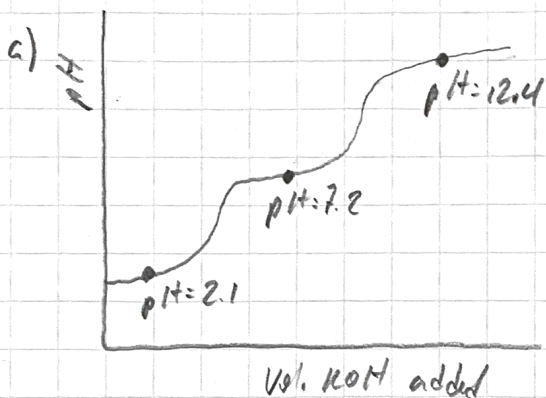


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QUESTION #1

$pK_a = 2.1, 7.2, 12.4$. Sketch titration curve for phosphoric acid if titrated w/ KOH



- b)
- At $pH = 1$: H_3PO_4 (no ions lost)
 - At $pH = 5$: $H_2PO_4^-$ (1 ion lost)
 - At $pH = 9$: HPO_4^{2-} (2 ions lost)
 - At $pH = 14$: PO_4^{3-} (all ions lost)

c) Phosphoric acid can not be used to make a good buffer at $pH = 4.5$ because a pH of 4.5 falls almost directly between the pK_a of 2.1 and pK_a of 7.2 , meaning that the equivalence point for H_3PO_4 is roughly 4.5 . Small additions of base lead to large increases in pH .

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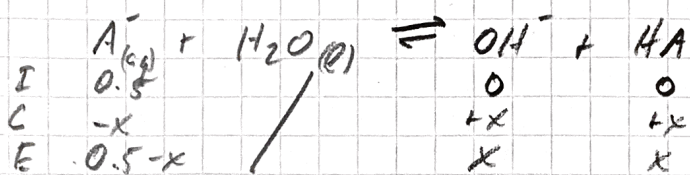
QUESTION # 2

a) 1L solution containing 0.5 moles of base w/ pKa of 9

$$[A^-] = \frac{0.5 \text{ moles}}{1L} = 0.5M$$

$$pK_b = 14 - pK_a = 14 - 9 = 5$$

$$-\log(K_b) = 5 \quad K_b = 10^{-5}$$



$$K_b = \frac{[HA][OH^-]}{[A^-]} = \frac{(x)(x)}{0.5-x} = 10^{-5}$$

$$\frac{[A^-]}{K_b} = \frac{0.5M}{10^{-5}} > 100, \text{ so ignore change}$$

$$10^{-5} = \frac{x^2}{0.5} \Rightarrow x = \sqrt{0.5(10^{-5})}$$

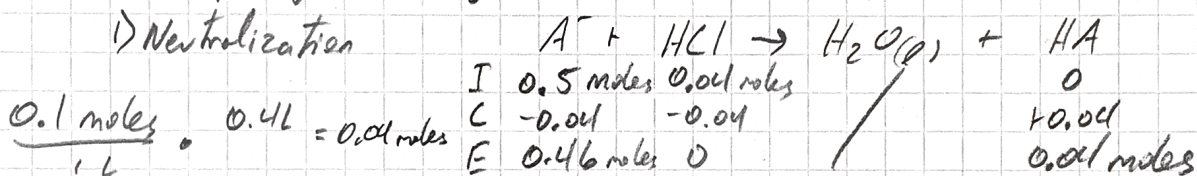
$$x = 2.24 \times 10^{-3}$$

$$p(OH) = -\log([OH]) = -\log(2.24 \times 10^{-3}) = 2.65$$

$$pH = 14 - p(OH) = \boxed{11.35}$$

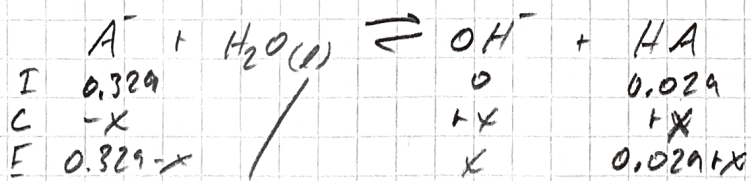
b) Calculate pH of solution if 400 mL 0.1 M HCl added

