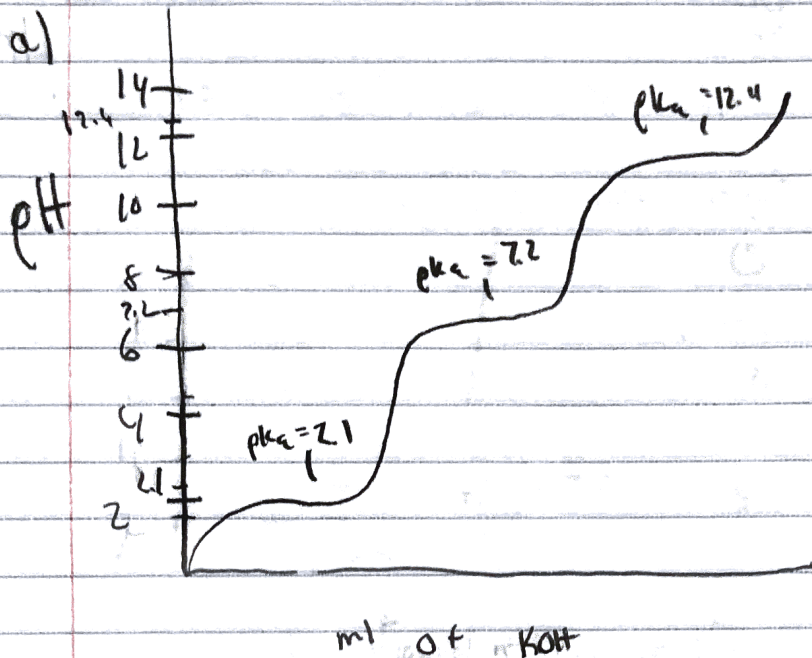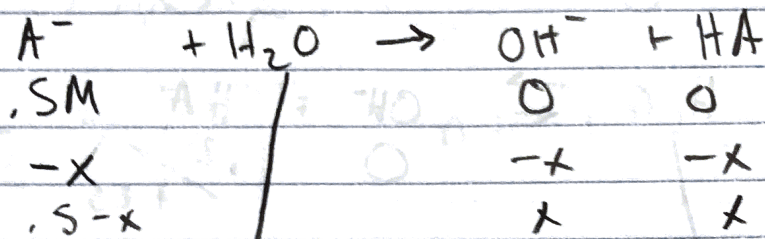# #1

a)

b) pH 1 : everything is protonated H_3PO_4
pH 5. : $H_2PO_4^{-1}$
pH 9. : HPO_4^{-2}
pH 14 : PO_4^{-3}

c) A pH 4.5 phosphoric acid cannot be used to make a good buffer since it is not within it's buffer region. The nearest pKa's are 2.1 and 7.2, and neither are within 1 of the pH of 4.5.
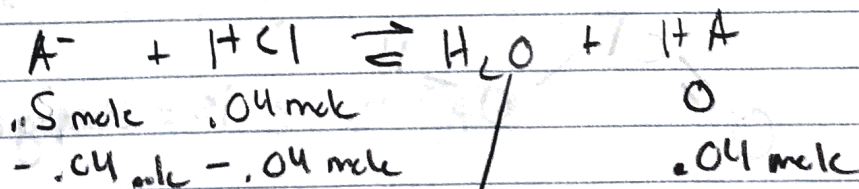
#2

