{T_2}\right)$

⇒ $\dfrac{R \cdot \ln 1000}{-Ea} - \dfrac{1}{T_1} = \dfrac{-1}{T_2}$

⇒ $\left(\dfrac{8.314 \, J\,mol^{-1}K^{-1} \cdot 6.908}{-32000 \, J\,mol^{-1}}\right) - \dfrac{1}{298K} = \dfrac{-1}{T_2}$ ✗✗

–0.5 if wrong units   (-70°C)   ∴ $T_2 = 194 \, K$

 # 6. (__/ 8 marks) Initial rates data were collected for the reaction of nitric oxide and hydrogen at 1100 K:

$$2NO(g) + 2H_2(g) \rightarrow N_2(g) + 2H_2O(g)$$
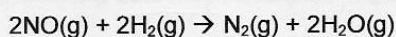
	Reactant Concentration (M)		Reaction rate (M/s)
Run	$[NO]_0$	$[H_2]_0$	$RATE_0$
1	5.00×10^{-3}	2.50×10^{-3}	3.0×10^{-3}
2	15.0×10^{-3}	2.50×10^{-3}	9.0×10^{-3}
3	15.0×10^{-3}	10.0×10^{-3}	3.6×10^{-2}

a) **(2 marks)** Use the initial rates data in the table to determine the observed rate law for this reaction.

2

$$[NO]_0 \times \left(\frac{15.0\times10^{-3}}{5.00\times10^{-3}}\right) \Rightarrow rate \times \left(\frac{9.0\times10^{-3}}{3.0\times10^{-3}}\right)$$

$\underbrace{\qquad}_{3} \qquad \underbrace{\qquad}_{3}$ ✓

Thus: 1st order in [NO]

$$[H_2]_0 \times \left(\frac{10.0\times10^{-3}}{2.50\times10^{-3}}\right) \Rightarrow rate \times \left(\frac{3.6\times10^{-2}}{9.0\times10^{-3}}\right)$$

$\underbrace{\qquad}_{4} \qquad \underbrace{\qquad}_{4}$

Thus: 1st order in [H_2] also. ✓

$$\boxed{Overall: \; rate_{obs} = k_{obs}\,[NO][H_2]}$$
$\quad\quad 0.25 \quad\quad 0.25 \quad 0.25 \quad 0.25$

b) **(2 marks)** Based on this experimentally observed rate law, does the balanced chemical equation for the reaction accurately summarize the mechanism of the reaction? Explain. ☐NO ✓

2

If the balanced reaction equation represented the mechanism, the rate law would have to be rate = $k\,[NO]^2[H_2]^2$. ✓ This would therefore need to be a single step reaction involving a collision between FOUR molecules (very improbable). Because the experimentally observed rate law is first order in each reactant, the rate limiting step is likely a bimolecular process. ✓ The mechanism must be more complex than the balanced equation suggests.

c) **(2 marks)** Calculate the average rate constant for this reaction at 1100 K.

2

Run 1: rate = $k_1\,[NO]_0[H_2]_0$

$$k = \frac{rate}{[NO]_0[H_2]_0}$$ ✓

$$= \frac{3.0\times10^{-3}\,Ms^{-1}}{(5.00\times10^{-3}M)(2.50\times10^{-3}M)}$$

$$= 240 \; M^{-1}s^{-1}$$ ✓ ✓

Similarly:

Run 2: $k = \frac{9.0\times10^{-3}\,Ms^{-1}}{(0.0150M)(0.0250M)} = 240 \; M^{-1}s^{-1}$

Run 3: $k = \frac{3.6\times10^{-2}\,Ms^{-1}}{(0.0150M)(0.0100M)} = 240 \; M^{-1}s^{-1}$ ✓

$$\boxed{\therefore \; average \; k = 240 \; M^{-1}s^{-1}}$$

d) **(2 marks)** Calculate the initial rate of this reaction at 1100 K if $[NO]_0 = [H_2]_0 = 8.0\times10^{-3}$ mol/L. Same T.