1) Neutralization



$$\text{New concentrations: } [A^-] = \frac{0.46 \text{ moles}}{1.4L} = 0.329M$$

$$[HA] = \frac{0.04 \text{ moles}}{1.4L} = 0.029M$$



$$\Rightarrow K_b \text{ is still } 10^{-5}$$

$$K_b = \frac{(0.029+x)(x)}{(0.329-x)}$$

$$\frac{[HA]}{K_b} = \frac{0.029}{10^{-5}} > 100$$

$$\frac{[A^-]}{K_b} = \frac{0.329}{10^{-5}} > 100$$

Ignore change

$$10^{-5} = \frac{(0.029)(x)}{(0.329)} \Rightarrow x = \frac{(0.329)(10^{-5})}{0.029}$$

$$x = 1.13 \times 10^{-4}$$

$$p(OH) = -\log([OH]) = -\log(1.13 \times 10^{-4}) = 3.95$$

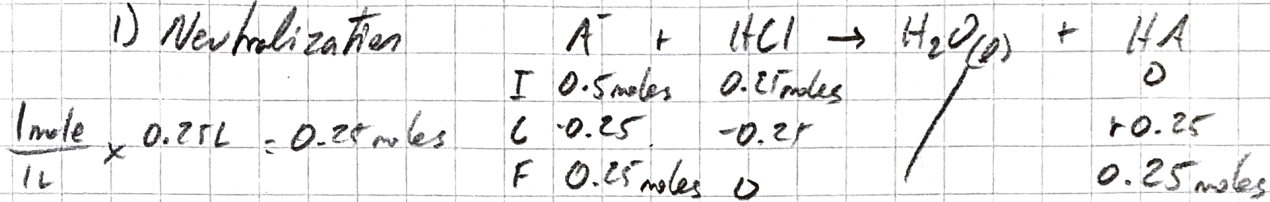
$$pH = 14 - p(OH) = \boxed{10.05}$$

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QUESTION #2 (cont.)

c. Calculate pH of solution from part A if 250 mL 1M HCl added

1) Neutralization



New Concentrations: $[A^-] = \frac{0.25 \text{ moles}}{1.25 L} = 0.2 M$

$[HA] = \frac{0.25 \text{ moles}}{1.25 L} = 0.2 M$

$\frac{[A^-]}{[HA]} = 0.1 < \frac{0.2}{0.2} < 10$, HH eqn applies

$pH = pK_a - \log\left(\frac{[HA]}{[A^-]}\right) = 9 - \log\left(\frac{0.2}{0.2}\right) = \boxed{9}$

d. Which is a stronger acid?

$HClO_2$ is the stronger acid

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QUESTION # 3

a. Determine rate expression.

$$\frac{\text{rate}_1}{\text{rate}_2} = \frac{k[A]^m[B]^n}{k[A_2]^m[B_2]^n} = \frac{10^{-3}}{3 \times 10^{-3}} = \frac{k[0.1]^m [0.1]^n}{k[0.3]^m [0.1]^n} \quad \frac{1}{3} = \left(\frac{1}{3}\right)^m \quad m=1$$

$$\frac{\text{rate}_1}{\text{rate}_3} = \frac{10^{-3}}{10^{-3}} = \frac{k[0.1]^m [0.1]^n}{k[0.1]^m [0.5]^n} \quad 1 = \left(\frac{1}{5}\right)^n \quad n=0$$

Rate expression: $\boxed{\text{rate} = k[A]}$

b. Calculate the rate constant.

$$10^{-3} = k[0.1] \quad k = \frac{10^{-3}}{0.1} = \boxed{10^{-2} \text{ s}^{-1}}$$

c. Calculate rate of rxn if $[A] = 5 \text{ mM}$, $[B] = 2 \text{ mM}$

$$[A] = 5 \times 10^{-6} \text{ M}, [B] = 2 \times 10^{-6} \text{ M}$$

$$\text{rate} = 10^{-2} \text{ s}^{-1} [A] = (10^{-2})(5 \times 10^{-6}) = \boxed{5 \times 10^{-8} \text{ M/s}}$$

d. What fraction of A remains after 110 s?