a) $pka = 9$ $pka = -\log [\,Ka\,]$

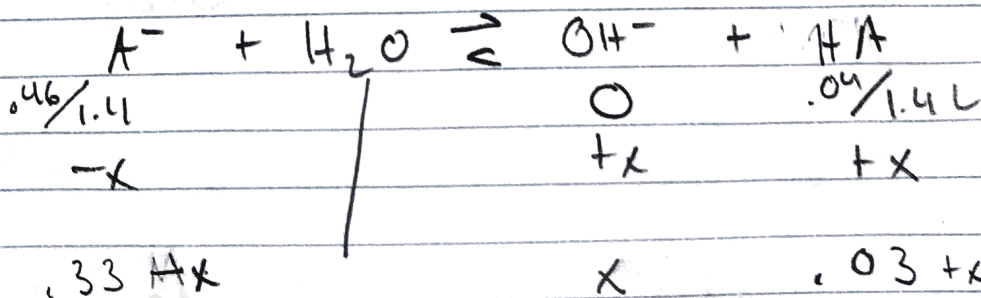$9 = -\log [Ka] \rightarrow$ $Ka = 10^{-9}$ $K_b = 10^{-5}$

$$A^- \quad + H_2O \rightarrow OH^- + HA$$

.5M	0	0
$-x$	$-x$	$-x$
$.5-x$	x	x

$$\frac{x^2}{.5 \cancel{-x}} = 10^{-5} \qquad x = 2.24 \times 10^{-3}$$

$pOH = -\log [2.24 \times 10^{-3}]$ $\boxed{pH = 11.35}$
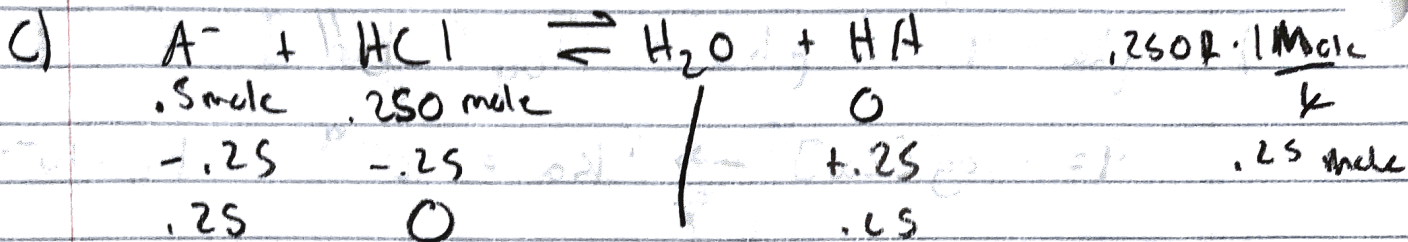
b) $.4L \cdot \dfrac{.1\ mol}{1L} = .04\ moles$

$$A^- \quad + HCl \rightleftharpoons H_2O + HA$$

.5 mole	.04 mole		0
$-.04$ mole	$-.04$ mole		.04 mole
.46 mole	0		.04 mole 1.4 L

$$A^- \quad + H_2O \rightleftharpoons OH^- + HA$$

$.46/1.4$	0	$.04/1.4L$
$-x$	$+x$	$+x$
.33 $-x$	x	$.03 + x$

$$\frac{(.03 \cancel{+x})\,x}{.33 \cancel{-x}} = 10^{-5} \qquad x = 1.1 \times 10^{-4}$$

$\boxed{pH = 10.04}$

c)
$$A^- + HCl \rightleftharpoons H_2O + HA \qquad .250\text{R} \cdot 1\frac{\text{Mole}}{\text{R}}$$