2
(-0.25 sf)

$$rate_0 = k\,[NO]_0[H_2]_0$$ ✓

$$= (240\,M^{-1}s^{-1})(0.0080M)(0.0080M)$$ ✓✓

$$= 0.01536 \; Ms^{-1}$$

$$\therefore rate_0 \doteq 1.5\times10^{-2} \; Ms^{-1}$$ ✓
$\qquad\qquad\qquad -0.25$ units

8

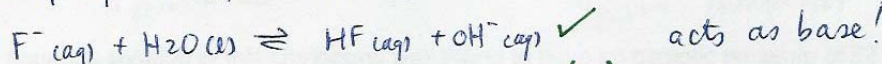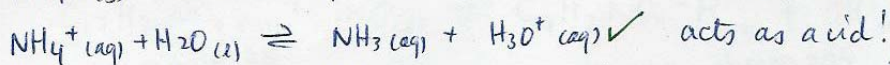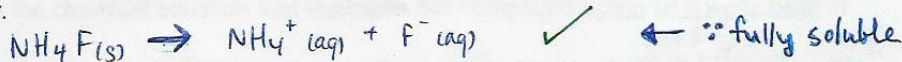**# 7.** (__/ 11 marks)   Imagine you are preparing a solution of ammonium fluoride, NH_4F, in water. The following data may be helpful: K_b of $NH_3 = 1.8 \times 10^{-5}$ K_a of HF $= 7.2 \times 10^{-4}$ $K_w = 1 \times 10^{-14}$

a) **(3 marks)**   Write balanced equations to illustrate all chemical processes that occur when $NH_4F_{(s)}$ dissolves in water.

3

$$NH_4F_{(s)} \rightarrow NH_4^+{}_{(aq)} + F^-{}_{(aq)}$$ ✓   ← ∴ fully soluble

$$NH_4^+{}_{(aq)} + H_2O_{(l)} \rightleftharpoons NH_3{}_{(aq)} + H_3O^+{}_{(aq)}$$ ✓ acts as acid!

$$F^-{}_{(aq)} + H_2O_{(l)} \rightleftharpoons HF_{(aq)} + OH^-{}_{(aq)}$$ ✓ acts as base!

$$(OR: NH_4^+{}_{(aq)} + F^-{}_{(aq)} \rightleftharpoons HF_{(aq)} + NH_3{}_{(aq)})$$ (✗) ← not a good choice actually.

b) **(4 marks)**   Will a solution of NH_4F be acidic, basic or neutral? EXPLAIN your conclusion (include any calculations that support your claims).

Both NH_4^+ and F^- will affect the pH of the solution. NH_4^+ is a <u>weak acid</u> ✗ while F^- is a <u>weak base</u> ✗ We must determine which will do<u>minate</u>.
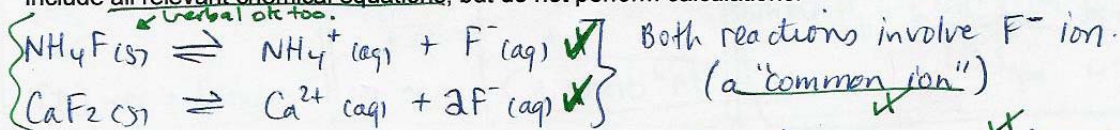
4

$$K_a\, NH_4^+ = \frac{K_w}{K_b\, NH_3} = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6 \times 10^{-10}\ ✗$$ } larger ∴ rxn more product- ✗ favoured.

$$\text{and } K_b\, F^- = \frac{K_w}{K_a\, HF} = \frac{1.0\times10^{-14}}{7.2\times10^{-4}} = 1.4 \times 10^{-11}\ ✗$$ ∴ will affect pH more.