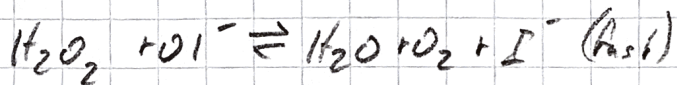
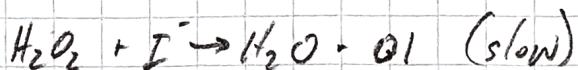
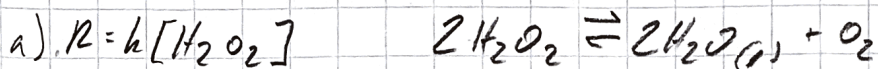
$$-\frac{d[A]}{dt} = k[A] \quad \int \frac{-d[A]}{[A]} = \int k dt \quad \ln\left(\frac{A_f}{A_i}\right) = -kt$$

$$e^{-kt} = \frac{A_f}{A_i} = \frac{-(10^{-2})(110)}{e} = 0.333$$

$\boxed{\frac{1}{3} \text{ of reactant A remains after 110 s.}}$

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QUESTION #4



$$\text{Rate} = \text{Rate}_{\text{slow}} = k_1 [H_2O_2] [I^-]$$

$$\text{Rate}_{-2} = k_{-2} [H_2O] [O_2] [OI^-] = k_2 [H_2O_2] [OI^-]$$

$$[OI^-] = \frac{k_2 [H_2O_2] [OI^-]}{k_{-2} [H_2O] [O_2]}$$

$$k_1 [H_2O_2] [OI^-] = k_{-2} [H_2O] [O_2] [OI^-]$$

$$[OI^-] = \frac{k_2 [H_2O_2] [OI^-]}{k_{-2} [H_2O] [O_2]} \quad \text{Rate} = \frac{k_1 k_2 [H_2O_2]^2 [OI^-]}{k_{-2} [H_2O]^2 [O_2]^2}$$

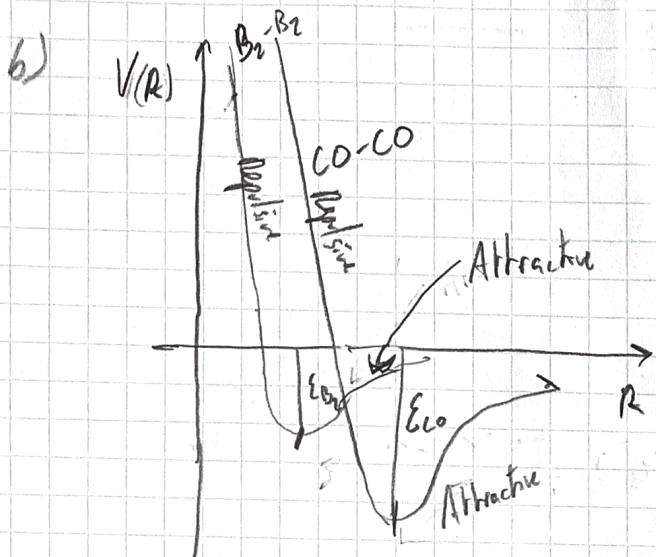
Proposed mechanism does not agree with rate law

b) Intermediates: OI^-
Catalyst: I^-

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QUESTION # 5

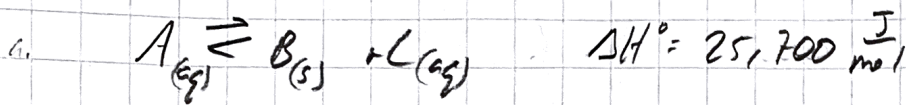
- a) CO has stronger intermolecular forces; there is an electronegativity difference between C and O, meaning that the molecule has a dipole. Thus, CO molecules interact through dipole-dipole forces. B_2 molecules have no dipoles so they interact through weaker induced-dipole induced-dipole forces.



- c) CO has a higher freezing point because the IMFs that want to bring the molecules closer together, and thus form a solid, are stronger.

