



Concordia
UNIVERSITY

Rogers

COURSE	GENERAL CHEMISTRY II	NUMBER	CHEM 206	SECTION	/4 01 & 52
EXAMINATION	Final Examination	DATE	April 20, 2006	TIME	1900-2200
INSTRUCTOR	Dr. Carrie ROGERS				

MATERIALS ALLOWED: ☒ NO ☐ YES (PLEASE SPECIFY)

CALCULATORS ALLOWED: ☐ NO ☒ YES programmable calculators must be reset

Chem 206 --- GENERAL CHEMISTRY II

LAST NAME: marking scheme 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.
- Read ALL questions quickly BEFORE starting the exam; do the "easy" questions first.
- Suggestion: spend <15 minutes per page to have 30 minutes left to check your work.

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

Page 2.	/	10	
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Page 5.	/	12	
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TOTAL:			/ 100 (MAXIMUM MARK = 105)

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1. (/ 10 marks) TRUE OR FALSE? Circle T or F to describe each of these statements.

T / ☒ F Chemical equilibrium is described as a dynamic state, because the concentrations of all species involved in the reaction change at equal rates at equilibrium.
 stay constant at eqm.

☒ T / F Most substances have higher solubility at higher temperatures, which suggests that dissolution is usually entropically favourable according to the system (where system = solute + solvent).
 *→ $\Delta G_{\text{dissolution}} < 0$ + becomes more favourable as $T \uparrow$.
 $\Delta S > 0$ $\Delta G = \Delta H - T\Delta S$ larger + when $T \uparrow$, so helps make $\Delta G < 0$...*

T / ☒ F If two reactions occur in sequence, the equilibrium constants for the reactions must be added together.
 multiplied.

☒ T / F During a chemical reaction that leads to an explosion, the system (i.e., the reactants &/or products) performs work on the surroundings.
 *releases gases $\therefore \Delta V > 0$ expands
 system pushes surroundings away \therefore performs work.*

T / ☒ F Hess's law can be used to calculate changes in thermodynamic functions that vary depending on the mechanism or path of the process.
 *state functions yes.
 \times path functions!*

T / ☒ F To minimize indicator error during the titration of an acid, it is best to choose an indicator that undergoes a dramatic colour change at a pH very close to the pK_a of the acid being titrated.
 NO. close to pH at equiv. point

T / ☒ F When an attractive interaction is broken, energy is released by the system.
 eg. a bond or intermolecular force

T / ☒ F Brønsted and Lowry derived an equation that helps explain why not all collisions between reactant molecules lead to reaction.
 → Arrhenius equation.

T / ☒ F A 1.0 M solution of sodium chloride (NaCl) would exert a lower osmotic pressure than a 1.0 M solution of glucose ($C_6H_{12}O_6$).
 *→ $i = 2$ $\therefore (\frac{n}{V})$ is larger $\approx 2.0M$
 $\hookrightarrow i = 1$ $(\frac{n}{V}) \approx 1.0M$
 $\pi = (\frac{n}{V})RT$ larger if $(\frac{n}{V})$ is larger*

T / ☒ F It is always possible to predict the relative solubilities of two ionic substances by comparing the values of their solubility product (K_{sp}) constants, without doing calculations.
 *no.
 only if have same ratio of ions!*

2. (/ 7 marks) The freezing point of a solution prepared by dissolving 1.00 mol of hydrogen fluoride (HF) in 500 g of water is -3.8°C , but the freezing point of a solution prepared by dissolving 1.00 mol of hydrogen chloride (HCl) in 500 g of water is -7.4°C . Explain. [Calculations are not required.]

Similarities: in H_2O , pure H_2O freezes at 0°C

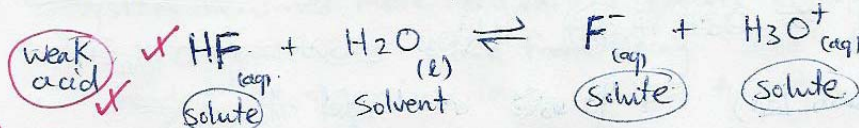
- both are solutions of an acid in water, same $[\text{HA}]_0$
- Solute interferes with freezing + facilitates melting
- so freezing point less than pure solvent ($T_f < 0.0^{\circ}\text{C}$)
- identity of solutes not important
- depression of f.p.