.5 mole	.250 mole		O
-.25	-.25		+.25
.25	O		.25

$$.25 \text{ mole}$$

$$\diagup 1.25 \text{ L}$$

$$A^- + H_2O \rightleftharpoons OH^- + HA$$

$\frac{.25}{1.25}$		O	$\frac{.25}{1.25}$
$-x$		$+x$	$+x$
$.2-x$		x	$.2+x$
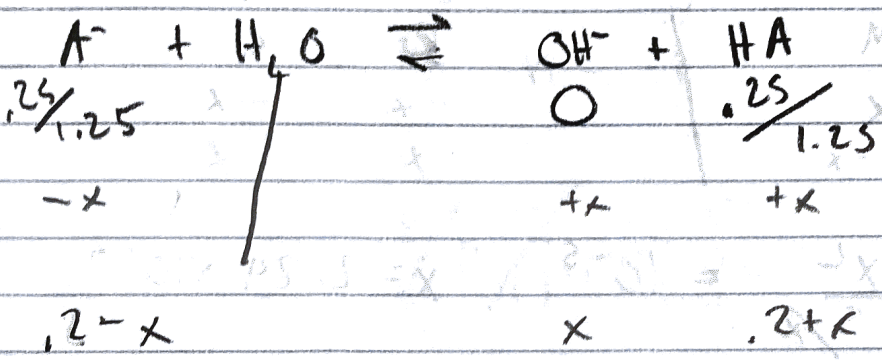
$$\frac{(.2+x)x}{.2-x} = 10^{-5} \qquad x = 10^{-5}$$

$$\boxed{pH = 9}$$

d)

$$O = \overset{Cl}{\underset{\diagdown}{}} \diagdown O - H \qquad \text{is stronger}$$
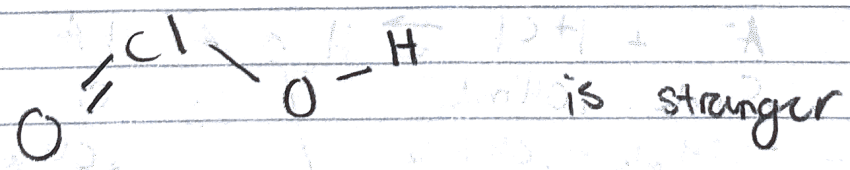
#3

a. $\text{Rate} = K[A]^n[B]^m$

b. $10^{-3} \text{ M/s} = K[.1]^n[.1]^m$
   $3 \cdot 10^{-3} \text{ M/s} = K[.3][.1]^m$

$$\frac{1}{3} = \left[\frac{1}{3}\right]^n \qquad n = 1$$

$10^{-3} \text{ M/s} = K[.1]^n[.1]^m$
$10^{-3} \text{ M/s} = K[.1]^n[.5]^m$

$$1 = \left[\frac{1}{5}\right]^m \qquad m = 0$$

New rate expression: $\text{Rate} = K[A]^1$

$10^{-3} \text{ M/s} = K[.1 \text{ M}]$

$K = .01 \text{ s}^{-1}$

c. $\text{Rate} = .01 \text{ s}^{-1}[A]^1$

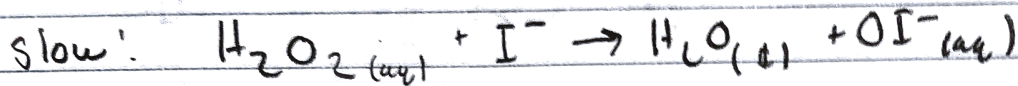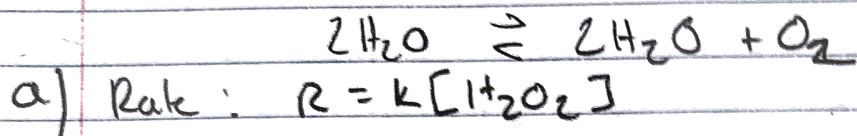$\text{Rate} = .01 \text{ s}^{-1}[5 \times 10^{-3} \text{ M}]$

$\text{Rate} = 5 \times 10^{-5} \dfrac{M}{s}$

d) First order: $\ln[A] - \ln[A_0] = -kt$

$\ln[A] = \ln[5 \times 10^{-3} \text{ M}] - (.01)(110 \text{ s})$

$[A] = 1.66 \times 10^{-3} \text{ M}$

#4

$$2H_2O \rightleftharpoons 2H_2O + O_2$$

a) Rate: $R = k[H_2O_2]$

slow: $H_2O_{2(aq)} + I^- \rightarrow H_2O_{(l)} + OI^-_{(aq)}$

Rate $= R = k_1[H_2O_2]^1[I^-]^1$

$\ast$ we use this because it is the Rate determining step $\ast$

We can conclude that proposed mechanism does not agree with the rate law because it includes the concentration of I^-. I^- is a catalyst and must be included since it influences the speed of the reaction. However it is not included in the overall reaction because it is not produced/destroyed it only facilitates the speed of the reaction.