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QUESTION #6



$$\Delta S^\circ = 95 \frac{J}{mol \cdot K}$$

a) Calculate T_{eq}

$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ \quad 0 = \Delta H^\circ - T\Delta S^\circ$$
$$\Delta H^\circ = T\Delta S^\circ \quad T_{eq} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{25,700}{95} = \boxed{270.53^\circ K}$$

b. Determine equilibrium constant for reaction at T_{eq}

$$\Delta G^\circ = -RT \ln(K) \quad 0 = -RT \ln(K) \quad \boxed{K=1}$$

c. Calculate Gibbs free energy @ $300^\circ K$. Is reaction spontaneous?

$$\Delta G = \Delta H - T\Delta S = 25,700 - 300(95) = \boxed{-2800 \frac{J}{mol}}$$

Since $\Delta G < 0$, reaction is spontaneous

d) Determine equilibrium constant for reaction @ $300^\circ K$ under standard conditions

$$\Delta G^\circ = -2800 \frac{J}{mol} = -(8.314)(300K) \ln(K)$$

$$K = e^{\frac{2800}{8.314 \times 300}} = \boxed{3.07}$$

e) If 1g reactant A dissolved in water, calculate equilibrium concentrations if A has molecular weight 100g/mole

$$K = \frac{[C]}{[A]} \quad 3.07 = \frac{[C]}{[A]}$$

$$1g \times \frac{1mol}{100g} = 0.01 \text{ moles}$$

$$3.07 = \frac{y \text{ moles}}{\frac{x \text{ Liter}}{0.01 \text{ moles}} \times 1 \text{ liter}}$$

$$3.07 = \frac{y \text{ moles}}{0.01 \text{ moles}}$$

$$y \text{ moles} = (3.07)(0.01) = 0.0307 \text{ moles}$$

The concentration of $[A] : [C]$ is $[0.01] : [0.0307]$

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QUESTION # 6 (Cont.)

f. Gibbs free energy of $[A] = 0.01M$, $[C] = 1M$

$$Q = \frac{[C]}{[A]} = \frac{1}{0.01} = 100 \quad \Delta G = RT \ln\left(\frac{Q}{K}\right)$$

$$\text{At } 280^\circ K: \Delta G = 25700 - 280(15) = -RT \ln(K) \Rightarrow -900 = -(8.314)(280) \ln(K)$$

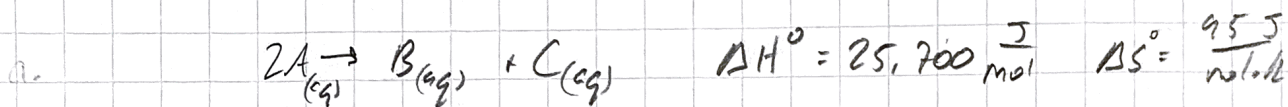
$$K = e^{\frac{900}{(8.314)(280)}} = 1.47$$

$$\Delta G = RT \ln\left(\frac{Q}{K}\right) = (8.314)(280) \ln\left(\frac{100}{1.47}\right) = \boxed{9823.61 \frac{J}{mol}}$$

Since $\Delta G > 0$, the reaction is NOT spontaneous.

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QUESTION # 7



6 moles of reactant A used to cool 1L of water @ 25°C
density $H_2O = \frac{1g}{mL}$, $C_N = 4.2 \frac{J}{g \cdot K}$

Equilibrium temperature for reaction: $\Delta G = \Delta H - T\Delta S = 0$

$$\Delta H = T\Delta S \quad T_{eq} = \frac{\Delta H^\circ}{\Delta S^\circ} = \frac{25,700 \frac{J}{mol}}{95 \frac{J}{mol \cdot K}} = \underline{270.53^\circ K}$$

$$q_{rxn} = -q_{water} \quad q_{rxn} = n\Delta H_{rxn} = 6(25,700 \frac{J}{mol}) = \underline{154,200 J}$$

$$154,200 = -mC_N \Delta T \Rightarrow 154,200 = -(1000g)(4.2 \frac{J}{g \cdot K})(T - 298^\circ K)$$

$$154,200 = -4200T + 1251600 \Rightarrow -1097400 = -4200T \quad T = \underline{261.3^\circ K}$$