In fact, any OH^- produced via reaction of F^- with water will be consumed by the H_3O^+ produced via reaction of NH_4^+ with water. Because the K_a of $NH_4^+ >$ ✗ K_b of F^-, more H_3O^+ will be present overall than OH^- So the overall solution will be <u>ACIDIC</u> ✗✗

note: HF vs NH_3 discussion max 2/4 remark. I for conclusion only based on HF vs NH_3

c) **(4 marks)**   Imagine you are preparing a <u>saturated solution</u> of NH_4F using water that already contains some calcium fluoride, CaF_2. Will the solubility of NH_4F be higher or <u>lower</u> than it is in pure water? Provide a written <u>explanation</u> of this phenomenon (note: naming the phenomenon is not enough). Include <u>all relevant chemical equations</u>, but do not perform calculations.
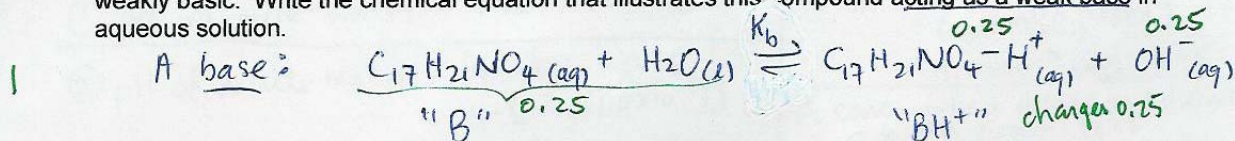
← verbal ok too.

4

{ $NH_4F_{(s)} \rightleftharpoons NH_4^+{}_{(aq)} + F^-{}_{(aq)}$ ✓ } Both reactions involve F^- ion.
{ $CaF_2{}_{(s)} \rightleftharpoons Ca^{2+}{}_{(aq)} + 2F^-{}_{(aq)}$ ✓ } (a "common ion") ✗

If CaF_2 is already present in the solution, some F^- ✗ <u>will already</u> be present. This is one of the products of dissolving $NH_4F_{(s)}$, therefore in order for the ion <u>product</u> $[F^-][NH_4^+]$ ✗ to equal K_{sp} for NH_4F, <u>not as much NH_4F will need to dis</u>~~solve~~ ✗✗ as in pure water. Thus, the <u>solubility of NH_4F will be lower</u> ✗✗ and in fact less NH_4F will be <u>able</u> to dissolve than in pure water. This is an example of the common ion effect.

for LeChâtelier explanation with no K_{sp} mentioned → remark 4 max.

11

 # 8. (__/ 10 marks) Imagine you have isolated an interesting new compound from a marine organism. You have determined that its formula is $C_{17}H_{21}NO_4$. You are now investigating its acid-base properties.

a) **(1 mark)** You notice that an aqueous solution of this compound turns litmus paper blue, and is therefore weakly basic. Write the chemical equation that illustrates this compound acting as a weak base in aqueous solution.

$\underline{A \ base}:$ $C_{17}H_{21}NO_4 (aq) + H_2O(l) \overset{K_b}{\rightleftharpoons} C_{17}H_{21}NO_4-H^+_{(aq)} + OH^-_{(aq)}$

"B" 0.25   0.25 "BH+" charges 0.25

b) **(3 marks)** A certain aqueous solution of this compound was found to have an osmotic pressure of 52.7 torr at 15°C. What was the total concentration of dissolved particles in this solution?

$\Pi V = nRT$ where $n = \underline{\text{total number of moles of dissolved particles (all solutes)}}$

$\boxed{\dfrac{n}{V} = \dfrac{\Pi}{RT}} = \dfrac{(52.7 \ torr)\left(\dfrac{1 \, atm}{760 \, torr}\right)}{(0.8206 \frac{L \cdot atm}{mol \cdot K})(288 \, K)}$

$\Pi = 0.0693 \ atm$

-0.25 SF/units
-0.5 silly math.

$= 0.002934 \ mol/L$

$\therefore \dfrac{n}{V} = 2.93 \times 10^{-3} \ M$
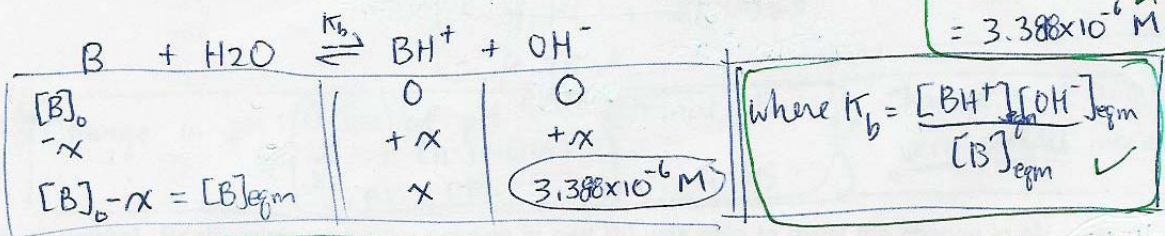$= 0.00293 M$

2 or 3 SF accepted (3 correct)

c) **(6 marks)** The solution analyzed in (b) was found to have a pH of 8.53. What is the compound's K_b?
[If you did not answer part (b), just explain what you would do].

