

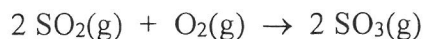
CHEMISTRY 104 – Summer 2022
Hour Exam I Answers

Multiple Choice (3 points each)

- | | | | |
|-----|---|-----|---|
| 1. | A | 14. | B |
| 2. | A | 15. | C |
| 3. | D | 16. | A |
| 4. | E | 17. | D |
| 5. | B | 18. | C |
| 6. | B | 19. | E |
| 7. | E | 20. | C |
| 8. | E | 21. | D |
| 9. | C | 22. | D |
| 10. | C | 23. | A |
| 11. | B | 24. | D |
| 12. | E | 25. | B |
| 13. | C | 26. | E |
| | | 27. | A |

WRITTEN OUT PROBLEMS – Show all work for partial credit.

28. Consider the following reaction and data:
(12 pts.)



$$\Delta H^\circ = \sum \Delta H_{f,i,\text{prod}}^\circ - \sum \Delta H_{f,i,\text{react}}^\circ$$

$$\Delta S^\circ = \sum S_{\text{prod}}^\circ - \sum S_{\text{react}}^\circ$$

Compound	ΔH_f°	S°
$\text{SO}_3(\text{g})$	-396 kJ/mol	257 J/K•mol
$\text{SO}_2(\text{g})$	-297 kJ/mol	248 J/K•mol
$\text{O}_2(\text{g})$	0	205 J/K•mol

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

- a) Calculate the value of ΔG° for the reaction at 25°C.

$$\Delta H^\circ = [2(-396)] - [2(-297) + 1(0)] = -198 \text{ kJ}$$

$$\Delta S^\circ = [2(257)] - [2(248) + 1(205)] = -187 \text{ J/K}$$

$$\Delta G^\circ = -198 \text{ kJ} - (298 \text{ K})(-0.187 \text{ kJ/K})$$

$$\Delta G^\circ = -198 \text{ kJ} + 55.7 \text{ kJ} = \boxed{-142 \text{ kJ}}$$

- b) Assuming ΔH° and ΔS° are temperature independent, calculate the temperatures at which this reaction is spontaneous (assuming all gases are at 1 atm).

At equilibrium, $\Delta G^\circ = 0$ (at standard concentrations).

$$\Delta G^\circ = 0 = \Delta H^\circ - T\Delta S^\circ, \quad \Delta H^\circ = T\Delta S^\circ, \quad T = \frac{\Delta H^\circ}{\Delta S^\circ}$$

$$T = \frac{-198 \text{ kJ}}{-0.187 \text{ kJ/K}} = 1060; \text{ this is the temperature where } \Delta G^\circ = 0.$$

Since both ΔH° and ΔS° are negative, this reaction will be spontaneous at $(T < 1060 \text{ K})$ where the favorable ΔH° term will dominate.

- c) At standard conditions, this reaction is allowed to react to reach equilibrium. If, at equilibrium, the partial pressures of $\text{O}_2(\text{g})$ and $\text{SO}_3(\text{g})$ are 0.50 atm and 2.0 atm respectively, calculate the equilibrium partial pressure of $\text{SO}_2(\text{g})$. Note: $T = 25^\circ\text{C}$

$$\Delta G^\circ = -RT \ln K, \quad \ln K = \frac{-\Delta G^\circ}{RT} = \frac{-(-142,000 \text{ J})}{8.3145 \text{ J/(K}\cdot\text{mol)}(298 \text{ K})} = 57.31$$

$$K = e^{57.31} = 7.76 \times 10^{24}$$

$$K = \frac{P_{\text{SO}_3}^2}{P_{\text{SO}_2}^2 \times P_{\text{O}_2}}, \quad 7.76 \times 10^{24} = \frac{(2.0 \text{ atm})^2}{P_{\text{SO}_2}^2 (0.50 \text{ atm})}$$

$$\text{Solving: } \boxed{P_{\text{SO}_2} = 1.0 \times 10^{-12} \text{ atm}}$$

$$\Delta G^\circ = -RT \ln K$$

29. Consider the following equilibrium constant vs. temperature data for some reaction:
(7 pts)

K	Temp
2.54×10^4	109°C
5.04×10^2	225°C
6.33×10^1	303°C
2.25×10^{-1}	412°C
3.03×10^{-3}	539°C

$\left. \begin{array}{l} < 25^\circ\text{C} \\ & \end{array} \right\} K > 1, \text{ so } \Delta G^\circ < 0$
 $\left. \begin{array}{l} & \\ & \end{array} \right\} K < 1, \text{ so } \Delta G^\circ > 0$

a) Is this reaction spontaneous at standard concentrations and $T = 25^\circ\text{C}$? Explain.

