CHEMISTRY 104 – Summer 2024
Hour Exam I Answers

Multiple Choice (3 points each)

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

Written out problems – Show all work for partial credit.

26. Ammonia (NH_3) is produced commercially for the following reaction. Utilizing the thermodynamic data given, answer the following five questions.

(15 pts.)

	$N_2(g)$	+ $3\ H_2(g)$	$\rightleftharpoons$ $2\ NH_3(g)$
ΔH°_f (kJ/mol)	$\overset{0}{?}$	$\overset{0}{?}$	–46
S° (J/K•mol)	192	131	193

a) Calculate ΔH° and ΔS° for this reaction.

2pts $\Delta H^\circ = [2(46\ kJ)] - [1(0) + 3(0)] = \boxed{-92\ kJ}$

2pts $\Delta S^\circ = [2(193\ J/k)] - [1(192\ J/k) + 3(131\ J/k)] = \boxed{-199\ J/K}$

2pts b) Calculate ΔG° for this reaction at 25° C.

$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ = -92\ kJ - (298\ k)(-0.199\ kJ/k)$

$\Delta G^\circ = -92\ kJ + 59.3\ kJ = \boxed{-32.7\ kJ = -33\ kJ = -3.3 \times 10^4\ J}$

3pts c) An industrial engineer is designing a plant to produce ammonia. Two important conditions to examine are temperature and pressure dependence of this reaction. Assuming standard pressures ($P_{N_2} = P_{H_2} = P_{NH_3} = 1.00$ atm) and assuming that ΔH° and ΔS° do not depend on temperature, what temperature conditions should be designed for in the plant? Be specific, i.e., give specific temperatures.

Because ΔH and ΔS are both negative values, this reaction will be spontaneous below some temperature.

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

$T = \frac{-92\ kJ}{-0.199\ kJ/K} = 462\ K = 460\ K$

This reaction will be spontaneous at temps below 460K, so this reaction should be run at $\boxed{T < 460\ K.}$

d) As mentioned previously, pressure dependence of this reaction is another important consideration. To examine this dependence, two experiments were run at two different initial conditions. They are:

Experiment 1: T = 25°C; $P_{N_2} = P_{H_2} = P_{NH_3} = 1.00$ atm

Experiment 2: T = 25°C; $P_{N_2} = P_{H_2} = P_{NH_3} = 10.0$ atm

Calculate ΔG for each of these experiments.

$$\Delta G = \Delta G^\circ + RT\ln Q = -3.3\times10^4\,J + \frac{8.3145\,J}{K\cdot mol}(298\,K)\ln\frac{P_{NH_3}^2}{P_{N_2}\times P_{H_2}^3}$$

1pt Exp 1: we are at standard concentrations, so $Q = 1$, $\ln Q = 0$ and $\boxed{\Delta G = \Delta G^\circ = -3.3\times10^4\,J = -33\,kJ}$

Exp3: $\Delta G = -3.3\times10^4\,J + 8.3145(298)\ln\frac{(10.0)^2}{10.0(10.0)^3}$

3pts

$$\Delta G = -3.3\times10^4\,J - 1.14\times10^4\,J$$

$$\boxed{\Delta G = -4.44\times10^4\,J = -4.4\times10^4\,J = -44\,kJ}$$

2pts

e) When designing the ammonia plant, should the reaction be run at high pressure or at low pressure? Explain. Hint: look at your answer to part d.

From the results in Exp2 at higher pressures, this reaction is more favorable (more negative ΔG) as the pressures increases. So higher pressure conditions are favorable for this reaction. At lower pressures, this reaction is less favorable thermodynamically and may even become nonspontaneous (ΔG > 0).