b) I^- - catalyst
       OI^- - intermediate

#5.

a) CO has the strongest IMF since it is polar
while B_2 is non polar. B_2 only experiences
LDF among other B_2

b)

V
(potential
energy)

CO B_2

r
Separation radius

repulsive

global
min
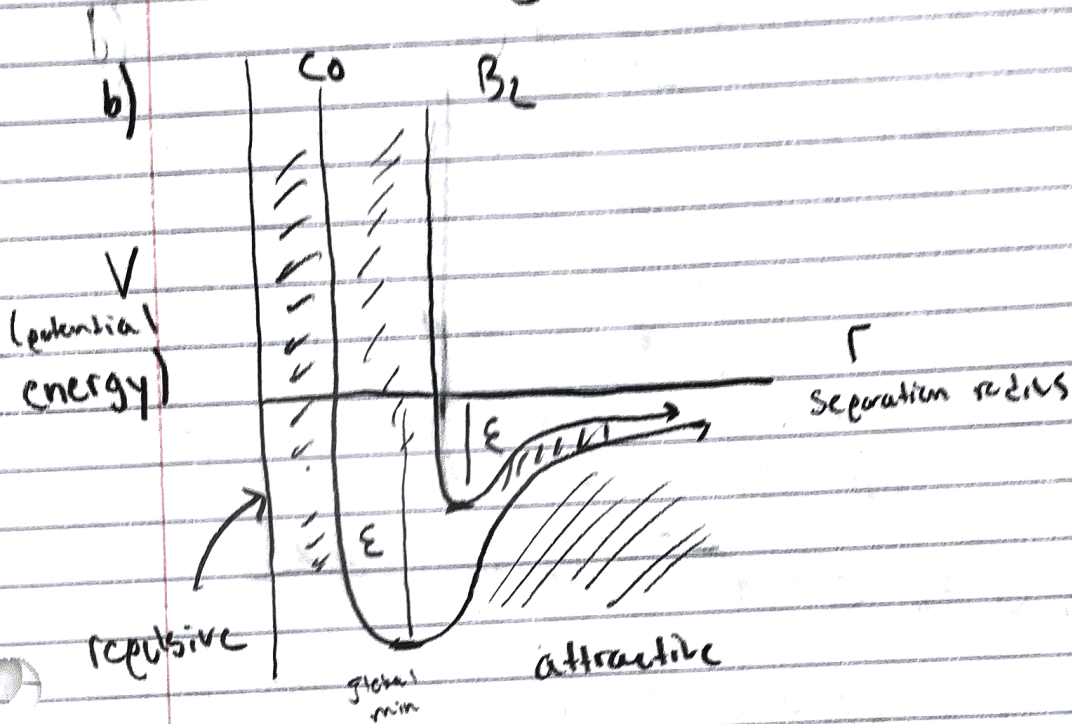
attractive

* Attractive where there are positive slopes ⊗

c) CO will have a higher freezing point
since it has stronger IMF. It already
has a tendency to bond more readily
with itself than B_2 so it will have
a higher temp.

#6

a) $\Delta G = 0$ at equilibrium

$\Delta G = \Delta H - T \Delta S$

$0 = 25700 \dfrac{J}{mol} - T \dfrac{95 J}{mol \cdot k}$

$T = \dfrac{25700 \; J/mol}{95 \; J/mol \cdot k}$

$T = 270.5 \; K$

b) $K = e^{\left(-\frac{\Delta G}{RT}\right)}$ at T_{eq}

$K = 1$ since $\Delta G = 0$ at equilibrium

c) $\Delta G = 25700 \dfrac{J}{mol} - 300 k \left(\dfrac{95 J}{mol \; k}\right)$

$\Delta G = -2800 \dfrac{J}{mol}$, since $\Delta G < 0$ it is Spontaneous

d) $K = e^{\left(\frac{2800}{(8.314)(300)}\right)}$

$K = 3.07$

Start w/ 1 M   end w/ 1 M

e) $1 \; gram \left(\dfrac{1 \; mole}{100 g}\right) = .01 \; moles$, so $.01 \; L$ of H_2O

