2007 Fall Semester Mid-term Examination
For General Chemistry II

Time Limit: 7:00 ~ 9:00 p.m.

Professor Name	Class	Student Number	Name

Problem No.	Scores (points)	Problem No.	Scores (points)	TOTAL
1	/12	**5**	/15	
2	/10	**6**	/15	
3	/10	**7**	/10	
4	/13	**8**	/15	**/100**

** This paper consists of 10 sheets with 8 problems. Please check all page numbers before taking the exam.

** Also, periodic table is attached on last page.

NOTICE: SCHEDULES on DISTRIBUTION and CORRECTION of Mid-term PAPER SCORED.
(채점답안지 분배 및 정정 일정)

1. Period, and Procedure

   1) Distribution and Correction Period: ***October 29 (Monday), Practice Hours; 7: 00 ~ 8:30***

   2) Procedure: During the practice hours, you can take your mid-term paper scored. If you have any claims on it, you can submit a claim paper with your opinion. After writing your opinions on any paper you can get easily, attach it to your mid-term paper scored (Please, write your name, professor, and class.). Submit them to your TA. The papers with the claims will be re-examined by TA.

   The correction is permitted only on the period. Keep that in mind!

2. Final Confirmation

   1) Period: November 6 (Tuesday)-November 7 (Wednesday), 2 days

   2) Procedure: During the period, you can check your score of the mid-term examination *on the website* again.

** For further information, please visit a *General Chemistry website* at www.gencheminkaist.pe.kr.

- Constants

$R = 0.08$ L atm mol^{-1} K^{-1}

$k_b = 1.381 \times 10^{-23}$ JK^{-1}

$N_0 = 6.022 \times 10^{-23}$ mol^{-1}

[1] (12 points total)

(a) (3 points) Give the number of translational, rotational and vibrational degrees of freedom for a water molecule.

Answers)

For a water molecule (H_2O), N=3. The total number of DF = 3N = 9.

Among these, Translational DF = 3, Rotational DF = 3 (since the water molecule is non-linear), Vibrational DF = 3.

+1   translational DFs

+1   rotational DFs

+1   vibrational DFs

(b) (3 points) If the water molecule dissociates into H and OH, how does the number of translational, rotational and vibrational degrees of freedom change?

Answers)

For H, N = 1. The total number of DF = 3.

Translational DF = 3, Rotational DF = 0, Vibrational DF = 0

For OH, N=2, The total number of DF = 3N=6.

Translational DF = 3, Rotational DF = 2 (since OH is linear), Vibrational DF = 3N-5=1.

In total, for H + OH, Translational DF = 6, Rotational DF = 2, Vibrational DF = 1.

So upon dissociation, it loses 3 translational DF and instead gain 2 rotational DF and 1 vibrational DF.

+0.5each   trans, rot, vib, DFs for H atom

+0.5each   trans, rot, vib, DFs for OH

(c) (3 points) Which of the following molecules will show a far-infrared or microwave spectrum?

ClF   Cl$_2$ NO$_2$ CS$_2$ C$_2$H$_4$ CH$_3$Cl

Answers)   ClF, NO$_2$, CH$_3$Cl

+1 each for correct molecule /-1 each for incorrect ones

(d) (3 points) Which of the molecules of (c) will show an infrared spectrum?

Answers)

ClF, NO$_2$, CS$_2$, C$_2$H$_4$, CH$_3$Cl

+1 each for correct molecule/   -1 each for incorrect ones

[2] (10 points Total) In the Dumas method for determination of molecular mass of volatile liquids, a compound of unknown molecular mass is vaporized completely into a flask with a pinhole over its mouth, driving out all the air. The liquid is then recondensed and weighed. If the vapor from 1.00g liquid was found to occupy a 400ml flask at 100°C and 700 torr, what is the molecular mass?

($R = 0.08$ L atm mol^{-1} K^{-1})

Answers)

$n = PV/RT = [(700torr)(1atm/760torr)(0.400L)] \div [0.082L \text{ atm mol}^{-1} \text{ K}^{-1}]$

Thus the molar mass is M = 1.00g/0.01204 mol = 83g/mol

For working:

 -1 for wrong unit

 -1 for blunder

 -2 for wrong conception (e.g. division by N, missing out division by 760 etc.)

