2008 FALL Semester Midterm Examination
For General Chemistry II

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

Professor Name	Class	Student Number	Name

Problem No.	points	Problem No.	points	TOTAL pts
1	/20	**4**	/20	
2	/22	**5**	/30	
3	/20			**/112**

** This paper consists of 12 sheets with 5 problems. Please check all page numbers before taking the exam.

Please take a good use of the reference materials (pages 10, 11 and 12), which include (a) Fundamental constants, (b) Conversion factors, (c) Atomization and bond energies, (d) Atomic weights of the elements, and (e) Standard reduction potentials in aqueous solution relative to standard hydrogen electrode.

No questions are allowed during the exam. You are not allowed to leave during the exam. You have to hold your nature call. Please write down the unit of your answer when applicable. You will get a deduction for a missing unit.

NOTICE: SCHEDULES on DISTRIBUTION and CORRECTION of the EXAM PAPER SCORED.
(채점답안지 분배 및 정정 일정)

1. Period, and Procedure

   1) Distribution and Correction Period: ***October 27 (Mon), 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 3 (Mon)-4 (Tue)

   2) Procedure: During this period, you can check final score of the examination *on the website* again.

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

[1] (20 pts)

(a) (8 pts) A thermodynamic engine operates cyclically and reversibly between two temperature reservoirs, absorbing heat from the high-temperature bath at 450 K and discharging heat to the low-temperature bath at 300 K. How much heat is discarded to the low-temperature bath, if 1500 J of heat is absorbed from the high-temperature bath during each cycle?

(Answers)

(a) Efficiency = $(T_h - T_l)/T_h = 1-T_h/T_h = 1- 300K/450K = 0.333$.

Efficiency = net work done / heat input = $0.333 = -W_{net}/1500J$

$W_{net} = -500J$

Therefore Discarded heat = 1500 J – 500 J = 1000J

(b) (12 pts) For ideal gases, heat capacity at constant pressure (C_p) is always larger than heat capacity at constant volume (C_v) ($C_p > C_v$). Using the given equation for the total energy of an ideal gas (E = 3/2 nRT) and equation of state (PV = nRT), probe that C_p is always larger than C_v. You have to show the detailed steps arriving at your final answer.

(Answers)

(b) *Isochoric process;* $\Delta V = 0$

if gas in a flask is heated → $w = - P \Delta V = 0$

$\therefore \Delta E = (3/2)nR\Delta T = q + w = q_V$ (at constant V)

Because $q = C(T_2 - T_1) \equiv C\Delta T$,

heat capacity C_v = 3/2 nR at constant volume.

Isobaric process ($\Delta P = 0$) → *heat, work are exchangeable*

$\Delta E = q + w = q_p - p\Delta V$

$\Delta E + p\Delta V = q_p$

$(E_2 + pV_2) - (E_1 + pV_1) = q_p$

The amount of heat measured in such a way is equal to E + PV which is path-independent (state variables).

$E + pV = H = 3/2$ nRT + nRT = 5/2 nRT, $\Delta H = q_P = C\Delta T$

heat capacity C_p = 5/2 nR at constant pressure

$C_p - C_v = nR$,

$\therefore C_p > C_v$

[2] (22 pts)

(a) (10 pts) Choose the substance from each pair with higher absolute entropy S^{o}_{298}. You will get 2 pt for a correct answer, 0 pt for no answer, and **-1 pt for a wrong answer**. You don't have to explain the reason for your answer.

A. $Fe^{3+}(aq)$, $Fe^{2+}(aq)$ (Answer) A. $Fe^{2+}(aq)$, _____

B. $NO_2^-(aq)$, $NO_3^-(aq)$ (Answer) B. $NO_3^-(aq)$, _____

C. $CH_3OH(l)$, $CH_3OH(g)$ (Answer) C. $CH_3OH(g)$, _____

D. $Cl_2O(g)$, $Cl_2(g)$ (Answer) D. $Cl_2O(g)$, _____

E. $Na(l)$, $Na(s)$ (Answer) E. $Na(l)$ _____

(b) (6 pts) For the following chemical reactions, guess the sign of $\Delta H°$. You will get 2 pt for a correct answer, 0 pt for no answer, and **-1 pt for a wrong answer**. You don't have to explain the reason for your answer.

A. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ (Answer) A. $\Delta H° < 0$, _____

B. $2CO_2(g) \rightarrow 2CO(g) + O_2(g)$ (Answer) B. $\Delta H° > 0$, _____

C. $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$ (Answer) C. $\Delta H° < 0$ _____

(c) (6 pts) For the following chemical reactions, guess the sign of $\Delta S°$. You will get 2 pt for a correct answer, 0 pt for no answer, and **-1 pt for a wrong answer**. You don't have to explain the reason for your answer.