3.0
+
0.5
+
0.5

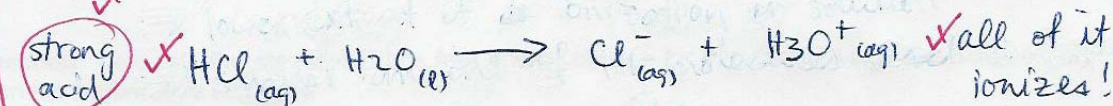
NOTE: $\Delta T_f = K_f m$
 \uparrow
 total solute particles

So if there are more dissolved solute particles, solution will freeze at lower temperature

- For acids: ionization/rxn with water leads to \uparrow # particles!



small fraction ionizes



all of it ionizes!

total 7

Thus: because HCl is a strong acid, it is fully converted to Cl^- and H_3O^+

so 1 mol HCl yields 2 mol solutes ($i=2$)

1.5 i 's

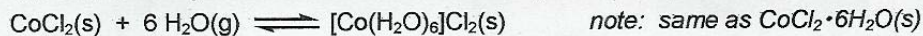
definition of i

because HF is a weak acid, 1 mol HF yields only slightly more than 1 mol solutes ($1 < i < 2$)

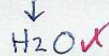
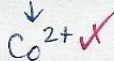
Thus: HCl solution contains more solutes, so freezes at a lower temperature than the HF solution of the same concentration.

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3. (/ 11 marks) A simple humidity sensor consists of a cardboard square that is blue in dry weather and red in humid weather. The colour change is due to the formation of a hydrated compound:



- a) (1 mark) The water molecules become bound to the cobalt ion via coordinate covalent bonds. Which of these two species is the Lewis acid, and which species is the Lewis base?



(will accept CoCl_2)

- b) (4 marks) Consider the reaction shown above. Briefly explain what causes this reaction to be:

- i. Exothermic ($\Delta H^\circ_{\text{rxn}} = -352 \text{ kJ} \cdot \text{mol}^{-1}$ at 25°C)

- forming 6 coordinate bonds between H_2O & $\text{Co}^{2+} \Rightarrow$ releases energy
- only needed to break 2 $\text{Cl}^- - \text{Co}^{2+}$ ionic bonds \Rightarrow requires energy
- but actually those 2 ionic interactions still exist in products
- \Rightarrow net formation of bonds \Rightarrow exothermic.

- ii. Entropically unfavourable ($\Delta S^\circ = -899 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$ at 25°C) — If misinterpret as ΔS_{univ} ... max 1.

- System becomes more organized (lower entropy)
- 6 H_2O molecules move from being "free" to being bonded to a metal ions \therefore less freedom of movement
- ie: 7 particles \rightarrow 1 particle
(really 10) (really 3)

- c) (4 marks) Calculate the standard Gibbs free energy change for this reaction on a hot summer day when the temperature is 35°C .

$$\begin{aligned} \Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= -352 \frac{\text{kJ}}{\text{mol}} - (273 + 35 \text{ K})(-0.899 \frac{\text{kJ}}{\text{mol} \cdot \text{K}}) \\ &= -352 \text{ kJ/mol} - (308 \text{ K})(-0.899 \text{ kJ/mol} \cdot \text{K}) \\ &= -352 \text{ kJ/mol} - (-276.89 \text{ kJ/mol}) \\ \therefore \Delta G^\circ &= -75. \text{ kJ/mol} \quad (\text{no decimal places for proper SF}) \end{aligned}$$

- d) (2 marks) Comment on the expected magnitude of the equilibrium constant for this reaction at this temperature.

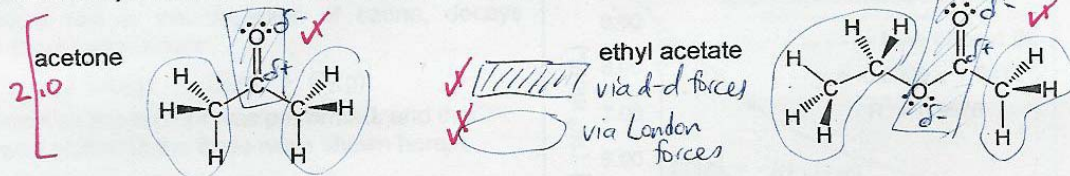
$\Delta G^\circ < 0 \therefore$ spontaneous forward, or product-favoured.
Thus, the equilibrium constant should be $\gg 1$ (LARGE).

or, $\Delta G^\circ = -RT \ln K, \quad K = e^{-\Delta G^\circ / RT}$

$$\begin{aligned} &= e^{-(-75000 \text{ J/mol}) / (8.314 \text{ J/mol} \cdot \text{K})(308 \text{ K})} \\ &= e^{+29.29} \\ \therefore K &= 5.2 \times 10^{12} \end{aligned}$$

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4. (/ 12 marks) Acetone, C_3H_6O , and ethyl acetate, $C_4H_8O_2$, are volatile liquids often used as solvents.



a) (5 marks) Name and describe two intermolecular forces that would exist between acetone and ethyl acetate molecules, and clearly indicate which parts of the molecules would be involved for each.