 +4 for PV=nRT

For answer:

 -3 for wrong figure

 -1 for small error

[3] (10 points total) Consider the Van der Waals equation of state. For the CO_2 vapor, a = 3.610 atm L^2 mol^{-2}, b = 0.04286 L mol^{-1}. At 400K, there is 2.0 mol of CO_2. Gas inside the volume of 1.0 L. Use the following R value for simplicity. R = 0.08 L atm mol^{-1} K^{-1}

-1 for wrong unit

a,b) +1 correct formula

 +1 correct calculation process

 +1 correct answer

c) If repulsive force, and attractive force is wrong -2 for each.

 (a) (3 points) What is the pressure?

 Answers)

 $P = \{(nRT) \div (V-nb)\} - a(n^2 \div V^2) = [\{(2 \text{ mol})(0.08 \text{ L atm mol}^{-1} \text{ K}^{-1})(400K)\} \div \{(1L)-(2mol \times 0.04286 \text{ L mol}^{-1})\}]$
 $- [3.610 \text{ atm L}^2 \text{ mol}^{-2} \{(2mol)^2 \div (1L)^2\}] = 70.00 - 14.4 = 55.6 \text{ atm}$

(b) (3 points) What would the pressure if this were ideal gas?

   Answers)

   P= nRT/V ={(2 mol)(0.08 L atm mol^{-1} K^{-1})(400K)}/1L = 64.0 atm

(c) (4 points) For the real gas, how much of pressure would increase or decrease by the repulsive force and attractive force compared with that of the ideal gas?

   Answers)

   Due to the repulsive force, 70.0 atm- 64.0 atm = 6.0 atm increases.
   Due to the attractive force, 14.4 atm decreases

[4] (13 points total) Following dimerization reaction, $2NO_2$ (g) $\rightleftharpoons N_2O_4$ (g)

-1 for wrong unit

a)
       +4 for correct formula
       +2 for correct answer
b)
       +5 for correct formula
       +2 for correct answer

(a) (6 points) Predict K at 100°C. $\Delta H^o_{298} = -13.67 kcal / mol$, $K_{298} = 6.97$.

   Answers)

$$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left[\frac{1}{T_2} - \frac{1}{T_1} \right]$$

$$\ln \frac{K_{373}}{6.97} = -\frac{-13,670\text{cal/mol}}{1.9872\text{cal/K} \cdot \text{mol}} \left[\frac{1}{373.15\text{K}} - \frac{1}{298.15\text{K}} \right] = -4.637$$

$$K_{373} = 6.97\text{e}^{-4.637} = 0.0675$$

(b) (7 points) Find the equilibrium partial pressures at that temperature and a total pressure of 1.3atm.
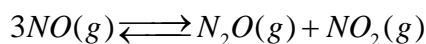
   Answers)

$x^2 - (2P + 1/K)x + P^2 = 0$

$x^2 - 17.4148x + 1.6900 = 0$

$x = 17.31720922 \qquad x = 0.9759078260$

P_{N2O4} = x = 0.0976 atm, P_{NO2} = P − x = 1.30 − 0.0976 = 1.20 atm

[5] (15 points total) Explain the effect of each of the following stresses on the position of the following equilibrium

$$3NO(g) \rightleftharpoons N_2O(g) + NO_2(g)$$

The reaction as written is exothermic. +3 for each correct answer

(a) (3 points) $N_2O(g)$ is added to the equilibrium mixture without change of volume or temperature.
Answers) (a) shifts left

(b) (3 points) The volume of the equilibrium mixture is reduced at constant temperature.
Answers) (b) shifts right

(c) (3 points) The equilibrium mixture is cooled
Answers) (c) shifts right

(d) (3 points) Gaseous argon (which does not react) is added to the equilibrium mixture while both the total gas pressure and the temperature are kept constant.
Answers) (d) shifts left

(e) (3 points) Gaseous argon is added to the equilibrium mixture without changing volume.
Answers) (e) no effect

[6] (15 points total) To make a buffer solution, 1.00 mol of formic acid (HCOOH) and 0.500 mol of sodium formate (HCOONa) are dissolved in 1.00 L of water. $K_a = 1.77 \times 10^{-4}$

-2 for wrong formula

a, b)   -2 for wrong answer

c)   0 point given when the cubic equation is not presented

(a) (5 points) Calculate the pH of the buffer solution.