A. $H^+(aq) + OH^-(aq) \rightarrow H_2O(l)$ (Answer) A. $\Delta S° > 0$, _____

B. $2CO_2(g) \rightarrow 2CO(g) + O_2(g)$ (Answer) B. $\Delta S° > 0$, _____

C. $HCl(g) + NH_3(g) \rightarrow NH_4Cl(s)$ (Answer) C. $\Delta S° < 0$ _____

[3] (20 pts)

(a) (4 pts) When nitrogen dioxide (NO_2) gas was allowed to dimerize into N_2O_4 gas until the reaction reached equilibrium at 25°C, the total pressure became 1.00 atm. What is the partial pressure of N_2O_4? The equilibrium constant K is 6.97 atm^{-1}.

(Answers)

(a) $2NO_2 \rightleftarrows N_2O_4$

$P_{NO_2} = P - x$ and $P_{N_2O_4} = x$

$K = x/(P- x)^2 \quad 0 \leq x \leq 1$

$x^2 - 2.1435\,x + 1.00 = 0$, $x = 0.686$

$P_{N_2O_4} = 0.686$ atm, $P_{NO_2} = 0.314$ atm

(b) (4 pts) Pure water is in equilibrium with its vapor at a given temperature. List the following H_2O's in the increasing order of molar Gibbs free energy of H_2O. Temperature = 298 K, and P = 1 atm.

A. Water vapor in air with 100% relative humidity.

B. Pure water.

C. Water in a mixture of 1 ethanol -1 water (molar ratio)

D. Water in a mixture of 10 ethanol - 1 water (molar ratio).

(Answers)

(b) D < C < B = A. Water vapor in air at 100%-humidity is in equilibrium with water. They have the same G. H_2O in the ethanol mixtures has a lower G than its pure state. Remember $\Delta G = \Delta G_0 + RT\,ln\,V_0/V$

(c) (4 pts) Calculate the boiling point of water at a high altitude where the atmospheric pressure is 0.5 atm. Assume that the enthalpy of vaporization of water is 10.5 kcal/mol.

(Answers)

(c) $H_2O(l) \rightleftarrows H_2O(g)$, $K = P_{H2O}$

Using $ln\frac{P_2}{P_1} = -\frac{\Delta H^0}{R}(\frac{1}{T_2} - \frac{1}{T_1})$

T = 82.6°C

(d) (4 pts) Express the equilibrium constant for the reaction between acetic acid (CH_3COOH) and ammonia (NH_3), in terms of K_a of acetic acid, K_b of ammonia, and the autoionization constant K_w of water. You do not have to show the detailed steps arriving at your final answer.

(Answers)

(d)

$$CH_3COOH + NH_3 \rightleftharpoons CH_3COO^- + NH_4^+$$

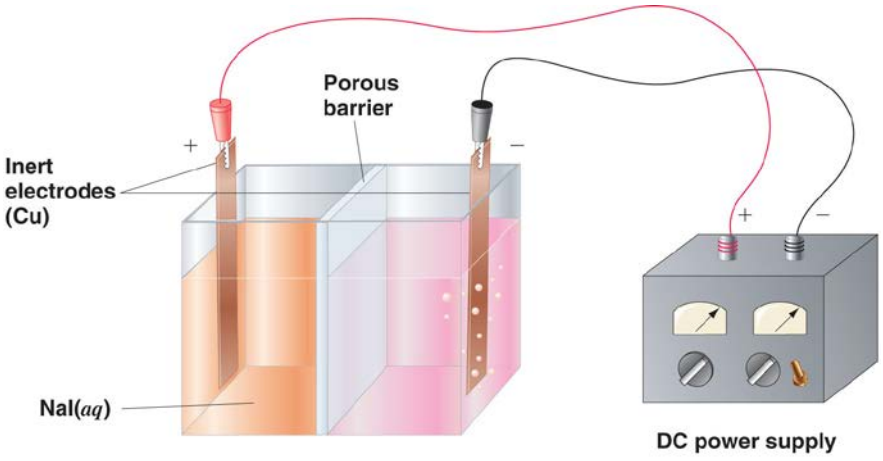
$$K = \frac{K_a K_b}{K_w}$$

(e) (4 pts) Many amine compounds (R-NH_2) act as a Bronsted-Lowry base in aqueous solution with base ionization constant (K_b) of around 10^{-4}. However, glycine which has a structure of $HOOCCH_2NH_2$ has very small K_b value around 10^{-12} in aqueous solution. Explain why.