① dipole-dipole interactions ✓
3.0 - permanent dipole moments in both molecules, so δ^- and δ^+ areas of neighbouring molecules will interact via electrostatic attraction ✓

② London dispersion forces ✓
(any type of induced-dipole force)
- nonpolar regions of molecules interact with each other via electron clouds distorting each other + inducing transient dipoles ✓

(5)

0.5 for saying NO hydrogen bonds!

* no marks for H-bonding, even if well-described, since no $\delta^+ H$ in either molecule! (need F-H, N-H, O-H...)

b) (7 marks) Consider a mixture of 25.0 g acetone and 25.0 g ethyl acetate, which you might use as a cleaning fluid. If this mixture behaves ideally, what would be the vapour pressure above the solution at 30°C? The pure liquids' vapour pressures at 30°C are: $P^\circ_{\text{acetone}} = 285 \text{ mm Hg}$; $P^\circ_{\text{ethyl acetate}} = 118 \text{ mm Hg}$.

Ideal 2-component-volatile solution:

$$P = P_{\text{acetone}} + P_{\text{ethyl acetate}} \quad \text{Sum...}$$

$$= X_{\text{ace}} P^\circ_{\text{ace}} + X_{\text{eth}} P^\circ_{\text{eth}} \quad \text{Raoult's law}$$

$$= (0.6027)(285 \text{ mmHg}) + (0.3973)(118 \text{ mmHg})$$

$$= 171.77 \text{ mmHg}_{\text{acetone}} + 46.88 \text{ mmHg}_{\text{ethyl acetate}}$$

$$(0.2260 \text{ atm} + 0.06168 \text{ atm})$$

$$= 218.65 \text{ mmHg} \quad (0.2877 \text{ atm})$$

$$\Rightarrow P = 219 \text{ mmHg total vapour}$$

This total vapour pressure results from each component exerting the vapour pressure corresponding to its fractional composition of the mixture.

$$X_{\text{acetone}} = \frac{n_{\text{acetone}}}{n_{\text{acetone}} + n_{\text{ethyl acetate}}}$$

$$n_{\text{ace}} = \frac{25.0 \text{ g}}{58.08 \text{ g/mol}} = 0.4304 \text{ mol}$$

$$n_{\text{eth}} = \frac{25.0 \text{ g}}{88.11 \text{ g/mol}} = 0.2837 \text{ mol}$$

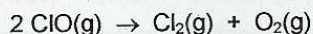
$$X_{\text{acetone}} = \frac{0.4304 \text{ mol}}{(0.4304 + 0.2837 \text{ mol})} = 0.6027$$

$$X_{\text{ethyl acetate}} = 1.000 - 0.6027 = 0.3973$$

Since only have 2 components, must add up to total (1).

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5. (1/8 marks) Chlorine oxide (ClO), which plays an important role in the depletion of ozone, decays rapidly at room temperature:



A single kinetics experiment was performed, and the data set was plotted in the three ways shown here.

- a) (2 marks) What is the rate law for this reaction?
How were you able to come to this conclusion?

2nd order in ClO: \checkmark
rate = $k [\text{ClO}]^2$ \checkmark

2 Based on plot of $\frac{1}{[\text{ClO}]}$ vs. time
being straight: \checkmark

- b) (1 mark) What is the value of the rate constant?
 \checkmark slope of line = $k = \frac{\text{rise}}{\text{run}} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}$

1 $\therefore k = \frac{2 \times 10^7}{0.25} \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1} \text{ (M}^{-1} \cdot \text{s}^{-1})$
 $\text{with } 0.75$

- c) (5 marks) How long would it take for the concentration of ClO to drop from $4.77 \times 10^{-6} \text{ M}$ to $1.0 \times 10^{-8} \text{ M}$?

Use (2nd order) integrated rate law. \checkmark
 $\frac{1}{[\text{ClO}]_t} = kt + \frac{1}{[\text{ClO}]_0}$ \checkmark for using right one!

$$kt = \frac{1}{[\text{ClO}]_t} - \frac{1}{[\text{ClO}]_0}$$

$$= \left(\frac{1}{1.0 \times 10^{-8} \text{ M}} \right) - \left(\frac{1}{4.77 \times 10^{-6} \text{ M}} \right)$$