27. Impure nickel (nickel that contains impurities) is converted into pure nickel by the Mond process. The equilibrium reaction involved in the Mond process is:

(10 pts.)

$$Ni(CO)_4(g) \rightleftharpoons Ni(s) + 4\,CO(g)$$

The Mond process consists of two steps. They are:

Step 1: Converting the nickel in the impure nickel sample to $Ni(CO)_4$ at $T = 25°C$.
At 25°C, the reverse reaction occurs. From the calculated K value which is very small, mostly reactants are present at equilibrium which is what we want.

Step 2: Separating out the $Ni(CO)_4$ formed from the first step, then increasing the temperature to 227°C.

The standard free energy changes ($\Delta G°$) for the above reaction at 25°C and at 227°C are:

$$\Delta G°_{25} = 78 \text{ kJ at } T = 25°C; \qquad \Delta G°_{227} = -38 \text{ kJ at } T = 227°C$$

$$\ln K = \frac{-\Delta G°}{RT}$$

4pts a) Calculate K for this reaction at 25°C and at 227°C.

$$25°C: \ln K = \frac{-(78{,}000\,J)}{8.3145\,(298\,K)} = -31.4805, \quad K = e^{-31.4805} = \boxed{2.1 \times 10^{-14}}\ 25°C$$

$$227°C: \ln K = \frac{-(-38{,}000\,J)}{8.3145\,(500.\,K)} = 9.1407, \quad K = e^{9.1407} = \boxed{9.3 \times 10^{3}}\ 227°C$$

3pts b) Why is the temperature increased in the second step of the Mond process? Be specific. In the second step, we want the forward reaction to dominate since we want to convert the Ni in $Ni(CO)_4$ into solid Ni. At 227°C, note that K is now greater than 1, indicating the reaction contains mostly products at equilibrium. The temperature is increased in the second step so the dominate reaction changes from the reverse reaction into the forward reaction. As a result, pure Ni(s) is formed.

3pts c) Is the Mond process reaction exothermic or endothermic? Explain your reasoning.

$\Delta G° = \Delta H° - T\Delta S°$; from the $\Delta G°$ values, this reaction becomes spontaneous (at standard concentrations) when the temperature increases. This is consistant with positive signs for both $\Delta H°$ and $\Delta S°$. Hence, the reaction is endothermic

28. Consider a weak acid, HX. If a 0.10 *M* solution of HX has a pH of 5.83 at 25°C, calculate ΔG° for the acid's dissociation reaction at 25°C.

(6 pts)

$HX(aq) \rightleftharpoons H^+(aq) + X^-(aq) \qquad \Delta G^\circ = ?$

I $\quad 0.10M \quad \sim 0 \quad 0$

E $\quad 0.10-x \quad x \quad x$

$$K_a = \frac{[H^+][X^-]}{[HX]} = \frac{x^2}{0.10-x}$$

From the problem:

$$pH = 5.83, \; [H^+] = x = 10^{-5.83} = 1.5\times10^{-6}\,M$$

$$K_a = \frac{(1.5\times10^{-6})^2}{0.10-1.5\times10^{-6}} = 2.25\times10^{-11}$$

$$\Delta G^\circ = -RT\ln K = -\frac{8.3145\,J}{K\cdot mol}\times 298K \times \ln(2.25\times10^{-11})$$

$$\boxed{\Delta G^\circ = 6.1\times10^{4}\,J = 61\,kJ}$$

29. Consider the following solutions for the next three questions.
(13 pts)

I. 100.0 mL of 0.50 *M* $(C_2H_5)_3N$ (K_b for $(C_2H_5)_3N = 4.0 \times 10^{-4}$) weak base
II. 50.0mL of 0.30 *M* $HClO_4$ strong acid
III. 50.0 mL of 0.30 *M* KOH strongbase
IV. 100.0 mL of 0.50 *M* $(C_2H_5)_3NHI$ $\rightarrow \underset{\text{weak acid}}{(C_2H_5)_3NH^+} + \underset{\text{garbage}}{I^-}$

3pts

a) Calculate the pH of solution IV. $(C_2H_5)_3NH^+$ is the conjugate acid of a weak base, so it is a weak acid.