From data, as temperatures decrease from 303°C , K increases to larger numbers greater than 1. So at $T = 25^\circ\text{C}$, $K > 1$ which means $\Delta G^\circ < 0$. So yes, this reaction is spontaneous at $T = 25^\circ\text{C}$ (assuming standard concentrations).

b) Predict the signs of ΔH° and ΔS° for the reaction. Explain.

As temperature increases, note that the data shows that K goes from a number greater than 1 to a value less than 1. This indicates that as temperature increases, ΔG° goes from a negative value to a positive value.

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

This can only be explained if both ΔH° and ΔS° are negative values. When this is the case, ΔG° is negative only below some temperature (as we have here).

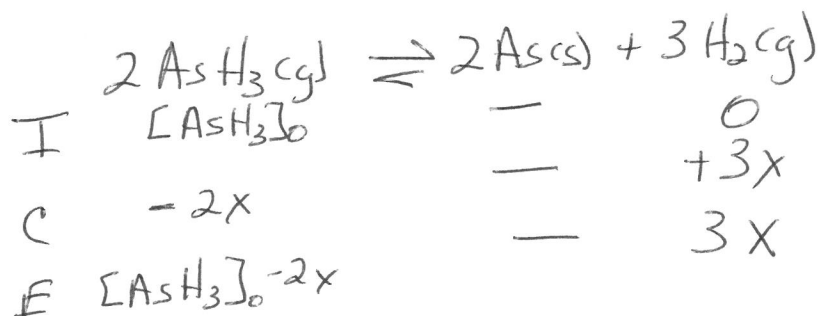
30. The gas arsine, AsH_3 , decomposes by the following reaction:

(8 pts)

Let $[\text{AsH}_3]_0 = \text{initial concentration of AsH}_3$



In an experiment, pure $\text{AsH}_3(\text{g})$ of unknown initial concentration is placed into a 2.0 L container. After equilibrium is reached, 6.0 moles of $\text{H}_2(\text{g})$ is produced and 12.0 moles of $\text{AsH}_3(\text{g})$ is also present. Determine the initial concentration of $\text{AsH}_3(\text{g})$ before the reaction took place ($[\text{AsH}_3]_{\text{initial}} = ?$). Also, calculate the value of the equilibrium constant for this reaction ($K = ?$). Show all work for credit.



From the problem:

$$[\text{H}_2]_e = \frac{6.0 \text{ mol}}{2.0 \text{ L}} = 3.0 \text{ M} = 3x, \quad x = 1.0 \text{ M}$$

$$[\text{AsH}_3]_e = [\text{AsH}_3]_0 - 2x = \frac{12.0 \text{ mol}}{2.0 \text{ L}}$$

$$[\text{AsH}_3]_0 - 2x = 6.0 \text{ M}, \quad [\text{AsH}_3]_0 - 2(1.0) = 6.0 \text{ M}$$

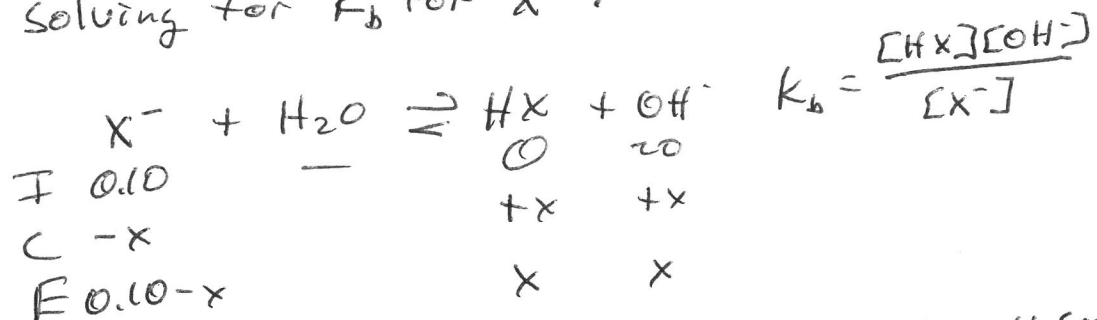
$$[\text{AsH}_3]_0 = 6.0 + 2.0 = \boxed{8.0 \text{ M}}$$