Answers)

(a)

$$HCOOH(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

Initial concentration (M)	1.00	≈ 0	0.500
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$1.00 - y$	y	$0.500 + y$

The equilibrium expression is

$$\frac{y(0.500 + y)}{1.00 - y} = K_a = 1.77 \times 10^{-4}$$

Because y is likely to be small relative to 1.00 and to 0.500, the expression is approximated as

$$\frac{y(0.500)}{1.00} \approx 1.77 \times 10^{-4}$$

$$y \approx 3.54 \times 10^{-4} \, M = [H_3O^+]$$

A glance verifies that y is indeed small relative to 1.00 and 0.500. Then

$$pH = -\log_{10}(3.54 \times 10^{-4}) = 3.45$$

(b) (5 points) Suppose 0.100 mol of a strong acid such as HCl is added to the above buffer solution. Calculate the pH of the resulting solution.

Answers)

(b)

The strong acid HCl ionizes essentially completely in dilute aqueous solution. Initially assume that *all* the hydrogen ions from HCl are taken up by formate ions, giving formic acid, after which some formic acid ionizes back to formate ion and H_3O^+. This is simply a way of looking at the route by which equilibrium is approached and not a statement of the sequence of reactions that actually occurs. The position of the final equilibrium does not depend on the route by which it is attained.

Because 0.10 mol of HCl reacts with an equal number of moles of $HCOO^-$, the concentrations of $HCOO^-$ and HCOOH *before* ionization are

$$[HCOO^-]_0 = 0.50 - 0.10 = 0.40 \, M$$

$$[HCOOH]_0 = 1.00 + 0.10 = 1.10 \, M$$

The chart to calculate the concentrations at equilibrium is

$$HCOOH(aq) + H_2O(\ell) \rightleftharpoons H_3O^+(aq) + HCOO^-(aq)$$

Initial concentration (M)	1.10	≈ 0	0.40
Change in concentration (M)	$-y$	$+y$	$+y$
Equilibrium concentration (M)	$1.10 - y$	y	$0.40 + y$

The equilibrium expression then becomes

$$\frac{y(0.40 + y)}{1.10 - y} = 1.77 \times 10^{-4}$$

Because y is again likely to be small relative to both 0.40 and 1.10,

$$y \approx \left(\frac{1.10}{0.40}\right)(1.77 \times 10^{-4}) = 4.9 \times 10^{-4}$$

$$pH = 3.31$$

Even though 0.10 mol of a strong acid was added, the pH changed only slightly, from 3.45 to 3.31. By contrast, the same amount of acid added to a liter of pure water would change the pH from 7 to 1.

(c) (5 points) Calculate the pH of a 1.00×10^{-5}M solution of HCN(aq) $K_a = 6.17 \times 10^{-10}$

(Hint: If you can't solve the pH, it's okay to write down the equation about $[H^+]$.)

Answers)

In a situation where H^+ produced by can not be neglected.

$$K_a = \frac{[H^+][A^-]}{[HA]} \qquad\qquad K_w = [H^+][OH^-]$$

$$[H^+] = [A^-] + [OH^-] \qquad \text{(charge balance)}$$

$$[HA]_o = [A^-] + [HA] \text{ (mole balance)}$$

And solve that equation we get $$K_a = \frac{[H^+]([H^+] - \dfrac{K_w}{[H^+]})}{[HA]_o - [H^+] + \dfrac{K_w}{[H^+]}}$$

Cubic equation about $[H^+]$ is $[H^+]^3 + K_a[H^+]^2 - (K_w + Ka[HA]_o) [H^+] - K_a K_w = 0$

$[H^+]^3 + 6.17 \times 10^{-10} [H^+]^2 - 1.617 \times 10^{-14} [H^+] - 6.17 \times 10^{-24} = 0$
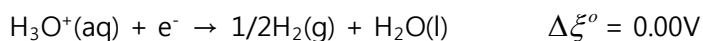
Carrying out the procedure gives $[H^+] = 1.27 \times 10^{-7}$M

pH = 6.90

[7] (10 points) A galvanic cell is constructed using a standard hydrogen half-cell(with platinum electrode) and a half-cell containing silver and silver chloride

$\quad\quad$ Pt l H_2(1atm) l H_3O^+(1M) ll Cl^-(1.00 × 10^{-3} M) + Ag^+(? M) l AgCl l Ag
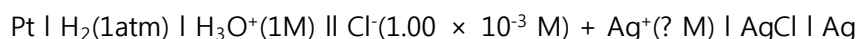
The H_2 l H_3O^+ half-cell is observed to be the anode, and the measured cell voltage is $\Delta\xi$ =0.397V.