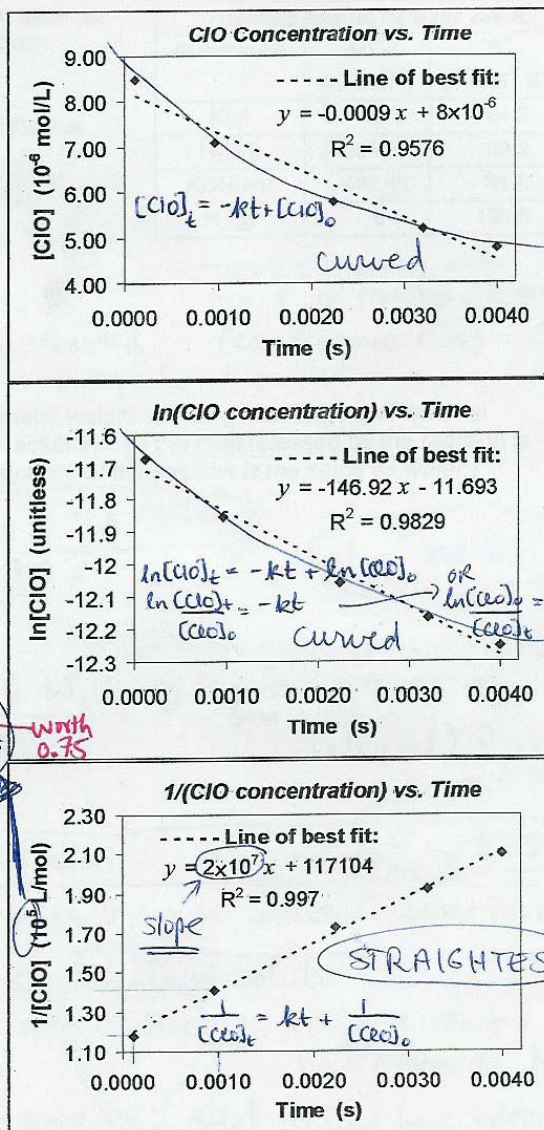
$$kt = 9.98 \times 10^7 \text{ M}^{-1}$$

$$t = \frac{9.98 \times 10^7 \text{ M}^{-1}}{2 \times 10^7 \text{ L} \cdot \text{mol}^{-1} \cdot \text{s}^{-1}} \checkmark \text{ for algebra!}$$

$$= 4.990 \text{ s}$$

$$\therefore t = 5 \text{ seconds} \checkmark \text{ units}$$

$$= 5 \text{ seconds (1 SF!)} \checkmark$$



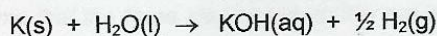
(very generous here!)

It would take only 5 seconds for the concentration to drop from $4.77 \times 10^{-6} \text{ M}$ to $1.0 \times 10^{-8} \text{ M}$.
... a very fast reaction...

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- # 6. (/ 10 marks) Potassium metal reacts violently with water to yield aqueous potassium hydroxide plus hydrogen gas:



- a) (2 marks) Calculate the standard enthalpy change for this reaction at 298 K.

$$\Delta H^\circ_{\text{rxn}} = \left[(1 \text{ mol}) \left(-482.4 \frac{\text{kJ}}{\text{mol}} \right) + \left(\frac{1}{2} \text{ mol} \right) \left(0 \frac{\text{kJ}}{\text{mol}} \right) \right] - \left[(1 \text{ mol}) \left(0 \frac{\text{kJ}}{\text{mol}} \right) + (1 \text{ mol}) \left(-285.8 \frac{\text{kJ}}{\text{mol}} \right) \right]$$

$$= -482.4 - (-285.8) \text{ kJ}$$

$$\therefore \Delta H^\circ_{\text{rxn}} = -196.6 \text{ kJ} \checkmark \text{ per mol K(s) reacted (exothermic rxn)}$$

-0.25 missing units
-0.5 if provide ΔS , ΔG also
-0.25 if given as per mol but species not specified.

- b) (8 marks) Imagine you drop a piece of potassium metal weighing 7.55 g into 400.0 g of water at 25.0°C. What would be the final temperature of the solution if all the heat released by the reaction is used to warm up the solution? [Assume the heat capacity of the solution is the same as water.]

Heat released by reaction: $q_{\text{rxn}} = n \times \Delta H^\circ_{\text{rxn}} \checkmark$

$$\# n_{\text{K(s)}} = \frac{7.55 \text{ g}}{39.098 \text{ g/mol}} \checkmark = 0.1931 \text{ mol} \checkmark$$

3.5 Every 1 mol K(s) \rightarrow $\frac{-196.6 \text{ kJ}}{0.1931 \text{ mol}} \checkmark \Rightarrow q_{\text{rxn}} = -37.96 \text{ kJ}$ (released) (should have 3 SF...)