(Answers)

(e) In aqueous solution near-neutral pH, most of Glycine exists as a zwitterion as a result of an internal proton transfer. The very small K_b arises from protonation of the carboxylate anion of the zwitterions, rather than the amine group, which is already protonated.

[4] (20 pts) Consider an electrolytic cell in operation with a NaI solution as electrolyte as in the following figure. A porous barrier was inserted into the initially uniform solution, and a voltage is being applied, plus-terminal to the left-handed electrode.



(a) (5pts) Write down two possible anode reactions (oxidation reactions) (1.5 pts for each correct reaction). In reality, which oxidation reaction occurs more readily (1 pt) and why (1 pt)?

(Answers)

(a)

Possible anode reactions

$2\ I^- \rightarrow I_2 + 2\ e^-$ -0.54 V
$2\ H_2O \rightarrow O_2 + 4\ H^+ + 4\ e^-$ -1.23 V

The first reaction occurs because it requires less voltage.

(b) (5 pts) Write down two possible cathode reactions (reduction reactions) (1.5 pts for each correct reaction). In reality, which reduction reaction occurs more readily (1 pt) and why (1 pt)?

(Answers)

(b)

Possible cathode reactions

$Na^+ + e^- \rightarrow Na(s)$ -2.71 V
$2\ H_2O + 2\ e^- \rightarrow 2OH^- + H_2$ -0.828 V

The second reaction occurs because it requires less voltage

(c) (5 pts) Write down the overall cell reaction (2.5 pts). What is the minimum applied voltage needed to cause this reaction to occur (2.5 pts)?

(Answers)

(c)

Overall cell reaction

$2\ I^- + 2\ H_2O \rightarrow I_2 + 2OH^- + H_2$ $\varepsilon^o = -1.37$ V

(d) (5 pts) Suppose a current of 1.0 A is drawn through the NaI cell for a total of 150 seconds. What is deposited at the anode (2 pts) and how many grams (3 pts)?

(Answers)

(d)

(4.0A)(150.s)
x(1 mol e^-/96500 C)
x(1 mol I_2/ 2 mol e^-)
X(254g I_2 / 1 mol I_2) = 0.79 g

0.79g of I_2 is deposited.

[5] (30 pts) Classify each of the following statements as 'True' or 'False'. You will get 1.5 pt for a correct answer, 0 pt for no answer, and **-1 pt for a wrong answer**.

(a) The molar heat capacity of argon gas is the same as that of helium gas.

(Answer) (a) T

(b) The molar heat capacity of 1 gram of water is smaller than that of 2 grams of water.

(Answer) (b) F

(c) A chemical reaction can occur spontaneously even if the entropy change of the reaction is negative under the reaction condition.

(Answer) (c) T

(d) The Gibbs free energy change of a reaction is zero where the reaction is in equilibrium.

(Answer) (d) T,

(e) The molar heat capacity of a gas at constant pressure is always larger than that at constant volume.

(Answer) (e) T

(f) The entropy change is negative for $H^+(aq) + OH^-(aq) \rightarrow H_2O(\ell)$ at 298 K.

(Answer) (f) F

(g) In the Joule's gas expansion, temperature of a gas can actually change if the gas has a significant intermolecular interaction.

(Answer) (g) T

(h) The absolute entropy of liquid helium at 0 K is zero, according to the 3rd law of thermodynamics.

(Answer) (h) F

(i) The molar heat capacity of H_2 gas is larger than that of the helium gas.

(Answer) (i) T

(j) The molar heat capacity of Cl_2 gas is larger than that of O_2 gas.

(Answer) (j) T

(k) The standard entropy of formation for H^+ in aqueous solution is zero regardless of the temperature.

(Answer) (k) F

(l) The molar heat capacity of H_2 gas at constant pressure approaches to 9R/2 as temperature increases.

(Answer) (l) T

(m) Reversible expansion of ideal gas yields a maximum amount of work.

(Answer) (m) T

(n) There are Carnot cycles that can work irreversibly.

(Answer) (n) F

(o) The standard Gibbs free energy of a species can change if temperature changes.

(Answer) (o) T

(p) There are other types of work besides the pressure-volume work.

(Answer) (p) T

(q) The molar heat capacity of a monolayer of iron is about 3R.

(Answer) (q) F

(r) The molar heat capacity of liquid water is larger than that of steam (gas water).

(Answer) (r) T

(s) Electrode potential is an extensive variable.

(Answer) (s) F

(t) The pH meter is a type of a concentration electrochemical cell.

(Answer) (t) T

Answer:

(a) T, (b) F, (c) T, (d) T, (e) T, (f) F, (g) T, (h) F, (i) T, (j) T, (k) F, (l) T, (m) T, (n) F, (o) T, (p) T, (q) F, (r) T, (s) F, (t) T