$$K = \frac{[\text{H}_2]^3}{[\text{AsH}_3]^2} = \frac{(3.0)^3}{(6.0)^2} = \frac{27}{36} = \boxed{0.75 = K}$$

31. A 0.10 M solution of the salt NaX has a pH of 11.50. Calculate the pH of a 1.0 M solution of HX.

(6 pts)

X^- must be a weak base, so HX is a weak acid. In order to solve for the pH of HX solution, we need to determine K_a for HX. We will do this by solving for K_b for X^- .

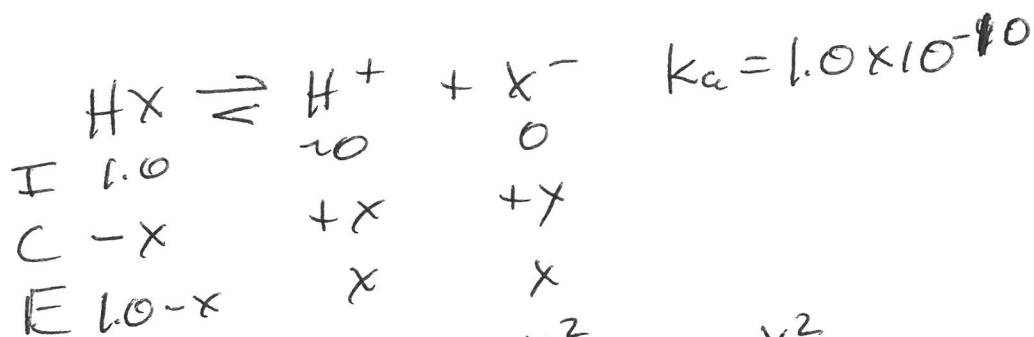


From problem, pH = 11.50, so pOH = 14 - 11.50 = 2.50.

$$[OH^-] = x = 10^{-2.50} = 3.16 \times 10^{-3} M$$

$$K_b = \frac{x^2}{0.10-x} = \frac{(3.16 \times 10^{-3})^2}{0.10 - 3.16 \times 10^{-3}}, \quad K_b = 1.0 \times 10^{-4}$$

$$\text{So } K_a \text{ for HX} = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.0 \times 10^{-4}} = 1.0 \times 10^{-10}$$



$$K_a = 1.0 \times 10^{-10} = \frac{x^2}{1.0-x} \approx \frac{x^2}{1.0}$$

$$\text{Solving: } x = 1.0 \times 10^{-5} M$$

Assumptions good.

$$[H^+] = 1.0 \times 10^{-5} M, \quad \text{pH} = -\log(1.0 \times 10^{-5}) = \boxed{5.00}$$

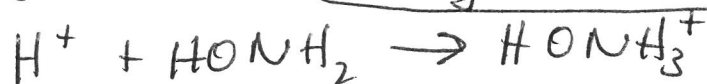
32. Consider 1.0 L of a solution composed of 1.60 M HONH_2 ($K_b = 1.1 \times 10^{-8}$) and 0.80 M HONH_3NO_3 . This is a buffer solution containing a weak base (HONH_2) and its conjugate acid (HONH_3^+).
(8 pts) a) Calculate the pH of this solution.

$$\text{pH} = \text{pK}_a + \log \frac{[\text{base}]}{[\text{acid}]} = -\log \frac{1 \times 10^{-14}}{1.1 \times 10^{-8}} + \log \left(\frac{1.60}{0.80} \right)$$

$$\text{pH} = 6.04 + \log 2 = 6.04 + 0.30 = \boxed{6.34}$$

- b) In order for this 1.0 L of solution to have $\text{pH} = \text{pK}_a$, would you add HCl or KOH? What quantity (moles) of HCl or KOH would you add to the solution in order to get $\text{pH} = \text{pK}_a$?