Heat is all used to warm up solution: $q_{\text{soln}} = -q_{\text{rxn}} \checkmark = +37.96 \text{ kJ}$

5.5 $q_{\text{soln}} = m_{\text{soln}} C_{\text{soln}} \Delta T$ using $C = 4.184 \text{ J/g} \cdot \text{K}$ solution same as water

$$\Delta T = \frac{q_{\text{soln}}}{m C}$$

where $m = \text{total mass of solution}$

$$= 400.0 \text{ g H}_2\text{O} + 7.55 \text{ g K reacted but now present as K}^+\text{(aq)}$$

$$= 407.55 \text{ g total (should have 1 decimal...)}$$

\rightarrow ignoring H_2 bubbling out!
407.36 g if H_2 leaves.
(also ignoring mass of H_2O consumed)

$$\Delta T = \frac{+37.96 \text{ kJ} \times (1000 \frac{\text{J}}{\text{kJ}})}{(407.55 \text{ g})(4.184 \text{ J/g} \cdot \text{K})}$$

$$= +23.43 \text{ K} \checkmark \text{ increase in temperature}$$

$$= +23.43^\circ \text{C} \text{ increase (should have 3 SF only } \therefore 1 \text{ decimal...)}$$

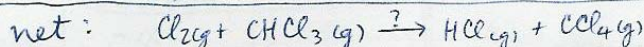
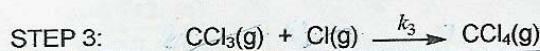
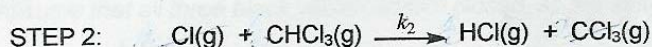
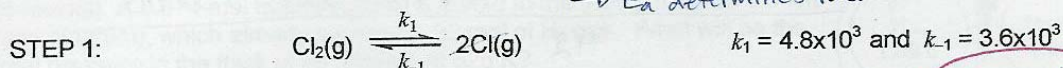
$$T_f = 25.0 + 23.43^\circ \text{C}$$

$$\Rightarrow T_f = 48.4^\circ \text{C} \checkmark \text{ The solution will heat up to } 48.4^\circ \text{C}$$

OR $47.3^\circ \text{C} / 320.5 \text{ K}$ within error...
-0.5 if say it gets colder!

Thermodynamic data for 298 K		
Substance	ΔH°_f (kJ·mol ⁻¹)	S°_f (J·mol ⁻¹ ·K ⁻¹)
K(s)	0	64.2
H ₂ O(l)	-285.8	69.9
KOH(aq)	-482.4	91.6
H ₂ (g)	0	130.6

7. (/ 8 marks) The following three-step mechanism has been proposed for the reaction of chlorine and chloroform. The numerical value (i.e., without units) of the rate constant for each step is provided. [Assume that the three steps have similar pre-exponential factors (frequency factors), A.] $k = Ae^{-E_a/RT}$
 $\hookrightarrow E_a$ determines rate...



Based on this mechanism, derive the predicted overall rate law for this reaction (include comments / explanation), and calculate the numerical value of the predicted overall rate constant.

The predicted rate law is based on the rate-limiting step:

rate_{RLS} = $k_2 [\text{Cl}][\text{CHCl}_3]$ ✓

RLS stuff (3)
remove (int) (1.5)

but Cl is an intermediate ✓
so its concentration must be expressed in terms of reactants ✓
(cannot have intermediates in obs. rate law) ✓

Intermediate Cl formed during step ①, which reaches eqm:

rate₁ = $k_1 [\text{Cl}_2] = k_{-1} [\text{Cl}]^2 = \text{rate}_{-1}$ when at eqm.

(0.5 for K_{eq} exp. for step 1)

1.5
find [Cl]
(1.5)

$\frac{k_1 [\text{Cl}_2]}{k_{-1}} = [\text{Cl}]^2$

$\left(\frac{k_1}{k_{-1}}\right)^{\frac{1}{2}} [\text{Cl}_2]^{\frac{1}{2}} = [\text{Cl}]$ ✓

Sub [Cl] expression into RLS rate law:

rate_{RLS} = $k_2 \left(\frac{k_1}{k_{-1}}\right)^{\frac{1}{2}} [\text{Cl}_2]^{\frac{1}{2}} [\text{CHCl}_3]$ ✓

k_{obs}
(1.0)

where $k_{\text{obs}} = (1.3 \times 10^{-2}) \left(\frac{4.8 \times 10^3}{3.6 \times 10^3}\right)^{\frac{1}{2}} = 1.5 \times 10^{-2}$

$\Rightarrow \text{rate}_{\text{predicted}} = 1.5 \times 10^{-2} [\text{Cl}_2]^{\frac{1}{2}} [\text{CHCl}_3]$

8

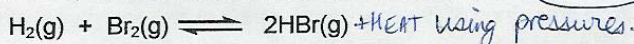
note: $\Delta n_{\text{gases}} = 0$, thus $(P_{\text{tot}})_0 = (P_{\text{tot}})_{\text{eqm}} !!!$

* if explained, get full marks!