$$\Delta S_{univ} = \Delta S_{reaction} + \Delta S_{water}$$

$$\Delta S_{rxn} = \int \frac{dq}{T} = \frac{q}{T} = \frac{n\Delta H}{T} = \frac{(6 \text{ moles})(25,700 \frac{J}{mol})}{270.53} = 570 \frac{J}{K}$$

$$\Delta S_{water} = \int \frac{dq}{T} = \int \frac{mC_N dT}{T} = (1000g)(4.2 \frac{J}{g \cdot K}) \ln\left(\frac{261.3}{298}\right) = -552 \frac{J}{K}$$

$$\Delta S_{univ} = 570 \frac{J}{K} - 552 \frac{J}{K} = \boxed{18 \frac{J}{K}} \quad \text{Since } \Delta S > 0 \text{ process is spontaneous}$$

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QUESTION # 8

Freezing point = 223°K
Boiling point = 323°K

$$C_{\text{solid}} = 1 \frac{\text{J}}{\text{g}\cdot\text{K}} \quad C_{\text{liquid}} = 2 \frac{\text{J}}{\text{g}\cdot\text{K}}$$

$$C_{\text{water}} = 20 \frac{\text{J}}{\text{g}\cdot\text{K}} \quad \Delta H_{\text{fusion}} = 250 \frac{\text{J}}{\text{g}}$$

$$\Delta H_{\text{vapor}} = 2000 \frac{\text{J}}{\text{g}}$$

2 grams of solid @ 173°K

room = 298°K

$$\Delta S_{\text{univ}} = \Delta S_{\text{substance}} + \Delta S_{\text{surr}}$$

$$\Delta S_{\text{substance}} = \Delta S_{\text{heat, solid}} + \Delta S_{\text{melt}} + \Delta S_{\text{heat, liquid}}$$

$$\Delta S_{\text{heat, solid}} = \int \frac{dq}{T} = \int \frac{m C_{\text{solid}} dT}{T} = m C_{\text{solid}} \ln\left(\frac{223^{\circ}\text{K}}{173^{\circ}\text{K}}\right)$$

$$\Delta S_{\text{melt}} = \int \frac{dq}{T} = \frac{m \Delta H_{\text{melt}}}{223^{\circ}\text{K}}$$

$$\Delta S_{\text{heat, liquid}} = \int \frac{dq}{T} = \int \frac{m C_{\text{liquid}} dT}{T} = m C_{\text{liquid}} \ln\left(\frac{298^{\circ}\text{K}}{223^{\circ}\text{K}}\right)$$

$$= (2\text{g})\left(1 \frac{\text{J}}{\text{g}\cdot\text{K}}\right) \ln\left(\frac{223}{173}\right) + \frac{(2\text{g})(250 \frac{\text{J}}{\text{g}})}{223^{\circ}\text{K}} + (2\text{g})\left(2 \frac{\text{J}}{\text{g}\cdot\text{K}}\right) \ln\left(\frac{298^{\circ}\text{K}}{223^{\circ}\text{K}}\right)$$

$$= 3.91 \frac{\text{J}}{\text{K}} = \Delta S_{\text{substance}}$$

$$\Delta S_{\text{surr}} = \int \frac{dq}{T} = \frac{q}{T} = \frac{-q_{\text{sys}}}{T}$$

$$q_{\text{sys}} = m C_{\text{solid}} \Delta T + m \Delta H_{\text{fusion}} + m C_{\text{liquid}} \Delta T$$

$$= (2\text{g})\left(1 \frac{\text{J}}{\text{g}\cdot\text{K}}\right)(223 - 173^{\circ}\text{K}) + (2\text{g})\left(250 \frac{\text{J}}{\text{g}}\right) + (2\text{g})\left(2 \frac{\text{J}}{\text{g}\cdot\text{K}}\right)(298 - 223^{\circ}\text{K})$$

$$= 900 \text{ J}$$

$$\Delta S_{\text{univ}} = 3.91 - 3.02 = \boxed{0.89 \frac{\text{J}}{\text{K}}}$$

$$\Delta S_{\text{surr}} = \frac{-900 \text{ J}}{298^{\circ}\text{K}} = -3.02 \frac{\text{J}}{\text{K}}$$

Since $\Delta S_{\text{univ}} > 0$, process is spontaneous