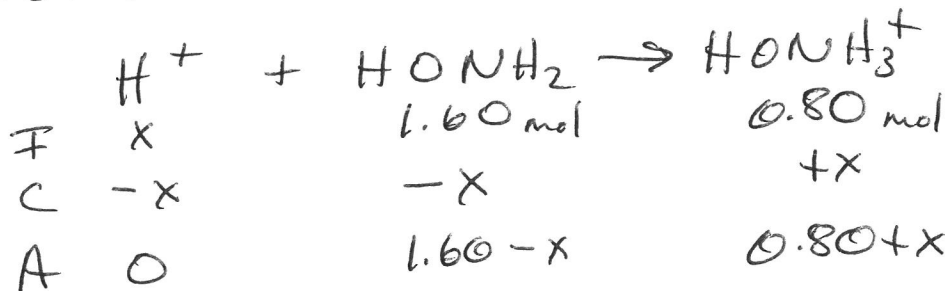
In order for $\text{pH} = \text{pK}_a$, we need a solution where $[\text{HONH}_2] = [\text{HONH}_3^+]$. We need to lower the HONH_2 concentration and raise the HONH_3^+ concentration. This will occur if ~~we~~ we add strong acid (HCl):



$$\text{mol HONH}_2 = 1.0 \text{ L} \times 1.60 \frac{\text{mol}}{\text{L}} = 1.60 \text{ mol}$$

$$\text{mol HONH}_3^+ = 1.0 \text{ L} \times 0.80 \frac{\text{mol}}{\text{L}} = 0.80 \text{ mol}$$

Let $x = \text{mol H}^+$ added from HCl



We want $[\text{HONH}_2] = [\text{HONH}_3^+]$ which will occur when $\text{mol HONH}_2 = \text{mol HONH}_3^+$.

$$1.60 - x = 0.80 + x, \quad 2x = 0.80, \quad x = 0.40 \text{ mol H}^+$$

0.40 mol HCl must be added to achieve $\text{pH} = \text{pK}_a$.

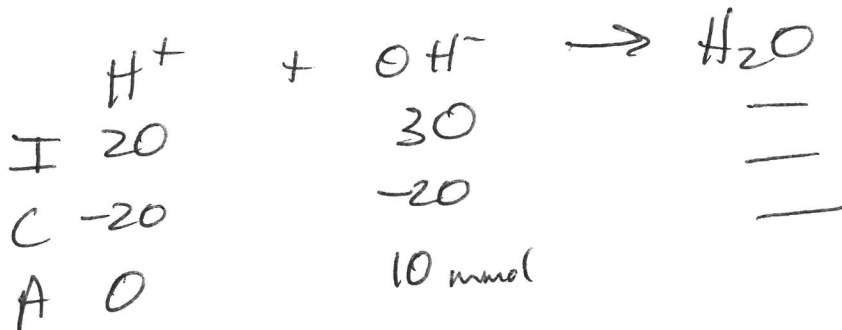
33. Consider the titration of 200.0 mL of 0.10 M HNO₃ titrated by 0.10 M Ca(OH)₂. Sketch the titration curve for this titration. On your plot, label the axis and indicate the pH and volume of the equivalence point. Also indicate the initial pH before any Ca(OH)₂ has been added as well as the pH at 150.0 mL of Ca(OH)₂ added.

(9 pts)

Initial pH: 0.10 M HNO₃
 $[H^+] = 0.10 M, pH = -\log(0.10) = 1.00$

pH at 150.0 mL Ca(OH)₂ added:

200.0 mL (0.10 M) = 20 mmol H⁺ initially
 150.0 mL (0.20 $\frac{mol}{L}$) = 30 mmol OH⁻ added



$\sum [OH^-]_{\text{excess}} = \frac{10 \text{ mmol } OH^-}{200.0 \text{ mL} + 150.0 \text{ mL}} = 2.86 \times 10^{-2} M$

$pOH = -\log(2.86 \times 10^{-2}) = 1.54, pH = 14 - 1.54 = 12.46$

In order to reach the equivalence point, we must add 20 mmol OH⁻, which occurs at 100.0 mL Ca(OH)₂ added.