A

at standard conditions   1 M

$K = \dfrac{[B][C]}{[A]}$

$3.07 = \dfrac{1+x}{1-x}$

$3.07 - 3.07x = 1 + x$

$2.07 = 4.07x$ M

$x = .509$

so $[C] = 1.509$ M $\quad$ 1M

and $[A] = .491$ M

f. $\quad \Delta G = RT \ln\left(\dfrac{Q}{k}\right)$

$Q = \dfrac{[C]}{[A]} = \dfrac{[1M]}{[.01M]}$

$\Delta G = RT \cdot \ln\left(\dfrac{Q}{k}\right)$

$\Delta G = 8.314 \cdot 280 \cdot \ln\left(\dfrac{100}{3.07}\right)$

$\Delta G = 2324.43$

It is not spontaneous since $\Delta G > 0$

3.

#7

$$2A \longrightarrow 2B + C$$

$$\Delta G_{eq} = \Delta H - T_{eq} \Delta S$$

$$0 = 25700 - T_{eq} \cdot 95 \frac{J}{mol \cdot k}$$

$$T_{eq} = 270 \text{ K}$$

ΔS ice pack: 6 moles $\cdot 95 \frac{J}{mole \cdot k}$

$$= 570 \frac{J}{k}$$

ΔS of water: $1000 m \ell \left(\frac{1g}{m\ell} \right) = 1000 g$

$$1000 \text{ grams} \left(4.2 \frac{J}{g \cdot k} \right) \left(\frac{270}{248} \right) k$$

$$= -371.9 \frac{J}{k}$$

$$\Delta S_{universe} = 570 \frac{J}{k} - 371.9 \frac{J}{k}$$

$$\Delta S_{univers} = 198.08 \frac{J}{k}$$

Since $\Delta S > 0$ it is spontaneous

#8

$$173K \qquad 223k \qquad -5$$

q_1 — from $-100°C$ to $-50°C$ $\qquad -100.$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad -50$

q_2 — enthalpy of fusion

q_3 — $-50°C$ to $25°C$

$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad q_T = 900 J$

Solid

$q_1 = (2g)\left(1 \frac{J}{g \cdot k}\right)(50 k') = 100 J$

$q_2 = 2g\left(\frac{250 J}{g}\right) = 500 J$

$q_3 = 2g\left(2 \frac{J}{g \cdot k}\right)(75 k) = 300 J$

$\Delta S_1 = (2g)\left(1 \frac{J}{g k}\right)^{ln}\left(\frac{223 K}{173 k}\right) = .508 \frac{J}{k}$

$\Delta S_2 = grams\left(\frac{\Delta H_{fusion}}{T_{fusion}}\right)$

$= (2 grams)\left(\frac{250 J}{gram}\right)\left(\frac{1}{223k}\right) = 2.24 \frac{J}{k}$

$\Delta S_3 = 2g\left(2 \frac{J}{g \cdot k}\right)^{ln}\left(\frac{298 k}{223 K}\right) = 1.16 \frac{J}{k}$

$=$

$\Delta S_{sys} = .508 \frac{J}{k} + 2.24 \frac{J}{k} + 1.16 \frac{J}{k} = 3.908 \frac{J}{k}$

$\Delta S_{sur} = \frac{-q_T}{T_{sur}} = \frac{-900 J}{298 k} = -3.07$

$\Delta S_{universe} = 3.908 \frac{J}{k} - 3.07 \frac{J}{k} = \boxed{.838 \frac{J}{k} > 0 \quad so \quad Spont}$