To find K_b, need equilibrium concentrations of $[B], [BH^+], [OH^-]$

$\checkmark$ $\boxed{[particles] = 0.002934M = [B] + [BH^+] + [OH^-]}$ where $\boxed{[OH^-] = 10^{-pOH}}$

related via equilibrium!

$= 10^{-(14-8.53)}$
$= 10^{-5.47}$
$= 3.388 \times 10^{-6} \ M$

B	+ H₂O	$\overset{K_b}{\rightleftharpoons}$ BH⁺	+ OH⁻
$[B]_o$		0	0
$-x$		$+x$	$+x$
$[B]_o - x = [B]_{eqm}$		x	$3.388 \times 10^{-6} M$

where $K_b = \dfrac{[BH^+][OH^-]_{eqm}}{[B]_{eqm}}$ ✓

Thus, $\boxed{[OH^-]_{eqm} = [BH^+]_{eqm}} = x$, so only unknown is $[B]_o$.

$\boxed{[B]_{eqm} = [particles] - [BH^+]_{eqm} - [OH^-]_{eqm}}$

$= 0.002934 - (3.388 \times 10^{-6}) - (3.388 \times 10^{-6}) \ M$

$= 2.927 \times 10^{-3} \ M.$

$\Rightarrow K_b = \dfrac{[3.388 \times 10^{-6}][3.388 \times 10^{-6}]}{(2.927 \times 10^{-3})} \doteq 3.92 \times 10^{-9}$ typical weak base.

 # 9. (__/ 10 marks) This question involves demonstrating and then explaining the nature of buffers.

→ full marks if presented vs 0.10M NaOH (pH = 13) instead of H₂O.

a) **(2 marks)** Calculate the change in pH that occurs when 10.0 mL of 0.10 M NaOH is added to 90.0 mL of pure water. [$K_w = 1.0 \times 10^{-14}$].

2

① pH of pure water = 7.00 0.25

② pH of dilute NaOH = 14 - pOH   0.25
$$= 14 - [-\log(1.0 \times 10^{-2})]$$
$$= 14 - 2$$
$$= 12.00 \quad 0.25 \quad (2SF)$$

⟹ Change in pH: 12 - 7 = +5.00 units! 0.25

#$n_{OH^-} = C \times V$ 0.25
$$= (0.10M)(0.0100L)$$
$$= 1.0 \times 10^{-3} \text{ mol} \quad 0.25$$

∴ conc. when added to 90.0mL H₂O
$$C = \#n / V_{TOT} \quad 0.25$$
$$= 1.0 \times 10^{-3} \text{mol} / 0.1000L$$
$$= 1.0 \times 10^{-2} M \quad 0.25$$

b) **(6 marks)** What is the change in pH that occurs if 10.0 mL of 0.10 M NaOH is added to 90.0 mL of a solution containing 1.0 M CH₃COOH, and 1.0 M CH₃COONa? [The K_a of CH₃COOH is 1.8×10^{-5}].

a. buffer

✗ | CH₃COOH   +   NaOH $\xrightarrow{\text{completion}}$ CH₃COO⁻ + H₂O

6

initial #$n = C \times V$
$$= (1.0M)(0.0900L)$$
$$= 0.0900 \text{ mol} \quad 0.25$$

#$n_{OH^-} = (0.10M)(0.0100L)$
$$= 0.0010 \text{ mol} \quad 0.25$$

#$n = (1.0M)(0.0900L)$
$$= 0.0900 \text{ mol} \quad 0.25$$

max 1.5 if correct
max 0.75 if keep in conc. !!