H_3O^+(aq) + e^- → $1/2H_2$(g) + H_2O(l) $\quad\quad\quad$ $\Delta\xi^o$ = 0.00V

Ag^+(aq) + e^- → Ag(s) $\quad\quad\quad\quad\quad\quad$ $\Delta\xi^o$ = 0.800V

Calculate the silver ion concentration in the cell and the K_{sp} of AgCl at 25℃

Answers)
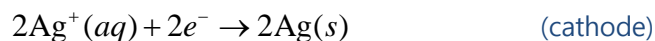
+2 for $\Delta\varepsilon^0$

+2 for Q

+2 for $\Delta\varepsilon$

+1 for n

+1 for [Ag^+]

+1 for [Ag^+][Cl^-]=K_{sp}

+1 for correct K_{sp}

Answers)

The half-cell reactions are

$$H_2(g) + 2H_2O(\ell) \rightarrow 2H_3O^+(aq) + 2e^- \quad\quad \text{(anode)}$$

$$2Ag^+(aq) + 2e^- \rightarrow 2Ag(s) \quad\quad\quad\quad \text{(cathode)}$$

$$\Delta\varepsilon^\circ = \varepsilon^\circ(\text{cathode}) - \varepsilon^\circ(\text{anode}) = 0.800 - 0.000V = 0.800V$$

Note that n=2 for the overall cell reaction, and the reaction quotient simplifies

$$Q = \frac{[H_3O^+]^2}{[Ag^+]^2 P_{H_2}} = \frac{1}{[Ag^+]^2}$$

Because $[H_3O^+] = 1M$ and $P_{H_2} = 1atm$. The Nernst equation is

$$\Delta\varepsilon = \Delta\varepsilon^\circ - \frac{0.0592V}{n}\log_{10} Q$$

$$\log_{10} Q = \frac{n}{0.0592V}(\Delta\varepsilon^\circ - \Delta\varepsilon) = \frac{2}{0.0592V}(0.800 - 0.397V) = 13.6$$

$$Q = 10^{13.6} = 4\times10^{13} = 1/[Ag^+]^2$$

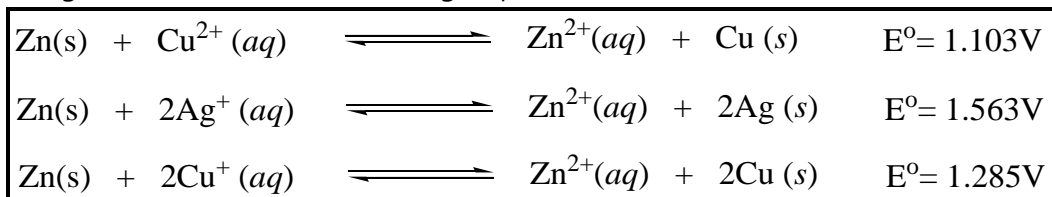This can be solved for the silver ion concentration $[Ag^+]$ to give

$$[Ag^+] = 1.6\times10^{-7}M$$

so that
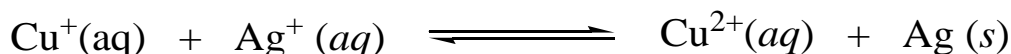
$$[Ag^+][Cl^-] = (1.6\times10^{-7})(1.00\times10^{-3})$$

$$K_{sp} = 1.6\times10^{-10}$$

[8] (15 points total) The following reactions proceed spontaneously to the right under standard condition with the given electrochemical cell voltages (potentials).
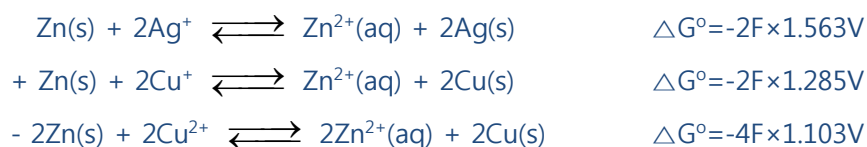
$Zn(s) + Cu^{2+}(aq)$ ⇌ $Zn^{2+}(aq) + Cu(s)$	$E^o = 1.103V$
$Zn(s) + 2Ag^+(aq)$ ⇌ $Zn^{2+}(aq) + 2Ag(s)$	$E^o = 1.563V$
$Zn(s) + 2Cu^+(aq)$ ⇌ $Zn^{2+}(aq) + 2Cu(s)$	$E^o = 1.285V$

For the following red-ox reaction;

$$Cu^+(aq) + Ag^+(aq) \rightleftharpoons Cu^{2+}(aq) + Ag(s)$$

+5 for each correct answers

a) (5 points) Which direction will the reaction proceed spontaneously?