* if NOT: max 3 for $(P_{\text{tot}})_{\text{initial}}$

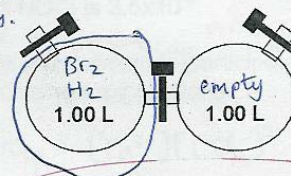
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8. (/ 15 marks) At 525 K, the exothermic reaction shown below has $K_p = 2.1 \times 10^2$ (data modified for this exam):



- a) (9 marks) A 0.974 mol quantity of Br_2 is added to the 1.00 L flask on the left (see diagram), which already contains 1.22 mol of H_2 gas. What will be the total pressure in the flask at equilibrium at 525 K?

Assume that all three black valves remain closed, so the volume is 1.00 L.



ICE table worth 3

	$\text{H}_2(\text{g})$	$+$	$\text{Br}_2(\text{g})$	\rightleftharpoons	$2\text{HBr}(\text{g})$
initial	52.56 atm		41.96 atm		0 atm
change	-x		-x		+2x
eqm	(52.56-x)		(41.96-x)		(2x)

$$K_p = 210 = \frac{(P_{\text{HBr}})^2}{P_{\text{H}_2} P_{\text{Br}_2}}$$

$$210 = \frac{(2x)^2}{(52.56-x)(41.96-x)}$$

approximation NOT valid.

Solving for x 3.5

$$52.5 = \frac{x^2}{2205 - 94.52x + x^2}$$

$$0 = 51.5x^2 - 4962.3x + 115762.5$$

$$x = 39.62 \text{ or } 56.74 \text{ atm (too large)}$$

$$x = 39.62 \text{ atm (should be 3sf, 1 decimal)}$$

$$PV = nRT$$

$$P = \left(\frac{n}{V}\right)RT \text{ with correct R.}$$

$$\text{initial } P_{\text{H}_2} = \left(\frac{1.22 \text{ mol}}{1.00 \text{ L}}\right) \left(\frac{0.08206 \text{ L atm}}{\text{mol K}}\right) (525 \text{ K})$$

$$= 52.56 \text{ atm}$$

$$\text{initial } P_{\text{Br}_2} = \left(\frac{0.974 \text{ mol}}{1.00 \text{ L}}\right) \left(\frac{0.08206 \text{ L atm}}{\text{mol K}}\right) (525 \text{ K})$$

$$= 41.96 \text{ atm}$$

$$\text{eqm } P_{\text{H}_2} = 52.56 - 39.62 = 12.94 \text{ atm}$$

$$\text{eqm } P_{\text{Br}_2} = 41.96 - 39.62 = 2.34 \text{ atm}$$

$$\text{eqm } P_{\text{HBr}} = 2(39.62) = 79.24 \text{ atm}$$

$$\text{Thus: } P_{\text{tot}} = 12.94 + 2.34 + 79.24 = 94.5 \text{ atm actual #...}$$

- b) (6 marks) Now consider disturbing this equilibrium mixture. How would the following changes affect the quantity of Br_2 present in the flask when equilibrium is re-established? Very briefly explain why.

Disturbance	Will the quantity of Br_2 increase, decrease or stay the same? Why?
Adding a substance that reacts with HBr	- react away HBr \rightarrow removes product - decreases rate of reverse rxn compared to forward rxn \Rightarrow net forward rxn (shifts right) $\therefore \text{Br}_2$ DECREASES
Decreasing the temperature to 400 K	- exothermic fwd rxn (can consider heat as product) - \downarrow temperature will affect endothermic direction more ie: slow down endothermic reverse rxn more \Rightarrow net forward rxn (shifts right) $\therefore \text{Br}_2$ DECREASES
Opening the valve that connects the two flasks	- increase volume $\Rightarrow \downarrow$ pressure - decreases concentration/partial P of all reactants/products - affects both directions equally since $\Delta n_{\text{gases}} = 0$ \therefore NO CHANGE

does not need to be rates... BUT must include some expl.