after rxn -0.0010 mol $- 0.0010$ mol   + 0.0010 mol
#$n = 0.0890$ mol 0.25   #$n_{OH^-} = 0$ 0.25   #$n_{A^-} = 0.0910$ mol 0.25
HA

Buffer: $pH = pK_a + \log \dfrac{[A^-]}{[HA]}$ ✗ = $-\log(1.8 \times 10^{-5})$ ✗ + $\log \left[\dfrac{0.0910 \text{mol} / 0.100L}{0.0890 \text{mol} / 0.100L} \right]$ ✗ final conc ✗ final conc

-0.5SF

$$= 4.74 + 0.00965$$
$$= 4.75 \text{ ✗}$$

⟹ Change in pH: ① Initial pH   ② Final pH   Change = + 0.01 ✗
✗ 1:1 [A⁻]:[HA]   very slight increase
✗ ∴ pH = pK_a = 4.74   4.75

c) **(2 marks)** Briefly explain why the solution in part (b) was able to resist the change in pH whereas water could not.   ⟶ a BUFFER (no marks for saying buffer!!)

2

In part (b), both a weak acid + its conjugate base were present, in equal concentrations. When OH⁻ was added, the weak acid reacted with the ✗ OH⁻ ions, preventing the ✗ OH⁻ ions from disrupting the H₂O + H₂O ⇌ OH⁻ + H₃O⁺ equilibrium + changing the pH. When OH⁻ ions are added to pure water, ✗ they essentially remain in the solution (since water's conjugate acid is present only at 10⁻⁷ M, they do not get consumed), so the solution's pH changes dramatically.

10

 # 10. (__/ 8 marks) People develop kidney stones when insoluble compounds like calcium phosphate, $Ca_3(PO_4)_2$, precipitate out of their urine. [The K_{sp} of calcium phosphate is 1×10^{-25}].

a) **(1 mark)** Write a balanced chemical equation for the equilibrium that occurs in a saturated solution of calcium phosphate.
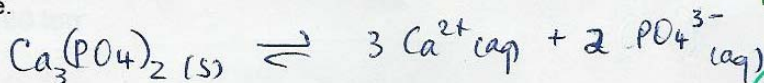
missing charges −0.5
balanced 0.5
phases 0.5
(no eqm ⇌ −0.5)

$$Ca_3(PO_4)_2 \, (s) \rightleftharpoons 3\, Ca^{2+} \, (aq) + 2\, PO_4^{3-} \, (aq)$$

b) **(1 mark)** Write an expression for the K_{sp} of $Ca_3(PO_4)_2$.

with solid (all else ok) 0.25
no solid 0.25
(no charges −0.5)
exponents 0.75

$$K_{sp} = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

c) **(6 marks)** Urine normally contains about 5.33 g/L of Ca^{2+} ions. What concentration of phosphate ions (in molarity) would cause calcium phosphate to begin precipitating from urine? Show calculations AND very briefly explain your answer.

→ equilibrium conc. $[Ca^{2+}] = 5.33$ g/L

→ requires $Q = K_{sp}$ for pptn to occur ✱

$$K_{sp} = 1 \times 10^{-25} = [Ca^{2+}]^3 [PO_4^{3-}]^2$$

to define limit of solubility

• known   solve for this
• need in molarity

$$[Ca^{2+}]_{eqm} = \frac{5.33\,g}{1\,L} \times \frac{1\,mol}{40.078\,g\,Ca} = 0.133\,mol/L$$

Thus: $1. \times 10^{-25} = (0.133\,M)^3 [PO_4^{3-}]^2$

$$[PO_4^{3-}]^2 = \frac{1 \times 10^{-25}}{(0.133)^3}$$

$$[PO_4^{3-}] = \sqrt{\frac{1 \times 10^{-25}}{(0.133)^3}} = \sqrt{\frac{1 \times 10^{-25}}{2.35 \times 10^{-3}}}$$

$$= \sqrt{4.25 \times 10^{-23}}$$

$$[PO_4^{3-}] = 6.52 \times 10^{-12}\,M$$

If the phosphate concentration exceeds ~ 7×10^{-12} M the solubility limit of $Ca_3(PO_4)_2$ will be exceeded + solid will precipitate. ✱

HAVE A GOOD SUMMER !