Answers)

$Zn(s) + 2Ag^+$ ⇌ $Zn^{2+}(aq) + 2Ag(s)$	$\triangle G^o = -2F \times 1.563V$
$+ Zn(s) + 2Cu^+$ ⇌ $Zn^{2+}(aq) + 2Cu(s)$	$\triangle G^o = -2F \times 1.285V$
$- 2Zn(s) + 2Cu^{2+}$ ⇌ $2Zn^{2+}(aq) + 2Cu(s)$	$\triangle G^o = -4F \times 1.103V$

$2Ag^+(aq) + 2Cu^+(aq)$ ⇌ $2Ag(s) + 2Cu^{2+}(aq)$ $\triangle G^o = -1.284V \times F$
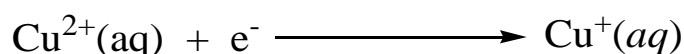
Therefore $\triangle G^o < 0$, the reaction proceed right.

b) (5 points) If one makes an electrochemical cell using this reaction, what will be the cell voltage under standard condition?

Answers)

$\triangle G^o = -nF\triangle E^o = -2F\triangle E^o = -1.284F$

$\triangle E^o = 0.642V$

c) (5 points) When reduction potential of Ag^+ is 0.800V, what is the reduction potential of the following reaction?

$$Cu^{2+}(aq) + e^- \longrightarrow Cu^+(aq)$$

Answers)

$Ag^+(aq) + Cu^+(aq) \rightarrow Ag(s) + Cu^{2+}(aq)$	$\triangle E^o = 0.642V$
$- Ag^+ + e^- \rightarrow Ag(s)$	$\triangle E^o = 0.800V$

$Cu^+(aq) \rightarrow Cu^{2+}(aq) + e^-$ $\triangle E^o = -0.158V$

Therefore $Cu^{2+}(aq) + e^- \rightarrow Cu^+(aq)$ $\triangle E^o = +0.158V$
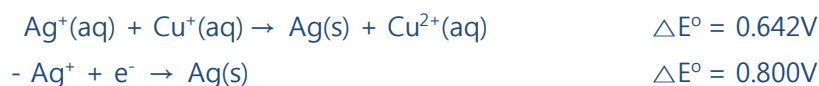
Periodic Table of The Elements

IA	IIA	IIIB	IVB	VB	VIB	VIIB	VIIIB			IB	IIB	IIIA	IVA	VA	VIA	VIIA	VIIIA
1 H 1.0079																	2 He 4.0026
3 Li 6.941	4 Be 9.0122											5 B 10.81	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984	10 Ne 20.1797
11 Na 22.9898	12 Mg 24.305											13 Al 26.9815	14 Si 28.086	15 P 30.9738	16 S 32.065	17 Cl 35.453	18 Ar 39.948
19 K 39.0983	20 Ca 40.078	21 Sc 44.9559	22 Ti 47.87	23 V 50.9415	24 Cr 51.996	25 Mn 54.9380	26 Fe 55.845	27 Co 58.9332	28 Ni 58.69	29 Cu 63.546	30 Zn 65.41	31 Ga 69.72	32 Ge 72.64	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62	39 Y 88.9059	40 Zr 91.224	41 Nb 92.9064	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.710	51 Sb 121.760	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 *La 138.906	72 Hf 178.49	73 Ta 180.948	74 W 183.84	75 Re 186.207	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 †Ac 227.028	104 Rf (260)	105 Db (261)	106 Sg (263)	107 Bh (267)	108 Hs (265)	109 Mt (266)	110 Ds (269)	111 Uuu (272)	112 Uub (277)	113 Uut (284)	114 Uuq (289)	115 Uup (288)	116	117	118

*Lanthanides

58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967

†Actinides

90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)