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Solution to the quadratic equation that I used on the previous page (both sides divided by 4 first):

$$\begin{aligned}
 x &= \frac{+4962.3 \pm \sqrt{24624421 - 206(115762.5)}}{103} \\
 &= \frac{4962.3 \pm \sqrt{777346}}{103} \\
 &= \frac{4962.3 \pm 881.7}{103} \\
 &= 56.74, 39.62 \text{ atm}
 \end{aligned}$$

Solution to the quadratic equation if you do not divide both sides by 4 first

$$\begin{aligned}
 463050 - 19849.2x + 210x^2 &= 4x^2 \\
 463050 - 19849.2x + 206x^2 &= 0 \\
 x &= \frac{+19849.2 \pm \sqrt{393990740 - 381553200}}{412} \\
 &= \frac{19849.2 \pm 3526.7}{412} \\
 &= 39.62, 56.74 \text{ atm}
 \end{aligned}$$

Solution to the whole problem if you use K_c rather than K_p :

Using K_c : $\Delta n_{\text{gases}} = 0$, $\therefore K_p = K_c = \frac{(2x)^2}{(1.22-x)(0.974-x)}$ ice = 1.5 here

$K_p = K_c(RT)^{\Delta n}$ ✓

$$\begin{aligned}
 (1.1883 - 2.194x + x^2) 210 &= 4x^2 \\
 (1.1883 - 2.194x + x^2) 52.5 &= x^2 \quad (\text{no approx}) \\
 51.5x^2 - 115.185x + 62.39 &= 0 \\
 x &= \frac{(115.185 \pm \sqrt{13267.6 - 12852.3})}{103} \\
 &= \frac{(115.185 \pm 20.38)}{103} \\
 &= 1.316, 0.920 \text{ M} \\
 &\text{too large} \quad \therefore x = 0.920 \text{ M}
 \end{aligned}$$

$p = \frac{nRT}{V}$ ✓

$[HBr]_{\text{eqm}} = 1.84 \text{ M} \Rightarrow 79.3 \text{ atm}$ ✓

$[H_2]_{\text{eqm}} = 0.30 \text{ M} \Rightarrow 12.9 \text{ atm}$ ✓

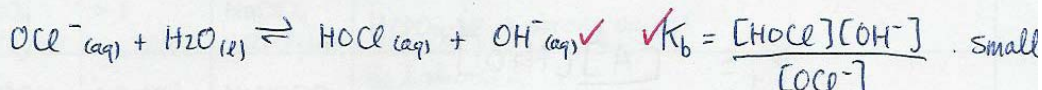
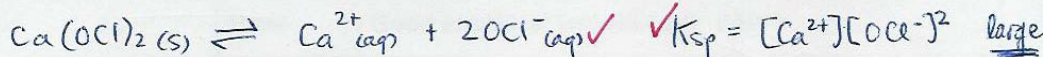
$[Br_2]_{\text{eqm}} = 0.054 \text{ M} \Rightarrow 2.33 \text{ atm}$ ✓

$P_{\text{tot}} = 94.6 \text{ atm}$ ✓

ID #: Rogers# 9. (/ 12 marks) Many home swimming pools are disinfected by adding calcium hypochlorite, $\text{Ca}(\text{OCl})_2$.Calcium hypochlorite is fully soluble in water, and the K_a of its conjugate acid HOCl is 3.5×10^{-8} .

total $\text{Ca}(\text{OCl})_2 + 2\text{H}_2\text{O} \rightleftharpoons \text{Ca}(\text{OH})_2 + 2\text{HOCl}$ not desired!

a) (4 marks) Write balanced chemical equations to illustrate the two equilibria this substance participates in when $\text{Ca}(\text{OCl})_2(s)$ is added to water. Include the appropriate equilibrium constant expressions.



missing phases: -0.25
not balanced: -0.5

missing label: -0.5
missing exponents: -0.5
including (s) or (l): -0.5

b) (8 marks) Calculate the pH of a pool with 0.100 M $\text{Ca}(\text{OCl})_2$. Is the water acidic, basic or neutral?

	$\text{OCl}^{-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HOCl}(\text{aq}) + \text{OH}^{-}(\text{aq})$	$\rightarrow 2\text{OCl}^{-} \rightarrow 1\text{Ca}(\text{OCl})_2$
initial	0.200 M \checkmark	0
change	-x	+x
eqm	0.200 - x \checkmark	x \checkmark

$[\text{OCl}^{-}]_0 = 0.200\text{M}$ \checkmark

$$K_b = \frac{K_w}{K_a} = \frac{[\text{HOCl}][\text{OH}^{-}]}{[\text{OCl}^{-}]} \quad \text{must match rxn eqn! (note: -1 if use HA)}$$

$$\frac{1 \times 10^{-14}}{3.5 \times 10^{-8}} = \frac{x^2}{0.200 - x}$$

$$2.86 \times 10^{-7} = \frac{x^2}{0.200 - x}$$

$$2.86 \times 10^{-7} \approx \frac{x^2}{0.200}$$

$$5.72 \times 10^{-8} = x^2$$

$$x = 2.39 \times 10^{-4} \text{ M} = [\text{OH}^{-}]_{\text{eqm}} \quad \text{(should have 2SF)}$$

$$\begin{aligned} \text{pH} &= 14 - \text{pOH} \checkmark \\ &= 14 - (-\log(1.69 \times 10^{-4})) \\ &= 14 - (+3.62) \end{aligned}$$

$\therefore \text{pH} = 10.37 \checkmark \Rightarrow$ The solution is basic (OCl^{-} is a weak base...).