$$\begin{array}{llll} & (C_2H_5)_3NH^+ \rightleftharpoons & (C_2H_5)_3N + & H^+ \\ I & 0.50M & 0 & \sim 0 \\ E & 0.50-x & x & x \end{array} \qquad K_a = \frac{K_w}{K_b} = \frac{1.0\times10^{-14}}{4.0\times10^{-4}}$$

$$K_a = 2.5\times10^{-11} = \frac{x^2}{0.50-x} \approx \frac{x^2}{0.50}$$

$x = [H^+] = \sqrt{0.50(2.5\times10^{-11})} = 3.54\times10^{-6}M$ (Assumptions good.)

$pH = -\log(3.54\times10^{-6}) = \boxed{5.45 = pH}$

5pts

b) Calculate the pH of the resulting solution when solutions I, III, and IV are mixed together.

mmol $(C_2H_5)_3N$ = mmol $(C_2H_5)_3NH^+$ = 100.0mL(0.50M) = 50. mmol

mmol OH^- = 50.0 mL(0.30M) = 15 mmol OH^-

OH^- reacts with best acid present to completion.

$$\begin{array}{llll} & OH^- + & (C_2H_5)_3NH^+ \longrightarrow & (C_2H_5)_3N + H_2O \\ I & 15\text{ mmol} & 50\text{ mmol} & 50\text{ mmol} \\ C & -15 & -15 & +15 \\ A & 0 & 35\text{ mmol} & 65\text{ mmol} \end{array}$$

A buffer solution is present after all of the OH^- reacts, Using H-H equation:

$$pH = pKa + \log\frac{[base]}{[acid]} = -\log(2.5\times10^{-11}) + \log\frac{(65/V_T)}{(35/V_T)}$$

$$pH = 10.60 + \log\left(\frac{65}{35}\right) = 10.60 + 0.27 = \boxed{10.87 = pH}$$

29. (cont.) Consider the following solutions for the next three questions.

I. 100.0 mL of 0.50 *M* $(C_2H_5)_3N$ (K_b for $(C_2H_5)_3N = 4.0 \times 10^{-4}$) weak base

II. 50.0mL of 0.30 *M* $HClO_4$ $\rightarrow H^+ + ClO_4^-$, ClO_4^- is a garbage ion

III. 50.0 mL of 0.30 *M* KOH $\rightarrow K^+ + OH^-$, K^+ is a garbage ion

IV. 100.0 mL of 0.50 *M* $(C_2H_5)_3NHI$ $\rightarrow (C_2H_5)_3NH^+ + I^-$, I^- is garbage ion

5 pts c) Calculate the pH of the resulting solution when solutions I, II, III, and IV are mixed together.

$100.0\,mL \times 0.50\,M = 50.\,mmol\,(C_2H_5)_3N$ (solution1)

$50.0\,mL \times 0.30\,M = 15\,mmol\,H^+$ (solution 2)

$50.0\,mL \times 0.30\,M = 15\,mmol\,OH^-$ (solution3)

$100.0\,mL \times 0.50\,M = 50.\,mmol\,((C_2H_5)NH^+$ (solution 4).

Whenever H^+ and/or OH^- are present, react them first. The reaction is best acid + best base. Also, because something strong is reacting, assume the reaction goes to completion.

$$H^+ + OH^- \rightarrow H_2O$$

	H^+	OH^-	H_2O
I	15mmol	15mmol	—
C	−15	−15	—
A	0	0	—

After reaction, all of the H^+ and OH^- are gone, we have a weak base $[(C_2H_5)N]$ and its conjugate acid $[(C_2H_5NH^+]$ present at the same time (with some garbage ions). we have a buffer. Using H-H equation:

$$pH = pKa + \log\frac{[base]}{[acid]} = 10.60 + \log\left(\frac{50}{50}\right) = \boxed{10.60 = pH}$$

As expected, pH = pKa because we have an equal concentration of weak base and conjugate acid present.