K_b expr \rightarrow approx 1.5

note: $K_b \ll [\text{OCl}^{-}]_0 \checkmark$
 \therefore approximation is valid

if sub into H-H eqn, lose 0.5 only.

10. (/ 12 marks) Imagine you are preparing to perform an experiment on a pH-sensitive compound, and you need the solution to be kept at pH 8.75 throughout the experiment.

a) (4 marks) Evaluate each of the pairs below in terms of their usefulness in a buffer for your experiment.
 ① weak HA/A⁻ pair
 ② conjugate pair
 ③ pKa HA near 8.75 (±1)

PAIR	Acid	K _a	Base	Good choice or bad choice? WHY?
1	HClO ₄ 100.45 g/mol	> 1	NaClO ₄ 122.45 g/mol	Bad choice ✓ HClO ₄ is a strong acid ✓
2	HCOOH 46 g/mol	1.8 × 10 ⁻⁴	NaHCOO 68 g/mol	Bad choice ✓ pKa of HCOOH is too low (3.74) ✓
3	NH ₄ Cl 53.5 g/mol	5.6 × 10 ⁻¹⁰	NH ₃ 17 g/mol	Good choice ✓ (weak HA/A ⁻ conjugate pair) pKa of NH ₄ ⁺ is 9.25, close to 8.75 ✓
4	H ₂ O ₂ 34 g/mol	1.8 × 10 ⁻¹²	Na ₂ O ₂ 78 g/mol	Bad choice ✓ Not a conjugate pair ✓ Also pKa too high (✓)

b) (3 marks) For the best choice from part (a), what is the ratio of [acid form] to [base form] necessary to maintain a pH of 8.75?

$$pH = pK_a + \log \frac{[NH_3]}{[NH_4^+]}$$

$$\log \frac{[NH_3]}{[NH_4^+]} = pH - pK_a$$

$$= 8.75 - (-\log K_a)$$

$$= 8.75 - 9.25 = -0.50$$

$$\log \frac{[NH_3]}{[NH_4^+]} = -0.50$$

$$\frac{[NH_3]}{[NH_4^+]} = 10^{-0.50} = 0.316$$

$$\text{So, } \frac{[NH_4^+]}{[NH_3]} = \frac{3.16}{1.0} \text{ is required.}$$

ok if leave it as base: acid.

If use pKa = 9.2
 $\Rightarrow 1 \text{ HA} : 0.35 \text{ A}^-$
 2.8 : 1

If use pKa = 9.3
 $\Rightarrow 1 \text{ HA} : 0.28 \text{ A}^-$
 3.5 : 1

c) (5 marks) If the total initial buffer concentration ([acid]₀ + [base]₀) must be 0.75 M in your experiment, what mass of each compound should you dissolve in water in order to prepare 1.0 L of buffer? (Note that you would be able to make minor adjustments to your buffer's pH after preparing it.)

$$\textcircled{1} [NH_4^+] + [NH_3] = 0.75 \text{ M}$$

and

$$\textcircled{2} [NH_4^+] = 3.16 [NH_3] \text{ needed.}$$

So, sub ② into ①:

$$3.16 [NH_3] + [NH_3] = 0.75 \text{ M}$$

$$\therefore [NH_3] = 0.180 \text{ M}$$

$$\text{Thus } [NH_4^+] = 0.570 \text{ M}$$

For 1.0 L buffer: need 0.180 mol NH₃ and 0.570 mol NH₄Cl

$$\Rightarrow m_{NH_3} = (0.180 \text{ mol})(17.030 \text{ g/mol}) = 3.065 \text{ g} \approx 3.1 \text{ g NH}_3$$

$$m_{NH_4Cl} = (0.570 \text{ mol})(53.488 \text{ g/mol}) = 30.5 \text{ g} \approx 31 \text{ g NH}_4\text{Cl}$$

$$\begin{aligned} MM_{NH_3} &= 17.030 \text{ g/mol} \\ MM_{NH_4Cl} &= 53.488 \text{ g/mol} \end{aligned}$$

with 2.8 HA : 1 A⁻ $\Rightarrow 3.4 \text{ g NH}_3$
 29 g NH₄Cl
 with 3.5 HA : 1 A⁻ $\Rightarrow 2.8 \text{ g NH}_3$
 32 g NH₄Cl

-1 if only calc. for NH₄⁺!