$M_AV_A = M_BV_B$, 0.100 M(50.0 mL) = 0.0500 M(V_B)

V_B = 100.0 mL of KOH necessary to reach equivalence point

30. Consider the titration 50.0 mL of 0.100 *M* $HClO_4$ by 0.0500 *M* KOH. Determine the pH at the **halfway point to equivalence** and the pH at the **equivalence point**. Also **sketch** the general shape of each **titration curve** showing the **volume and pH** of the two points that you calculated. Determine all pH values to 2 decimal places.

(9 pts) This is a strong acid titrated by a strong base.

½ way pt. / 3 pts

100.0 mL of KOH is required to reach the equivalence point, so 50.0 mL KOH added is required to reach ½ way point.

mmol H^+ = 50.0 mL × 0.100 M = 5.00 mmol H^+

mmol OH^- added = 50.0 mL × 0.0500 M = 2.50 mmol OH^-

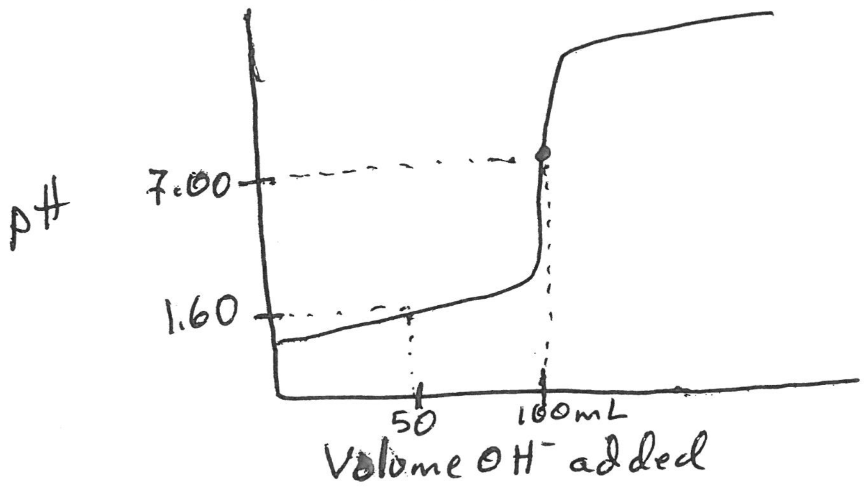
	H^+	+ OH^-	$\rightarrow H_2O$
I	5.00 mmol	2.50 mmol	—
C	−2.50	−2.50	—
A	2.50 mmol	0	—

After reaction, $[H^+] = \frac{2.50\text{ mmol}}{(50.0+50.0)\text{ mL}} = 0.025$ M

$pH = -\log(0.025) = \boxed{1.60 = pH}$

3pts

At equivalence point, H^+ and OH^- will run out at the same time. All that is left are garbage ions (ClO_4^- and K^+) in water. So $\boxed{pH = 7.00}$ at equivalence point (100.0 mL KOH added).



3pts

31. Consider the reaction:
(5 pts)

$$2\ CO(g) + O_2(g) \leftrightarrow 2\ CO_2(g) \qquad K = 2.0$$

An equilibrium mixture contains 4.0 *M* CO_2 and 2.0 *M* O_2 in a 3.0 L container. How many moles of CO are present in this equilibrium mixture?

$$K = 2.0 = \frac{[CO_2]^2}{[CO]^2[O_2]} = \frac{(4.0)^2}{[CO]^2(2.0)}$$

$$[CO]^2 = \frac{16.}{(2.0)2.0} = 4.0$$

3pt $$[CO] = \sqrt{4.0} = 2.0\ M$$

2pt $$\text{mol CO} = \frac{3.0\ \text{L}}{} \Big| \frac{2.0\ \text{mol CO}}{\text{L}} = \boxed{6.0\ \text{mol CO}}$$